MODERN
INORGANIC CHEMISTRY

ACCORDING TO THE NEW SYLLABUS 2005-07

For

B.Sc. & B.S. (Hons.) Students

By

Dr. Haq Nawaz Bhatti
M.Sc. (Pb) Gold Medalist
PhD (UAF), MCSP
Department of Chemistry
University of Agriculture
Faisalabad

Dr. Bashir Ahmad Nasir (Late)
M.Sc. & PhD (Pb)
Postgraduate Dimploa (Tokyo)
Post Doctoral Research (Bristol)
Institute of Chemistry
University of the Punjab, Lahore.

THE CARAVAN BOOK HOUSE
Kachehri Road, Lahore. Phones: 7212091, 7122955, 7352296
e.mail. caravanlhr@hotmail.com

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Dr. Bashir Ahmad Nasir

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PREFACE TO THE SECOND EDITION

In recent years drastic revision has taken place in the Curriculum of Chemistry by Higher Education Commission (HEC), at National level. Different courses of Chemistry have been revised and updated at both graduate and postgraduate levels to cater the needs of future trends. Keeping in view the profound changes in the Syllabi, the text book is revised. Some new chapters namely, **Solvent extraction, Chromatography, Spectroscopy, Evaluation of analytical data, Chemical industries** etc. have been added to increase the utility of the book.

We are grateful to our numerous colleagues who have sent their valuable suggestions and extended their whole- hearted cooperation especially, **Professor Dr. Jamil Anwar Ch.**, Director, Institute of Chemistry, University of the Punjab, Lahore **Professor Dr. Iftikhar Imam Naqvi**, Chairman Department of Chemistry University of Karachi, **Professor Dr. Mohammad Ali,** Chairman Department of Chemistry University of Sargodha, **Professor Dr. Bushra Khan,** Lahore College University for Women, Lahore, **Professor Dr. Muhammad Akram Kashmiri,** Chairman, Department of Chemistry G.C. University, Lahore, **Professor Dr. Shahida B. Niazi**, Chairperson Department of Chemistry, Baha-ud-Din Zakria University Multan, **Professor Dr. Sher Khan** Chairman. Department of Chemistry, Gomal University D.I. Khan, **Dr. Muhammad Asfaq**, Department of Chemistry, Islamia University Bahawalpur **Dr. Abdul Jabbar,** Department of Chemistry, Govt. College University Faisalabad, **Dr. Zill-i–Huma Nazli**, & **Mrs. Ambreen Ashar,** Govt. College for Women, Faisalabad for their encouragement and moral support. It will be sheer ingratitude if we fail to appreciate the help extended by our students, especially **Khalid Mahmood Zia, Muhammad Asif Hanif** and **Nadia.**

As always, we wish to record our thanks to **Ch. Ahmad Najeeb** for giving open offer to publish this book.

For Suggestions
hnbhatti2005@yahoo.com
03336528455

Authors

UNIVERSITY OF THE PUNJAB

SYLLABUS INORGANIC CHEMISTRY (WRITTEN)

PAPER 'B'

1. Periodicity

Modern periodic table; Similarities and differences in first row elements; the diagonal and vertical relationship with other elements; electronegativity of elements (Pauling and mulliken scales); Polarizability and polarizing power of ions; periodicity in the properties of transition and inner transition elements.

2. Theories of Chemical Bonding

Nature and types of Chemical Bonding. Modern concept of Valence Bond Theory (VBT), Molecular Orbital Theory (MOT) and their applications to Homo and hetero di- and polyatomic inorganic molecules, explaining the convertional and modified MO diagrams. Valence Shell Electron Pair Repulsion Theory (VSEPR), explaining the shapes of inorganic molecules (i.e. AB_2, AB_3, AB_2E, AB_4, AB_3E, AB_2E_2, AB_5, AB_4E, AB_3E_2, AB_2E_3, AB_6, AB_5E, AB_4E_2) and directed valence theory (Hybridization), Metallic bonds (detailed concept).

3. Acid-Base Concept

General concept of acids and bases. Detail of Lewis concept of acids and bases. Soft and Hard Acid-Base (SHAB) concept and its applications. Relative strength of acids and bases based on Pk values. Chemical reactivity of acids and Bases. Relationship between redox reactions and acid base reactions. Significance of pH, pOH, and buffers. Indicators and theories of indicators.

4. Chemistry of d-Block Elements

Electronic configuration of transition elements. Metallurgy of chromium, nickel and copper. Theories of coordination compounds, Valence Bond Theory (VBT), Molecular Orbital Theory (MOT) and Crystal Field Theory (CFT) for tetrahedral and octahedral complexes). Nomenclature, Isomerism in coordination compounds. Chelates. Application of coordination compounds.

5. Nuclear Chemistry

Natural and artificial radioactivity. Stability of nuclei. Nuclear transformations. Rate of radioactivity disintegration. Measurement of nuclear radiations. (Wilson's cloud chamber and Geiger count chamber). Nuclear reactions (Fission and Fusion). Use of radioisotopes in various fields. Biological effects of nuclear radiation.

6. Solvent Extraction and Chromatographic Techniques

Basis of solvent extraction process; Distribution Law and Distribution co-efficient; Simple extraction, Double extraction and multiple extraction systems; applications of solvent extraction in chemistry and industry; Basic principle of chromatographic techniques; Classifications of Chromatographic techniques on the basis of mobile and stationary phases; introduction to column and Paper chromatography.

7. Evaluation of Analytical Data and Essentials of Chemical Analysis

Some fundamental concepts like mole, activity and activity co-efficient; Concepts of mean, median, accuracy, precision, significant figures; Standard deviation; Relative standard deviation. Law of mass action and its applications; precipitation and solubility product; common ion effect; Co-precipitation, fractional precipitation.

8. Spectroscopy

Electromagnetic radiation and its interaction with matter; Nature of different transitions possible in atoms and molecules; Electronic, vibrational, rotational and other possible transitions by absorption of radiation by molecules and atoms. Development of spectroscopic analytical techniques employing various transitions. Classification of spectroscopic techniques on the basis of type of radiation, phenomenon accruing and the nature of the matter. Basic introduction to atomic and molecular spectroscopic techniques including flame emission, spectrophotometry, UV and IR spectroscopy.

9. Chemical Industries

Glass, Soda ash & Soap.

BAHAOUDIN ZAKIRIYA UNIVERSITY MULTAN

Paper 'B' **INORGANIC CHEMISTRY (THEORY)** 50 Marl

1. Basis of Periodic Classification of Elements and Periodic Table

Periodic law, classification of elements based on s, p, d, and f-orbitals, placement of elements based on electronic configuration, group trends and periodic properties: atomic radii, ionization potentials, electron affinities and electronegativities redox potential (elementary treatment), electro-chemical series and its applications.

2. Chemical Bonding

Nature and types of chemical bond, born-haber cycle, theories of chemical bonding: valence bond theory and molecular orbital theory, interpretation of shapes of inorganic molecules based on Valence Shell Electron Pair Repulsion (VSEPR) Model and hybridization.

3. Acid Base Equilibria

General concepts of acids and bases, relative strengths of acids, significance of pK, pH and buffers, theory of indicators.

4. Theoretical Principles of Inorganic Analysis

Applications of the law of mass action principles of solubility product and common ion effect in inorganic qualitative analysis.

5. Chemistry of p-block elements

General characteristics of the following group of p-block elements with reference to the aspects given against each.

(a) Boron and Aluminium: Gradation of the characteristic properties within the group, electron deficient molecules such as hydrides of boron and aluminium including their structures.

(b) Carbon and Silicon: Gradation of the characteristic properties, production of pure silicon for solar energy cells and silicon chips. Structural aspects of ortho- and meta- silicates, industrial applications of meta-silicates in cement and glass industry.

(c) Nitrogen and Phosphorus: Gradation of the characteristic properties within the group, oxides and oxyacids of nitrogen and their role in environmental pollution.

(d) Oxygen and Sulphur: Gradation of the characteristic properties within the group, role of sulphur dioxide in air pollution, thionic acids and use of 'hypo' in photography.

(e) Halogens: Gradation of the characteristic properties within the group. Industrial preparation of halogens, oxyacids of halogens, interhalogens: structural and chemical aspects, rules governing AB, AB3, AB5, AB7 types.

(f) Zero Group Elements: Chemistry of noble gases, reactivity, bonding and structure of xenon compounds, laboratory and commercial utilization of inert gases.

6. Transition Elements

General characteristics of d-block elements, electronic configurations, coordination compounds: nomenclature, nature of coordinate bond, applications of Werner valence bond, molecular orbital and crystal field theories to explain the structure of the coordination compounds.

7. Metallurgies and Industries

(a) Metallurgy of Aluminium, Copper, Steel and Iron:

(b) Chemical Industries with special reference to chemical processes and scope in Pakistan:

Caustic soda, Sulphuric acid, Glass, Cement and Fertilizers (N and P based).

HEC PROPOSED SYLLABUS

Paper 'B' **INORGANIC CHEMISTRY (THEORY)** 50 Mark

1. The Periodic Law and Periodicity

Development of periodic table; Classification of elements based on s, p, d, and f-orbitals, group trends and periodic properties: atomic radii, ionization potentials, electron affinities, electronegativities and redox potential.

2. Chemical Bonding in Main Block Elements

Nature and types of chemical bonding, Lewis concepts, ionic, covalent, coordinate covalent bond; Valence Bond Theory (VBT), Molecular Orbital Theory (MOT). Interpretation of shapes of inorganic molecules based on Valence Shell Electron Pair Repulsion (VSEPR) Model and hybridization.

3. Acid and Bases

Concepts of acids and bases including soft and hard acid base concepts. Relative strengths of acids and bases, significance of pH, pK_a pK_b and buffers solutions. Theories of indicators: (acid base, redox adsorption). Solubility, solubility product, common ion effect and their industrial application.

4. Chemistry of p-block elements

General characteristics of the following group of p-block elements with reference to the aspects given against each.

(a) **Boron and Aluminium**: group anamolies: Boron and aluminium hydrides: Structures, properties and industrial application.

(b) **Carbon and Silicon**: group anamolies. Fullerenes and their applications. Production of pure silicon for solar energy cells and silicon chips, silicates, and silicones and industrial applications.

(c) **Nitrogen and Phosphorus**: group anamolies preparation, structures, properties and the environmental role of oxides of nitrogen. Industrial preparation of nitric acid, urea and superphosphate fertilizers. Causes of fog and smog.

(d) **Oxygen and Sulphur**: group anamolies. preparation, structures, properties and the environmental role of oxides and oxy acids of sulphur, manufacturing of sulphuric acid and its reactions. Thionic acids and use of 'hypo' in industry.

(e) **The Halogens:** anamolous behaviour of fluorine. Industrial preparation of chlorine. Peparation, structures, properties and uses of oxides, oxyacids of chlorine, interhalogens and pseudohalogens.

(f) **The Noble Gases** Preparation, properties structures and uses of xenon fluorides; commercial uses of noble gases.

5. Chemistry of d-block elements

Electronic configuration. General characteristics of d-block elements, Werner's concepts of coordination. Nomenclature. nature of coordinate covalent bond, Valence Bond, Molecular Orbital and Crystal Field theories to explain the structure of the polymer coordination compounds. Introduction to chelates. Industrial application of transtition metals.

6. Introduction to Nuclear Chemistry

natural and artificial radioactivity; Nuclkear reaction, fission and fusion. Uses of radioisotopes in variouys fields. Nuclear hazards and safety measures.

7. Chromatography

Classification and introduction to paper, column and thin layer chromatography.

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Chapter One

CHEMICAL PERIODICITY AND THE PERIODIC TABLE

1.1 INTRODUCTION

The concept of chemical periodicity is central to the study of inorganic chemistry. No other generalization rivals the periodic table of the elements in its ability to systematize and rationalize known chemical facts or to predict new ones and suggest fruitful areas for further study. Chemical periodicity and the periodic table now find their natural interpretation in the detailed electronic structure of the atom; indeed, they played a major role at the turn of the century in elucidating the mysterious phenomena of radioactivity and the quantum effects, which led ultimately to Bohr's theory of the hydrogen atom. Because of this central position it is perhaps not surprising that innumerable articles and books have been written on the subject since the seminal papers by Mendeleev in 1869, and some 700 forms of the periodic table (classified into 146 different types or subtypes) have been proposed.

There is no single best form of the periodic table since the choice depends on the purpose for which the table is used. Some forms emphasize chemical relations and valence, whereas others stress the electronic configuration of the elements or the dependence of the periods on the shells and sub-shells of the atomic structure. The most convenient form for our purpose is the so-called "long form" with separate panels for the lanthanide and actinide elements. There has been a lively debate during the past decade as to the best numbering system to be used for the individual groups in the table; we will adopt the 1-18 numbering scheme recommended by IUPAC.

1.2 THE ELECTRONIC STRUCTURE OF ATOMS

The ubiquitous electron was discovered by J.J. Thompson in 1897 some 25 y after the original work on chemical periodicity by D.I. Mendeleev and Lothar Meyer; however, a further 20 y were to pass before G.N. Lewis and then I. Langmuir connected the electron with valency and chemical bonding. Refinements continued via wave mechanics and molecular orbital theory, and the symbiotic relation between experiment and theory still continues today. It should always be remembered, however, that it is incorrect to "deduce" known chemical phenomena from theoretical models; the proper relationship is that the currently accepted theoretical models interpret the facts and suggest new experiments— they will be modified (or discarded and replaced) when new results demand it. Theories can never be proved by experiment— only refuted, the best that can be said of a theory is that it is consistent with a wide range of information which it interprets logically and that it is a fruitful source of predictions and new experiments.

Our present views on the electronic structure of atoms are based on a variety of experimental results and theoretical models, which are fully discussed in many elementary texts. In summary, an atom comprises a central, massive positively charged nucleus surrounded by a more tenuous envelope of negative electrons. The nucleus is composed of neutrons ($^1_0$n) and protons ($^1_1$p, i.e. $^1_1$H$^+$) of approximately equal mass tightly bound by the force field of mesons. The number of protons (Z) is called the atomic number and this, together with the number of neutrons (N), gives the atomic mass number of the nuclide ($A = N + Z$). An element consists of atoms all of which have the same number of protons (Z) and this number determines the position of the elements in the periodic table (H.G.J. Moseley, 1913). Isotopes of an element all have the same value of Z but differ in the number of neutrons in their nuclei. The charge on the electron (e^{-1}) is equal in size but opposite in sign to that of the proton and the ratio of their masses is 1/1836.2

1.3 CONCEPT OF ATOMIC ORBITAL

If a line is drawn enclosing a region where an electron can be found, say 90 to 95% of time, such a region or space is called an atomic orbital. Thus:

"The three-dimensional region or space around the nucleus of an atom where there is maximum probability of finding an electron having certain energy is called atomic orbital."

Or

"An atomic orbital represents the space around the nucleus in an atom where the electron spends most of its time while in constant motion."

To clarify the concept of electron probability let us assume that we take a set of instantaneous pictures of an electron with a specific energy moving around a nucleus. If all these sequential pictures, with the electron appearing as small dot in each picture, were superimposed, a cloud would result as shown in Fig. 1.1. This picture is called an electron density representation. The density of dots in a given spatial region is a pictorial representation of the probability density in that region.

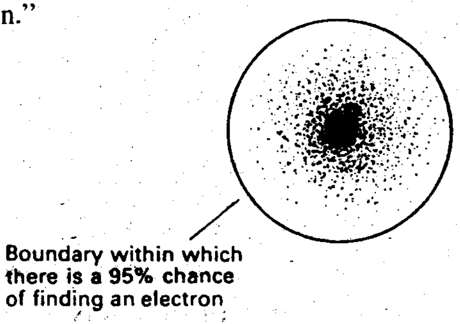

Fig. 1.1 The dot population picture of an orbital.

Shapes of Orbitals

The shapes of orbitals depend on the quantum numbers *l* and m. (see latter).

s-orbitals

s-orbitals are shown in Fig. 1.2. The important points regarding their shapes are:

1. All s-orbitals are spherically symmetrical.
2. The effective size of *s*-orbitals increases as n increases.
3. Each orbital has regions of high electron density (shown as spherical shells) equal to *n*.

4. In between the spherical shells there are nodes (having zero probability) equal to $n - 1$.

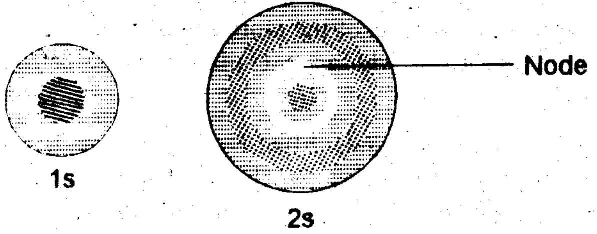

Fig. 1.2. Shapes of 1s and 2s orbitals.

p-orbitals

There are three *p*-orbitals, designated as p_x, p_y and p_z, which are oriented along the three mutually perpendicular axes x, y and z. Each orbital consists of two lobes symmetrical about a particular axis and has ***dumb bell*** shape. The two lobes are separated by a nodal plane. Higher *p*-orbitals have similar shapes except that they have additional smaller regions of high electron density (called lobes) separated from the major lobes by the nodal surface. The number of such regions is $(n - 2)$ on each side.

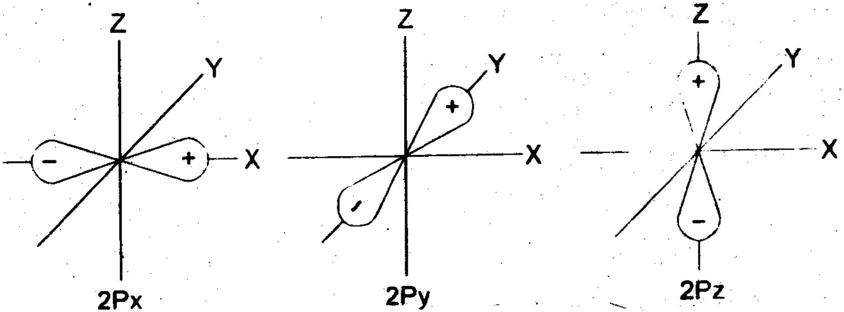

Fig. 1.3. Shapes of 2p-orbitals.

d-orbitals

There are five d-orbitals designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. These are shown in Fig. 1.4.

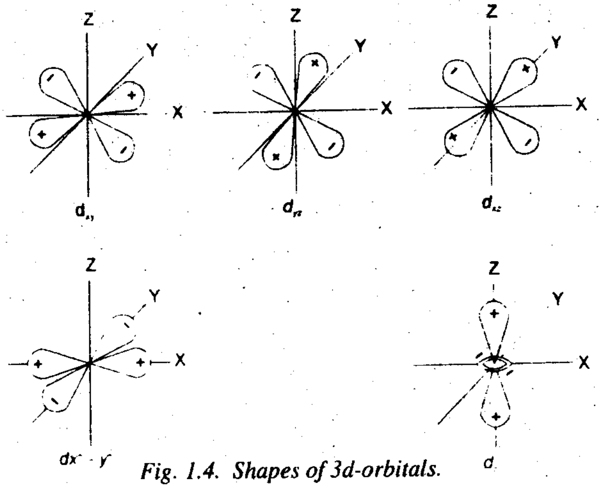

Fig. 1.4. Shapes of 3d-orbitals.

1.4 QUANTUM NUMBERS

The term quantum number is used to identify the various energy levels available with the atom in which the electron of the atom can reside. The word *quantum* is used to signify that all the energy levels which are available to an electron are governed by laws of quantum mechanics.

Just as a college student is identified by *(i)* his name *(ii)* the name of his college *(iii)* class in which he is studying and *(iv)* the locality of his college, an electron in an atom is completely described by its four quantum numbers. Thus the quantum numbers serve as *identification numbers* which completely define the electron in an atom i.e., these numbers

(i) specify the position (or location) of an electron in an atom.

(ii) predict the direction of spin or self-rotation of the electron, and

(iii) determine the energy and angular momentum of the electron.

Four quantum numbers which are required to completely specify the character of an electron are:

1. Principal quantum number (n)
2. Azimuthal quantum number (l)
3. Magnetic quantum number (m)
4. Spin quantum number (m_s)

Each quantum number refers to a particular character of an electron in an atom.

1. Principal Quantum Number (*n*)

This quantum number n defines the energy level or shell in which the electron is present. The average distance of the electron from the nucleus, and the energy associated, depend on n. It can have whole number values as

$$n = 1, 2, 3, 4, ...$$

2. Azimuthal or Angular Quantum Number (*l*)

This quantum number denotes the *sublevel* or *sub shell* in a given principal energy level. This quantum number is related to the angular momentum of the electron. In multi-electron atoms, the energy, besides depending on n, also depends on l. Corresponding to each value of n there are n possible values of l

$$l = 0, 1, 2, ..., (n - 1)$$

These various sub shells are called *s*, *p*, *d*, *f*, ... depending upon the value of l

Value of l	0	1	2	3	.....
Sublevel	*s*	*p*	*d*	*f*	.....

3. Magnetic Quantum Number (*m*)

The third quantum number m is called the magnetic quantum number for it is only in an applied magnetic field that it is possible to define a direction within the atom with respect to which the orbital can be directed. In general, the magnetic quantum number can take up $2l+1$ values (i.e. 0, ±1, ……± l), thus an *s* electron (which is spherically symmetrical and has zero orbital angular momentum) can have only one orientation, but a *p* electron can have three (frequently chosen x, y and z directions in Cartesian coordinates). Likewise there are five possibilities for the *d*-orbitals and seven for *f*- orbitals.

4. Spin Quantum Number (m_s)

This is designated by m_s and describes the spin orientation of the electron. Since the electron can spin only in two ways — clockwise and anticlockwise, s can have only two values: + ½ and - ½, which are also expressed by arrows pointing up (↑) and down (↓), respectively. It determines the orientation of spin angular momentum.

It can now bee seen that there is a direct and simple correspondence between this description of electronic structure and the form of the periodic table. Hydrogen with 1 proton and 1 electron is the first element, and, in the ground state it has the electronic configuration $1s^1$ with zero orbital angular momentum. Helium, Z = 2, has the configuration $1s^2$, and this completes the first period since no other unique combination of $n = 1$, $l = m = 0$, $m_s = \pm ½$ exists. The second period begins with lithium (Z = 3), the least tightly bound electron having the configuration $2s^1$. The same situation obtains for each of other periods.

In so far as the chemical (and physical) properties of an element derive from its electronic configuration, and especially the configuration of its least tightly bound electrons, it follows that chemical periodicity and the form of the periodic table can be elegantly interpreted in terms of electronic structure.

Example 1.1

An electron is in 4*f* orbital. What possible values for the quantum numbers, *n*, *l*, *m* and m_s it can have?

Solution

We know that for 4*f* orbital $n = 4$ and $l = 3$. Now when $l = 3$, m = 0, ± 1, ± 2 and ± 3 (seven values). Seven values of m imply that the electron may be in any of the seven 4*f* orbital and for this electron *m* may have any of the seven values. For this electron s = + ½ or - ½.

Example 1.2

Which of the orbitals namely 1*p*, 2*s*, 2*p* and 3*f* are not possible? Give reason for your answer.

Solution

The orbitals which are not possible are 1*p* and 3*f*. The reason for their non-existence is given as follows:

We know that when $n = 1$ (1st shell), $l = 0$. $l = 0$ value means that first shell has only one sub-shell namely 1*s* for which $l = 0$. Thus first shell does not contain 1*p* orbital.

It is also known to us that when $n = 3, l = 0, 1, 2$. Three values of l mean that 3rd shell has only three sub-shells namely 3s ($l = 0$), 3*p* ($l = 1$) and 3*d* ($l = 2$). Thus 3rd shell does not contain 3*f* orbital.

Example 1.3

What designations are given to the orbitals having

(i) $n = 2$ $l = 1$

(ii) $n = 1$ $l = 0$

(iii) $n = 3$ $l = 2$

(iv) $n = 4$ $l = 3$

Solution

(i) When $n = 2$ and $l = 1$ the orbital is 2*p*

(ii) When $n = 1$ and $l = 0$ the orbital is 1*s*

(iii) When $n = 3$ and $l = 2$ the orbital is 3*d*

(iv) When $n = 4$ and $l = 3$ the orbital is 4*f*

1.5 PAULI'S EXCLUSION PRINCIPLE

We have seen that four quantum numbers *n*, *l*, *m* and *s* are essential to describe the state of an electron in an atom. Pauli in 1925 introduced a principle known as Pauli's exclusion principle for assigning quantum numbers to the electrons. According to this principle,

"No two electrons in an atom can have the same values of all the four quantum numbers."

Thus for $n = 1$ in 1*s* orbital, only two electrons can exist with the quantum numbers given as:

Electron Number	**Quantum Numbers**				**Set of Values**
	n	***l***	***m***	***s***	
1st electron (↑)	1	0	0	$+\frac{1}{2}$	$(1, 0, 0, +\frac{1}{2})$
2nd electron (↓)	1	0	0	$-\frac{1}{2}$	$(1, 0, 0, -\frac{1}{2})$

It is obvious that although the values of three quantum numbers *n*, *l* and *m* are identical, but the value of fourth quantum number s is different, i.e., $+\frac{1}{2}$ and $-\frac{1}{2}$. Any attempt to introduce the third electron in the 1*s* orbital would inevitably lead to the duplication of one of the above sets of quantum numbers, which is contrary to the Pauli's principle. Hence *s*-orbitals cannot contain more than two electrons.

The maximum number of electrons for each principal quantum number is given by $2n^2$. This would give the maximum number of electrons in successive shells as 2, 8, 18, 32 and 50. For example, according to $2n^2$ rule, $n = 2$ must have eight electrons. According to Pauli's principle, we can arrange them, having the following combinations:

$n = 2, \quad l = 0, \quad m = 0, \quad s = +\frac{1}{2}$

$n = 2, \quad l = 0, \quad m = 0, \quad s = -\frac{1}{2}$

$n = 2, \quad l = 1, \quad m = 0, \quad s = +\frac{1}{2}$

$n = 2, \quad l = 1, \quad m = 0, \quad s = -\frac{1}{2}$

$n = 2, \quad l = 1, \quad m = +1, \quad s = +\frac{1}{2}$

$n = 2, \quad l = 1, \quad m = +1, \quad s = -\frac{1}{2}$

$n = 2, \quad l = 1, \quad m = -1, \quad s = +\frac{1}{2}$

$n = 2, \quad l = 1, \quad m = -1, \quad s = -\frac{1}{2}$

Two electrons are accommodated in $2s$ orbital ($l = 0$), while the six electrons are accommodated in all the three $2p$ orbitals ($l = 1$), two electrons each in $2p_x$ $(m = +1)$, $2p_y$ $(m = -1)$ and $2p_z$ $(m = 0)$. Similarly we can account for other levels.

Significance of the Principle

The significance of the principle is that each orbital in an atom can hold a maximum of two electrons, provided these two electrons have opposite spins. Knowing this fact and using the rules, we can determine the largest possible number of electrons that can occupy each energy level.

1.6 DISTRIBUTION OF ELECTRONS IN ORBITALS

As we pass from one element to another along the periodic table, we find that one electron is added every time to the next atom. Where should the incoming electron go? Filling of the different orbitals by electrons proceeds in accordance with the following rules:

(a) The maximum number of electrons in any orbit or shell is $2n^2$, where n is the number of orbit or principal quantum number.

(b) The maximum number of electrons in a sub-shell (s, p, d or f) is equal to $2(2l + 1)$ where $l = 0, 1, 2$ or 3 (Azimuthal quantum number). Thus these sub-shells can have a maximum of 2, 6, 10 and 14 electrons, respectively.

(c) The orbitals are filled up in order of increasing energy. As a working rule a new electron enters the orbital where $n + l$ value is minimum. When $(n + l)$ has the same value for two or more orbitals, the new electron enters the orbital where n is the minimum. This is known as *Building up Principle* or *Pauli's Aufbau Principle* (Aufbau is a German expression meaning building up). As each electron shell has sub-shells and their energy difference is very much less, the orbitals having lower energy are filled first. It is seen that the order of energy of various orbitals is the following.

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

The above order, for the sake of simplicity can be represented by a simple diagram. (Fig. 1.5).

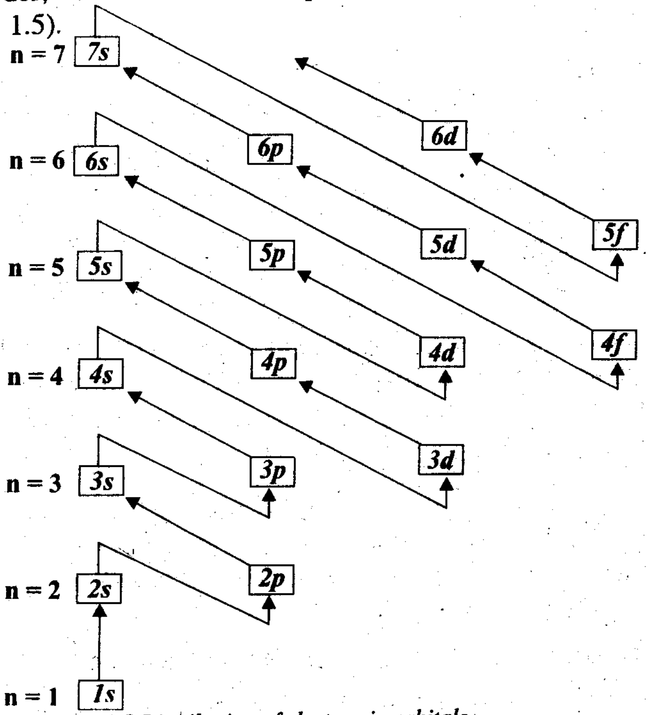

Fig. 1.5 Distribution of electron in orbitals.

(d) There can be one *s* orbital, three *p* orbitals, five *d* orbitals and seven *f* orbitals. Each one of these orbitals can hold only two electrons with spin + ½ and – ½.

(e) When several orbitals of same energy are available, electrons would prefer to occupy separate orbitals and remain unpaired rather than to live in the same orbital and leave the other empty. This is known as *Hund's Rule of Maximum Multiplicity*. For example, three *p* orbitals are of equal energy but are concentrated in different regions of space at right angles to each other. Electrons can minimize the repulsive forces between themselves by occupying different orbitals and having parallel spins. This explains their preference to enter different orbitals as long as possible. In other words, pairing must begin with the introduction of the second electron in the *s* orbital, the fourth in the *p*-orbitals the sixth in the *d*-orbitals and the eighth in the *f*-orbitals. If we represent *p*-orbitals as boxes and electrons by arrows (↑ for + ½s and ↓ for -½s), then if two electrons are added to p-sub-shell, there exists two possibilities I and II.

p_x	p_y	p_z
↑↓		

I

p_x	p_y	p_z
↑	↑	

II

In the first arrangement, two electrons are in the same orbital (*i.e.*, p_x) but it is not permitted by Hund's rule, so the II arrangement is right as this satisfies the rule. If we add 3rd electron, it will go to p_z (empty orbital) rather than to p_x and p_y.

1.7 THE ELECTRONIC CONFIGURATION OF ELEMENTS

The distribution of electrons in various shells, sub-shells and orbitals of an atom is called its complete electronic configuration or simply electronic configuration. The distribution of electrons in various sub-shells and orbitals of the valence-shell (or outermost shell) is called valence shell configuration.

Representation of Electronic Configuration

The electronic configuration of an atom is written in terms of nl^x notation where l indicates the sub-shell as given below:

value of l :	0	1	2	3	.....
sub-shell :	*s*	*p*	*d*	*f*	.....

In the notation nl^x, super-script x written at the top of 'l' indicates the number of electrons present in the sub-shell given by l, while n written to the left of l^x indicates the number of shell to which the sub-shell denoted by l belongs. For example, $3p^2$ in which n = 3, x = 2 and l = 1 (*p* sub-shell) indicates that two electrons (x = 2) are present in *p*-sub-shell (l = 1) which belong to 3rd main shell.

Number of electrons
Shell number ⟶ nl^x
Sub-shell

Actual electronic configuration of atoms of all the elements of the periodic table are given in Table 1.2. We find that these configurations are by and large the same as predicted by the Aufbau procedure. However, there are quite a few elements which exhibit slight variations from the standard pattern.

Table 1.1. Ground State Electronic Configuration of Elements

Atomic Number	Symbol	Electron Configuration	Atomic number	Symbol	Electron Configuration
1.	H	$1s^1$	39.	Y	$[Kr]5s^2 4d^1$
2.	He	$1s^2$	40.	Zr	$[Kr]5s^2 4d^2$
3.	Li	$[He]2s^1$	41.	Nb	$[Kr]5s^1 4d^4$
4.	Be	$[He]2s^2$	42.	Mo	$[Kr]5s^1 4d^5$
5.	B	$[He]2s^2 2p^1$	43.	Tc	$[Kr]5s^2 4d^5$
6.	C	$[He]2s^2 2p^2$	44.	Ru	$[Kr]5s^1 4d^7$
7.	N	$[He]2s^2 2p^3$	45.	Rh	$[Kr]5s^1 4d^8$
8.	O	$[He]2s^2 2p^4$	46.	Pd	$[Kr]4d^{10}$
9.	F	$[He]2s^2 2p^5$	47.	Ag	$[Kr]5s^1 4d^{10}$
10.	Ne	$[He]2s^2 2p^6$	48.	Cd	$[Kr]5s^2 4d^{10}$

11.	Na	[Ne]$3s^1$	49.	In	[Kr]$5s^2 4d^{10} 5p^1$
12.	Mg	[Ne]$3s^2$	50.	Sn	[Kr]$5s^2 4d^{10} 5p^2$
13.	Al	[Ne]$3s^2 3p^1$	51.	Sb	[Kr]$5s^2 4d^{10} 5p^3$
14.	Si	[Ne]$3s^2 3p^2$	52.	Te	[Kr]$5s^2 4d^{10} 5p^4$
15.	P	[Ne]$3s^2 3p^3$	53.	I	[Kr]$5s^2 4d^{10} 5p^5$
16.	S	[Ne]$3s^2 3p^4$	54.	Xe	[Kr]$5s^1 4d^{10} 5p^6$
17.	Cl	[Ne]$3s^2 3p^5$	55.	Cs	[Xe]$6s^1$
18.	Ar	[Ne]$3s^2 3p^6$	56.	Ba	[Xe]$6s^2$
19.	K	[Ar]$4s^1$	57.	La	[Xe]$6s^2 5d^1$
20.	Ca	[Ar]$4s^2$	58.	Ce	[Xe]$6s^2 4f^1 5d^1$
21.	Sc	[Ar]$4s^2 3d^1$	59.	Pr	[Xe]$6s^2 4f^3$
22.	Ti	[Ar]$4s^2 3d^2$	60.	Nd	[Xe]$6s^2 4f^4$
23.	V	[Ar]$4s^2 3d^3$	61.	Pm	[Xe]$6s^2 4f^5$
24.	Cr	[Ar]$4s^1 3d^5$	62.	Sm	[Xe]$6s^2 4f^6$
25.	Mn	[Ar]$4s^2 3d^5$	63.	Eu	[Xe]$6s^2 4f^7$
26.	Fe	[Ar]$4s^2 3d^6$	64.	Gd	[Xe]$6s^2 4f^7 5d^1$
27.	Co	[Ar]$4s^2 3d^6$	65.	Tb	[Xe]$6s^2 4f^9$
28.	Ni	[Ar]$4s^2 3d^8$	66.	Dy	[Xe]$6s^2 4f^{10}$
29.	Cu	[Ar]$4s^1 3d^{10}$	67.	Ho	[Xe]$6s^2 4f^{11}$
30.	Zn	[Ar]$4s^2 3d^{10}$	68.	Er	[Xe]$6s^2 4f^{12}$
31.	Ga	[Ar]$4s^2 3d^{10} 4p^1$	69.	Tm	[Xe]$6s^2 4f^{13}$
32.	Ge	[Ar]$4s^2 3d^{10} 4p^2$	70.	Yb	[Xe]$6s^2 4f^4$
33.	As	[Ar]$4s^2 3d^{10} 4p^3$	71.	Lu	[Xe]$6s^2 4f^{14} 5d^1$
34.	Se	[Ar]$4s^2 3d^{10} 4p^4$	72.	Hf	[Xe]$6s^2 4f^{14} 5d^2$
35.	Br	[Ar]$4s^2 3d^{10} 4p^5$	73.	Ta	[Xe]$6s^2 4f^{14} 5d^3$
36.	Kr	[Ar]$4s^2 3d^{10} 4p^6$	74.	W	[Xe]$6s^2 4f^{14} 5d^4$
37.	Rb	[Kr]$5s^1$	75.	Re	[Xe]$6s^2 4f^{14} 5d^5$
38.	Sr	[Kr]$5s^2$	76.	Os	[Xe]$6s^2 4f^{14} 5d^6$
77.	Ir	[Xe]$6s^2 4f^{14} 5d^7$	94.	Pu	[Rn]$7s^2 5f^6$
78.	Pt	[Xe]$6s^1 4f^{14} 5d^9$	95.	Am	[Rn]$7s^2 5f^7$
79.	Au	[Xe]$6s^1 4f^{14} 5d^{10}$	96.	Cm	[Rn]$7s^2 5f^7 6d^1$
80.	Hg	[Xe]$6s^2 4f^{14} 5d^{10}$	97.	Bk	[Rn]$7s^2 5f^9$
81.	Tl	[Xe]$6s^2 4f^{14} 5d^5 6p^1$	98.	Cf	[Rn]$7s^2 5f^{10}$
82.	Pb	[Xe]$6s^2 4f^{14} 5d^5 6p^2$	99.	Es	[Rn]$7s^2 5f^{11}$
83.	Bi	[Xe]$6s^2 4f^{14} 5d^5 6p^3$	100.	Fm	[Rn]$7s^2 5f^{12}$

84.	Po	[Xe]$6s^2 4f^{14} 5d^5 6p^4$
85.	At	[Xe]$6s^2 4f^{14} 5d^5 6p^5$
86.	Rn	[Xe]$6s^2 4f^{14} 5d^5 6p^6$
87.	Fr	[Rn]$7s^1$
88.	Ra	[Rn]$7s^2$
89.	Ac	[Rn]$7s^2 6d^1$
90.	Th	[Rn]$7s^2 6d^2$
91.	Pa	[Rn]$7s^2 5f^2 6d^1$
92.	U	[Rn]$7s^2 5f^3 6d^1$
93.	Np	[Rn]$7s^2 5f^4 6d^1$
101.	Md	[Rn]$7s^2 5f^{13}$
102.	No	[Rn]$7s^2 5f^{14}$
103.	Lr	[Rn]$7s^2 5f^{14} 6d^1$
104.	Rf	[Rn]$7s^2 5f^{14} 6d^2$
105.	Db	[Rn]$7s^2 5f^{14} 6d^3$
106.	Sg	[Rn]$7s^2 5f^{14} 6d^4$
107.	Bh	[Rn]$7s^2 5f^{14} 6d^5$
108.	Hs	[Rn]$7s^2 5f^{14} 6d^6$
109.	Mt	[Rn]$7s^2 5f^{14} 6d^7$
110	Ds	[Rn]$7s^2 5f^{14} 6d^8$
111	Rg	[Rn]$7s^2 5f^{14} 6d^9$

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* The symbol [He] is called the *helium core* and represents $1s^2$. [Ne] is called the *neon core* and represents $1s^2 2s^2 2p^6$. [Ar] is called *argon core* and represents [Ne]$3s^2 3p^6$. [Kr] is called the *krypton core* nd represents [Ar]$4s^2 3d^{10} 4p^6$. [Xe] is called the *xenon core* and represents [Kr]$5s^2 4d^{10} 5p^6$. [Rn] is called the *radon core* and represents [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$.

1.8 DEVELOPMENT OF THE PERIODIC TABLE

One of the most important scientific activities is the search for order. If a large number of observations or objects can be arranged into categories according to their common features, it becomes easier to describe them. Moreover, it may be possible to discover an underlying cause for a particular order. This in turn may lead to a significant scientific discovery.

In the section 1.7 we discussed the building up or Aufbau, principle for writing the ground state electronic configuration of the elements. As we will see shortly, elements with similar outer electron configurations behave alike in many ways. This fact helps us in grouping the elements according to the positions they now occupy in the periodic table. But this is not the way the original periodic table was constructed in the 19th century. The chemists of that time had only a vague idea of atoms and molecules and did not know of the existence of protons and electrons. Instead, they constructed the periodic table using their knowledge of atomic masses. Accurate measurements of the atomic masses of many elements had already been made. Arranging elements according to their atomic masses in a periodic table seemed logical to those chemists, who felt that chemical behaviour should somehow be related to atomic mass.

1. Dobereiner's Triad

In 1829 Johann Dobereiner (1780-1849) observed that some of the known elements could be grouped in three's (*triads*) according to similarities in their chemical and physical properties. In these triads the central member has an atomic weight that is roughly the average of other two as illustrated in Table 1.2.

Since Dobereiner's triads included only a few elements, this relationship was not considered a good classification. Other attempts to relate the properties of the elements to their atomic masses were not successful, partly because of the poor reliability of the available values for atomic masses. Dobereiner's concept of triads inspite of its limitations has provided the background to seek further information for the classification of elements.

Table 1.2. Dobereiner's Triads

No.	Elements with Atomic Weights			Mean Atomic Weights
1.	Li = 7	Na = 23	K = 39	$\frac{7+39}{2} = 23$
2.	Cl = 35.5	Br = 80	I = 127	$\frac{35.5+127}{2} = 81.25$
3.	Ca = 40	Sr = 88	Ba = 137	$\frac{40+137}{2} = 88.5$
4.	S = 32	Se = 79	Te = 128	$\frac{32+128}{2} = 80$

2. Newlands Octaves

In 1864 the English chemist John Newlands noticed that when the known elements were arranged in order of atomic mass, every eight element had similar properties. Newlands referred to this peculiar relationship as the *law of octaves.* However, this "law" turned out to be inadequate for elements beyond calcium. Though ridiculed for leaving blank spaces for the yet undiscovered elements, he was the first forerunner of the present periodic table, and was awarded the Davy Medal by the Royal Society (1887) in recognition of his contribution.

Table 1.3. Newlands arrangement of elements in Octaves

I	II	III	IV	V	VI	VII
Li	Be	B	C	N	O	H
Na	Mg	Al	Si	P	S	F
K	Ca	Cr	Ti	Mn	Fe	Cl

3. Mendeleev's Periodic Table and Periodic Law

The major portion of the credit for the development of the periodic system must go to the Russian, Dimitrii Ivanovich Mendeleev, and to the German, Julius Lother Meyor. Both observed independently that *properties of the elements can be represented as periodic functions of their atomic weights.* Mendeleev published the first account of his periodic system in 1869, a few months before the publication of the table by Meyer. Their work was recognized by the Royal Society in 1882 by the presentation of the Davy Medal to both.

Mendeleev arranged the known elements in order of their increasing atomic weights. He found that if elements are arranged in order of their increasing atomic weights, their properties vary in a regular manner, from one member to another in series.

He concluded that *"physical and chemical properties of elements are periodic functions of their atomic weights"*. This is known as *Mendeleev's Periodic Law.* Mendeleev's arrangement of the elements are shown in Table 1.5.

Table 1.4. Mendeleev's Periodic Table of 1871

Sr. No.	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII - RO_4
1.	H = 1							
2.	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3.	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4.	K = 39	Co = 40	- = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Co = 59 Ni = 59 Cu = 63
5.	(Cu = 63)	Zn = 65	– = 68	– = 72	As = 75	Se = 78	Br = 80	
6.	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	– = 100	Ru=104 Rh=104 Pd=106 Ag=108
7.	(Ag=108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125		
8.	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	–	–	–	----
9.	(–)	–	–	–	–	–	–	
10.	–	–	?Er = 178	?La = 180	Ta = 182	W = 184	–	Os=195 Ir=197 Pt=198 Au=199
11.	(Au=189)	Hg = 200	Ti = 204	Pb = 207	Bi = 208			
12.	–	–	–	Th = 231	–	U = 240	–	- - - -

Salient Features of Mendeleev's Table

The salient features of the Mendeleev's table of elements are:

(i) The vertical columns are called Groups. These are numbered I to VIII.

(ii) The horizontal rows are called Periods.

(iii) Groups I to VIII are sub-divided into sub-groups A and B. Group 0 is the group of noble gases. Since noble gases were known at the time Mendeleev compiled his periodic table these were assigned group 0.

(iv) Two consecutive elements were expected to have a difference of at least one unit (and upto four units) in the atomic weights.

(v) Blank spaces were left for unknown elements. For example, blank space was left for Eka-silicon (germanium), and its properties predicted.

(vi) When the table had no space for the known element on the basis of the properties, Mendeleev, without any experimental evidence, changed its atomic weight by a factor that would change the atomic weight of the element to fill up a gap in the table.

Advantages of Mendeleev's Table

The modern version of the Mendeleev's periodic table has the following advantages:

(i) The regular gradation in physico-chemical properties is similar in all the groups.

(ii) The group number (except for group VIII) gives the highest valence state possible for the elements.

(iii) Elements of the second row of group I, II and III show a diagonal relationship to the next elements of group II, III and IV respectively.

(iv) From the positions of the gaps in the table, Mendeleev predicted the properties of the missing elements.

(v) Mendeleev used his periodic classification to rectify the atomic weights of elements. For example, he changed the atomic weights of Al and B from 40.5 and 16 to 27 and 10.7 respectively. Thus Al could fill the gap between Mg (24) and Si (28) whereas B could be placed between Be (9) and C (12).

Defects / Limitations of Mendeleev's Table

Mendeleev's periodic table despite its advantages suffers from certain drawbacks. These are:

(i) Position of hydrogen which resembles both alkali metals and halogens is not clear. Like alkali metals it gives H^+ ion while like halogens, it gives hydride.

(ii) Certain chemically similar elements, *e.g.*, Cu and Hg or Au and Pt, are placed in different groups while some dissimilar elements are grouped together. For example, alkali metals, copper, silver and gold have been placed in the same group though they are dissimilar.*

(iii) Lanthanides and actinides do not find any proper place in the table.

(iv) Certain elements of higher atomic weight, preceed others with lower atomic weight;

Argon (40 preceeds potassium (39).

Cobalt (59) preceeds nickel (58.6).

(v) No place is offered to isotopes and isobars in different groups.

(vi) No explanation is available for the stability of valence states differing by units of two (inert pair effect).

(vii) No explanation is provided for the anomalous behaviour of the first member of a group.

(viii) Though the group number indicated the maximum valence state of the elements, this is not true for group VIII elements except for ruthenium and osmium.

4. Lother Meyer's Work

In December 1869, shortly after the publication of Mendeleev's first paper on the periodic classification of the elements, Lother Meyer submitted a paper entitled "The Nature of the Chemical Elements as functions of Their Atomic Weights". In this publication, emphasizing the physical properties of the elements, Meyer pointed out that in general properties of the elements are periodic functions of their atomic weights. This periodicity was very clearly shown by Meyer by means of the atomic volume curves. The atomic volume of an element is obtained by dividing its atomic weight by its density. He plotted atomic volume vs. atomic weight giving a curve shown in Fig. 1.6. The peaks in the curve are always occupied by alkali metals.

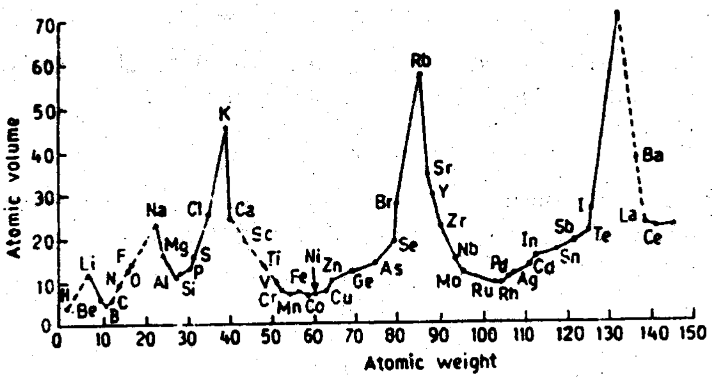


Fig. 1.6. Atomic volume curve of Lothar Meyer.

1.9 MODERN PERIODIC LAW

On studying the shortcomings (limitations) in the Mendeleev's table, it became apparent that atomic weight is not the fundamental property of elements. There is something else in the structure of elements that brings about periodicity of properties in elements. The clue to this problem was provided by Moseley who studied the characteristic X-ray spectra of elements.

Moseley's Work

In 1913, H.G.J. Moseley carried out the first detailed study of the characteristic X-ray spectra emitted by different elements. Using the Bragg crystal spectrometer, Moseley studied the spectra of 38 elements. He showed that the characteristic lines could be separated into two distinct series which then could be related to the K and L radiations observed earlier by Barkla and Sadler (Barkla and Sadler studied the characteristic radiation around 1908. They studied the absorption properties of these radiations and named more penetrating radiation, K-radiation and less penetrating radiation. L radiation). A typical X-ray spectrum is shown in Fig. 1.7.

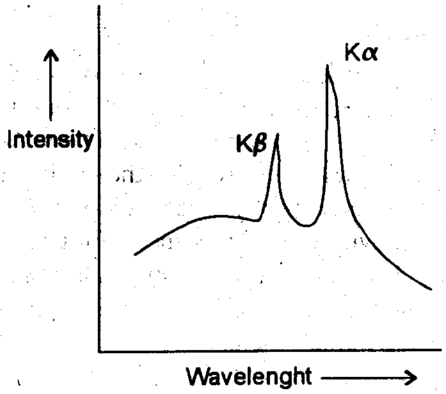


Fig. 1.7 A typical X-ray spectrum.

Empirically, Moseley found that the frequency ν of the characteristic X-ray line could be related to the atomic number by means of the relation

$$\sqrt{\nu} = a\,(Z - b)$$

where 'a' and 'b' are both constants, and Z is the atomic number (or nuclear charge) of the element. The accuracy of this relation is readily determined by plotting frequency against the atomic number as shown in Fig. 1.8.

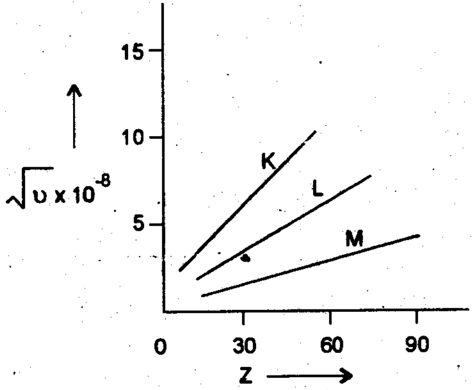


Fig. 1.8 A plot of frequency of the characteristic X-ray vs. atomic number.

In order to explain the relation between frequency and atomic number, Moseley utilized Bohr's model for the H-atom. From the Bohr's model it is reasonable to conclude that an X-ray resulted from an electron transition in the K or L shell. The energy of an electron in an atom depends on the nuclear charge Z (atomic number). As the charge increases, the force holding the electron also increases. Hence the energy and frequency of X-rays emitted by metal targets must depend on the atomic number of the target element. Moseley found that the frequency and hence the energy at the bright lines of the X-ray spectrum increases in a regular way as the atomic number increases.

From these observations, Moseley concluded that the atomic number is a measure of the positive charge on the nucleus of an atom. This property appeared to be more fundamental property and the periodic law was modified as follows:

"The properties of the elements are periodic functions of their atomic numbers".

The above statement is known as modern periodic law. With this change in the basis of classification, defects (4) and (5) of the Mendeleev's table disappear. The various anomalous pairs are found to occupy their proper places and different isotopes of the same element do not require separate positions.

1.10 MODERN PERIODIC TABLE

The first comprehensive classification of elements was made independently by Dimitrii Mendeleev in Russia and Lother Meyer in Germany. While Lother Meyer was primarily interested in the relationships obtained by plotting the magnitude of physical properties against atomic weights, Mendeleev based his system of classification on chemical characterization as a periodic function of atomic weights — *the periodic law.* After an elucidation of atomic structure and the discovery of isotopes, it was realized that the atomic number of an element is a more fundamental property of an element than the atomic weight. Thus in its revised form the periodic law is stated as:

"The properties of elements are periodic functions of their atomic number."

In other words, when the elements are listed in the order of increasing atomic numbers, elements having closely similar properties will fall at definite intervals along the list. *This tabular arrangement of elements having similar properties placed in vertical columns is called a periodic table.* A large number of versions of the periodic table have been proposed but the one that is easiest to use and which is most closely related to the electronic structures of the atoms is the so-called *long form* shown in Fig. 1.9 The long form of the periodic table may be regarded as an extended form of the Mendeleev's table.

The main features of the Bohr's long table are summarized as follows:

1. There are 18 vertical columns which constitute 16 *groups* of elements. These are numbered 1A, IIA, IIIB, ..., VIIB, VIIIB, 1B, IIB, IIIA, ..., VIIA and zero (or VIIIA) according to the traditional system of nomenclature.

   According to the new IUPAC (*International Union of Pure and Applied Chemistry*) recommendation adopted in 1984, the groups are numbered 1 to 18 as shown also in Fig. 1.10. Thus, the alkali metal group IA becomes, 1; while group 2 is Be, Mg and other alkaline earths. The *d*-block elements are labeled from group 3 (Sc, Y, La, Ac) to 12 (Zn, Cd, Hg). Thus Fe, Ru and Os constitute group 8, Co, Rh and Ir group 9 and Ni, Pd and Pt group 10. The boron group — B, Al, Ga, In and Tl becomes group 13 and the remaining main groups constitute upto group 18 — the noble gases. The numbering in the *p*-block thus differs from the old scheme by adding 10 and using Arabic instead of Roman numerals.

MODERN PERIODIC TABLE

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	→ IUPAC
I A	II A	III B	IV B	V B	VI B	VII B		VIII		I B	II B	III A	IV A	V A	VI A	VII A	VIII A	→ CONVENTIONAL
1 H																	2 He	
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 • La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 : Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq		116 Uuh		118 Uuo	

•	Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
:	Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig 1.18 The long form of the periodic Table

2. Elements of groups IA(1), IIA(2), IIIA(13), IVA(14), VA(15), VIA(16) and VIIA(17) have their outermost shells incomplete. These are called normal elements or representative elements or non-transition elements.
3. Elements of group IIIB(3), IVB(4), VB(5), VIB(6), VIIB(7) VIIIB(8, 9, 10), IB(11) and IIB(12) are known as transition elements. These have their outermost as well as penultimate shell incomplete. The electrons in them occupy (n -1)*d* sub-shell in preference to *np*.
4. Elements of group VIIIA or zero (18) show little reactivity and are termed noble gases.
5. Horizontal rows are called *periods*. There are seven periods in the table:
   - *(i)* The first period is a short period of two elements (H — He).
   - *(ii)* Second and third are two short periods of 8 elements each (Li — Ne and Na — Ar).
   - *(iii)* Fourth and fifth are long periods of 18 elements each (K — Kr and Rb — Xe) while sixth is a long period of 32 elements (Cs — Rn) including the rare-earths elements (At. No. 57 — 71) which are all placed in the same group of the periodic table. These rare earths (Ce — Lu) are listed separately at the bottom of the table. These are also known as *lanthanides*.
   - *(iv)* Seventh is an incomplete period of 23 elements. The 14 elements (Th — Lr) extracted from the seventh period are also placed at the bottom of the period table and are called *actinides*.
   - *(v)* The elements after Uranium (Z = 92) are called *transuranic elements*. These elements are the result of atomic research and hence are synthetic elements.
6. The noble gases have been grouped at the extreme right of the periodic table.
7. In this table the long periods have been extended and short periods have been broken so as to accommodate the transition elements at their proper places.

Merits of the Long Form of the Periodic Table

The long form of the periodic table has a number of merits over the Mendeleev's periodic table in the following respects:

(i) The classification of the elements is based on a more fundamental property viz. atomic number.

(ii) It relates the position of an element to the electronic arrangement in its atoms and is, therefore, nearly an ideal arrangement.

(iii) It reflects the similarities, differences and the trends in the chemical properties more clearly across the long periods.

(iv) The inert gases having completely filled shells have been placed at the end of each period. Such a location of the inert gases represents a logical completion of each period.

(v) In this form of the periodic table, the elements of the two sub-groups have been placed separately and thus dissimilar elements do not fall together.

(vi) It provides a clear demarcation of different types of the elements like active metals, transition metals, non-metals, metalloids, inert gases, lanthanides and actinides.

(vii) The properties of transition elements are more clearly understood and their place in a long period is justified in the light of their electronic configuration.

(viii) The position of lanthanides and actinides as a separate group in the table, again, is based on their analogous chemical behaviour.

(ix) It is easier to remember, understand and reproduce.

Defects of the Long Form of Periodic Table

Although the long form of the periodic table is superior to Mendeleev's periodic table in many respects, it retains some of the defects as such. These are listed below:

(i) The group nomenclature A and B as mentioned earlier is arbitrary and confusing. The designation is often inverted for groups III to VII. To overcome this problem use is being made of new IUPAC nomenclature along with the traditional nomenclature.

(ii) The problem of the position of hydrogen still remains unsolved.

(iii) The presence of transition elements between s and p blocks interrupts the regular change in character along the *s* and *p*-blocks rows. There is little chemical justification for the presence of these elements between *s* and *p*-blocks.

(iv) Zn, Cd and Hg are not typical transition elements. They are in fact fairly typical representative elements, but do not fit easily into the scheme.

(v) In the long form of the periodic table there is no attempt to systematize the elements into the useful classification of metals and non-metals.

(vi) The terms usually associated with the elements in the long form of the table such as representative, transition, etc. should be regarded merely as convenient labels and have no definite associated meaning.

(vii) Like the Mendeleev's table, it fails to accommodate the lanthanides and actinides in the main body of the table.

(viii) The arrangement is unable to reflect the electronic configuration of many elements.

IUPAC Nomenclature for New Elements

Elements beyond uranium ($Z = 92$) are not found in nature. They are artificially prepared and named after the person or place of discovery. In recent years conflicts have arisen between scientists on the nomenclature of the artificially prepared elements. To avoid such anomalies the international Union of Pure and Applied Chemistry (IUPAC) in 1997-98 has recommended the name and symbol of new elements having atomic number beyond 103.

Atomic Number	**Name**	**Symbol**	**Atomic Mass**
104	Rutherfordium	Rf	261
105	Dubnium	Db	262
106	Seaborgium	Sg	266
107	Bohrium	Bh	264
108	Hassium	Hs	265
109	Meitnerium	Mt	268
110	Darmstadtium	Ds	271
111	Roentgenium	Rg	272

All these are synthetic elements created via nuclear bombardment. Few atoms of these elements have been made and their properties are very poorly understood.

1.11 ELECTRONIC BASIS FOR THE PERIODIC CLASSIFICATION

It is interesting to note that the number of elements in each period is related to the order of filling up of the various energy levels. On inspection, it can be seen that a new period begins when the first electron occupies a new energy shell (principal quantum level). Thus each new period begins with an element whose outermost shell configuration is ns^1. A period terminates when the s and p orbitals are fully occupied, i.e. the configuration is $ns^2\ np^6$. This, however, is not true for the first period as for $n = 1$ no p-orbitals exist.

The number of elements in each period is equal to the number of electrons that are required to fill up the various orbitals of a particular n value. This may be illustrated as follows:

For the first period $n = 1$ and other configuration for hydrogen, the first element is $1s^1$. Since in this level one more electron could be accommodated before the higher quantum shell ($n = 2$) starts filling up, we can have one more element in this period, having the configuration $1s^2$. This element is helium.

The second period starts with the electrons entering the second energy level ($n = 2$). Since there are only four orbitals (one s and three p) to be filled which can accommodate eight electrons, the second period accommodates eight elements (lithium, $2s^1$ to neon, $2s^2\ sp^6$).

In the third period, the electrons start entering the third energy level ($n = 3$). Of the nine orbitals of this energy level (one s, three p and five d), the five d orbitals have higher energy than $4s$ orbitals and hence only four orbitals (one s and

MODERN PERIODIC TABLE

s - orbital block **Groups** **p - orbital block**

d - orbital block

f - orbital block

1 S^1	2 S^2	3 d^1S^2		4 d^2S^2	5 d^3S^2	6 d^5S^1	7 d^5S^2	8 d^6S^2	9 d^7S^2	10 d^8S^2	11 $d^{10}S^1$	12 $d^{10}S^2$	13 S^2p^1	14 S^2p^2	15 S^2p^3	16 S^2p^4	17 S^2p^5	18 S^2p^6
1 H																		2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc		22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y		40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	• 58 71 Ce ⟶ Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	: 90 103 Th ⟶ Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq		116 Uuh		118 Uuo

• Lanthaanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
: Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig 1.19 The s, p, d & f blocks of periodic Table

three *p*) corresponding to $n = 3$ are filled. Consequently there are only eight elements in this period (sodium, $3s^1$ to argon, $3s^2\ 3p^6$).

In the fourth period ($n = 4$) the $4d$ and $4f$ orbitals are high energy orbitals. According to Aufbau order $3d$, $4s$ and $4p$ orbitals are to be filled up. Thus there are nine orbitals to be filled up and eighteen elements in this period.

The fifth period similarly begins with an element of $5s^1$ configuration and consists of eighteen elements corresponding to the filling up of $5s$, $4d$ and $5p$ orbitals.

For the sixth period ($n = 6$) we have sixteen orbitals (one $6s$, seven $4f$, five $5d$ and three $6p$) to be filled up and thus thirty two elements.

The seventh period ($n = 7$) begins with $7s^1$ configuration and can accommodate thirty two elements. However at present there are only 23 elements.

This relationship is summarized in Table 1.5.

Table 1.5. Number of Elements in Each Period

Period	Principal quantum number n	Orbitals being filled	No. of electrons needed to fill the orbitals	No. of elements
First	1	$1s$	2	2
Second	2	$2s$, $2p$	2 + 6	8
Third	3	$3s$, $3p$	2 + 6	8
Fourth	4	$4s$, $4d$, $4p$	2 + 10 + 6	18
Fifth	5	$5s$, $4d$, $5p$	2 + 10 + 6	18
Sixth	6	$6s$, $4f$, $5d$, $6p$	2 + 14 + 10 + 6	32
Seventh	7	$7s$, $5f$, $6d$, $7p$	2 + 14 + 10 + 6	23

1.12 CLASSIFICATION OF ELEMENTS BASED ON *s*, *p*, *d* AND *f* ORBITALS

A careful examination of the electronic configurations of the elements reveals that they may be divided into four sections or blocks in the long form of the periodic table. This division is on the basis of that whether the last electron goes to *s*, *p*, *d* or *f*-orbital. Thus the elements in the long form of the periodic table are divided into *s*, *p*, *d* and *f*-blocks. Figure 1.19 shows how the elements in which s, p, d and f-orbitals are being filled up are grouped naturally in the long form of the periodic table. For the purpose of this type of division of elements we consider the orbital of the highest energy into which the last electron goes. This orbital may not always belong to the outermost shell.

1. *s*-Block Elements

These are the elements in which the last electron enters the *s*-orbital of the outermost energy level. They have configuration ns^1 and ns^2 where *n* represents the last energy level. The elements of group 1 (H to Fr), group 2 (Be to Ra) and He (zero group) belong to this block, since their valence shell configuration is ns^1 and ns^2 respectively. The elements of this block are collectively known as *normal elements* or *representative elements.*

2. *p*-Block Elements

In the atoms of these elements the last electron enters the *p*-orbital of the ultimate (outermost) shell. In other words, in these elements *np* orbital is being progressively filled. Hence the name *p*-block elements. In the atoms of these elements the *ns* orbital is completely filled and hence the valence shell configuration of these elements varies from ns^2p^1 to ns^2p^6. The elements of group 13 (B to Tl), 14 (C to Pb), 15 (N to Bi), 16 (O to Po) 17 (F to At) and 18 (Ne to Rn) belong to this block. The elements of this block, like *s*-block elements, are also called *normal elements* or *representative elements.*

3. *d*-Block Elements

In these elements, either in their atomic state or in any of their common oxidation state, the last electron enters the *d*-orbital of the penultimate (inner to ultimate) shell, i.e., the last electron goes to $(n-1)d$ orbital. Hence the name *d*-block elements. The valence shell configuration of most of these elements varies from $(n-1)\,d^1\,ns^2$ to $(n-1)d^{10}\,ns^2$. The elements of the group 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 belong to this block. These elements are located in the middle of the periodic table and consist of metals only. *d*-block elements are also called *transition metals,* since their properties are intermediate between those of *s* and *p*-block elements.

4. *f*-Block Elements

In these elements, either in their atomic state, or in any of their common oxidation state, the last electron goes to $(n-2)$ *f*-orbital. In other words, in these elements, $(n-2)\,f$-orbital is being progressively filled. Hence the name *f*-block elements. The valence shell electronic configuration of the atoms of these elements is represented as:

$$(n-2)\,f^{1,\,\ldots\ldots,\,7,\,9,\,\ldots\ldots,\,14}\,(n-1)\,d^{0,\,1},\,ns^2$$

These elements are located in group IIIB and have been given a separate place at the bottom of the periodic table. *f*-block elements are also called *inner transition elements* and are classified into two series viz. 4*f* and 5*f* corresponding to the filling of 4*f* and 5*f* orbitals.

1.13 THE TYPES OF ELEMENTS

On the basis of electronic configurations we may classify elements into four general types; the inert gas elements, the representative elements, the transition elements, and the inner transition elements. The classification of the elements into these groups is dependent on whether the particular orbitals (*s*, *p*., *d* or *f*) are complete or incomplete.

1. Inert Gas Elements

With the exception of helium which has the configuration $1s^2$, all of the members of this group of elements may be characterized by the configuration $ns^2\,np^6$. This is the smallest class of elements, all of which are chemically inert because of the high stability associated with the completed *s* and *p* orbitals.

2. Representative Elements (or Non-Transition Elements)

The members of this group of elements have their outer electron shell incomplete. Thus, any atom with an outer electron configuration from ns^1 to $ns^2\ np^6$ belongs to this class. There will be 44 members in this group if the above electronic arrangement is strictly followed. This includes the copper and zinc families. Some authors prefer to consider these latter six metals as transition elements because of their physical and chemical similarities with the transition metals.

The chemical behaviour of the representative elements will be determined to a large extent by the tendency for these atoms to gain, lose, or share electrons in such a manner as to attain the electronic configuration of the inert gas of next higher or lower atomic number, or the so called pseudo-inert gas configuration $(n-1)s^2\ p^6\ d^{10}$. Many of the metals, and all of the nonmetals and metalloids constitute the group of representative elements.

3. Transition Elements

The transition elements have their two outer principal quantum shells incomplete and are characterized specifically by their incomplete $(n-1)\ d$ orbitals. Because of the extra stability which is associated with empty, half-filled and filled sub shells, there are some apparent anomalies in electronic arrangements in the transition series. This is illustrated by the chromium and copper configurations in the first transition series:

$$\text{Cr} : 3d^5\ 4s^1$$

$$\text{Cu}: 3d^{10},\ 4s^1$$

There are four transition series corresponding to unfilled $3d$, $4d$, $5d$ and $6d$ orbitals. The series begins with the group IIIA (or Group 3) elements Sc, Y, La and Ac, and the first three series end, by definition, with Ni, Pd and Pt, respectively. These elements show striking similarities to each other, particularly in their physical properties. The oxidation states are numerous, compound are highly coloured and coordination compounds are stable and large numbers are known.

4. Inner Transition Elements

By definition, these elements are transition series elements, but they have an additional feature in their electronic arrangement, i.e. the outer three principal quantum levels are incomplete due to incomplete $(n-2)f$ orbitals. In general, the configuration for this class may be given as $(n-2)f^{1-14}\ (n-1)s^2\ p^6\ d^{1 \text{or} 0}\ ns^2$. The empty, half-filled and filled sublevel stability rule is valid here also, and indeed this is invoked to explain the oxidation states other than 3 among the lanthanides. An important feature of these elements is the similarity in chemical and physical properties which they exhibit.

The first series ($4f$) begins at cesium (atomic number 58) and ends at lutetium (71). The second inner transition series exists in which $5f$ orbitals are being occupied. This series starts with thorium (At.No.90) and ends with lawrencium (At. No. 103).

1.14 MODERN TRENDS IN PERIODIC TABLE BASED ON CHEMICAL REACTIVITIES OF ELEMENTS

In the block-wise division of the periodic table four blocks clearly identified are — *s*-block, *p*-block, *d*-block and *f*-block. In the build up of atoms, elements belonging to a particular block receive electrons in *s*, *p*, *d* or *f* orbitals in their atoms. Further, the elements of a particular block are also characterized by a certain set of physical and chemical properties. The elements of *s* and *p*-blocks are collectively known as *representative elements.* The *d*-block elements are known as *transition elements* and *f*-block elements as *inner transition elements.* The chemistry of the representative elements is so much entirely different from the chemistry of transition and inner transition elements that a separate study of the representative elements is not only desirable but necessary.

The properties of different compounds depend upon the nature of constituting elements. We can find a number of correlations between the properties of compounds and the position of their constituent elements in the periodic table. Such correlations are especially clear in hydrides, oxides, halides and salts of oxoacids.

1. Hydrides

It is the general name for all the hydrogen binary compounds and the specific name for the hydrogen compounds of group IA and IIA elements. The hydrides of alkali and alkaline earth metals are salt like compounds. The hydrides of transition metals are hard compounds having high melting points. The hydrides of metalloids are usually gases or liquids with low boiling points. Hydrides of non-metals are also gases or liquids with low boiling points. It is observed that except for group IA and IIA, as we proceed down a group the stability of hydrides decreases. The chemical behaviour of the hydrogen compounds is dependent to a large extent on the relative electronegativities of the other element and hydrogen.

2. Oxides

All the representative elements except some of the noble gases form oxides; almost all the elements form more than one oxides. Since oxygen is the most electronegative element (except flourine), the partial charge on oxygen in all oxides except OF_2 and O_2F_2 is negative. Oxides of alkali and alkaline earth metals are generally ionic solids. Oxides of metallic elements towards the middle of the table and of semi-metals are solid and not usually ionic. Oxides of non-metals are discrete molecules and exist as liquids or gases at room temperature.

Ionic oxides react with water to form basic hydroxides.

$$CaO + H_2O \longrightarrow Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-_{(aq)}$$

Covalent oxides react with water to give oxoacids, these oxides are known as acid anhydrides.

$$SO_3 + H_2O \longrightarrow H_2SO_4 \longrightarrow H^+_{(aq)} + HSO_4^-$$

The elements of IIIA group such as Al forms amphoteric oxide which does not dissolve in water but does dissolve in acidic or basic medium.

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O \longrightarrow 2Al(OH)_4{}^-_{(aq)}$$

The following trends are observed in the nature of oxides in the periodic table.

(i) The general trend in a given period from left to right is the increase of acidity and decrease of basicity.

(ii) The general trend within a group, downward is toward increased basicity and (or) decreased acidity of oxides.

(iii) For any element the oxide tends to become more acidic, the higher the oxidation of the element.

3. Halides

With the exception of few elements, all other elements combine with halogens. Each halogen is the most electronegative element in its period. In general the halides of the electropositive metallic elements, such as those of 1A and IIA are ionic salts. The ionic character increases on proceeding down the group of the metals and up the group of halogens.

Ionic character of the halides decreases on proceeding from left to right across a period. Thus LiCl is an ionic compound, $BeCl_2$ has considerable covalent character and BCl_3 is a typical covalent compound. The halides of non-metals are typically gases such as BCl_3 and NCl_3 and volatile liquids such as CCl_4.

The halides of most non-metals hydorlyse to give the oxoacid of the element and the corresponding hydrohalogen acid. As the metallic properties of the central atom increase, as is the trend in going down a group, hydrolysis is incomplete, e.g.,

$$SbCl_3 + 3H_2O \longrightarrow SbOCl + 2H_3O^+ + 2Cl^-$$

Carbon tetrachloride, CCl_4 is one of the four non-metallic halides that resists hydrolysis. It is immiscible with water and relatively inert. In contrast to CCl_4, $SiCl_4$ reacts vigorously with water.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{silicic acid}}{Si(OH)_4} + 4HCl$$

In group IVA $GeCl_4$ and $SnCl_4$ are easily hydrolysed by water, $PbCl_4$ is very unstable and decomposes to give lead (II) chloride.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

4. Salts of Oxoacids

The tendency to form salts of oxoacids is a reflection of the electropositive character of an element. The most electropositive elements, the alkali metals, form salts even with weak acids. With decreasing metallic character in a period on proceeding from left to right the tendency to form cations decreases and hence, the tendency to form oxosalts. In the same group this tendency increases in going down a group. For example caesium salts are much more ionic than those of lithium or sodium.

1.15 PERIODICITY OF PROPERTIES

Most of the chemical and physical properties of the elements are related to electronic configurations of their atoms. As we have seen, the electronic configurations of the elements show a periodic variation with increasing atomic number. Consequently, the elements also display periodic variations in their physical and chemical behaviour.

The term periodicity of properties indicates that the elements with similar properties reappear at certain regular intervals of atomic number in the periodic table. In order to understand the concept of periodicity of properties we may consider the properties of the elements of groups 1 (*Alkali metals*) and 17 (*Halogens*). The members of these groups along with the valence shell configurations are given in Table 1.6.

Table 1.6. Elements of Group 1 and 17

Periodic Number	Group 1	Group 17
1	H (1) $1s^1$	
2	Li (3) $2s^1$	F (9) $2s^2p^5$
3	Na (11) $3s^1$	Cl (17) $3s^2p^5$
4	K (19) $4s^1$	Br (35) $4s^2p^5$
5	Rb (37) $5s^1$	I (53) $5s^2p^5$
6	Cs (55) $6s^1$	At (85) $6s^2p^5$
7	Fr (87) $7s^1$	

The examination of the properties of these elements will show that the elements belonging to the same group have similar properties. In other words we can say that the atomic number intervals at which the elements with similar properties reappear are 2, 8, 8, 18, 18 and 32, i.e., we have to pass 2, 8, 8, 18, 18 and 32 elements before we come across an element with similar properties. This repetition of the elements with similar properties in the order of increasing atomic number as in the periodic table is known as *periodicity of properties* and the number 2, 8, 18 and 32 are called *magic numbers*.

Cause of Periodicity of Properties

What is the cause of periodicity of properties, i.e., why do the elements placed in the same group have similar properties?

In order to answer this question, we may again consider the valence shell electronic configurations, for example, of the elements of groups 1and 17 as shown in Table 1.7. An examination of the valence shell configurations of the elements shows that the elements show periodicity of properties, i.e., the elements belonging to the same group have the same valence-shell electronic configuration. Thus we see that in any group similar valence shell electronic configurations of the elements reoccur after certain regular intervals of atomic number. It is this reoccurrence of similar valence-shell electronic configurations of the elements at certain regular intervals of atomic number which becomes the cause of periodicity of properties.

We have already said that, according to the modern periodic law, the properties of the elements like atomic volume, atomic and ionic radii, ionization potential, electron affinity, electronegativity etc. are periodic functions of their atomic numbers. Here the word *periodic* means that with the rise of atomic number of the elements in the same period or group, there is a gradual variation (i.e., increase or decrease) in a particular property of the element. These properties depend on the electronic configuration of the atoms of the elements. Some of such properties which are more useful to the students of chemistry are: *(i)* Atomic volume *(ii)* Size of atoms and ions *(iii)* Ionization potential *(iv)* Electron affinity *(v)* Electronegativity *(vi)* Bond energy *(vii)* Charge density of ions.

1.16 SOME IMPORTANT CONCEPTS

Before discussing the periodic properties we shall discuss some important concepts which are very useful in having a clear understanding of periodic properties. These concepts are:

- *(i)* Shielding or screening effect.
- *(ii)* Effective nuclear charge.
- *(iii)* Penetration of orbitals.

Now we shall discuss each concept separately.

1. Shielding or Screening Effect

In a multi-electron atom the valence-shell electrons are attracted by the nucleus and also at the same time repelled by the electrons present between the nucleus and the valence-shell electrons. Thus the nucleus exerts an attractive force on the valence shell electrons while the inner-shell electrons exert a repulsive force on the valence-shell electrons. The combined effect of these two forces is that the actual force exerted by the nucleus on the valence-shell electrons is partially decreased or weakened by the presence of repulsive forces exerted by the inner-shell electrons on the valence-shell electrons. Thus the valence shell electrons experience less attraction or pull towards the nucleus. This decrease in the attractive force exerted by the nucleus on the valence-shell electrons due to the presence of intervening electron is known as *shielding* or *screening effect.* This concept has the following applications:

- *(i)* The concept of shielding effect has been used to explain why the ionization potential values of the elements of a given group decrease on descending the group.
- *(ii)* This concept has also been used to explain that when we proceed from an inert gas to alkali metal, a large decrease in the ionization potential is observed.

2. Effective Nuclear Charge

It is due to the shielding effect of the inner-electrons on the outer-electrons that the valence electrons experience less attraction or pull from the nucleus. The decrease in the attractive force reduces the nuclear charge, Z represented by the atomic number of the element. This decreased nuclear charge is called the *effective nuclear charge* and is represented by Z_{eff}. It is given by the relation:

$$Z_{eff} = Z - \sigma$$

Here σ is constant which is called *screening constant* and Z is the actual nuclear charge. This constant is a measure of the extent to which the other electrons in an atom are able to screen the nucleus from the chosen electron. Thus, effective nuclear charge is defined as the difference between the nuclear charge (Z) and the screening constant (σ).

Greater is the number of intervening electrons between the nucleus and the outer electrons, more will be the magnitude of σ and hence the magnitude of effective nuclear charge will decrease. The effective nuclear charge is a concept often used in qualitative explanation of many properties and trends in properties. For example,

(i) Why 4*s* orbital is filled before 3*d* orbital?

(ii) Why 4*s* electrons are removed before 3*d* electrons in the conversion of 3*d* transition elements into cations?

(iii) The successive ionization potentials of an atom are in the following order:

$$I_1 < I_2 < I_3 \ .....$$

This order can be explained on the basis of effective nuclear charge.

(iv) A cation is smaller in size than its parent atom.

(v) An anion is bigger in size than its parent atom etc.

3. Penetration of Orbitals

The extent to which an orbital of a shell interacts with the lower quantum shell orbitals is referred to as the *penetration of the orbitals.* We are familiar with the fact that the energy of 4*s* orbital is lower than that of 3*d* orbitals and that the filling of 4*s* orbital commences even before the third shell has been completely filled. This is known as the penetration of the 3*d* orbitals by the 4*s* orbital.

The penetration is more as the shell number increases. Thus 5*s* orbital penetrates the 4*d* and 4*f* orbitals. The penetration of the orbitals of a given quantum shell follows the following order:

$$s > p > d > f$$

1.17 SIZE OF ATOMS AND IONS

(Atomic and Ionic Radii)

According to the wave-mechanical picture of the atom, the electron cloud around the nucleus extends to infinity. The size of an atom is therefore difficult to define. However, the distance between the nucleus and a point where the electron density is effectively zero (i.e., negligible), may be defined as the *atomic radius.* Again though the boundary surface of the nucleus is not well-defined, its central point may be considered to represent the nucleus and may be taken as reference point. The distance between two nuclei can be determined by X-ray spectroscopy. Thus, to define atomic radius is quite arbitrary and due to this vagueness in concept, a number of radii have been defined for an atom which pertain to different types of bonding between the atoms. Some of these radii are:

- *(i)* Atomic or metallic radius.
- *(ii)* Ionic radius.
- *(iii)* Covalent radius.
- *(iv)* Van der Walls radius.

1. Atomic Radius

The atomic radius of an atom is defined as one-half of the inter nuclear distance between two identical atoms in a chemical bond. For example, the atomic radius of bromine is measured with the help of Br — Br bond in Br_2 as under:

The bond length of $Br_2 = 2.66$ Å

The atomic radius of Br = ½ (2.66) = 1.33 Å

The atomic radius as obtained from the metallic crystalline structure of a metal is referred to the *crystal* or *metallic radius.* Thus it is used for metal atoms which are assumed to be closely packed spheres in the metallic crystal and is defined as one-half of the distance between the nuclei of two adjacent atoms in the metallic close-packed crystal lattice in which the metal exhibit a coordination number of 12. For example, the internuclear distance between two adjacent Na atoms in a crystal of sodium metal is 3.80 Å and hence the atomic radius of sodium metal = 3.80/2 = 1.90 Å.

Since we cannot isolate an individual atom and measure its diameter the way we can measure the diameter of a gold-ball, atomic sizes are determined indirectly. The arrangement of the atoms or ions in the molecules can be elucidated by the techniques of X-ray diffraction, electron diffraction and infrared spectroscopy. It is thus possible to evaluate the distance between the nuclei of adjacent atoms or ions. Atomic or ionic radii then can be obtained by assuming that the internuclear distance is the sum of the radii of two touching spherical atoms or ions. For a homonuclear diatomic molecule, the atomic radius is simply one-half of the internuclear distance as shown in Fig. 1.12. Similarly, in a metallic element the atomic (metallic radius) is one-half of the internuclear distance between the nearest atoms.

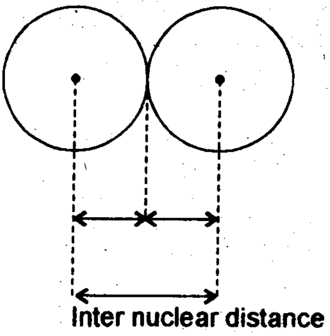


Fig. 1.12. The atoms as two touching spheres.

Atomic radii are useful for comparison of the sizes of different atoms, but they depend upon the method of measurement and the physical state of the sample. Metallic radii of some common elements are given in Table 1.7. These values are for coordination number 12.

Table 1.7. Atomic radii of some common elements (in Å)

Li	Be											B	C	N	O	F
1.57	1.12											0.88	0.77	0.74	0.66	0.64
Na	Mg											Al	Si	P	S	Cl
1.91	1.60											1.43	1.18	1.10	1.04	0.99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
2.35	1.97	1.64	1.47	1.35	1.29	1.37	1.26	1.25	1.25	1.28	1.53	1.53	1.22	1.21	1.04	1.14
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
2.50	2.15	1.82	1.60	1.47	1.40	1.35	1.34	1.37	1.37	1.44	1.52	1.67	1.58	1.41	1.37	1.33
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
2.72	2.24	1.72	1.59	1.47	1.41	1.37	1.35	1.36	1.39	1.44	1.55	1.71	1.75	1.82		

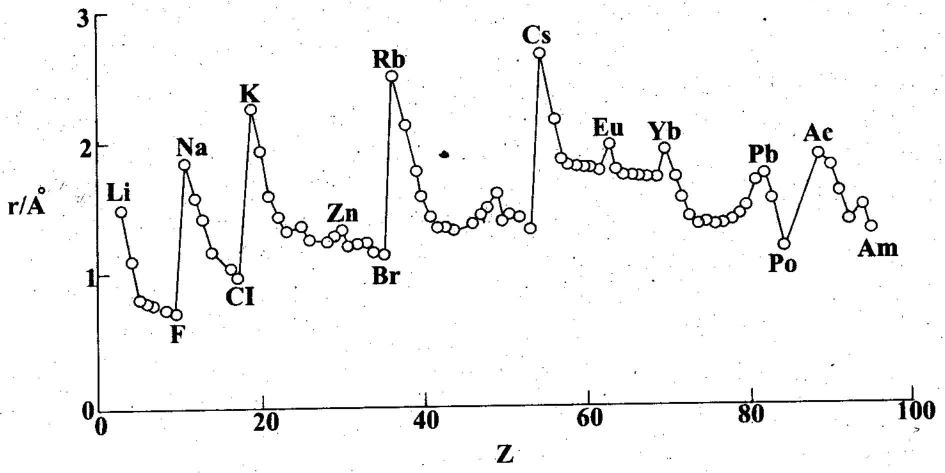


Fig. 1.13. The variation of atomic radii through the period table. Note the contraction of radii following the lanthanides in Period 6. Metallic radii have been used for the metallic elements and covalent radii have been used for the nonmetallic elements.

Units of Atomic Radii

The unit that has long been used to describe atomic dimensions is the Angstrom (Å). In SI units the other units such as nanometer (nm) and picometer are in use.

$$1\ \text{Å} = 1 \times 10^{-10}\ \text{m} = 1 \times 10^{-8}\ \text{cm} = 0.10\ \text{nm} = 100\ \text{pm}$$

Periodic Trends in Atomic Radii

(a) Variation in a Period

We know that the number of shells in all the elements of a given period remains the same but the value of effective nuclear charge increases from left to right. The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of the atoms and ions goes on decreasing from left to right. Thus in going from left to right in a period of *s* and *p*-block elements atomic and ionic radii decrease with the increase of atomic number.

(b) Variation in a Group

As we move down a group, atomic as well as ionic radii increase with the increase of atomic number. On descending a group the magnitude of the effective nuclear charge acting on the valence shell electrons of the elements remains the same. Thus the concept of effective nuclear charge cannot be used to explain the successive increases in the atomic and ionic radii of the elements in a given period. However, the other factor namely the number of shells or principal quantum number (*n*) can be used to explain the increase. As the number of shells or principal quantum number (n) increases from 2 to 6, the outermost shell electrons get farther and farther away from the nucleus and hence atomic and ionic radii increase. Thus it is due to the progressive addition of a new shell that the atomic or ionic radii increase when we proceed from top to bottom in a group.

(c) Variation in Transition Elements

As we proceed horizontally across the transition series of elements there is a gradual decrease in atomic and ionic radii. However, this decrease is not uniform and is slight when compared to the decrease observed within a given period of representative elements. The reason for this behaviour is that in case of transition elements the differentiating electrons enter the inner shell which is $(n - 1)d$ sub-shell. The added electrons effectively screen much of the added nuclear charge from the outer ns electron, and the size of the atom remains almost the same. However in a given family (i.e., group) both the radii increase with increase in atomic numbers.

2. Ionic Radius

Ions are produced when neutral atoms gain or lose electrons. Ionic radius may be defined as the distance between the nucleus of an ion and the point upto which the nucleus is able to exert its influence on the electron cloud. Ionic radii together with covalent or metallic radii are listed for certain elements in Table 1.8.

The calculation of ionic radii is not simple as in the case of covalent or metallic radii since like atoms do not form ionic bonds. The measured distance between the nuclei held by ionic bonds cannot be halved to give the desired ionic radii. The internuclear distances in ionic solids give sums of ionic radii. Therefore they indicate only differences in Ionic size. For example, in NaF the internuclear distance between Na^+ and F^- is 2.31 Å and that in NaCl is 2.76 Å. These values indicate that the radius of the Cl^- ion is greater than that of F^- ion by 0.45 Å, but the values give no indication of the ionic size. Since like atoms do not form ionic bonds with each other, the size of an ion can be determined only when that of another atom is known.

Table 1.8. Ionic Radii (in Å) of Some Elements

Li^+	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F^-
0.59(4)	0.27(4)	0.12(4)			1.71	1.35(2)	1.28(2)
0.76(6)						1.38(4)	1.31(4)
						1.40(6)	1.33(6)
						1.42(8)	
Na^+	Mg^{2+}	Al^{3+}			P^{3-}	S^{2-}	C^{l-}
0.99(4)	0.49(4)	0.39(4)			2.12	1.84(6)	1.67(6)
1.02(6)	0.72(6)	0.53(6)					
1.16(8)	0.89(8)						
K^+	Ca^{2+}	Ga^{3+}			As^{3-}	Se^{2-}	Br^-
1.38(6)	1.00(6)	0.62(6)			2.22	1.98(6)	1.96(6)
1.51(8)	1.12(8)						
1.59(10)	1.28(10)						
1.60(12)	1.35(12)						
Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sn^{4+}		Te^{2-}	I^-
1.49(6)	1.16(6)	0.79(6)	1.22(8)	0.69(6)		2.2(6)	20.6(6)
1.60(8)	1.25(8)	0.92(8)					
1.73(12)	1.44(12)						
Cs^+	Ba^{2+}	Tl^{3+}					
1.67(6)	1.49(6)	0.88(6)					
1.74(8)	1.56(8)						
1.88(12)	1.75(12)						

*Numbers in parentheses are the coordination number of the ion. 1Å ≐ 100 pm.

Source: R.D. Shannon, Acta Crystallogr. A32, 751 (1976). The readius of the six-coordinate NH_4^+ ion is approximately 1.46 Å

Ionic radii can thus be computed from the internuclear distances in the ionic crystals, provided the ionic radius of one ion is known.

Periodic Trends in Ionic Radii

Like atomic radii ionic radii also decrease along a period as we proceed from left to right in a periodic table and increase along a period with the increase of atomic numbers. This has already been explained in periodic trends of atomic radii.

A Cation is smaller in Size than its Parent Atom

The decrease in the size of cation as compared to its parent atom can be explained on the basis of the concept of effective nuclear charge. A cation is formed by the removal of one or more electrons from the atom. Thus a cation has lesser number of electrons than its parent atom. With the decrease of the number of electrons the magnitude of screening constant, σ also decreases. The decrease in the magnitude of σ

increases the magnitude of effective nuclear charge. The increased effective nuclear charge pulls the electron cloud of cation inward nearer to the nucleus and thus makes the cation smaller in size than its parent neutral atom. Thus alkali metal cations are smaller in size than the alkali metal atoms as shown below:

Elements	Atomic Radius (Å)	Cation	Radius of Cation (Å)
Li	1.22	Li^+	0.60
Na	1.54	Na^+	0.85
K	2.03	K^+	1.33

Size of Cations of the Same Element but in Different Oxidation States

The size of the cations of the same element in different oxidation states decreases with the increase in the oxidation state, e.g., in case of the pair: Fe^{2+} — Fe^{3+}, the radius of Fe^{2+} ion is greater than that of Fe^{3+} ion ($Fe^{2+} = 0.76$ Å, $Fe^{3+} = 0.64$ Å).

The decrease in size with the increase in oxidation state can also be explained on the basis of similar arguments as explained above in case of cationic size.

An Anion is Bigger in Size than its Parent Atom

The increase in the size of the anion as compared to its parent atom can also be explained on the basis of the concept of effective nuclear charge. We know that an anion is formed by adding one or more electrons to the neutral atom. Thus an anion has more electrons than its parent atom. With the increase of number of electrons the magnitude of screening constant, σ also increase. The increase in the magnitude of σ decreases the magnitude of effective nuclear charge. The decreased effective nuclear charge pulls the electron cloud of anion less tightly from the nucleus and thus makes the anion larger in size than its parent atom. Thus halide ions are bigger in size than the halogen atoms from which they have been derived as shown below:

Elements	Atomic Radius (Å)	Anion	Radius of Anion (Å)
F	0.72	F^-	1.36
Cl	0.99	Cl^-	1.81
Br	1.14	Br^-	1.95

Size of Iso-electronic Species

Iso-electronic species are the atoms or ions which have the same number of electrons and the electronic configuration but different magnitude of nuclear charge. For example, N^{3-}, O^{2-}, F^-, Ne, Na^+, etc. are iso-electronic species, since these have the same number of electrons (10 electrons) and same configuration viz. Ne-type configuration

$(1s^2, 2s^2 p^6)$. The size of iso-electronic species decreases with the increase of their atomic number (nuclear charge) as shown in Table 1.9.

Table 1.9 Ionic or Atomic Radii (in Å) of Iso-electronic Species

Electron	**Charge on the Ion**						
Configuration	**–3**	**2–**	**–1**	**0**	**1**	**2**	**3**
$2s^2$			H 1.50	He 1.20	Li 0.66		
$2s^2\,2p^6$	N 1.50	O 1.40	F 1.36	Ne 1.40	Na 0.97	Mg 0.67	Al 0.55
$3s^2\,3p^6$	P 1.90	S 1.84	Cl 1.81	Ar 1.70	K 1.33	Ca 0.99	Sc 0.81

The decrease in size with the increase in atomic number can be explained on the basis of effective nuclear charge. With the increase in atomic number, the magnitude of effective nuclear charge in a period also increases. The increased effective nuclear charge pulls the electron cloud of the iso-electronic species inward nearer to the nucleus and thus decreases their size successively.

Example 1.4

Ionic radius of Na^+ ion is 0.95 Å and the internuclear distance between the ion-pairs in NaCl ionic crystal is equal to 2.76 Å. Calculate the radius of Cl^- ion.

Solution

$$d(Na^+ — Cl^-) = r_{Na^+} + r_{Cl^-}$$

$$\therefore \quad 2.76 = 0.95 + r_{Cl^-}$$

$$\therefore \quad r_{Cl^-} = 2.76 - 0.95 = 1.81 \text{ Å}$$

Example 1.5

Referring to a periodic table, arrange the following atoms in order of increasing radius: P, Si, N.

Solution

Note that N and P are in the same group (Group 15) so that radius of N is smaller than that of P (atomic radius increases as we go down a group). Both Si and P are in the 3rd period, and Si is to the left of P. Therefore, the radius of P is smaller than that of Si (atomic radius decreases as we move from left to right across a period). Thus the order of increasing radius is

$$N < P < Si$$

Example 1.6

In each f the following pairs, indicate which one of the two species is larger:

(i) N^{3-} or F^-

(ii) Mg^{2+} or Ca^{2+}

(iii) Fe^{2+} or Fe^{3+}

Solution

(i) N^{3-} and F^{-} are isolectronic anions. Since N^{3-} has three negative charges and F^{-} has one negative charge, N^{3-} is larger.

(ii) Both Mg and Ca belong to group 2. Thus the Ca^{2+} ion is larger than Mg^{2+} ion because Ca lies below Mg.

(iii) Both ions have the same nuclear charge, but Fe^{2+} has one more electron and hence greater electron-electron repulsion. The radius of Fe^{2+} ion is larger.

1.18 IONIZATION POTENTIAL OR IONIZATION ENERGY

The ionization energy of an element is the minimum amount of energy required to remove an electron from a gaseous atom in its ground state. Thus, ionization energy for an element X is the energy required to carry out the reaction

$$X_{(g)} \longrightarrow X^{+} + e$$

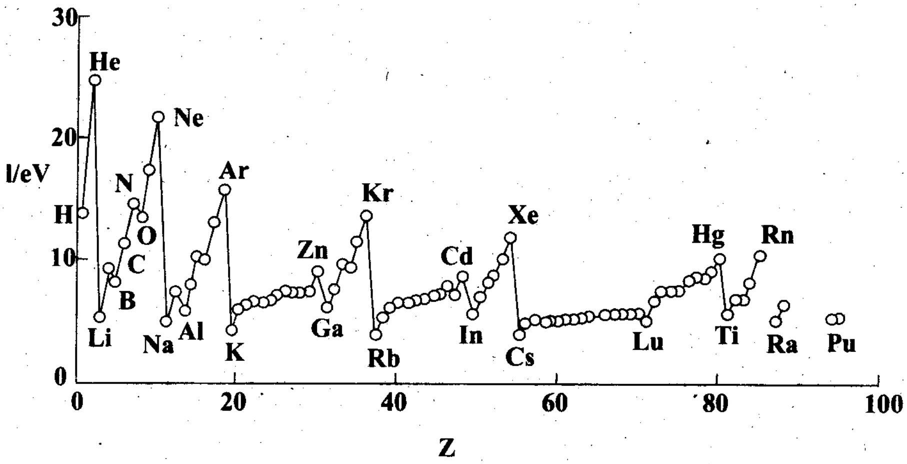


Fig. 1.14. The variation of first ionization energies through the periodic table.

Ionization energy is an atomic property which is shown by the atoms of all the elements. The magnitude of ionization energy is a measure of the effort required to force an atom to give up an electron, or of how "tightly" the electron is held in the atom. The higher the ionization energy, the more difficult it is to remove the electron. With the help of this property a number of other properties of the elements like reducing power, metallic character etc. can be explained.

Ionization energy is also called *ionization potential,* since it represents the amount of potential (voltage) required to remove the most loosely bound electron from the gaseous atom of an element to get a gaseous cation. Since in the gaseous phase the atom and the ion are isolated from all external influences, the ionization energy is exactly the energy with which the atom binds its electron. It, therefore, gives a quantitative measure of the stability of the isolated atom. Ionization energies are usually expressed in electron volts (eV) per atom, or in kilo joules per mole of atoms (kJ mol^{-1}) or in kilo calories per mole.

$$1 \text{ eV atom}^{-1} = 96.48 \text{ kJ mol}^{-1} = 23.06 \text{ kcal mol}^{-1}$$

Values of first ionization energies (in kJ mol^{-1}) of representative elements are shown in Table 1.10.

Table 1.10. First and Higher Ionization Energies (in eV) of Representative Elements

H							He
13.60							24.59
							54.51
Li	Be	B	C	N	O	F	Ne
5.32	9.32	8.30	11.26	14.53	13.62	17.42	21.56
75.63	18.21	25.15	24.38	29.60	35.11	34.97	40.96
122.4	153.85	37.93	47.88	47.44	54.93	62.70	63.45
Na	Mg	Al	Si	P	S	Cl	Ar
5.14	7.64	5.98	8.15	10.48	10.36	12.97	15.76
47.28	15.03	18.83	16.34	19.72	23.33	23.80	27.62
71.63	80.14	28.44	33.49	30.18	34.65	39.65	40.71
		119.96					
K	Ca	Ga	Ge	As	Se	Br	Kr
4.34	6.11	6.00	7.90	9.81	9.75	11.81	14.00
31.62	11.87	20.51	15.93	18.63	21.18	21.80	24.35
35.71	50.89	30.71	34.22	28.34	30.82	36.27	36.95

Rb	Sr	In	Sn	Sb	Te	I	Xe
4.18	5.69	5.79	7.34	8.64	9.01	10.45	1[illegible]13
27.28	11.03	18.87	14.63	18.59	18.60	19.13	[illegible]
40.42	43.63	28.02	30.50	25.32	27.96	33.16	32.[illegible]
Cs	Ba	Tl	Pb	Bi	Po	Ar	Rn
3.89	5.21	6.11	7.42	7.29	8.42	9.64	10.[illegible]
25.08	10.00	20.43	15.03	16.69	18.66	16.58	
35.24	37.51	29.83	31.94	25.56	27.98	30.06	
	Ra						
	5.28						
	10.15						
	34.20						

*To convert-to kJ mol^{-1}, multiply by 96,485..

Source: C.E. Moore, Atomic energy levels, NBS Circular 467 (1949-58)

Ionization Energies of Many-Electron Atoms

For a many-electron atom, the amount of energy required to remove the first electron from the atom in the ground state,

$$\text{Energy} + X_{(g)} \longrightarrow X^{+}_{(g)} + e^{-} \qquad \text{..... 1.30}$$

is called the *first ionization energy (I_1)*. In equation 1.30, X represents an atom of any element, e is an electron, and g denotes the gaseous state. Unlike an atom in the condensed phases (liquids and solids), an atom in the gaseous phase is virtually uninfluenced by its neighbours. The *second ionization energy (I_2)* and the *third ionization energy (I_3)* are shown in the following equations:

$$\text{Energy} + X^{+}_{(g)} \longrightarrow X^{2+}_{(g)} + e^{-} \qquad \text{second ionization}$$

$$\text{Energy} + X^{2+}_{(g)} \longrightarrow X^{3+}_{(g)} + e^{-} \qquad \text{third Ionization}$$

The pattern continues for the removal of subsequent electrons.

After an electron is removed from a neutral atom, the repulsion among the remaining electrons decreases. Removal of a second electron from a singly charged positive gaseous ion $X^{+}_{(g)}$ needs more energy than for the removal of the first electron. This is so because attraction between the positive ion and electron is greater than between the neutral atom and the electron. Similarly, removal of a third electron from the ion is even more difficult. Thus, ionization energies always increase in the following order:

$$I_1 < I_2 < I_3 < \text{.....}$$

In comparing ionization energies, we must be careful to compare the energy for ionization of species with the same charge.

Factors Affecting Ionization Energies

The first ionization energy is a measure of the strength with which the nucleus holds the outermost electron. Thus, the magnitude of ionization energy depends upon:

1. **Effective Nuclear Charge.** Greater is the magnitude of effective nuclear charge, greater is the electrostatic force of attraction exerted by the nucleus on the outer electrons. Thus it would be more difficult to remove the outer shell electron from an atom with higher effective nuclear charge.
2. **Size of the Atom.** Greater is the size of an atom, more far is the outermost shell electron from the nucleus and hence lesser will be the force of attraction exerted by the nucleus on the valence electron. Thus with the increase of atomic size, it would be more and more easy to remove an electron from the outer-most shell.
3. **Shielding Effect.** Greater is the magnitude of shielding effect working on the valence-shell electron, smaller is the magnitude, of the force of attraction between the nucleus and valence shell electron and hence lower is the amount of energy (ionization energy) to remove the valence-shell electron.
4. **The Extent of Penetration of Valence-Electrons.** It has been found that the extent of penetration of valence-electrons in a given principal energy level decreases in the order:

   $$s > p > d > f$$

   This corresponds to the extent of binding of various electrons. An ns electron is more tightly bound than any *np* electron, which, in turn, is more tightly bound than any *nd* electron etc.
5. **The Nature of Configuration.** According to Hund's rule, half-filled (ns^1, np^3, nd^5) or completely-filled (ns^2, np^6, nd^{10}) orbitals are comparatively more stable and hence more energy is needed to remove an electron from such orbitals. Thus ionization energy of an atom having half-filled or completely filled atomic orbitals in its electronic configuration is relatively higher than that expected normally from its position in the table.

Periodic Trends in Ionization Energies

(a) **Variation in a Group.** When we proceed from top to bottom in a group of representative elements, the ionization energy values of the elements go on decreasing. On descending a group the size of the atom (i.e., the value of principal quantum number) and shielding effect caused by the intervening electrons on the valence-electrons increase, which result in the decrease of ionization energy.

The Group IA metals have very low first ionization energies, as is expected since these elements have only one electron in their highest energy levels (..... ns^1). The first electron added to a principal energy level is easily removed.

The first ionization energies for the Group IIA elements decrease in moving down the group but are significantly higher than those of Group IA elements in the same periods. This is due to the fact that Group IIA elements have smaller atomic radii and high effective nuclear charges. Thus, their valence-electrons are held more tightly than those of the preceding alkali metals of the same period. Moreover, since a pair of electrons in an *s*-orbital is more stable than a single electron, more energy is required to remove an electron from the filled outermost *s*-orbital of Group IIA elements than to remove the single electron from the half-filled outermost *s*-orbitals of the alkali metals.

(b) **Variation in a Period.** In general, as we move from left to right in a period, the ionization energies of the elements increase due to successive increase in the nuclear charge and decrease in atomic size. Both effects are due to the fact that on moving across a period from one element to the other, electrons are being successively added to the same principal energy level while the nuclear charge is increasing. These electrons shield each other poorly from the increasing nuclear charge. As a result, there is an increase in the effective nuclear charge along the period. This causes a decrease in atomic radius and an increase in ionization energy along the period. However there are certain elements which show irregular trends.

Boron (B) has lower ionization energy than that of beryllium (Be). It is due to the fact that it has only single electron in its outermost p-orbital, hence it requires less energy to remove a p-electron than an s-electron from the same principal energy level since an np orbital is higher in energy than an ns orbital.

The ionization energy of oxygen (O) is slightly less than that of nitrogen (N). The electronic configuration of nitrogen is $1s^2, 2s^2, 2p^3$ in which the three *p*-orbitals are occupied by one electron each. The additional electron in oxygen must enter in one of these *p*-orbitals. It will then encounter repulsion and will therefore be less stable and easier to remove from the oxygen atom.

Similarly in the 3rd period higher ionization energies of Mg as compared to Al and P as compared to S can also be explained on the same line of arguments.

1.19 ELECTRON AFFINITY

The electron affinity (EA) of an element is defined as the amount of energy released when an electron is added to an isolated gaseous atom to form an anion. The current convention is to assign a negative value when energy is released and a positive value when energy is absorbed. This is consistent with thermodynamic convention. Thus electron affinity for an atom $X_{(g)}$ can be defined by the following process:

$$X_{(g)} + e^- \longrightarrow X^-_{(g)} + \text{energy released}$$

The above process which depicts the addition of an electron to a gaseous atom is an *exothermic process,* since in the addition of an electron energy is released.

The addition of a second electron to a uni-negative ion is usually *endothermic,* so electron affinities of anions are usually positive. This is because of the fact that the addition of an electron to a negative ion must overcome the repulsion due to the existing negative charge. hence the process is endothermic i.e., energy is absorbed. For example, with oxygen the process involves the following two values in two stages, the second of which is endothermic.

$$O_{(g)} + e^- \longrightarrow O^-_{(g)} \qquad EA_1 = -142\ kJ\ mol^{-1}$$

$$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)} \qquad EA_2 = +780\ kJ\ mol^{-1}$$

Electron affinity is an atomic property which gives us an idea of the tendency of the element to accept the electron to form an anion. With the help of this property a number of properties of the elements like oxidizing power and non-metallic character can will be explained. It is a precise and quantitative term, like ionization energy, but it is difficult to measure. It is also expressed in electron volt (eV) or kilo joule per mol. Table 1.11 shows electron affinity for representative elements.

Factors Affecting the Magnitude of Electron Affinity

The factors on which the magnitude and sign of electron affinities depend are, in general, similar to those which determine the ionization energies but in the reverse order. These factors are:

1. **Atomic radius:** Larger the atomic radius, lesser the tendency of the atom to attract the additional electron towards itself, lesser the force of attraction exerted by the nucleus on the extra electron being added to the outer-shell of the atom and hence lesser the amount of energy released when the extra electron is added to the atom to form an anion. Thus smaller atoms have higher electron affinities.

2. **Effective nuclear charge:** Higher the effective nuclear charge, greater the tendency of the atom to attract the additional electron towards itself, greater the force of attraction exerted by the nucleus on the extra electron being added to the outer-shell of the atom and hence higher the amount of energy released when the extra electron is added to the atom. Thus the atoms with higher effective nuclear charge have higher electron affinities.

3. **Electronic configuration:** The effect of this factor on the magnitude of electron affinity of an element can be explained by the following examples.

(a) *Electron affinity values of the elements of group IIA:* *ns* orbital of the valence-shell of the atoms of these elements is completely filled and hence the addition of any extra electron from outside to these *ns* orbital is not possible. Consequently the elements of group 11A have practically zero electron affinity.

(b) *Electron affinity values of N and P.* The valence-shell electronic configuration of N and P are:

$$N \longrightarrow 2s^2p^3\ ;\ P \longrightarrow 3s^2p^3$$

2*p* and 3*p* orbitals in N and respectively are half-filled and hence are extra ordinarily stable. Thus the addition of any extra electron from outside to these orbitals is not possible. Consequently N and P have very low electron affinity values (N = + 20.1 kJ/mole, P = -74 kJ/mole).

(c) *Electron affinity values of halogens.* The valence-shell configuration of halogen atoms (ns^2p^5) has an appetite for one electron to stabilize its configuration by attaining the noble gas configuration (ns^2p^6) which is very stable. Thus halogen atoms have a strong tendency to accept an extra electron from outside and the addition an extra electron makes the configuration of the resulted halide ion similar to that of the noble gas and hence very stable. Consequently the halogen atoms have very high values of electron affinity.

(d) *Electron affinity values of noble gases.* The noble gases which have extraordinarily stable configuration namely ns^2p^6 show no tendency to accept the additional electron from outside. Hence the electron affinity values of inert gases are practically zero.

Variation of Electron Affinity in a Period and a Group.

It is difficult to make general views about the periodic variation of electron affinity of various elements for the following reasons:

(i) The electron affinities of only a very few atoms are known with certainty.

(ii) The elements like Be, Mg and noble gases have practically zero electron affinity values, and N and P have very small values.

(iii) The elements of 2nd period of the periodic table do not follow the general trend of decrease of electron affinity values on moving from top to bottom in a group.

However, the general trend of variations of electron affinity of various elements can be discussed as follows:

(a) In a period: On moving from left to right in a period, the size of the atoms decreases and the effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted by the nucleus on the electron. Consequently the atom has a greater tendency to attract an extra electron from outside towards itself and hence its electron affinity increases from left to right. Thus the metals (e.g. alkali metals) which lie at the left hand portion of the periodic table have low values of electron affinity while the non- metals (e.g. halogens) which lie at the right hand portion of the periodic table have high values of electron affinity.

Exceptions: There are certain elements in each period which have abnormal values. For example in 2nd period Li, Be, N and Ne have abnormal values. Similarly in 3rd period Na, Mg, P and Ar have abnormal values. The abnormal values of Li and Na cannot be explained by simple mechanism while those of Be, N, Mg, P, Ne and Ar have already been explained.

(b) In a group: On moving down a group both the size of the atom and the effective nuclear charge increase. The increase in atomic size tends to decrease the electron affinity values. The net result is that the effect produced by the progressive increase of the atomic size outweighs the effect produced by the progressive increase in nuclear charge and consequently the electron affinity goes on decreasing as we move from top to bottom in a group as is evident from EA values of (i) alkali metals (ii) C, Si and Ge (Group IVA) (iii) S, Se and Te (Group VIA) (iv)) O, S and Se for two electrons (Group VIA) and (v) Cl, Br and I (Group VII A).

Exceptions: Although the elements of 2nd period of the periodic table have smaller size than the elements of 3rd period, the EA values of some of the elements of 2nd period are lower than the Ea values of the elements lying just below them in 3rd period. For example B<A1, N<P, O<S and F<Cl. The lower values for the elements of 2nd period are explained by saying that, due to the smaller size of the atoms of the elements of 2nd period, the addition of an extra electron to these atoms produces high electron density round the resulted anions. This high electron density increases the repulsion between the electron (called electron— electron repulsion) already present in the relatively compact 2*p* orbital of the 2nd shell of these atoms and the electron being added, Due to this electron— electron repulsion, the atoms of the elements of 2nd period show lesser tendency to attract the extra electron from outside and hence lower values of electron affinity for these elements.

Table 1.11 Electron affinities of the main-group elements (in eV)*

H							He
0.754							-0.5
Li	Be	B	C	N	O	F	Ne
0.618	≤0	0.277	1.263	-0.07	1.461 -8.75	3.399	-1.2
Na	Mg	Al	Si	P	S	Cl	Ar
0.548	≤0	0.441	1.385	0.747	2.077 -5.51	3.617	-1.0
K	Ca	Ga	Ge	As	Se	Br	Kr
0.502	+0.02	0.30	1.2	0.81	2.021	3.365	-1.0
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.486	+0.05	0.3	1.2	1.07	1.07	3.059	-0.8

*To convert to kJ mol^{-1}, multiply by 96.485

The first values refer to the formation of the ion X^- from the neutral atom X; the second value to the formation of X^{2-} from X^-.

Source: H. Hotop and W.C. Lineberger, J. Phys. Chem. Ref. Data 14,731 (1985).

Example 1.7 Account for the large decrease in electron affinity between lithium and beryllium despite the increase in nuclear change.

Answer The electron configuration of the two atoms are $[He]2s^1$ and $[He]2s^2$. The additional electron enters the 2*s* orbital of lithium, but it must enter the 2*p* orbital of beryllium, and hence is much less tightly bound. In fact, the nuclear charge is so well shielded in beryllium that electron gain is endothermic. Similarly the decrease in the decrease in electron affinity between carbon and nitrogen can be accounted.

1.20 ELECTRONEGATIVITY

When two different atoms in a molecule are bonded together by a covalent bond, the electron pair forming the covalent bond is not shared equally by both the atoms. Rather, the electron pair lies nearer to one atom than the other. The relative tendency or ability of a bonded atom to attract the shared electrons towards itself is termed its *electronegativity.* This definition was given by Pauling in 1932.

Electronegativity is an inherently fundamental property of the atom and is fundamentally different from electron affinity, since electron affinity represents the tendency of an *isolated gaseous atom* to attract the electrons while electronegativity represents the tendency of a *bonded* atom to attract the shared electron pair.

Electronegativity is not a directly measurable quantity. It is not a precise quantity; it is rather a relative value. Thus, the electronegativity of an element is only defined in terms of the electronegativities of other elements. Moreover, it depends upon the environment of an atom in the molecule. Accordingly, the electronegativity assigned to an element can only be an average value for its most common valency state. It is obvious that the higher the oxidation state of an element in a compound the more strongly its atom attracts electrons.

Electronegativity Scales

Various methods have been used to construct electronegativity scales for the comparison of electronegativity of the elements. The various electronegativity scales include those of Pauling, Mulliken, Allred and Rochow and Sanderson. Of these Pauling scale is the earliest and probably the most widely used.

The Pauling's Scale

Historically Pauling was the first to introduce the concept of electronegativity. He defined electronegativity difference for two atoms A and B (in the molecule A — B) in terms of deviation (Δ) of the A — B bond energy from geometric mean of A — A and B — B bond energies.

Pauling suggested that if two atoms A and B, had the same electronegativity, the bond energy of the A — B bond would be equal to the geometric mean of A — A and B — B bond energies. This would be so since the electrons in the bond would be equally shared in purely covalent bonds in all three cases. Thus, the A — B bond energy could be expressed as

$$E_{A-B} = [E_{A-A} \times E_{B-B}]^{1/2}$$

Pauling, however, observed that for the majority of A — B bonds the energy exceeds the geometric average because generally the atoms A and B have different electronegativities and there is an ionic contribution to the bond in addition to the covalent one. Let the difference between two be Δ, then

$$\Delta = E_{A-B} - [E_{A-A} \times E_{B-B}]^{1/2}$$

This "excess" energy is known as the *ionic resonance energy.* Pauling proposed that this "excess" energy Δ could be used as an empirical basis to determine electronegativity differences. If X_A and X_B represent the electronegativities of A and B respectively, the difference $X_A - X_B$ could be related to Δ as follows:

$$X_A - X_B = \left(\frac{\Delta}{96.5 \text{ kJ mol}^{-1}}\right)^{1/2}$$

The factor 96.5 kJ mol^{-1} converts Δ from kJ mol^{-1} (SI units) to electron volts (eV) per molecule.

Example 1..8

The bond energies of H_2, Cl_2 and HCl are:

$$E_{H-H} = 436 \text{ kJ mol}^{-1}$$

$$E_{Cl-Cl} = 243 \text{ kJ mol}^{-1}$$

$$E_{H-Cl} = 431 \text{ kJ mol}^{-1}$$

Evaluate $X_{Cl} - X_H$.

Solution

$$\Delta_{HCl} = E_{H-Cl} - [E_{H-H} \times E_{Cl-Cl}]^{1/2}$$

$$= 431 - (436 \times 243)^{1/2}$$

$$X_{Cl} - X_H = \left(\frac{\Delta}{96.5 \text{ kJ mol}^{-1}}\right)^{1/2}$$

$$= \frac{106}{96.5} = 1.05$$

Thus, $X_{Cl} - X_H = 1.05$

Pauling $X_H = 2.1$ as a standard so that all electronegativity values would be positive. Pauling's scale extends from cesium, with electronegativity 0.7 to fluorine with electronegativity 4.0. Fluorine is the most electronegative element followed by oxygen. Hydrogen and semi-metallic elements are in the middle of the scale having electronegativity values of about 2.0.

Mulliken's Scale

According to Mulliken, electro-negativity is determined, partly by the tendency of an atom to bind an additional electron and partly by its tendency to hold on the those it already has. On Mulliken's scale, the electro-negativity is taken as the mean value of the first ionization energy and the first electron affinity; both qualities are given a positive value if loss of electron involves absorption of energy and gain of electron involves release of energy. Thus

$$\chi_M = \frac{1E + EA}{2}$$

The commonly accepted values (in terms of Pauling's scale) may be obtained from the relation.

$$\frac{\text{ionization energy + Electron affinity}}{544}$$

where both 1E and EA are measured in kJ mol^{-1}. One of the outstanding features of the Muliken definition of electro-negativity is that allowance can be made for hybridization and atomic charge. However, a complete electro-negativity scale cannot be constructed based upon Mulliken's concept since electron affinities (EA) are known for only a few atoms.

If both IE and EA both are measured in eV units, Mulliken's electronegativity χ_M is related to Pauling,s electronegativity χ_P as follows,

$$\chi_P = 0.3\,\chi_M — 0.2$$

Table 1.12 Pauling (italics), χ_P, and Mulliken electro-negativities χ_M

H							He
2.20							
3.06							5.5
Li	Be	B	C	N	O	F	Ne
0.98	*1.57*	*2.04*	*2.55*	*3.04*	*3.44*	*3.98*	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
Na	Mg	Al	Si	P	S	Cl	Ar
0.93	*1.31*	*1.61*	*1.90*	*2.19*	*2.58*	*3.16*	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
K	Ca	Ga	Ge	As	Se	Br	Kr
0.82	*1.00*	*1.81*	*2.01*	*2.18*	*2.55*	*2.96*	*3.0*
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.82	*0.95*	*1.78*	*1.96*	*2.05*	*2.10*	*2.66*	*2.6*
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
Cs	Ba	Tl	Pb	Bi			
0.79	*0.89*	*2.04*	*2.33*	*2.02*			

***Source:* Pauling values: A.I. Allred, J. Inorg. Nucl. Chem. 17, 215 (1961); L.C. Allen and J.E. Huheey, ibid, 42, 1523 (1980); Mulliken values: L.C. Allen, J. Am. Chem. Soc. 111, 9003 (1989). The Mulliken values have been scaled to the range of the Pauling values.**

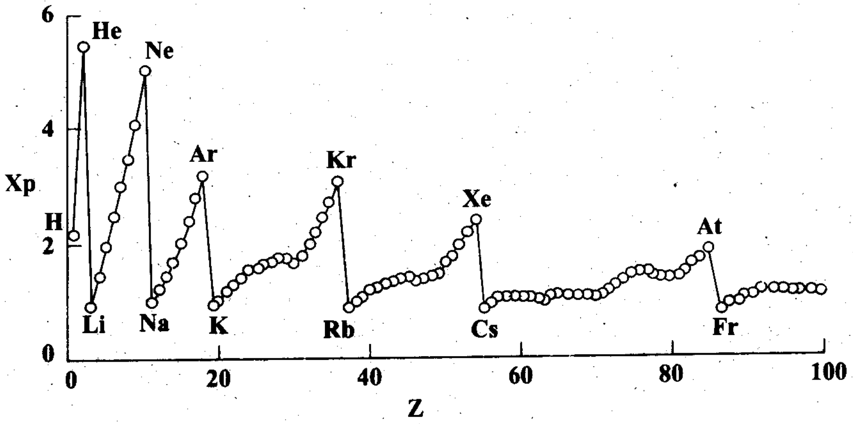


Fig. 1.15 The variation of Pauling electro-negativity through the periodic table.

Periodic Trends of Electronegativity

In going from left to right in a period of representative elements, the electronegativity values increase. On moving from left to right in a period, there is a decrease in the size of the atoms. Smaller atoms have greater tendency to attract the electrons towards themselves i.e., smaller atoms have higher electronegativity values.

Electronegativity usually decreases from top to bottom within groups. As we move down a group, there is an increase in the size of the atoms as well as more shielding electrons are present. With the increase in the size of atoms and shielding electrons, their electronegativity values decrease.

Electronegativity and Nature of Chemical Bond

The concept of electronegativity can be used to predict the nature of the chemical bond formed, between two similar or dissimilar atoms, i.e., the concept of electronegativity can predict whether the bond between two similar or dissimilar atom is non-polar covalent bond, polar covalent bond or ionic bond as discussed below:

(i) When $(X_A - X_B) = 1.7$, the A — B bond is 50% ionic and 50% covalent.

(ii) When $(X_A - X_B) < 1.7$, the A — B bond is predominantly covalent.

(iii) When $(X_A - X_B) > 1.7$, the A — B bond is predominantly ionic.

1.21 OXIDATION-REDUCTION REACTIONS

The term *oxidation* was originally used to represent a process in which a substance acquired oxygen in a chemical reaction and the term *reduction* was used for a process in which oxygen was removed from the substance. Today these terms are used to represent processes in which oxygen may not play any role whatsoever. Redox reactions are now described in terms of *electron gain* and *electron loss.*

Oxidation is defined as a process in which one or more electrons are lost by an atom, ion or a molecule and reduction as a process in which electrons are added. Since loss or gain of electrons are relative terms, the gain or loss of electrons takes place simultaneously in a chemical reaction. Thus the oxidation (i.e., loss of electron) and the reduction (i.e., the gain of electron) reactions go hand in hand and such reactions in which oxidation and reduction take place simultaneously are known as *oxidation-reduction reactions* or *redox reactions.* Redox reactions are very much a part of the world around us. They range from combustion of fossil fuels to the action of household bleaching agents. Most metallic and non-metallic elements are obtained from their ores by the process of oxidation or reduction.

Consider the reaction between Zn and $CuSO_4$ solution shown as:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

or

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

is a redox reaction, since Zn atom (valency = 0) by losing two electrons is oxidized to Zn^{2+} ion (valency = +2) while Cu^{2+} ion (valency = +2) by gaining the same number of electrons lost by Zn atom gets reduced to Cu atom (valency = 0). Thus we see that a redox reaction consists of two reactions — one involves oxidation and the other involves reduction. Each of these reactions is called *half-reaction.* The reaction showing oxidation is called *oxidation half reaction* while that representing reduction is called *reduction half reaction.* Thus the two half-reactions of the above mentioned redox reaction are:

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad \text{Oxidation half-reaction}$$

and,

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{Reduction half-reaction}$$

It may be noted that the number of electrons lost or gained in two opposite half-reactions of a redox reaction is equal and the reaction mixture of a redox reaction is electrically neutral.

Types of Redox Reactions

There are three important types of redox reactions:

1. Displacement Reaction

It is one in which an ion (or atom) in a compound is replaced by another ion (or atom) of another element. It is represented by

$$A + BC \longrightarrow AC + B$$

Most displacement reactions can be conveniently divided into three major categories: hydrogen displacement, metal displacement, and halogen displacement.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

$$Cu_{(s)} + 2AgNO_{3(aq)} \longrightarrow Cu(NO_3)_{2(aq)} + 2Ag_{(s)}$$

$$Cl_{2(g)} + 2KBr_{(aq)} \longrightarrow 2KCl + Br_{2(g)}$$

2. Disproportionation Reaction

It is a special type of redox reactions. In disproportionation reaction an element in one oxidation state is both oxidized and reduced. One reactant in a disproportionation reaction always contains an element that can have at least three oxidation states. The reactant itself is in one of these states, and there are both a higher and a lower possible oxidation state for the same element. For example,

$$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

$$Cl_{2(g)} + 2OH^-_{(aq)} \longrightarrow OCl^-_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$

3. Decomposition Reaction

A reaction which produces one or more free element is known as decomposition reaction. For example,

$$2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$$

$$2HgO_{(s)} \longrightarrow 2Hg_{(l)} + O_{2(g)}$$

Moreover all *combustion reactions* (which involve elemental oxygen) as well as many reactions *involving elements* are redox in nature.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

$$3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(s)}$$

1.22 STANDARD ELECTRODE POTENTIAL

The electrode potential is defined as the potential difference of the electrical double layer formed at the contact (interface) of electrode metal and electrolyte. It is also called *single electrode potential.* The electrode potential is the measure of tendency of an electrode to lose or gain the electrons, when it is in contact with its own ions. Thus we have oxidation potential and reduction potential. Electrode potential or half cell potential is denoted by the symbol E.

Oxidation and Reduction Potentials

The cell reaction consists of two half cell reactions of which one is oxidation reaction and the other is reduction reaction. Electromotive force (emf) of a cell may be regarded as being made up of two single electrode potentials. Their algebraic sum equals to the emf of cell.

$$E_{cell} = E_{anode} + E_{cathode}$$

1. E_{anode} would be the measure of tendency of anode to lose the electrons. Since loss of electrons is oxidation.

$$M \longrightarrow M^{n+} + ne^-$$

the E_{anode} would be called oxidation potential. Hence we can define *oxidation potential* as the measure of the tendency of an electrode to lose the electrons. It is denoted by E_{oxi}.

2. $E_{cathode}$ stands for the potential electrode at which reduction occurs.

$$M^{n+} + ne^- \longrightarrow M$$

Hence *reduction potential* is the measure of tendency of electrode to gain the electrons. It is denoted by E_{red}. Since cell reaction is essentially a redox-process, we can also write

$$E_{cell} = E_{oxi} + E_{red}$$

The reduction potential of an electrode is the same as its oxidation potential with the sign changed.

Standard Electrode Potential

It is defined as the potential of the electrode when all of the ionic concentrations are 1.00 M, the temperature is 25°C, and any gases that are involved in the cell reaction are at a pressure of 1 atmosphere. It is denoted by the symbol E°.

Measurement of Electrode Potential

Unfortunately there is no way to measure the single electrode potential of an isolated half-cell. All we can measure is the difference that is produced when two half cells are connected. In order to determine single electrode potentials, it would be necessary to couple an electrode with a reference or standard electrode. The potential of the reference electrode is arbitrarily assigned a zero value and the potentials of all other electrodes are then referred to it. Two such reference electrodes are used *(i)* standard hydrogen electrode and *(ii)* calomel electrode.

Although the standard electrode potentials are fixed, changes in the concentration of the ions and temperature may alter their values. The potential of an electrode under changed condition is given by *Nerst equation.*

$$E = E^\circ - \frac{RT}{nF} \ln a_{ion}$$

where E = Electrode potential

E° = Standard electrode potential

R = Gas constant

T = Absolute temperature

n = Number of electrons transferred

F = Faraday

a_{ion} = Activity of the ion

Significance of Redox Potential

We can determine the feasibility of a chemical reaction by its redox potential. A cell can be constructed by utilizing a redox reaction. If the voltage of the cell is positive then the reaction is feasible, and if negative, the reaction is not feasible. Let us take the example of Daniel cell.

$$Zn_{(s)} + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu_{(s)}$$

The reaction occurs in two steps.

$$Zn_{(s)} \rightleftharpoons Zn^{2+} + 2e^- \qquad E_{oxi} = 0.76\ V$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E_{red} = 0.34\ V$$

$$Zn_{(s)} + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu \qquad E_{cell} = 1.10\ V$$

As the value of voltage is positive, hence the reaction is feasible in forward direction.

Sign of Electrode Potentials

1. According to IUPAC system — the electrode potential is given *positive sign* if the electrode reaction involves reduction when connected to SHE. For example when copper electrode is connected with SHE, reduction occurs at copper electrode.

   At SHE $H_{2(g)} \rightleftharpoons 2H^+ + 2e^-$ (oxidation)

   At copper electrode: $Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}$ (reduction)

   $$H_{2(g)} + Cu^{2+} \rightleftharpoons 2H^+ + Cu_{(s)}$$

   Hence potential of copper electrode will have *positive sign.*

   That is, $E^\circ_{(Cu^{2+}/Cu)} = 0.337$ volts

2. The electrode potential is given *negative sign,* if the electrode reaction involves oxidation, when connected with SHE. For example, when zinc electrode is connected with SHE, oxidation occurs at the zinc electrode.

   $$Zn_{(s)} + 2H^+ \rightleftharpoons Zn^{2+} + H_{2(g)}$$

   Hence the electrode potential of Zn/Zn^{2+} electrode will be negative and is equal to –0.763 volt. The values of oxidation electrode potential and reduction electrode potential are numerically equal but opposite in sign.

An arrangement of electrode systems in order of increasing standard electrode potential (reduction potential) is given in Table 1.13. This is known as *standard reduction electrode potential series.* In some books, standard oxidation potential series is followed. These series are called *electrochemical series* or *activity series.*

1.23 ELECTROCHEMICAL SERIES

The list of elements or ions arranged in the increasing or decreasing order of their standard reduction potential values is called *electrochemical* or *e.m.f* or *activity series.* The electrochemical series is shown in Table 1.13.

The magnitude of the standard electrode potential is a measure of the tendency for reduction to occur. The reduced form of a half-cell higher up in the series has a greater tendency to donate electrons and be oxidized than the reduced form of the half-cell which is below it in the series. Similarly, the oxidized form of the half-cell lower in the series has a greater tendency to accept electrons and be reduced than the oxidized form of the half-cell which is above it in the series.

Uses of Electrochemical Series

1. The magnitude of E° value of a metal or a non-metal gives a measure of its tendency to gain electrons to get reduced and hence to act as an oxidizing agent or to lose electrons to get oxidized and hence to act as a reducing agent. The species having positive E° values i.e., the species lying below the hydrogen show a strong tendency to gain electrons to undergo reduction and hence they are *strong oxidizing agents,* e.g. F_2 is the strongest oxidizing agent. On the other hand, species having negative E° values show a strong tendency to lose electrons to undergo oxidation and hence they are *strong reducing agents,* e.g., Li is the strongest reducing agent.
2. We can determine electropositive character of metals by consulting electrochemical series. Metals like Na, K, Ca etc. which lie at the top of the series lose outer-most electrons to form metal cations and hence are *strongly electropositive.* On the other hand, metals which lie at the bottom are *less electropositive,* e.g., Ce, Co etc.
3. By consulting electrochemical series one can determine whether a given metal will be displaced by another metal or not. A metal will displace another metal from the aqueous solution of its salt that lies below it in the series. For example, Zn will displace Cu.
4. The values of standard reduction potentials given in the series can also be used to calculate the e.m.f. of a given Galvanic cell. The standard e.m.f. of a cell is equal to the difference of the standard reduction potential of the cathode and the standard reduction potential of the anode. Thus

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

5. We can predict whether a given redox reaction is likely to occur or not. A given redox reaction will take place spontaneously in the direction as represented by a given net equation, if E°_{cell} is positive, because in that case the standard free energy change of the reaction (ΔF°) would be negative ($\Delta F^\circ = -nFE^\circ$). If E°_{cell} is a negative quantity, the given redox reaction will not take place in the given direction. Let us see whether the reaction.

$$Cu_{(s)} + Zn^{2+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Zn_{(s)}$$

will take place or not.

Oxidation half reaction: $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$ $E^\circ = -0.34$ V

Reduction half-reaction: $Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$ $E^\circ = -0.76$ V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= -0.76 - (+0.34)$$

$$= -1.10 \text{ volt}$$

Due to negative value of E°_{cell} the above reaction is not feasible.

6. We can predict whether a given non-metal will displace another non-metal from aqueous solution of its salt. A non-metal with higher standard reduction potential can displace another non-metal with lower standard reduction potential. For example, Cl_2 can displace I_2 and Br_2.

Table 1.13. Standard Electrode Potentials at 298 K

Elextrode	E°(V)	Electrode Reaction
$Li^+ \mid Li$	– 3.045	$Li + e^- \rightleftharpoons Li$
$K^+ \mid K$	– 9.925	$K^+ + e^- \rightleftharpoons K$
$Ca^{2+} \mid Ca$	– 2.870	$Ca^{2+} + 2e^- \rightleftharpoons Ca$
$Na^+ \mid Na$	– 2.714	$Na^+ + e^- \rightleftharpoons Na$
$Zn^{2+} \mid Zn$	– 0.762	$Zn^{2+} + 2e^- \rightleftharpoons Zn$
$Fe^{2+} \mid Fe$	– 0.441	$Fe^{2+} + 2e^- \rightleftharpoons Fe$
$Cr^{2+}, Cr^{3+} \mid Pt$	– 0.410	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$
$Cd^{2+} \mid Cd$	– 0.403	$Cd^{2+} + 2e^- \rightleftharpoons Cd$
$Tl^+ \mid Tl$	– 0.336	$Tl^+ + e^- \rightleftharpoons Tl$
$Co^{2+} \mid Co$	– 0.277	$Co^{2+} + 2e^- \rightleftharpoons Co$
$Ni^{2+} \mid Ni$	– 0.250	$Ni^{2+} + 2e^- \rightleftharpoons Ni$
$I^- \mid AgI \mid Ag$	– 0.152	$AgI + e^- \rightleftharpoons Ag + I^-$
$Sn^{2+} \mid Sn$	– 0.140	$Sn^{2+} + 2e^- \rightleftharpoons Sn$
$Pb^{2+} \mid Pb$	– 0.126	$Pb^{2+} + 2e^- \rightleftharpoons Pb$
$H^+ \mid H_2 \mid Pt$	0.000	$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$
$Br^- \mid AgBr \mid Ag$	+ 0.093	$AgBr + e^- \rightleftharpoons Ag + Br^-$
$Sn^{4+}, Sn^{2+} \mid Pt$	+ 0.150	$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$
$Cl^- \mid AgCl \mid Ag$	+ 0.2225	$AgCl + e^- \rightleftharpoons Ag + Cl^-$
$Cu^{2+} \mid Cu$	+ 0.337	$Cu^{2+} + 2e^- \rightleftharpoons Cu$
$I^- \mid I_2 \mid Pt$	+ 0.5355	$I_2 + 2e^- \rightleftharpoons 2I^-$
$SO_4^{2-} \mid Hg_2SO_4 \mid Pt$	+ 0.614	$HgSO_4 + 2e^- \rightleftharpoons 2Hg + SO_4^{2-}$
$Fe^{3+}, Fe^{2+} \mid Pt$	+ 0.771	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
$Ag^+ \mid Ag$	+ 0.799	$Ag^+ + e^- \rightleftharpoons Ag$
$Br^- \mid Br_2 \mid Pt$	+ 1.0652	$Br_2 + 2e^- \rightleftharpoons 2Br^-$
$Cl^- \mid Cl_2 \mid Pt$	+ 1.3595	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$

$Ce^{4+}, Ce^{2+} \mid Pt$	+ 1.61	$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$
$Co^{3+}, Co^{2+} \mid Pt$	+ 1.82	$Co^{3+} + e^- \rightleftharpoons Co^{2+}$
$O_2 \mid O_3$	+ 2.07	$O_3 + 2H^+ + e^- \rightleftharpoons O_2 + H_2O$
$F^- \mid F_2 \mid Pt$	+ 2.85	$F_2 + 2e^- \rightleftharpoons 2F^-$

1.24 POLARIZABILITY AND POLARIZING POWER OF IONS

When a cation, C^+ of an ionic molecule, C^+A^- approaches closely the anion, A^-, it withdraws the electrons (i.e. electron cloud) of the anion towards itself and the electron cloud of the anion gets distorted from its symmetrical shape. Thus the electron cloud of the anion no longer remains symmetrical but is elongated towards cation. In other words we say that the A^- anion is distorted (or deformed or polarized) by C^+ cation and this phenomenon is called distortion (or deformation or polarization) of A^- anion by C^+ cation (Fig.1.16)

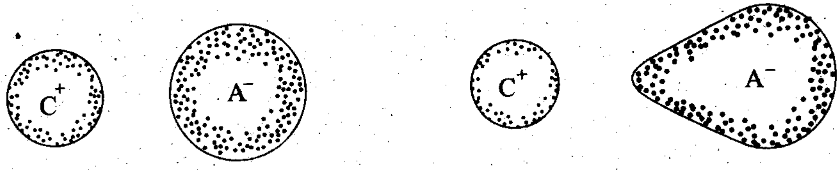


Fig. 1.16. Schematic representation of polarization of an anion, A- by a caution, C^+ in C^+A^- ionic molecule. (a) No polarization (b) Polarised anion.

The cation, C+ is also deformed by the anion, A-, but due to smaller size of the cation, its electron are strongly held to the nucleus and hence the cation is not polarized to an appreciable extent by a nearby anion i.e. the polarization of a cation by an anion is regarded as negligible and hence we generally do not consider the polarization of a cation by anion.The ability of a cation to polarize a nearby anion is called its polarizing power or polarizing ability and the tendency of an anion to get distorted or polarized by a cation is called its polarisability.

Factors Affecting the Magnitude of Polarising Power of a Cation and Polarizeability of an Anion — Fajans's Rules

Following are the factors on (which the magnitude of polarizing power of a caution to polarize a nearby anion and the polarisability of an anion depends. These factors have been suggested by Fajans and hence are called Fajans's Rules.

1. Chare on cation or anion. The cation with higher positive charge attracts the electron cloud of the anion more strongly towards itself than the caution with smaller positive charge and hence polarizes the anion more strongly. Consequently higher the positive charge on the cation, greater its polarizing power to polarize a given nearby anion. For example in LiCl, $BeCl_2$, BCl_3 and CCl_4 molecules, the polarizing power of Li+, Be^{-}. B^{3+} and C^{4+} cations (cations of the same period) to polarize Cl^{-} anion increases with the increase of positive charge on them.

An anion with higher negative charge repels the electron cloud of its outer-most shell towards the caution more effectively and hence is polarized by the cation more strongly it will be polarized by a given cation i.e. more will be its polarisability of C^{4-}, N^{3-}, O^{2-} and F^{-} anions (anions of the same period) to be polarized by H^{+} caution decreases from C^{4-} to F^{-}, since the magnitude of negative charge on these anions also decreases in the same direction.

2. Size of the cation. The nucleus of a smaller cation is shielded to a lesser extent by the electron shells and, therefore, such a cation attracts the electron cloud of the anion more strongly than a large cation. This means that smaller is the size of the cation, higher is its polarizing power to polarize a given nearby anion. For example in $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ molecules the polarizing power of Be^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} cations (cations of the same group) to polarize Cl^{-} ion decreases with the increase of their size.

3. Size of the anion. The electrons of the outer-most shell of a large anion are less firmly bound to its nucleus and hence can be withdrawn by the cation more easily. Consequently a larger anion will be polarized by the cation more easily than a smaller anion. This means that larger is the size of the anion, more strongly or easily it will be polarized by a given cation i.e., more will be its polarisability. For example in halides of a given caution (e.g. MX halides) the polarisability of halids ions (anions of the same group) will increase from F^{-} to I^{-}, since the size of these ions also increases in the same direction.

A cation with 18-electron valence shell configuration ($ns^2p^6d^{10}$ configuration) has greater polarizing power than that with 8-electron valence-shell configuration ($ns^2p^6d^{10}$ valence-shell configuration is because of the fact that the *d*-electrons of the 18-electron shell shield the nuclear charge of the caution less effectively than the *s*- and *p*-electrons of 8-electron shell. Hence the caution with 18-electron valence shell configuration behaves, as if it has greater nuclear charge on it. Greater nuclear charge increase the polarizing power of the caution having 18-electron valence-shell configuration . This Ag^{+} caution ($4s^2p^6d^{10}$) has greater polarizing power than k^{+} caution ($3s^2p^6$).

Variation of Polarizing Power of Cautions in a Period and a Group of the Periodic Table

(a) **In a period.** In moving from left to right in a period, the size of the cations decreases and the positive charge increases. Both these factors increase the polarizing power of the cations of 2nd period viz Li^{+}, Be^{2+} and C^{4+} to polarize Cl^{-} anion in LiCl, $BeCl_2$, BCl_3 and CCl_4 molecules increases from Li+ to C^{4+} with the decrease of their size and increase in their positive charge from + 1 to + 4..

(b) **In a group.** On descending a group the magnitude of positive charge on the cations remains the same and hence it is the size of the cation alone which affects the magnitude of the polarizing power of the given cation. On moving down group the size of the cautions increases and hence the polarizing power of the cations goes on decreasing. For example the polarizing power of the cations of the elements of Group IIA viz. Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} to polarize Cl^- ion in $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ molecules, decreases with the increase of their size.

Variation of Polariability of Anions in a Period and a Group of the Periodic Table.

(a) **In a period.** We know that on proceeding from left to right in a period, both negative charge on the anions and their size decrease. Both these factors decreases the polarisability of the anions by a given cation from left to right in a period of the long form of periodic table. For example the polarisability of C^{4-}, N^{3-}, O^{2-} and F^- anions (anions of 2nd period) to be polarized by M^+ caution in M_4C, M_3N, M_2O and MF molecules decreases from C^{4-} to F^-, since both negative charge on these anions and their size also decrease in the same direction.

(b) **In a group.** On descending a group, the magnitude of negative charge on the anions remains the same and hence it is the size of the anion alone which affects the magnitude of polarisability of a given anion. On moving down a group the size of the anions increases and hence the polarisibility of a anions also goes on increasing. For example in the halides of a given cation (e.g. MX type halides) the polarisability of halide ions (anions of the same group) will increase from F^- to I^- since the size of these anions also increases in the same direction.

1.25 ANOMALIES IN FIRST ROW ELEMENTS

The "anomalous" properties of the elements in the second short period (from lithium to fluorine) are interesting, because some of the properties of these elements are different from those of the other elements in their respective groups. These anomalous properties of the respective elements can be attributed to their small size, high electronegativities, high ionization potential etc. Similarities and differences in first row elements, their diagonal and vertical relationship with other elements are discussed as under:

Anomalous Properties of Lithium: Dissimilarities with Other Alkali Metals

From the general properties of alkali metals it may be seen that Li differs in many properties from the other alkali metals.

The main reasons due to which it shows anomalous properties are:

(a) The size of Li atom and Li^+ ion is the smallest of all the alkali metal ions.

(b) The polarizing power of Li^+ ion is the greatest of all the alkali metal ions.

(c) Li has the highest ionization energy and electronegativity as compared to other alkali metals.

Points of Differences. Following are the main points of differences between Li and other alkali metals.

1. The greatest polarizing power of Li^+ ion results in its tendency towards solvation and covalent bond formation. Thus the salts of Li are covalent and are, therefore, more soluble in non-polar solvents (e.g. organic solvents).

2. Li is the only alkali metal which reacts with nitrogen and silicon to form ionic lithium nitride (Li_3N) and lithium silicide (Li_6Si_2).

3. Li is much harder and lighter than the other alkali metals.

4. Its melting and boiling points are rather high and it can be melted in dry air without losing its brilliancy.

5. Due to its high ionization energy, Li does not react with O_2 below 0°C; reacts slowly with H_2O to liberate H_2 or with liquid Br_2.

6. Li is the least reactive metal of all the alkali metals.

7. Li^+ ion shows a tendency to form complexes with NH_3, H_2O (to form hydrates) and forms a large number of organo lithium compound.

8. When burnt in air, Li gives only the monoxide, Li_2O (O^{2-}) while other alkali metals form peroxide (O_2^{2-}) and super oxides (O_2^-).

9. When acetylene gas is passed over heated Li metal, it does not form lithium acetylide, while other alkali metals do form metal acetylides.

10. Li when heated in NH_3 forms imide, Li_2NH while other alkali metals form amides, MNH_2.

11. Li is the only alkali metal whose salts (e.g. LiCl) may undergo hydrolysis.

12. Li_2O dissolves in H_2O quietly while other oxides do so more energetically.

13. LiOH is considerably less soluble in H_2O and is a much weaker base than NaOH or KOH.

14. LiCl is deliquescent and is soluble in a alcohol as well as in pyridine. It forms the hydrate, $LiCl_2H_2O$. Chlorides of other alkali metals do not show this behaviour.

15. $LiCO_3$ decomposes on heating to from Li_2O and CO_2 while other carbonates do not decompose. The small size of Li^+ ion makes LI_2O lattice more stable than Li_2CO_3 lattice. However, the large size of other alkali metals ions make M_2O lattices less stable than M_2CO_3 lattice and hence they decompose.

Diagonal Relationship of Li with Mg: Similarities between Li and Mg

It has been observed that Li resembles more in its many properties with the elements, Mg, lying at its right in 3rd period (i.e. diagonally opposite element) than with other members of its own sub-group IA. This type of similarity between Li and Mg is called diagonal relationship.

1. The atomic radii of Li and Mg are comparable (Li = 1.225Å, Mg = 1.365 Å). The ionic radius of Li+ (= 0.60 Å) is closer to that of Mg^{2+} (=0.5 Å) than to that of Na^+ (= 0.95 Å)

2. The atomic volumes of solid Li and Mg are quite similar (Li = 12.97 c.c. Mg = 13.97 c.c.)
3. Electro-negativities of Li and Mg are quite comparable (Li = 1.00, Mg = 1.20)
4. Li^+ and Mg^{2+} both the ions have high polarizing power, i.e., charge\radius ratio of both the ions is high.

It is due to this high polarizing power that both the ions have great tendency to form hydrates with a definite number of water molecules.

Because of the strong polarizing power of Li^+ and Mg^{2+} ions on the charge cloud of the ions like NO_3^- and CO_3^{2-}, their nitrates and carbonates show low thermal stability, i.e., they decompose easily on heating to give out NO_2 and CO_2 respectively.

$$4LiNO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$

$$2Mg(NO_2)_3 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

$$MgCO_3 \xrightarrow{\Delta} MgO_2 + CO_2$$

5. Enthalpies of both the elements are comparable.
6. Li and Mg have higher melting points than the other members of their respective groups. Their melting points are comparable with each other (Li =1336°C, Mg = 1100°C)
7. Li and Mg are harder than the other members of their respective groups. Hardness of Li is comparable with that of Mg.
8. Like Mg, Li decomposes water slowly to liberate H_2.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

9. Both the elements combine with N_2 on heating to form their ionic nitrides. Li_3N aad Mg_3N_2.
10. Both the elements form their chlorides, LiCl and $MgCl_2$, on heating with dry Cl_2.

$$2Li + Cl_2 \longrightarrow 2LiCl$$

$$Mg + Cl_2 \longrightarrow MgCl_3$$

Both the chlorides have many similar properties, e.g. (i) Both are deliquescent solids (ii) Both are soluble in water and alcohol (iii) Both form hydrates viz. $LiCl. 2H_2O$ and $MgCl_2 6H_2O$ (iv) Both undergo hydrolysis in hot water.

11. On heating, both the elements combine with carbon to form the carbides, Li_2C_2 and MgC_2.

12. Li, when burnt in air or O_2, forms lithium oxide, Li_2O (which is a normal oxide). Mg ribbon, under similar conditions, forms magnesium oxide, MgO (which is also a normal oxide) Like Li_2O, MgO does not combine with further quantity of O_2 to form the peroxide (M_2O_2) or super-oxide (MO_2).

13. Of all the alkali metal hydroxides, LiOH is less soluble in water, less basic and decomposes on healing to form Li_2O. Likewise $Mg(OH)_2$ is also sparingly soluble, less basic and decomposes on heating to form MgO.

$$2LiOH \longrightarrow Li_2O + H_2O$$

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$

14. The solubility of lithium salts resembles that of the corresponding magnesium salts, e.g. fluorides, carbonates and phosphates of the both the metals are insoluble in water while the chlorides, bromides, iodides and perchlorates are soluble in oxygenated organic solvents.

15. $MgSO_4$, Li_2SO_4 does not form alums.

16. Due to their covalent nature, the alkyls of Li and Mg are soluble in organic solvent, e.g., $LiAlH_4$, RMgX are soluble in either. Akyls of Li undergo reactions similar to Grignard reagents (RMgX),

17. Li+ and Mg^{2+} ions are strongly hydrated.

Cause of Diagonal Relationship. Why Li resembles in its many properties whit its diagonally opposite element viz., Mg can be explained as follows on the basis of the concept of electronegativity.

We know that electro-negativity increases from left to right in a period and decreases on descending a group. Thus, Be is more electronegative than Li (Be=1.5 Li=1.0; Be> Li) and Mg is slightly less electronegative than Be. (Be=1.5, Mg=1.2; Be> Mg). Li and Mg being slightly less electronegative than Be have almost the same value of electronegativity and hence have many similar properties, i.e., they show diagonal relationship with each other.

Anomalous Behavior of Beryllium: Dissimilaries with other Alkaline Earth Metals

Beryllium, the first element of the group differs from rest of alkaline earth metals due to its small atomic size (0.90 Å) and comparatively high electro-negativity (1.5). The main points of difference are:

1. Beryllium is the hardest of all the elements of its group.
2. The melting and boiling points of beryllium are the highest.

3. Beryllium has a tendency to form covalent compounds. Thus, when it reacts with another element, the electronegativity difference is not so large and the bond is, therefore, covalent.

4. Beryllium does not react with water even at high temperatures. Other alkaline earth metals decompose water liberating H_2 gas.

$$Mg + H_2O \longrightarrow MgO + H_2$$

5. Beryllium does not react with hydrogen directly to form its hydride. Its hydride, however, has been prepared indirectly. The rest of the alkaline earth metals combine with hydrogen to form hydrides. The hydrides of Be and Mg are covalent, whereas the hydrides of other metals are ionic.

6. Beryllium reacts with alkalies to form hydrogen.

$$Be + 2NaOH \longrightarrow \underset{\substack{\text{Sodium}\\ \text{beryllate}}}{Na_2BeO_2} + H_2 \uparrow$$

Other alkaline earth metals do not react with alkalies.

7. The oxides and hydroxides of beryllium are amphoteric, i.e., dissolve in both acids and alkalis to form salts.

$$BeO + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

The oxides and hydroxides of other alkaline earth metals are basic.

8. Beryllium carbide is decomposed by water to form methane (CH_4).

$$BeC + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

The carbides of other alkaline earth metals are decomposed by water to form acetylene (C_2H_2). For example:

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

9. Be_3N_4 is volatile while the nitrides of other alkaline earth metals are non-volatile.

10. The salts of Be^{2+} ion cannot have more than four molecules of water of crystallization while other alkaline earth metals have more than four molecules of water of crystallization.

11. Be^{2+} ion, on account of its small size, forms many stable complex compounds like $[BeF_3]^-$, $[BeF_4]^{2-}$ while M^{2+} ions derived from other alkaline earth metals form very few complex compounds.

Diagonal Relationship between Be and Al: Similarities between Be and Al

Since Be is placed diagonally opposite to Al in the periodic table, it shows diagonal relationship with Al, i.e., both these elements show many similar properties. In fact the similarity between Be and Al is so striking that Be—Al pair is considered to be an ideal diagonal pair in the periodic table and hence the similarity between Be and Al is the best example of diagonal relationship. Their diagonal relationship is attributed because of the following reasons:

(i) Polarizing powers (i.e., ionic potentials), which are equal to charge/radius ratio, of Be^{2+} (=6.45) and Al^{3+} (=6.00) are of similar magnitude as shown below:

Ion:	Be^{2+}	Al^{3+}
Charge on ion;	+2	+3
Ionic radius (Å);	0.31	0.50
Charge/radius ratio:	2/0.31=6.45	3/0.50=6.0

(ii) The standard oxidation potential of Be (+1.70 volts) for the electrode reaction:

$$Be \longrightarrow Be^{2+} + 2e^-, E^\circ_{ox} = +1.70 \text{ volts}$$

is very close to that of Al(+1.67 volts) for the electrode reaction:

$$Al \longrightarrow Al^{3+} + 3e^-, E^\circ_{ox} = +1.67 \text{ volts}$$

(iii) The electronegativity values of both the elements are the same (Be=1.5, Al=1.5)

(iv) Both the metals are weakly electropositive.

The following points show that Be and Al have many similar properties, i.e, they show diagonal relationship.

1. The ionic radius of Be^{2+} (0.31 Å) is comparable with that of Al^{3+} (0.50 Å)
2. Both the metals are obtained by the electrolysis of their fused salts in the presence of fluoride.
3. Heats of vaporization of both the elements at their boiling points are comparable (Be = 73.9 k.cal/g.atom, Al=67.9 k.cal/g.atom).
4. In nature both the elements occur together in beryl, $3BeO.Al_2O_3.6SiO_2$.
5. Both the elements form the polymerized hydrides which are covalent in nature.
6. Both Be and Al have small size and higher charge density and as such they have a strong tendency to form covalent compounds. Thus the compounds of both the elements have lower melting points, are soluble in organic solvents and get hydrolysed by water.
7. Both Be and Al are rendered passive by HNO_3 due to the formation of an inert and imperious film of their oxide on the surface of the metals.
8. Both the metals dissolve in boiling alkalies liberating H_2 and forming beryllates and aluminates respectively, e.g.

$$\mathrm{Be} + 2\mathrm{NaOH} \longrightarrow \underset{\text{Sodium beryllate}}{\mathrm{Na_2BeO_2}} + \mathrm{H_2} \uparrow$$

$$\mathrm{Al} + 2\mathrm{NaOH} + 2\mathrm{H_2O} \longrightarrow \underset{\text{Sodium aluminate}}{2\mathrm{Na_2AlO_2}} + 3\mathrm{H_2} \uparrow$$

9. Both the metals burn in O_2 and form oxides. The oxides and hydroxides of both the metals are amphoteric in nature, i.e., they are soluble in acids and alkalis.

10. Both the metals react with halogens and from halides.

$$\mathrm{Be} + \mathrm{Cl_2} \longrightarrow \mathrm{BeCl_2} : 2\mathrm{Al} + 3\mathrm{Cl_2} \longrightarrow \mathrm{AlCl_3}$$

These halides have low melting points and are hydrolyzed by water. The anhydrous halides (excepting fluorides) are covalent in nature and as such they dissolve in organic solvents and fume in moist air. Their halides also behave as Lewis acids.

11. Both the metals form carbides (Be_2C and Al_3C_3) which evolve methane on hydrolysis.

$$\mathrm{BeC} + 4\mathrm{H_2O} \longrightarrow \mathrm{CH_4} + 2\mathrm{Be(OH)_2}$$

$$\mathrm{Al_4C_3} + 12\mathrm{H_2O} \longrightarrow 3\mathrm{CH_4} + 4\mathrm{Al(OH)_3}$$

12. Be^{2+} and Al^{3+} ions have strong tendency to form chelate type complexes.

13. Salts of both the metals like nitrates, sulphates and chlorides crystallize from aqueous solutions as hydrates. They get easily hydrolysed in solution. The extent of hydrolysis of the salts of both the metals is almost comparable.

    The carbonates of both the metals are unstable, except in an atmosphere of CO_2.

14. Both the ions give hydrated ions in aqueous solution like $[Be(H_2O)_4]^{2+}$ and $[Al(H_2O)_6]^{3+}$.

15. Both the metals form bridged chlorides in vapor form.

16. Both the metals combine with N_2 and form nitrides. These nitrides are decomposed by water to form NH_3.

$$3\mathrm{Be} + \mathrm{N_2} \longrightarrow \mathrm{Be_3N_2}$$

$$2\mathrm{Al} + \mathrm{N_2} \longrightarrow 2\mathrm{AlN}$$

$$\mathrm{Be_3N_2} + 6\mathrm{H_2O} \longrightarrow \mathrm{Al(OH)_2} + 2\mathrm{NH_3}$$

$$\mathrm{AlN} + 3\mathrm{H_2O} \longrightarrow \mathrm{Al(OH)_3} + \mathrm{NH_3}$$

Anomalous Properties of Boron: Dissimilarities of Boron with Other Elements of Group III A. In many properties boron differs from the other elements of its own sub-group. The main points of difference are:

B has a very small atomic radius. The hypothetical B^{3+} ion has very small size, high charge and hence high charge density. This value is so high that B^{3+} ion does not exist. All the compounds of boron are, therefore, covalent.

2. Boron has less than four valence-electrons and this gives it a great election accepting power, i.e., its compounds behave as strong Lewis acids and hence forms a large number of complex compounds exhibiting its tendency to acquire a stable octet.
3. Boron shows a maximum covalency of four while all other elements show a covalency of six or more.
4. It does not exhibit inert pair effect.

Diagonal Relationship between B and Si: Similarities between B and Si

Boron resembles silicon in many of its properties with which it is diagonally related. Some common properties showing the similarities between B and Si are given below:

1. Both the elements can be prepared by reducing their oxides with Mg.

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

2. Both the elements dissolve in alkalies (boron only in fused while silicon in fused as well as aqueous), forming meta-borate (BO_2^-) and meta-silicate (SiO_3^{2-}) and liberate H_2.

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2\uparrow$$

$$Si + 2NaOH + H_2O \longrightarrow NaSiO_3 + 2H_2\uparrow$$

3. None of the elements is attacked by water and non-oxidising acids.
4. None of these elements occurs in the free state. Both are found as oxy-compounds, e.g. borates and silicates.
5. Chemically both the elements are typical non-metals and are bad conductors of heat and electricity.
6. Both the elements exist in two allotropic forms viz. amorphous and crystalline. The crystalline form of both the elements is harder and elements are almost the same.
8. Both the elements have high melting points (B=2300°C, Si=1420°C).

9. Both the elements form mainly covalent compounds like hydrides (e.g. B_2H_6, SiH_4) halides (e.g. BX_3, SiX_4), oxides (e.g. B_2O_3, SiO_2).

10. Both the elements are normally inert at ordinary temperature. For example they are not oxidized in air and do not react with other elements or with dilute acids. However, the reactivity can be increased by increasing the temperature. At high temperatures these elements react with a number of metals and non-metals.

11. Both the elements combine with metals like Mg and form borides and silicides respectively.

$$2B + 3Mg \longrightarrow Mg_3B_2 \quad \text{(Boride)}$$

$$Si + 2Mg \longrightarrow Mg_2Si \quad \text{(Silicide)}$$

12. Boron and silicon combine with O_2, at elevated temperature to form the stable oxides viz. B_2O_3 and SiO_2.

$$4B + 3O_2 \longrightarrow 2B_2O_2$$

$$Si + O_2 \longrightarrow SiO_2$$

13. BCl_3 and $SiCl_4$ can be prepared by passing dry Cl_2 over a heated mixture of the oxide (B_2O_3 or SiO_2) and carbon.

$$B_2O_3 + 3C + 3Cl_2 \longrightarrow 2BCl_3 + 3CO$$

$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

14. No oxy-salts of boron and silicon containing cationic boron and silicon are known.

15. B and Si form similar hydrides known as boranes and silanes respectively.

16. Both the elements combine with sulphur at elevated temperatures to form sulphides (B_2S_3 and SiS_2). These sulphides are attacked by water with the liberation of H_2S.

$$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$

$$SiS_2 + 4H_2O \longrightarrow H_4SiO_4 + 2H_2S$$

17. Nitrides (BN and Si_3N_4) can be obtained either by the direct combination of the elements with N_2 or by passing N_2 over heated mixture of the oxide and carbon. These nitrides decompose steam, liberating NH_3.

$$BN + 3H_2O\ \text{(steam)} \longrightarrow H_3BO_3 + NH_3 \uparrow$$

$$Si_2N_4 + 12H_2O\ \text{(steam)} \longrightarrow 3H_4SiO_4 + 4NH_3$$

18. The carbides, viz B_4C and SiC are obtained by heating the elements with carbon in an electric furnace. On a commercial scale these are obtained by heating their oxides with carbon in an electric furnace.

19. Both the elements form complexes, e.g., hydrofluoboric acid, HBF, and fluosilicic acid, H_4SiF_6.

Anomalous Properties of Oxygen: Dissimilarities with Other Elements of Group VIA. Oxygen, the first element of group VI A, like carbon (group IV A) and nitrogen (group V A) differs considerably from the rest of the elements of group VI A because of the following inherent characteristics of oxygen; (i) Small size (ii) Higher electronegativity (iii) Non-availability of *d* orbital in the electronic oxygen and the remaining members of group VI A are given below:

(i) Oxygen is a gas while the other members are solids.

(ii) Oxygen is the most abundant of all the elements and constitutes 46.6% of the earth's crust.

(iii) Oxygen molecule is diatomic (O_2) while the molecules of the other elements are more complex, e.g. sulphur and selenium have octatomic molecules (i.e. S_8 and Se_8) with puckered ring structures.

(iv) Oxygen does not show any positive oxidation state except in oxygen difluoride, OF_2 in which it shows +2 oxidation state, while the other members of this group show both positive and negative oxidation states. Positive oxidation states are more frequent.

(v) On account of higher electronegativity of oxygen atom, dinegative anion O^{2-} (oxide anion) is more common while the S^{2-}, Se^{2-} and Te^{4-} ions are less probable.

(vi) The maximum covalency of oxygen is two because of the absence of *d*-orbitals in its valence-shell. Other elements, on the other hand, exhibit a maximum covalency of six due to the presence of *d*-orbitals in which *s*-and *p*-electrons can be promoted and thus can be made unpaired.

(vii) Since oxygen is highly electronegative , hydrogen bonding is found to occur in oxygen compounds like H_2O etc. Other elements, because of low electronegativity, do not form compounds having hydrogen bonding. Recently, however, weak hydrogen bonding involving sulphur has been proved to exist.

(viii) The hydride of oxygen (H_2O) is a colorless, odorless and non-poisonous liquid while the hydrides of other elements are inflammable gases with an unpleasant smell and are poisonous.

(ix) Oxygen shows paramagnetic behavior.

(x) Metals like Cu, Ag, Hg etc. show lesser tendency to react with O_2 to form oxides than with sulphur to form sulphides. This is because of the fact that a stronger bond is formed when larger S^{2-} ion is polarized by the small Cu^{2+}, Ag^{+}, Hg^{2+} ions. It is because of this reason that in nature weaker metals tend to occur as sulphides rather than as oxides.

Anamalous Behviour of Fluorine: Dissimilarities of Fluorine with Other Halogens. Like other element such as C. N and O which are the first members of their respective groups, fluorine also differs from the other members of its own sub-group due to (a) its small size (b) its high electro-negativity and (c) non-availability of *d*-orbitals in its valence shell. The main differences are: (i) Due to its maximum electronegativity, it shows only a negative oxidation state of –1. It does not show any positive oxidation state. The other members show negative as well as positive oxidation states of +1, +3, +5 and +7. (ii) Fluorine is the most reactive element among halogens. This is due to the minimum value of F – F bond dissociation energy. (iii) On account of high electro-negativity of fluorine atom hydrogen bonding occurs in HF molecule while it is absent in HCl, HBr and HI molecule. The presence of hydrogen bonding in HF explains why (a) HCl, HBr and HI are gaseous while HF is a liquid with an abnormally high boiling point (b) HF forms a number of compounds containing HF_2^- ion (e.g. $K^+HF_2^-$) while such compouns (e.g. $K^+HCl_2^-$, $K^+HBr_2^-$ etc.) are not given by other HX molecules. (iv) HF ionizes only slightly in aqueous solution and is, therefore a weak acid. HCl, HBr and HI, on the other hand, ionize almost completely and are thus strong acids. (v) Fluoride of silver is soluble while other halides of silver are insoluble. Similarly fluoride of calcium is insoluble and other halides of calcium are soluble. (vi) Fluorides are ionic while other halides have frequently molecular lattices. (vii) F^- ion has a great tendency to give complex ions like $[AlF_6]^{3-}$, $[FeF_6]^{3-}$ etc. The remaining halide ions show this tendency to a much lesser extent. (viii) Fluorine, being the most electronegative, gives SF_6 while other members do not form hexahalides with sulphur. (ix) Because of the absence of *d*-orbitals in its valence shell, fluorine does not combine with F^- ions to give polyhalide ion, F_3^- while other members of the group give such ions (e.g. Cl_3^-, Br_3^-, I_3^-, I5- etc.) because they contain *d*-orbitals.

1.26 PERIODICITY IN PROPERTIESOF TRANSITION ELEMENTS

The elements from Sc_{21} to Zn_{30} (ten elements), Y_{39} to Cd_{48} (10 elements), La_{57}, Hf_{72} to Hg_{80} (ten elements), Ac_{89}, Rf_{104}, Db_{105}, Sg_{106} Rg_{111} etc. are called transition metals. Since the last electron in the atoms of these elements enters *d*-subshell belonging to penultimate shell [i.e. (*n*-1) the shell], these elements are also called *d*-block elements. Thus in these elements the last electron goes to (*n*-1) *d* sub-shell.

The transition elements show several properties. Some of these properties and their trends of variation are discussed below:

1. Atomic radii

The atomic radii of the atoms of *d*-block elements are given in Table 1.14. The following trends may be observed:

(i) Variation of atomic radii in a given period. The atomic radii of the elements of a particular series decrease gradually up to the midway element and then these values remain almost constant up to the element of group 11 (Cu, Ag and Au). The last element of each series (Zn, Cd and Hg) shows in increase in its atomic radius.

For example, for the elements of 1st transition series the atomic radii decrease gradually from Sc to Mn but from Fe to Cu these values remain practically constant. The atomic radius of Zn is higher than that of Cu. Similar behavior has been observed for the elements of 2nd and 3rd transition series.

Table 1.14. Atomic radii (pm) of *d*-block elements

	IIIB (3)		IV B (4)	VB (5)	VI B (6)	VII B (7)	← VIII (8)	(9)	→ (10)	IB (11)	IIB (12)
1st	Sc_{21}		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
series	162		147	134	127	126	126	125	124	128	138
2nd	Y_{39}		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
series	180		160	146	139	136	134	134	137	144	154
3rd	La_{57}	Ce_{58}—Lu_{71}	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
series	187	165 156	158	146	139	137	135	136	138	144	157

↑

14 lanthanides

Explanation. For the elements from Sc to Mn the atomic radii decrease. This decrease is because of the gradual increase in nuclear charge with the increase in atomic number. The increased nuclear charge makes the atom to shrink in size and hence the size of the atom decreases. However, since the electrons added to 3 *d* orbital screen the 4*s* electron(s), the attraction between the nucleus and the 4*s* electron(s) decrease, i.e., due to the screening effect caused by d electrons the magnitude of nuclear charge decreases and consequently the atomic radii for the elements from Fe to Cu remain almost uncharged. Towards the end of each series, there is an increase in electron-electron repulsion between the electrons being added to 3 *d* orbital. This increase in repulsion becomes greater than that of the attraction between the nucleus and the 4*s* electron(s). Because of the greater of electron-electron repulsion, the electron cloud of Zn expands and hence it size also becomes greater than that of Cu.

(ii) Variation of atomic radii in a given group. The covalent radii of the atoms of the elements of group. (Sc, Y and La) increase (as expected) from top to bottom as the atomic number increases. When we compare these values for the elements of other groups of transition elements, it is found that these values for the elements of 2nd transition series are higher (as expected) than those for the elements of 1st transition series, but these values for the elements of 3rd transition series are almost equal to those for the elements of 2nd transition series. The similarity in the covalent radii for the elements of 2nd and 3rd series is due to lanthanide contraction which takes place among lanthanides (Ce_{58} to Lu_{71} = 14 elements). These 14 lanthanides are present between La_{57} (group 3) and Hf_{72} (group 4) in 3rd transition series.

Due to the similarity in the covalent radii of the elements of 2nd and 3rd transition series, these elements show close similarity in their properties while the elements of 1st and 2nd transition series do not exhibit so close similarity. For example the solubility of the salts of the elements of 2nd and 3rd transition is very close and hence the separation of these elements by precipitation method is difficult. Examples of the pairs of elements which show similar properties and hence are difficult to separate are Rh-Ir, Pd-Pt, Ag-Au. The above discussion shows that due to lanthanide contraction the elements of 2nd and 3rd transition series resemble each other much more than the elements of 1st and 2nd transition series.

2. Ionic radii

The ionic radii of the common cations derived from transition metals have been given in Table 1.15 The following trends in their values may be noted:

(i) Since the transition metals show many oxidation states (variable oxidation states), the radii of the ions in different oxidation states are also different.

(ii) In general the ionic radii of different cations of the same element in different oxidation states decrease with the increase in oxidation state. For example, $Ti^{2+} > Ti^{3+} > Ti^{4+}$; $Cr^{2+} > Cr^{3+} > Cr^{4+} > Cr^{5+} > Cr^{6+}$; $Cu^{+} > Cu^{2+}$ etc.

(iii) Ionic radii of the cations of different elements in the same oxidation state generally decrease with the increase in nuclear charge or atomic number. Thus the ionic radii of the bivalent cations derived from the elements of 1st transition series decrease as we move from left to right in the series, i.e., $Ti^{2+} > V^{2+} > Cr^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$.

(iv) These values for the cations of the elements of group 3 (i.e., Sc^{3+}, Y^{3+} and La^{3+}) increase as $Sc^{3+} < Y^{3+} < La^{3+}$, but these values for the cations derived from most of the elements of 3rd transition series are almost the same as those of the corresponding cations derived from the elements of 2nd transition series. The similarity in their ionic radii is due to the presence of 14 lanthanides (Ce_{58} to Lu_{71}) between La_{57} (group 3) and Hf_{72} (group 4)

Table 1.15. Ionic radii (pm) of the common cations derived from *d*-block elements

	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1st series	Sc_{21} +2=81 +3=88.5	Ti +2=91 +3=76 +4=74.5	V +2=88 +3=74 +4=72 +5=68	Cr +2=84 +3=69 +4=68 +5=63 +6=58	Mn +2=80 +3=66 +7=60	Fe +2=76 +3=64	Co +2=76 +3=63	Ni +2=72	Cu +1=91 +2=69	Zn_{30} +2=74
2nd series	Y_{39} +3=104	Zr +4=86	Nb +3=86 +4=82 +5=78	Mo +3=83 +4=79 +5=75 +6=73	Tc +4=78.5 +5=74 +7=70	Ru +3=82 +4=76 +5=70.5	Rh +3=80.5 +4=74 +5=69	Pd +2=100 +3=90 +4=75.5	Ag +1=129 +2=108 +3=89	Cd_{48} +2=109
3rd series	La_{57} +3=117.2	Hf_{72} +4=85	Ta +3=86 +4=82 +5=78	W +4=80 +5=76 +6=74	Re +4=77 +5=72 +6=69 +7=67	Os +4=77 +5=71.5	Ir +3=82 +4=76.5 +5=71	Pt +2=94 +4=76.5 +5=71	Au +1=51 +3=99 +5=71	Hg_{80} +1=133 +2=116

3. Metallic character

All the transition elements show metallic character, i.e., all these elements are metals.

Since the transition elements have low values for their ionization energies, *ns* electrons can easily be lost by them to form M^+ or M^{2+} cations and thus these elements show metallic character.

As usual, the metallic character of these elements increases on descending the group, e.g., basic character of the peroxides of the elements of group 5 (V_2O_5, Nb_2O_5 and Ta_2O_5) increases as $V_2O_5 < Nb_2O_5 < Ta_2O_5$. Thus V_2O_5 is amphoteric (but more basic than acidic) while Nb_2O_5 and Ta_2O_5 are more basic than acidic.

The metallic character of the transition elements is evident from the following properties of these elements (i) electrical conductivity (ii) hardness and (iii) crystalline structure.

4. Atomic volumes and densities

The atomic volumes (in ml) and density (in g/cm^3) of transition elements are given below in Table 1.16. The values given against ml are atomic volumes while those given against g/cm^3 represent densities.

Table 1.16. Atomic volumes (ml) and densities (g/cm3) of d-block elements.

	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
	Sc_{21}	Ti_{22}	V	Cr	Mn	Fe	Co	Ni	Cu	Zn_{30}
ml	15.02	10.60	8.35	7.23	7.39	7.10	6.70	6.60	7.10	9.20
g/cm^3	3.01	4.51	6.10	7.19	7.43	7.86	8.90	8.90	8.96	7.14
	Y_{39}	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd_{48}
ml	19.8	14.1	10.8	9.4	—	8.3	8.3	8.9	10.4	13.1
g/cm^3	4.47	6.49	8.40	10.21	11.50	12.20	12.40	12.00	10.51	8.65
	La_{71}	Hf_{72}	Ta	W	Re	Os	Ir	Pt	Au	Hg_{80}
ml	20.50	13.60	10.91	9.53	8.85	8.43	8.54	9.10	10.22	14.80
g/cm^3	6.17	13.10	16.60	19.30	21.00	22.60	22.50	22.40	19.30	13.60

Atomic volumes of *d*-block elements are much lower than those of the elements of *s*- and *p*-blocks.

We know that density and atomic volume are inversely proportional to each other. All the transition metals have low values for their atomic volumes and hence their densities are high. The atomic volumes are low because the electrons are added to $(n - 1)$ *d* orbtals and not to ns orbital. The increased nuclear charge is partly screened by $(n - 1)$ d electrons and ns electrons are strongly attracted by the nucleus. Consequently the densities of transition metals are high.

Variation of atomic volumes in a given series. In a given transition series, the density of the elements increases on moving from left to right and attain a maximum value for the elements of group 9. They then start increasing as we proceed further to the elements of group 11 and 12.

Variation of densities in a given sub-group. Densities of elements belonging to the same sub-group increases on moving down the sub-group. The densities of the elements of 2nd transition series are only slightly higher than those of the corresponding elements of 1st transition series while these values for the transition elements from Hf_{72} to Hg_{80} (elements of 3rd transition series) are almost double these values for the elements from Zr_{40} to Cd_{48} respectively (elements of 2nd transition series). Note that the density of La_{57} (=6.17) is not double that of the value for Y_{39} (=4.47).

The variation of densities of transition series elements in a given sub-group, as discussed above, can be explained as follows:

(a) The atomic weights of the elements of 3rd transition series are almost double the atomic weights of the corresponding elements of 2nd transition series. This makes the densities of the elements of 3rd transition series almost double those of the corresponding elements of 2nd transition series.

(b) Because of lanthanide contraction occurring in lanthanides, the atomic sizes of the elements of 3rd transition series coming after Lu_{71} (i.e. elements from Hf_{72} to Hg_{80}) become very small. Consequently the packing of the atoms in their metallic crystals become so much compact that their densities become very high. Thus the densities of the elements of 3rd transition series become almost double the densities of the corresponding elements of 2nd transition series.

5. Melting and boiling points

The melting and boiling points of transition metals are given in Table 1.17 these values suggest that these are very high values. The high values are due to the fact that transition metals have strong metallic bonding between their atoms.

Table 1.17. Melting and boiling points (°C) of *d*-block elements.

3d-seires elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
M.P.(°C)	1539	1668	1900	1875	1245	1536	1495	1453	1083	419.5
B.P.(°C)	2730	3260	3450	2665	2150	3000	2900	2730	2595	906.00
4d-series elements	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
M.P.(°C)	1509	1852	2415	2610	2200	2500	1966	1552	960.8	320.9
B.B.(°C)	2927	1500	3300	5560	—	4900	4500	3980	2210	765
4d-series elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
M.P.(°C)	920	2222	2996	3410	3180	2700	2454	1769	1063	-32.4
B.P.(°C)	3470	5400	5425	5930	5900	5500	5300	4530	2920	357

As we proceed along a particular series, the melting points increase from Sc to Cr in 1st series (V and Cr have almost equal melting points), from Y to Mo in 2nd series and from La to W in 3rd series, and then decrease. This variation can be explained as follows:

We know that the strength of metallic bonding is roughly related with the number of unpaired electrons present in the valence-shell of the element. In general, greater in the number of unpaired electrons, stronger is the metallic bonding and hence greater is the melting point of the element. As we move along a particular series, since the number of unpaired electrons increases up to Cr (in 1st series) Mo (in 2nd series) and W (in 3rd series), the melting points of the elements also increase up to these elements and then with decrease in the number of unpaired electrons, their melting points are the lowest in their respective periods. Their melting points are so low that these elements can be volatilized off easily. In fact, Hg is a liquid at room temperature.

Although Mn, Tc and Te also have the maximum number of unpaired electrons, these elements have lower values of their melting points than Cr, Mo and W respectively. Their low values are due to the fact that the metallic bonding in these elements is relatively weak.

6. Ionization energies

The values of first ionization energy (in kJ/mole) of 1st, 2nd and 3rd transition series elements are given in Table 1.18. From this table the following points may be noted:

(i) The values of ionization energy increase as we move from left to right in each series, although the increase is not quite regular, i.e., the increase in ionization energies is quite gradual or slow. The reason for the gradual increase is given below.

Explanation: We know that when we move from left to right in a given series, the nuclear charge increases. The increased nuclear charge would attract the ns^2 electron cloud with greater force and hence the ionization energies are expected to increase at each step. However, as the electron is added to $(n-1)$ d sub-shell at each next element, the ns^2 electrons are shielded more and more. The effect of increasing nuclear charge is opposed by the additional screening effect of the nucleus and consequently, the ionization energies increase but quite slowly along a given series.

Table 1.18. Ionization energies (kJ mol^{-1}) of d-block elements

Groups →	(3)		(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
1st or 3rd series (4th period) →	Sc$_{21}$ 631		Ti$_{22}$ 658	V$_{23}$ 650	Cr$_{24}$ 652.8	Mn$_{25}$ 717.4	Fe$_{26}$ 759.4	Co$_{27}$ 758	Ni$_{28}$ 736	Cu$_{29}$ 745.5	Zn$_{30}$ 906.4
2nd or 5d series (6th period) →	Y$_{39}$ 616		Zr$_{40}$ 660	Nb$_{41}$ 664	Mo$_{42}$ 685	Tc$_{43}$ 702	Ru$_{44}$ 711	Rh$_{45}$ 720	Pd$_{46}$ 805	Ag$_{47}$ 731	Cd$_{48}$ 867.7
3rd or 5d series (6th period) →	La$_{57}$ 538.1	(Ce$_{58}$ – Lu$_{71}$)	Hf$_{72}$ 654	Ta$_{73}$ 761	W$_{74}$ 770	Re$_{75}$ 760	Os$_{76}$ 840	Ir$_{77}$ 870	Pt$_{78}$ 870	Au$_{79}$ 890	Hg$_{80}$ 1007

These values have been taken from Table 2.2A, page 40-42, "Inorganic Chemistry: principles of Structure and Reactivity" (2nd edition) by Jannes E. Huheey.

(ii) When we proceed from top to bottom in group 3, ionization energy values decrease as Sc$_{21}$ > Y$_{39}$ > La$_{57}$. However, in most of the remaining groups the ionization energies increase in the same direction, i.e., the ionization energies of the elements lying after La$_{57}$ in 3rd series are greater than those of their corresponding elements lying in 1st and 2nd series.

Explanation. In the atoms of 14 elements following La$_{57}$ (Ce$_{58}$ to Lu$_{71}$), $4f$ orbitals are completely filled and hence cannot shield the nucleus effectively. Due to ineffective (i.e., poor) shielding of the nucleus by the $4f$ electrons, the elements lying after La$_{57}$ in 3rd series have greater effective nuclear charge acting on the ns^2 electrons. Therefore, the ionization energies of the elements following La$_{57}$ in 3rd series are higher than those of their corresponding elements lying in 1st and 2nd series.

(iii) In each series the elements of group 12 (Zn, Cd and Hg) have the highest values for their ionization energy. This is due to the extra stability associated with their completely-filled (n – 1) d and ns orbitals ($Zn_{30} = 3d^2$, $Cd^{48} = 4d^{10}\,5s^2$ and $Hg_{80} = 5d^{10}\,6s^2$).

(iv) When we compare these values of *d*-block elements with those of *s*-and *p*-block elements, we find that these values are higher than those of *s*-block elements but lower than those of *p*-block elements. It is also seen that in any particular series, the difference in ionization energies between any two successive *d*-block elements is much less as compared to the difference in case of successive *s*-block or *p*-block elements.

7. Variable oxidation states

With the exception of a few elements, most of the *d*-block elements show more than one oxidation state (i.e., variable or several oxidation states). The following two reasons have been given to explain why *d*-block elements show several oxidation states:

(i) (*n* – 1) *d* and *ns* orbitals in the atoms of *d*-block elements have almost the same energies and hence electrons can be removed from (*n* – 1) *d* orbitals as easily as they can be removed from *ns* orbital.

(ii) After removing *ns* electron(s) the remainder is called core or kernel (penultimate shell).

In case of most the *d*-block elements, the core is unstable and hence can lose one or more electrons, resulting in the formation of cations having different oxidation states, i.e., the removal of one or more electrons from the unstable core gives several oxidation states to transition metals.

Various oxidation states shown by transition elements are given in Table 1.19 oxidation states shown in bracket are unstable oxidation states.

Table 1.19. Various oxidation states of transition metals.Unstable oxidation states are shown in brackets.

Elements of 1st transition series (3d-series) (*n* =No. of unpaired electrons)

Sc	$3d^1 4s^2$	($n = 1$)	+2, +3
Ti	$3d^2 4s^2$	($n = 2$)	(0, -1), +2, +3, +4
V	$3d^3 4s^2$	($n = 3$)	(-1, 0, +1) +2, +3, +4, +5
Cr	$3d^5 4s^1$	($n = 6$)	(0, +1), +2, +3, (+4, +5), +6
Mn	$3d^5 4s^2$	($n = 5$)	(-1, 0, +1), +2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	($n = 4$)	(-2, 0, +1), +2, +3, (+4, +5. +6)
Co	$3d^7 4s^2$	($n = 3$)	(-1, +0, +1). +2, +3, (+4)
Ni	$3d^8 4s^2$	($n = 2$)	(0, +1), +2, +3, +4

Cu	$3d^{10}4s^1$	($n = 1$)	+1, +2, (+3)
Zn	$3d^{10}4s^2$	($n = 0$)	+2

Elements of 2nd transition series (4d-series)

Y	+3
Zr	(0, +3), +4
Nb	(-1, 0, +1, +2, +3, +4), +5
Mo	(0, +1), +2, +3, +4, +5, +7
Tc	(0), +2, (+3, +4, (+5, +6, +7)
Ru	(0), +2, +3, +4, (+5, +6, +7, +8)
Rh	(0, + 1), +2, +3, +4, (+6)
Pd	(0) +2, (+3), +4
Ag	+1, (+2, +3)
Cd	+2

Elements of 3rd transition series (5d- series)

La	+3
Hf	(+3), +4
Ta	(-1, +1, +2, +3, +4), +5
W	(0, +1), +2, (+3), +4, +5, +6
Re	(-1, 0, +1, +2), +3, +4, +5, (+6), +7
Os	(0), +2, +3, +4, (+5), +6, (+7), +8
Ir	(0, + 1), +2, +3, +4, (+6)
Pt	(0), +2, (+3), +4, (+5, +6)
Au	+1, +3
Hg	+1, +2

No. of various oxidation states shown by elements. When we proceed from Sc (Sc = $3d^1$ $4s^2$, n = 1) to Mn (Mn = $3d^54s^2$ n = 5) in the series, the number of unpaired electrons (n) increases from 1 (in Sc) to 5 (in Mn) (do not consider Cr which has 6 unpaired electrons) and hence the number of various oxidation states shown by the elements increases from Sc to Mn. On proceeding further from Mn to Zn (Z = $3d^{10}$, $4s^2$, n = 0) the number of unpaired electrons decreases from 5 in Mn to zero in Zn and hence the number of various oxidation states shown by Mn is maximum while that shown by the elements lying at the right and left of Mn goes on decreasing when we proceed in either direction of Mn.

Oxidation state of Zn. $3d^{10}$ orbitals in Zn^{2+} ion ($Zn^{2+} = 3d^{10}4s^0$), being completely-filled, are stable and hence do not lose any more electrons. Thus Zn atom cannot show any oxidation state higher than +2.

Relative stability of various oxidation states. (a) The relative stability of various oxidation states of a given element can be explained on the basis of the stability of d^0, d^5 and d^{10} orbitals. For example. Ti^{4+} ($3d^0.4s^0$) is more stable than Ti^{3+} ($3d^1.4s^0$) because of the presence of $3d^0$ orbital in Ti^{4+} ion. Mn^{2+} (($3d^5.4s^0$) is more stable than Mn^{3+} ($3d^4 4s^0$), since Mn^{2+} ion has $3d^5$ orbital.

The stability of +2 oxidation state increases as we proceed from Sc to Zn in the series, i.e., the reducing power of M^{2+} ions decreases from left to right. For example the salts of V^{2+} (vanadous states) and Cr^{3+} (chromous salts) are powerful reducing agents while the salts of other orbital ($Mn^{2+} = 3d^5$) Ni^{2+} and Cu^{2+} don't have reducing property.

The stability of +3 oxidation state decreases on proceeding from Sc to Cu (Zn does not show +3 is a stable oxidation state) in the series, i.e., the oxidizing power of M^{3+} ions increases along readily oxidized to Ti^{4+} ion. V^{3+} and Cr^{3+} ions do not act as oxidizing agents (i.e., these ions are stable), since they do not get reduced to cations with lower oxidation states. Mn^{3+} ion acts as an oxidizing agent (i.e., this ion is unstable), since it is reduced to Mn^{2+} ion. Fe^{3+} ion ($3d^5.4s^0$) is stable because of the presence of stable half-filled $3d$-orbtals in it.

The stability of a given high oxidation state of different transition metals of the same sub-group increases as we move down the group, e.g., the compounds of V(+5) are oxidizing agents (i.e., unstable) while those of Nb (+5) and Ta (+5) are stable. Similarly permangnates containing Mn (+7) are strong oxidizing agents while perrhenates containing Re (+7) are stable.

1.27 PERIODICITY IN PROPERTIES OF INNER TRANSITION ELEMENTS

The elements from Ce_{58} to La_{71} (14 elements) and from Th_{90} to Lw_{103} (14 elements) are called **inner-transition elements**. These elements have been shown at a separate place at the bottom of the periodic table. The first series of 14 elements lies between La_{57} and Hf_{72} in 6th period while the other series of 14 elements lies between Ac89 and Rt_{104} in 7th period (incomplete period).

The elements of 1st series are called **lanthanides** or **lanthanones** (rare earth elements) while those of the 2nd series are called **actinides** or **actinones**. The names lnthanides and actinides have been given, since these elements follow La_{57} and Ac_{89} respectively with which these elements show close similarities.

Since the last electron (differentiating electro) in the atoms of these elements enters the f-sub-shell belonging to anti-penultimate shell [i.e. (n – 2) the shell], these elements are also called ***f*-block elements**. Thus the last electron enters $(n-2)f$ sub-shell in inner-transition elements.

Since lanthanides are present in 6th period ($n = 6$) of the periodic table, the last electron in these elements goes to $(6-2)f$ or $4f$ sub-shell. Thus actinides are also called **4*f*-block elements**. i.e., lanthanides can be defined as those elements in which the last electron goes to $4f$ sub-shell.

Similarly since actinides are present in 7th period ($n = 7$) of the periodic table, the last electron in these elements goes to $(7-2)f$ or $5f$ sub-shell. Thus actinides are also called **5*f*-block elements**. i.e., actinides are those elements in which the last electron enters $5f$ sub-shell.

Valence-shell electronic configuration of the atoms of *f*-block elements can be represented as $(n-2)f^{0-14}.\ (n-1)d^{0-2}.\ ns^2$ which shows that in these elements are outermost three shells are partially-filled while the remaining inner shells are completely-filled.

Atomic and ionic radii of M^{3+} ions: Lanthanide contraction

Atomic and ionic radii of M^{3+} ions have already been given in Table 1.20. A look at these values shows that there in a stead decrease in these values as we move from Ce to Lu and from Ce^{3+} to Lu^{3+}.

Table 1.20. Oxidation states, atomic radii and ionic radii (of M^{3+} ions) of lanthanides.

Lanthanides	Oxidation states	Atomic radii (pm)	Ionic radii (M^{3+} ions) (pm)
La	+3	169	106
Ce	+3, +4	165	103
Pr	+3, +4	165	101
Nd	+2, +3, +4	164	100
Pm	+3	—	98
Sm	+2, +3	166	96
Eu	+2, +3	185	95
Gd	+3	161	94
Tb	+3, +4	159	92
Dy	+3, +4	159	91
Ho	+3	158	89
Er	+3	157	88
Tm	+2, +3	156	87
Yb	+2, +3	170	86
Lu	+3	156	85

The steady decrease in the atomic and ionic radii (M^{3+} ions) of lanthanide elements with increasing atomic number is called **lanthanide contraction**.

When we say that there is a steady decrease in the values of atomic and ionic radii, this means that he decrease is very small. For example on moving from Ce to Lu the atomic radii decrease from 165 pm to 156 pm and the decrease is only equal to $165 - 156 = 9$ pm. Similarly, the ionic radii decrease from $103 - 85 = 18$ pm. Thus we see that although the atomic number or nuclear charge increases by +14 units which is a large number, the decrease in atomic and ionic radii is only equal to 9 pm and 18 pm respectively. This decrease in atomic and ionic radii is very small as compared to that found in the elements of other groups and periods.

It may be seen from the table that although the atomic radii show some irregularities e.g., (the atomic radii of Eu and Yb are abnormally high), the ionic radii of M^{3+} ions contract steadily.

Cause of lanthanide contraction

We know that as we proceed from one element to the next one in lanthanide series, the nuclear charge (i.e., atomic number) increases by +1 at each next element. Thus as we move from Ce to Lu, the attraction between the nucleus and the outermost shell electron increases gradually at each step. It is also known that as we move from Ce to Lu, the addition of extra electron takes place to 4*f* orbitals. Since 4*f* orbitals have very diffused shape, the electrons in these orbitals are not able to shield (decrease) effectively the attraction of the nucleus for the electrons in the outer-most shell as the atomic number of lanthanides increases. Thus it is only due to the gradual increase in the nuclear charge (i.e., increase in the attraction between the nucleus and the outer-most shell electrons) that the size of the lanthanide atoms and M^{3+} ions decreases gradually with atomic number. The above discussion show that it is due to the poor shielding effect of 4*f* electrons and gradual increase in the nuclear charge that the lanthanide contraction takes place among lanthanides.

Oxidation states of Actinides

Important oxidation states exhibited by actinides are given in Table 1.21. Most oxidation states are shown in circles while unstable ones are given in brackets.

It may be seen from these oxidation states that +2 state is shown by two elements namely Am and The in its few compounds like $ThBr_2$, ThI_2, ThS etc. +3 oxidation state is shown by all the actinides +3state becomes more and more stable as the atomic number increases. +4 oxidation state is shown by Th, Pa, U, Np, Pu, Am and Cm while +5 state is shown by the Th, Pa, U, Np, Pu and Am. +6oxidation state is exhibited by U, Np, Pu and Am while +7 oxidation state is shown by Np and Pu.

The principal cations given by actinide elements are M^{3+}, M^{4+} and oxo-cations like MO^{+2} (Oxidation state of M = +5) and MO_2^{2+} (oxidation state of M = +6). Examples of MO_2^{+} ion are UO_2^{+} and PuO_2^{+} while those of MO_2^{2+} are UO_2^{2+} and PuO_2^{+}. These oxo-cations are stable in acid and aqueous solutions.

U^{3+} ion in aqueous solution liberates H_2 on standing. Np^{3+} and Pu^{3+} are stable in water but are readily oxidized by air to Np^{4+} and Pu^{4+} respectively. All the remaining M^{3+} ions up to Md^{3+} are stable in aqueous solution. U^{4+} and Np^{4+} ions are stable in aqueous solution but are slowly oxidized by air to UO_2^{2+} (U = +6) and PuO_2^{2+} (Pu = 6)ions respectively.

Table 1.21. Important oxidation states shown by actinides. Unstable states are given in bracket.

Actinides	Oxidation states
Ac_{89}	+2, +3, +4
Th_{90}	+2, (+3), +4, +5
Pa_{91}	(+3), +4, +5
U_{92}	+3, +4, +5, (+6)
Np_{93}	+3, +4, +5, +6, +7
Pu_{94}	+3, +4, +5, +6, +7
Am_{95}	+2, +3, (+4), +5, +6
Cm_{96}	+3, (+4)
Bk_{97}	+3
Cf_{98}	+3
Es_{99}	+3
Fm_{100}	+3
Md_{101}	+3
No_{102}	+3
Lw_{103}	+3

Radii of M^{3+} and M^{4+} ions: Actinide contraction

Table 1.22. Radii of tripositive (M^{3+}) and tetrapositive (M^{4+}) actinide cations.

M^{3+} ions	Radii(Å)	M^{4+} ions	Radii (Å)
Ac^{3+}	1.11	Ac^{4+}	0.99
Th^{3+}	1.08	Th^{4+}	0.96
Pa^{3+}	1.05	Pa^{4+}	0.93
U^{3+}	1.03	U^{4+}	0.92
Np^{3+}	1.01	Np^{4+}	0.91
Pu^{3+}	1.00	Pu^{4+}	0.90
Am^{3+}	0.99	Am^{4+}	0.89
Cm^{3+}	0.98	Cm^{4+}	0.88

A look of the values of radii of M^{3+} and M^{4+} cations reveals that these values for both the caution decrease as we move from Ac to Cm. This decrease in the size of M^{3+} and M^{4+} cations in the actinide series is called actinide contraction which is analogous to lanthanide contraction found in lanthanides.

Causes of actinide contraction

We known that as we proceed from one element to the next one in the actinide series, the nuclear charge (i.e., atomic number) increases by +1 at each next element and the addition of extra electron takes place in 5*f* orbital. Again it is also known that the shielding of one electron in 5*f* orbital by the other one residing in the same orbital is very poor. Due to the negligible amount of mutual shielding effect between the electrons residing in 5*f* orbital, the increase in nuclear charge by +1 at each next element in the actinide series brings the valence-shell nearer to the nucleus and hence the size of M^{3+} and M^{4+} cautions goes in decreasing as we move from one element to the next one in the series.

QUESTIONS

Q.1. Explain the term atomic orbital. Draw the shapes and orientation of s, p and d-orbitals.

Q.2. What do you understand by the term "quantum number"? How many quantum numbers has an electron in an orbital? Name and explain them. Also explain the significance of each quantum number.

Q.3.*(a)* Write the name of the orbital for which the quantum numbers are $n = 2$ and $l = 1$.

(Ans. 2*p* sub-shell)

(b) What are the restrictions on the values of *n* and *l*?

(c) What are the possible values of *s* for an electron with $m = 0$.

Q.4. State and illustrate the following with examples:

(a) Pauli's exclusion principle.

(b) Aufbau principle.

(c) Hund's rule of maximum multiplicity.

Q.5.*(a)* What is meant by electronic configuration of atoms? State various rules for writing electronic configuration of a given atom.

(b) State electronic configurations of the following elements and locate their position in various blocks and consequently in groups: *(i)* $_{15}P$ *(ii)* $_{19}K$ *(iii)* $_{24}Cr$
(iv) $_{29}Cu$ *(v)* $_{64}Gd$ and *(vi)* $_{92}U$.

Q.6.*(a)* Give the electronic configurations of the following elements and locate their positions in the periodic table: *(i)* ${}_{13}Al$ *(ii)* ${}_{27}Co$ *(iii)* ${}_{30}Zn$ *(iv)* ${}_{42}Mo$.

(b) Give the orbital configurations and predict the magnetic behaviour of the following atoms in their ground state: *(i)* ${}_{15}P$ *(ii)* ${}_{4}Be$ *(iii)* ${}_{54}Xe$ *(iv)* ${}_{27}Co$ *(v)* ${}_{83}Bi$.

Q.7. Briefly discuss the contributions of Dobereiner and Newlands in the development of periodic classification of elements.

Q.8. What are the salient features of Mendeleev's periodic table? Discuss its merits and limitations.

Q.9.*(a)* What is periodic law? Describe Moseley's contribution towards the development of the modern form of the periodic table.

(b) What is the relationship between the atomic number and the periodic classification of elements?

Q.10. Enumerate the weaknesses of Mendeleev's form of the periodic table of elements. How valid is the table in the light of modern discoveries?

Q.11.*(a)* Give a brief account of the Modern periodic table. How is this superior to Mendeleev's table.

(b) Discuss some limitations of the Modern periodic table.

Q.12. What is periodic law? Describe the salient features of the long form of the periodic table.

Q.13. Discuss the classification of elements on the basis of electronic configuration.

Q.14.*(a)* Discuss the various groups and periods on the basis of atomic structure.

(b) Explain how the elements in the long form of the periodic table have been classified into *s*, *p*, *d* and *f*-blocks.

Q.15. Briefly discuss the various types of elements existing in the long form of the periodic table.

Q.16.*(a)* What do you understand by periodicity of properties? What is the cause of periodicity of properties?

(b) Explain the terms screening effect and effective nuclear charge.

Q.17.*(a)* What do you understand by size of an atom? Discuss the various modes in which the size of an atom can be expressed.

(b) Which of the following pairs would have a larger size? Explain giving reasons.

(i) K or K^+ *(ii)* Br or Br^- *(iii)* O^{2-} or F^-

(iv) Li^+ or Na^+ *(v)* P or As *(vi)* Na^+ or Mg^{2+}.

Q.18.*(a)* Define atomic radius. Does the size of an atom have a precise meaning?

(b) How does the atomic radius change as we move *(i)* from left to right across a period and *(ii)* from top to bottom in a group.

(c) Why are the atomic radii of alkali metals very large?

Q.19.*(a)* Define ionic radius. How does the size change when an atom is converted to *(i)* an anion and *(ii)* a cation?

(b) List the following ions in order of increasing ionic radius:

N^{3-}, Na^{+}, F^{-}, Mg^{2+}, O^{2-}

(c) Arrange the following anions in order of increasing size:

O^{2-}, Te^{2-}, Sc^{2-}, S^{2-}. Explain your sequence.

Q.20.*(a)* Define atomic, covalent and ionic radii for an element. How will you distinguish between the different values?

(b) On the basis of their position in the periodic table, select the atom with the larger atomic radius in each of the following pairs:

(i) Na, Cs; *(ii)* Be, Ba; *(iii)* N, Sb; *(iv)* F, Br; *(v)* Ne, Xe.

(c) Arrange the following atoms in order of decreasing atomic radius:

Na, Al, P, Cl, Mg.

(d) Explain which of the following pairs is larger and why:

(i) Cu^{+} or Cu^{2+} *(ii)* N^{3-} or P^{3-} *(iii)* Pb^{2+} or Pb^{4+}

Q.21.*(a)* Define ionization energy. Ionization energy measurements are usually carried out with atoms in the gaseous state, why?

(b) Justify the following:

1st I.P. < 2nd I.P. < 3rd I.P.

Q.22.*(a)* What is ionization energy of an element. How does it vary across a period and down the group in a periodic table?

(b) What factors affect the ionization energies?

(c) Define successive ionization energies for an element.

Q.23.*(a)* Why is the ionization energy of *(i)* B is less than Be *(ii)* O and S are less than that of N and P.

(b) Arrange the following species in iso-electronic pairs:

O^{+}, Ar, S^{2-}, Ne, Zn, Cs^{+}, N^{3-}, As^{3+}, N, Xe.

Q.24.*(a)* Define electron affinity. How does it differ from ionization energy?

(b) Ionization energy is always a positive quantity, whereas electron affinity may be either positive or negative. Explain.

(*c*) Arrange the elements in each of the following groups in increasing order of the most exothermic electron affinity:

(*i*) Li, N, K; (*ii*) F, Cl, Br.

Q.25.(*a*) Briefly discuss the significance of electron affinity.

(*b*) Which of the following pairs of elements would have a higher electron affinity? Explain.

(*i*) N or O (*ii*) F or Cl.

(*c*) Explain why alkali metals have a greater electron affinity for electrons than alkaline earth metals.

(*d*) Discuss the periodic trends of electron affinity.

Q.26.(*a*) Explain the term electronegativity of an element. Discuss the estimation of relative electronegativity by Pauling method and Mulliken methods.

(*b*) Electronegativity increases as moving across a period and decreases from top to bottom in a group. Explain.

(*c*) Explain the relationship between the electronegativity of atoms and the type of bond formed.

Q.27.(*a*) Explain the terms (*i*) electron affinity (*ii*) ionization potential and (*iii*) electronegativity.

(*b*) Which of the following pairs is more electronegative and why?

(*i*) K or Cs (*ii*) Br or Cl (*iii*) Mg or Al (*iv*) P or As

(*v*) Al or Ga (*vi*) Li or Be and (*vii*) Cu or Ag

Q.28. What are REDOX reaction. Discuss various types of such reactions giving suitable examples in each case.

Q.29.(*a*) What is REDOX potential? How is it determined?

(*b*) Briefly discuss the significance of REDOX potential.

Q.30. What are electrochemical series? Discuss various applications of the series.

Q.31. (*a*) What do you understand by polarizability and polarizing power of the ions? Discuss various factors affecting polarizability of anion.

(*b*) Discuss periodic trends of polarizability of anions.

(*c*) Discuss periodic trends of polarizing power of cations.

Q.32. Explain the trends in the periodicity of properties of transition elements.

Q.33. Discuss the periodicity of properties of inner transition elements.

Q.34. Discuss the lanthanide contraction. What is the cause of lanthanide contraction?

Q.35. Discuss various oxidation states of lanthanides and actinides.

Q.36.(*a*) Discuss anomalous properties of Li and O with other members of their groups.

(*b*) Explain diagonal relationship between the following pairs

(i) Li and Mg (ii) Be and Al (iii) B and Si

Q.37. Justify / comment on the following statements:

(*a*) The common oxidation state of lanthanide is +3.

(*b*) Li resemble with Mg

(*c*) The atomic radii of lanthanides decrease along a period.

(*d*) The atomic radii of *d*-block elements decrease along a period.

(*e*) Quantum numbers are identification numbers for an electron.

(*f*) The order of energy of various orbitals is
$1s < 2s < 2p < 3s < 3p < 4s < 3d$ etc.

(*g*) The electronic configuration is Ca is [He] $4s^2$.

(*h*) Properties of the elements are periodic functions of their atomic weights.

(*i*) The element having atomic number 104 is known as unnilpentium.

(*j*) *d*-block elements are known as transition elements.

(*k*) Al_2O_3 is an acidic oxide while Na_2O is an amphoteric oxide.

(*l*) A cation is smaller in size than its parent atom.

(*m*) An anion is bigger in size than its parent atom.

(*n*) The ionization energy of B is less than Be.

(*o*) The ionization energy of O is less than N.

(*p*) Cl^- is larger than Cl°, but K^+ is smaller than K°.

(*q*) The electron affinity values for Be and Mg are positive.

(*r*) The first ionization potential of Mg is larger than Na.

(*s*) The first ionization potential of B is lower than Be.

(*t*) N^{3-}, O^{2-}, Ne, Na^+ are isolectronic species.

(*u*) Electron affinities of alkaline earth metals are all positive.

(*v*) *f*-block elements are known as inner transition elements

(*w*) Second ionization energy is always greater than the first ionization energy.

(*x*) Electron affinity of an anion is always positive

(*y*) The size of an anion affects its polarizability

(*z*) Lanthanides exhibit variable oxidation states

Chapter Two

CHEMICAL BONDING

2.1 INTRODUCTION

In nature we come across many substances. These range from very hard solids such as rocks, to very soft substances such as butter. There are liquids and gases too. If we carefully examine these substances we shall note that substances rarely occur as free atoms in nature. On the other hand they are composed of clusters of aggregates of atoms joined together. These clusters are called *molecules*. Since the tendency of the atoms is to remain together rather to fly apart, we can conclude that there must be some force that is holding the atoms together. This force which holds the atoms together in a molecule is called a *chemical Bond.*

Cause of Chemical Combination

During the development of atomic theory various ideas were also entertained about the combinations of atoms that lead to chemical compound. In compounds, atoms are held together by forces known as chemical bonds in which electrons play a key role. It is interesting to note that one of the first real clues about chemical bonding came from a group of elements that show little tendency to form chemical compounds at all. These are the noble (inert) gases.

It was observed that the atoms of the noble gases had little tendency to combine with one another or with atoms of other elements, because of the greater stability of their ns^2p^6 electronic configurations. In the case of other elements, atoms combine with each other or with atoms of other elements to acquire noble gas configuration. This tendency of the atoms to attain a maximum of eight electrons in the valence shell is known as the *octet rule* or *rule of eight*. Since helium atom has only two electrons, this rule is called *doublet rule*, in case of helium. However, this rule could not be made universal because of the formation of compounds like PF_5, SF_6, BCl_3 etc., where the central atom has more or less eight electrons in the valence shell. Moreover, it has been found that even the noble gases combine to form compounds like XeF_2, XeF_4, $XeOF_3$, XeO_3 etc.

According to the modern theory of chemical bonding, atoms form bonds because it leads to decrease in energy of the system. For example, when two atoms of hydrogen approach each other, attractive and repulsive forces operate simultaneously. The attractive forces tend to bring two atoms close to each other and decrease the potential energy of the system, whereas the repulsive forces tend to push the atoms apart and increase the potential energy. It has been found that the magnitude of the attractive forces, in the case of two hydrogen atoms, is more than the repulsive forces and, therefore, the potential energy decreases as the two atoms approach each other.

Eventually, a state is reached (corresponding to a distance of 0.74Å, called bond length) where the attractive forces balance the repulsive forces. At this stage the potential energy of the system is minimum and the hydrogen atoms are said to be bonded to form a stable molecule.

In case the repulsive forces dominate over the attractive forces, as when two helium atoms approach each other, the energy of the system increases and leads to instability. Consequently, a bond is not formed.

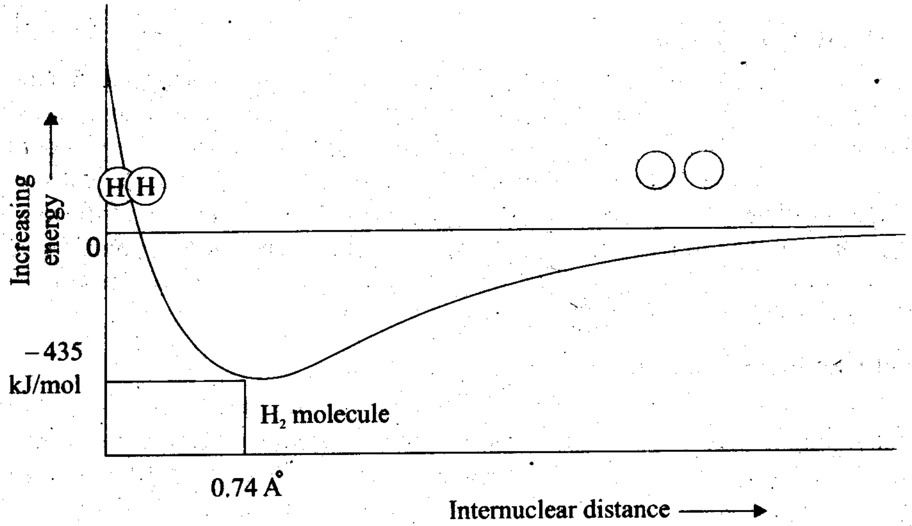


Fig. 2.1. Variation of potential energy with the distance between two H-atoms

2.2 TYPES OF CHEMICAL BONDS

Achievement of eight electrons in the outermost shell is brought about by rearrangement of electrons between the atoms undergoing a chemical change. This rearrangement takes place mainly in four ways giving rise to four types of chemical bonds.

1. Electrovalent or Ionic bond
2. Covalent bond
3. Coordinate covalent bond
4. Metallic bond

All these four bonds are called *strong bonds*. There are, however, attractive interactions between the atoms which are comparatively weaker than the bonds mentioned above. These weaker interactions are called *weak bonds*. In these bonds the bonding atoms do not lose their identity. These weaker bonds are of two types which we shall study later on. These are:

1. Hydrogen bond
2. Vander Waals interaction

1. Ionic Bond

An ionic bond is formed between two atoms by the transfer of one or more valence electrons from one atom to the other. Ionic bonding occurs most easily when elements with low ionization energies (metal) react with elements with high electronegativity and very negative electron affinities (non-metals). Many metals lose electrons easily, and many non-metals gain electrons readily. The elements which have a tendency to lose one or more electrons are called *electropositive elements*. Alkali metals and alkaline earth metals are the examples of this type. Those which have a tendency to gain one or more electrons are called *electronegative elements*. Halogens, oxygen, nitrogen, etc., are the examples of this type.

One of the combining atoms has excess of electrons than the stable number (2 or 8) in its valence-shell while the other atom is short of electrons and hence needs electrons to complete its octet. When atoms of electropositive and electronegative elements combine, one or more electrons are transferred from former to latter. The electropositive atoms are converted to cations (positively charged ions) by loss of electrons and electronegative atoms are converted to anions (negatively charged ions) by gain of electrons. Cations and anions so formed possess stable electronic configuration, usually that of the nearest noble gas. The oppositely charged ions are held together by electrostatic force of attraction. Because of the electrostatic nature of binding force, the bond is also known as *electrovalent bond*. The relative number of atoms in an ionic compound depends upon the number of electrons which are lost or gained.

Examples of ionic compounds

1. **NaCl molecule.** In the formation of this molecule Na atom loses its one excess electron from its outermost shell (Na → 2, 8, 1) which is taken by Cl atom (Cl → 2, 8, 7). Thus Na atom acquires the configuration of Ne (2, 8) and Cl acquires the configuration of Ar (2, 8, 8). This converts Na atom into Na^+ ion and Cl atom into Cl^- ion. The two ions thus formed attract each other by electrostatic force of attraction which leads to the formation of an ionic bond between Na^+ and Cl^- ions.

$$\begin{array}{lcll}
Na - 1\bar{e} & \longrightarrow & Na^+ & \\
(2, 8, 1) & & (2, 8) & \text{Neon configuration} \\
Cl + 1\bar{e} & \longrightarrow & Cl^- & \\
(2, 8, 7) & & (2, 8, 8) & \text{Argon configuration} \\
Na^+ + Cl^- & \longrightarrow & Na^+Cl^- & \text{crystal.}
\end{array}$$

2. **MgO molecule.** In the formation of this molecule Mg atom loses its two electrons from its outermost shell (Mg → 2, 8, 2) which are taken up by O atom (O → 2, 6). This converts Mg into Mg^{2+} ion and O into O^{2-} ion. The ions thus formed attract each other and form MgO molecule.

$$\begin{array}{lcl} Mg - 2\bar{e} & \longrightarrow & Mg^{2+} \\ (2, 8, 2) & & (2, 8) \\ O + 2\bar{e} & \longrightarrow & O^{2-} \\ (2, 6) & & (2, 8) \\ Mg^{2+} + O^{2-} & \longrightarrow & Mg^{2+}O^{2-} \quad \text{Crystal} \end{array}$$

3. **CaF_2 molecule.** In the formation of this molecule each Ca atom loses two electrons and is converted into Ca^{2+} ion. Each F atom accepts one electron and is converted to $\bar{F}$) ions and forms CaF_2 molecule.

$$\begin{array}{lcl} Ca - 2\bar{e} & \longrightarrow & Ca^{2+} \\ (2, 8, 8, 2) & & (2, 8, 8) \\ 2F + 2\bar{e} & \longrightarrow & 2\bar{F} \\ (2, 7) & & (2, 8) \\ Ca^{2+} + 2\bar{F} & \longrightarrow & F^{-}Ca^{2+}F^{-} \text{ or } Ca^{2+}F^{2-} \quad \text{crystal} \end{array}$$

Electrovalency

Electrovalency of an element is its combining capacity in an ionic compound, i.e., when an element forms electrovalent bond, its valency is known as electrovalency. It is equal to the number of electrons lost by an atom of an element in forming a positive ion or gained by it in forming a negative ion, both having the noble gas configuration (ns^2p^6) in their outermost shell. The elements which lose electrons show positive electrovalency while the elements which gain electrons show negative electrovalency. For example in the formation of NaCl the electrovalency of Na is equal to +1 while that of Cl is equal to −1. An element which gains or loses one, two, three, four etc. electrons is called mono (or uni) valent, di (or bi) valent, trivalent, tetravalent etc. element. Examples are:

Na, K, Cl, F	Monovalent elements
Mg, Ca, O,	Divalent elements
Al, B,	Trivalent elements
C, Si	Tetravalent elements

There are many elements which show different values of electrovalency in different electrovalent compounds. This phenomenon is called *variable electrovalency* which is due to the following reasons:

1. Unstable configuration of the core
2. Inert electron pair effect

1. **Unstable Configuration of the Core.** The outermost levels of the elements like Fe, Co, Ni, Cu etc. contain only one or two electrons. When these electrons are lost, the remaining part which is called the *core or kernel* is unstable and hence some more electrons from the core can be further lost, giving variable electrovalency to the ion. For example:

(i) The variable electrovalency to iron equal to +2 in ferrous compounds and equal to +3 in ferric compounds can be explained as follows:

Fe (26) ⟶ $1s^2, 2s^2p^6, 3s^22p^6, 3s^23p^63d^6, 4s^2$?

Fe^{2+} (24) ⟶ $1s^2, 2s^2p^6, 3s^22p^6, 3s^23p^63d^6$

$3s^2p^6d^6$ configuration is unstable and hence loses one more electron and thus forms Fe^{3+} ion.

Fe^{3+} (23) ⟶ $1s^2, 2s^2p^6, 3s^22p^6, 3s^23p^63d^5$

(ii) The variable electrovalency of copper equal to +1 (cuprous ion) and +2 (cupric ion) is easily understood from the electronic configuration given below:

Cu (29) ⟶ $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^1$

Cu^+ (28) ⟶ $1s^2, 2s^22p^6, 3s^23p^63d^{10}$

Cu^{2+} (27) ⟶ $1s^2, 2s^22p^6, 3s^23p^63d^9$

2. **Inert electron pair effect.** Some of the heavier elements of groups IIIA, IVA, VA and VIA show two oxidation states as shown below:

Group IIIA (G=3) ⟶ Ga (+1, +3) In (+1, +3)

Group IVA (G=4) ⟶ Sn (+2, +4) Pb (+2, +4)

Group VA (G=5) ⟶ As (+3, +5) Sb (+3, +5)

Group VIA (G=6) ⟶ Te (+4, +6) Po (+4, +6)

It is evident that the two oxidation states differ from each other by two units. The higher oxidation state for most of the elements is equal to their group number, G while the lower ones are equal to (G–2) as shown above. Group number oxidation state is obtained when all the ns and np electrons of P-block elements are lost while the lower oxidation state is obtained when only np electrons are lost and the ns electron pair, due to its extra stability, remains inert. Such a pair of ns an electron is called *inert electron pair* and the effect caused by it is called *inert electron pair effect.*

General Characteristics of Ionic Compounds

1. **Physical state.** Ionic compounds consist of solid aggregates of cations and anions arranged in a well–organized manner known as a crystal lattice. The lattice extends in all three–dimensions. Thus ionic compounds are crystalline solids at room temperature.

2. **Melting and boiling points.** Due to the powerful electrostatic force between the cation and the anion in a crystal of an ionic compound, considerable energy is

needed to overcome these forces and break down the crystal lattice. Hence such compounds are quite hard and possess high melting and boiling points, high heats of fusion and vaporization.

3. **Conductance.** In the solid state since the ions are not mobile, ionic solids have extremely low conductance. When any ionic compound is in the molten state or dissolved in a solvent of high dielectric constant, such as water, the binding forces in the crystal lattice are overcome and the component ions become mobile. Under the influence of applied electric field the ions being charged are attracted towards the electrodes and thus act as carriers of the current. Hence they melts or solution conduct electricity.
4. **Crystal structure.** X-ray studies of the ionic compounds have revealed that the components of the crystals are ions, and not molecules. Thus in the crystal of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride ion in turn is surrounded by six sodium ions in a regular manner.
5. **Solubility.** Ionic compounds dissolve in polar solvents like water because the molecules of the polar solvent interact strongly with the ions of the crystal and the solvation energy is sufficient to overcome the attraction between the ions in the crystal lattice. Another factor that favors solubility is the high dielectric constant of the solvents such as water, since this weakens the interionic attractions in the resulting solution.

   Non-polar solvents such as benzene and carbon tetrachloride have low dielectric constant and are poor solvents for ionic compounds. Ionic compounds like sulphates of barium and lead are insoluble in water. This can be attributed to the high lattice energies of these compounds. In these cases hydration of ions fails to liberate sufficient energy to offset the lattice energy.
6. **Brittleness.** Ionic solids are highly brittle and if some external force is applied these can be easily broken to powder form. In an ionic solid, there are parallel layers consisting of anions and cations placed at alternate positions so that there exist net attractive forces. When an external force is applied the attractive forces become repulsive due to anion-anion and cation-cation repulsions, and hence the crystal breaks up.
7. **Isomorphism.** Ionic solids made up of ions with identical electronic configurations show an identity of crystalline form which is called isomorphism. Two such pairs of isomorphous compounds are *(i)* NaF and MgO and *(ii)* $CaCl_2$ and K_2S.
8. **Non–directional behaviour.** The ionic bonds are held together by electrostatic force of attraction between oppositely charged ions. These coulombic forces are non–directional in character.
9. **Density.** The electrostatic force of attraction existing between the cations and anions in an ionic crystal brings these ions very close to one another. This decreases the volume of the crystal and consequently the ionic crystals have high density.

2. Covalent Bond

A covalent bond is a type of chemical bond which is formed by the mutual sharing of electrons between combining atoms of the same or different elements. According to the orbital concept, a covalent bond is formed between two atoms when a half-filled valence orbital of one atom overlaps with a half-filled valence orbital of the other atom.

In 1916 G. N. Lewis, an American Chemist, suggested that there are atoms which can combine with each other or with other atoms by sharing the unpaired electrons in their outermost shells. In this way the occupied orbitals of the outermost shell of each of the participating atoms are filled with two electrons which have opposite spins. Consequently the paired electrons are shared by both the atoms and circulate about the nuclei of both the atoms. The attractive force of the two nuclei for the shared pair of electrons holds the atoms together and gives rise to the formation of a bond which is called *covalent bond* or *electron pair bond.* The compounds containing covalent bonds are called *covalent compounds.* Each of the two combining atoms contributes the shared electron pair.

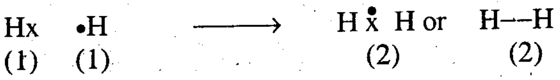
According to the Lewis concept when two atoms form a covalent bond, each of the atoms attains the stable configuration of the nearest noble gas, by completing its octet (i.e., 8 electrons in the outermost shell) or doublet (i.e., 2 electrons in case of hydrogen). However, there are many covalent molecules in which the central atom which is covalently bonded with other atoms has electrons either less than eight (incomplete octet) or more than eight (expansion of octet) in its outermost shell. In this way we come across many molecules which have *non–octet structure*, e.g., $BeCl_2$, BCl_3, BF_3, PCl_5, IF_7, NO etc.

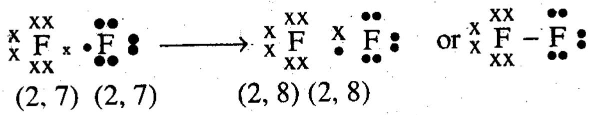
Covalent bonds are formed between the same or different kinds of atoms which should have high electronegativity, since the elements with high electronegativity do not ionize and have an equal attraction for electrons to complete their octets. Such elements are mostly located in right hand portion of the periodic table.

Types of Covalent Bond

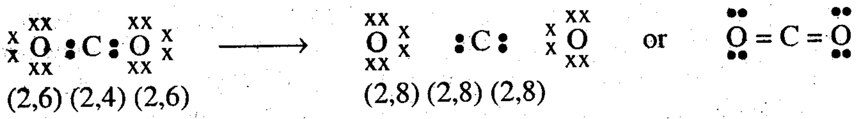
Depending upon the number of electrons shared, the covalent bond has following types:

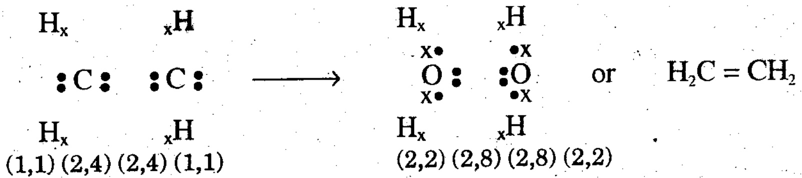
1. **Single Covalent Bond.** It is the covalent bond which is formed by the sharing of one electron pair between the participating atoms. For example, H_2 molecule is composed of two hydrogen atoms, each having one valence electrons. Each contributes an electron to the shared pair and both atoms acquire helium configuration. Thus stable H_2 molecule results. In F_2 molecule each F-atom (2, 7) has seven valence electrons. The two F atoms acquire a stable electron octet by sharing a pair of electrons.



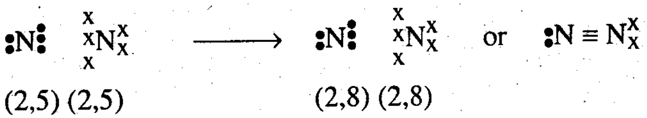


2. **Double Covalent Bond.** If two atoms share two pair of electrons, the covalent bond is called a double bond. Double bonds are found in molecules like CO_2 and ethylene (C_2H_4).

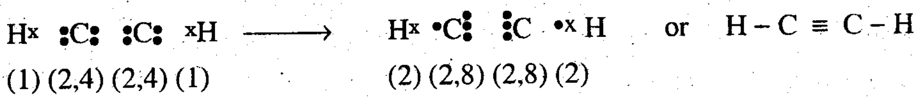




3. **Triple Covalent Bond.** A triple bond arises when two atoms share three pairs of electrons, as in the nitrogen molecule (N_2):



The acetylene molecule (C_2H_2) also contains a triple bond, in this case between two carbon atoms:



Double and triple covalent bonds are called *multiple bonds.*

Covalency

The valency of an element in a covalent compound is called its *covalency.* Covalency of an element in a covalent compound is equal to the number of electrons contributed by one atom of it in the shared electron pairs. Consequently, the covalency of an element in a covalent compound is equal to the number of covalent bonds formed by one atom of it with the neighboring atoms. Thus:

Covalency of Cl in Cl_2 molecule	= 1
Covalency of H in H_2, H_2O and HCl molecules	= 1
Covalency of O in O_2 and H_2O molecules	= 2
Covalency of N in N_2 molecule	= 3
Covalency of C in CH_4 molecule	= 4

Element	Covalency	Compound
P	3	PCl_3
	5	PCl_5
S	2	SCl_2
	4	SF_4
	6	SF_6
I	1	ICl
	3	ICl_3
	5	IF_5
	7	IF_7

Generally the covalency of an element which has only *s* and *p* orbitals in its valence-shell (e.g., H, N, O, F) is a fixed quantity and is equal to the number of unpaired electrons in *s* or *p* orbitals. However, the elements containing vacant d-orbitals (e.g., P, Cl, S etc.) show different values of covalency in different covalent compounds. This phenomenon is called *variable vovalency* and is due to the presence of vacant d-orbitals in the Valence-shell of these elements. Variable covalency of an element arises due to the increase in the number of unpaired electrons in the different excited states of the atom. Examples of the elements showing different valencies in different covalent compounds are given below.

General Characteristics of Covalent Compounds

1. **Physical state.** Covalent compounds usually consist of discrete molecules and the force of attraction between adjacent covalent molecules is weak. It is due to these weak forces that most of the covalent compounds exist as gases or liquids or soft solids under the normal conditions of temperature and pressure.

2. **Melting and boiling points.** With the exception of covalent solids consisting of giant molecules (e.g., diamond, SiC, AlN etc.), other covalent compounds have relatively low melting and boiling points than the ionic compounds. The covalent molecules are held together in the solid crystal lattice by weak forces.

3. **Conductance.** Covalent solids consisting of giant molecules are bad conductors of electricity, since they do not contain charged particles or electrons to carry the current. However, the covalent solids having layer lattices (e.g., graphite) are good conductors of electricity, since in such solids electrons can pass from one layer to the other and thus current can be carried.

4. **Solubility.** Generally covalent solids are insoluble in polar solvents like H_2O but are readily soluble in non-polar solvents like CCl_4, C_6H_6 etc. Their solubility in non-polar solvents is due to the similarity in covalent nature of the molecules of the solute and solvent, i.e., the solubility is based on the principle: "*like dissolves like*". Some of the covalent compounds like alcohol; amines etc. are soluble in water due to hydrogen bonding.

5. **Molecular reactions.** The covalent compounds give reactions where th molecule as a whole undergoes a change. Since there are no strong electrica forces to speed up the reaction between molecules, these reactions are slow tha ionic reactions.

6. **Isomerism.** Since covalent bonds are rigid and directional, they can give rise to different arrangements of atoms in space. This means that covalent compounds can show isomerism and this phenomenon is mostly shown by organic compounds.
7. **Neither hard nor brittle.** While ionic compounds are hard and brittle, covalent compounds are neither hard nor brittle. Rather they are soft and waxy, since they usually consist of separate molecules. There are weak forces holding the molecules in the solid crystal lattice.
8. **Directional character.** Whereas the ionic bonds are non-directional, the covalent bonds are directional in character. Hence individual covalent compounds possess definite shapes of their molecules.

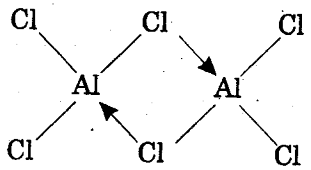
3. Co-ordinate Covalent Bond

A covalent bond which is formed by the sharing of two electrons both of which are provided entirely by one of the linked atoms (or ions) is called a *co-ordinate covalent bond* or simply *co-ordinate bond.*

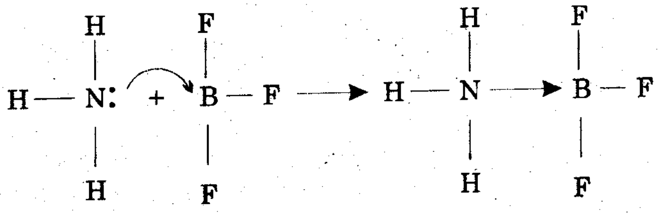
We have seen that in the formation of a normal-covalent bond each of the two bonded atoms contributes one electron for the shared pair of electrons. However in some compounds the formation of covalent bond between two atoms takes place by the mutual sharing of two electrons by one of the bonded atoms. This bond is called the Co-ordinate bond and is also sometimes referred to as *dative bond.* The pair of shared electrons is called *lone pair.* The atom which furnishes the electron pair is called *donor* or *ligand* while the other atom which accepts the electron pair is called *acceptor.* The electron pair donor atoms are usually called Lewis bases and electron pair acceptors as Lewis acids. Lewis acid-base reactions would result in the formation of co-ordinate covalent bonds. The process of such bond formation is called *coordination.* A co-ordinate bond is represented by an arrow which points away from the donor to the acceptor.

Examples of co-ordinate compounds or ions

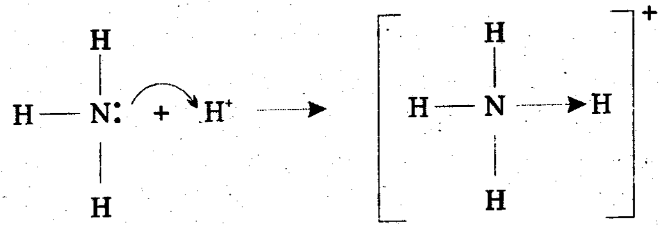
1. **Aluminium chloride, Al_2Cl_6.** Al-atom has three valence-electrons which it shares with three Cl-atoms, forming three covalent bonds. Thus the Al-atom acquires six electrons in its outer shell. Now Cl atom has three lone pairs, one of which is donated to the Al-atom of another molecule $AlCl_3$. Thus both Al-atoms achieve octet and stable Al_2Cl_6 results.



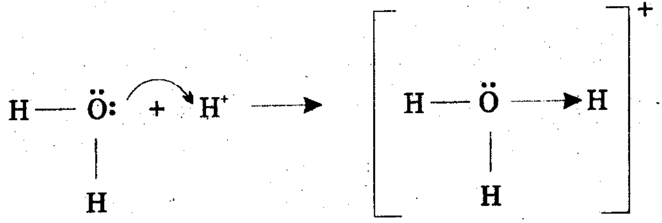
2. **Addition Compounds.** Co-ordinate bond is also formed between two atoms of both of which are the parts of a stable molecule. For example, this type of bond is found in boron fluoride-ammonia complex, $H_3N \rightarrow BF_3$.



3. **Ammonium (NH_4^+) and hydroxonium (H_3O^+) ions.** NH_4^+ ion may be regarded as being obtained by the combination of NH_3 molecule and H^+ ion. In NH_3 molecule each of three H-atoms is linked to N-atom by a covalent bond. Thus N-atom in this molecule is left with a lone pair of electrons after completing its octet by sharing three of its five valence electrons with three H-atoms. The electrons of the lone pair on N-atom are donated to H+ ion and thus a N→H coordinate bond is established.



H^+ ion in aqueous solution is found always in association with H_2O as H_3O^+ ion due the coordination of the H^+ ion with neutral H_2O molecule.



General Characteristics of Co-ordinate Compounds

1. **Physical state.** These compounds are gases, liquids or solids under ordinary conditions of temperature and pressure.
2. **Melting and boiling points.** We know that a co-ordinate bond is, in a way, a combination of an ionic bond and a covalent bond. It is for this reason that co-ordinate compounds have melting and boiling points which are higher than those of pure covalent compounds but lower than those of purely ionic compounds.
3. **Conductivity.** Like covalent compounds, co-ordinate compounds are also non-ionic i.e., they do not conduct electric current through their aqueous solutions or fused masses.

4. **Solubility.** They are usually insoluble in polar solvents like water but are soluble in non-polar solvents.
5. **Semi-polar character.** These compounds are semi-polar in character (A^+-B^-) i.e., they are more polar than covalent compounds but less polar than the ionic compounds.
6. **Molecular reactions.** There are two types of co-ordinate compounds, labile and inert. The labile complexes undergo rapid reactions but inert complexes show very slow reactivity with other substituents.
7. **Stability.** Co-ordinate compounds are as stable as the covalent compounds. But when they are made up of two different stable molecules (molecular compounds), they are less stable.
8. **Isomerism.** Co-ordinate compounds also show isomerism. Since the co-ordinate bond is rigid and directional, different space models (i.e., stereoisomers) of a single co-ordinate compound are possible.
9. **Paramagnetism.** Many of the coordination compounds of transition metals are paramagnetic, which indicates the presence of unpaired electronic spins.

2.3 THEORIES OF CHEMICAL BONDING

Ionic bonding is basically understandable in terms of coulombic forces of attraction between oppositely charged species–cations and anions. The description of covalent bonding is limited to writing Lewis structures. According to the Lewis concept a covalent bond is formed by the sharing of electrons between the combining atoms. It serves as a guide for writing structural formulae of various covalent compounds. However, it does not explain:

(i) How does sharing of electrons lead to the formation of a bond?
(ii) What is the nature of bonding forces?
(iii) It tells nothing about the shapes of molecules, bond energies and bond lengths.

It was only after the development of wave mechanics that two alternative theories were put forward to provide plausible answers to these questions. These two approaches are:

(i) Valence bond theory (VBT)
(ii) Molecular orbital theory (MOT)

There is only one molecule for which an exact solution of the wave equation has been obtained analytically, namely, the hydrogen molecule ion H_2^+. For other relatively simple molecules only approximate solutions are possible but these are sufficient to explain the influences which lead to bond formation, and to the behaviour of electrons in such bonds.

2.4. VALENCE BOND THEORY

The first quantum mechanical treatment to explain the formation of a covalent bond for the hydrogen molecule was developed by W. Heitler and F-London in 1927. It was later improved and extended by Linus Pauling and J.C. Slater in 1931. According to Valence bond model:

(i) A covalent bond is formed between two atoms by the overlap of half–filled valence atomic orbitals of each atom containing one unpaired electron.

(ii) The overlap of two atomic orbitals gives rise to a single bond orbital which is localized orbital and is occupied by both the electrons.

(iii) The two electrons that occupy the bond orbital have opposite spins.

(iv) Each electron occupies the entire bond orbital and hence may be considered to belong to both the atomic orbitals.

(v) There is a maximum electron density somewhere between the two atoms as a result of overlapping.

(vi) A large part of the bonding force of covalent bond results from the electrostatic attraction between the nuclei and the accumulated electron clouds between them.

(vii) The strength of a covalent bond is proportional to the extent of overlapping between the atomic orbitals.

(viii) The atoms retain their identities, only the outer valence shell electrons are affected as a result of bond formation.

Let us consider the formation of hydrogen molecule, H_2. The two hydrogen atoms involved in the bonding may be represented as $H_A(1)$ and $H_B(2)$ in which the electrons (1) and (2) are supposed to be part of two hydrogen nuclei H_A and H_B. Let these two H–atoms, H_A and H_B, be at an infinite distance from each other so that no appreciable interaction may occur. If $\Psi_A(1)$ and $\Psi_B(2)$ represent the orbital wave functions of the two atoms H_A and H_B, then the combined wave function for the separated atoms is given by

$$\Psi = \Psi_A(1)\,\Psi_B(2) \qquad \text{..... 2.1}$$

As the two atoms approach each other, they experience attractive forces due to the attraction between the nucleus of one and electron cloud of the other. They also experience repulsive forces due to mutual nucleus–nucleus and electron–electron repulsions. However the attractive forces overweigh the repulsive forces. Consequently, as the atoms approach closer and closer, work is done by the system resulting in decrease of potential energy. At a certain distance between the nuclei of the two atoms, the potential energy is at a minimum. At this distance, called the *bond distance,* the atoms are said to be bonded together. The bonding energy corresponding to this wave function calculated as a function of internuclear distance is only 25 $kJmol^{-1}$. Compared to the experimental value of 435 $kJmol^{-1}$, this value is very low. This shows that the total wave function Ψ is not the correct wave function for H_2 molecule.

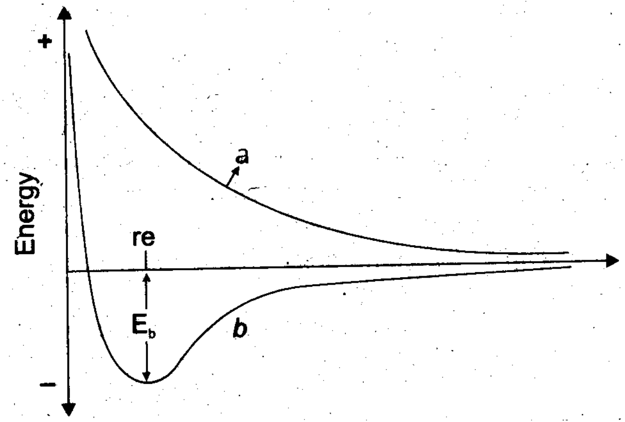


Fig. 2.2 Potential energy curve for H_2 molecule

One of the obvious discrepancies is our assumption that the electrons of two hydrogen atoms are distinguishable as $H_A(1)$ and $H_B(2)$. When the two atoms are close enough, the electrons labeled 1 and 2 could no longer be associated with H_A and H_B. Thus there are two possible equivalent structures of H_2 molecule which are indistinguishable once the bond has been formed.

$$H_A(1)\,H_B(2) \qquad H_A(2)\,H_B(1)$$
$$\text{(I)} \qquad\qquad \text{(II)}$$

In structure (I) we have the nucleus H_A with electron 1 and nucleus H_B with electron 2. In structure (II) the electrons have been exchanged. Now the acceptable wave functions corresponding to these two forms are:

$$\Psi_I = \Psi_A(1)\,\Psi_B(2) \qquad .....2.2$$

$$\Psi_{II} = \Psi_A(2)\,\Psi_B(1) \qquad .....2.3$$

The true wave function Ψ can be calculated by applying the law of linear combination.

$$\Psi = C_1\Psi_I + C_2\Psi_{II}$$

or
$$\Psi = C_1\Psi_A(1)\,\Psi_B(2) + C_2\Psi_A(2)\,\Psi_B(1) \qquad ....2.4$$

Where C_1 and C_2 are the mixing coefficients. They are adjusted in such a way so as to give the lowest energy. Since the H_2 molecule is symmetrical, the two component wave functions contribute equally, therefore $C_1 = \pm C_2$. Moreover, coefficients are relative quantities, we can pat $C_1 = 1$ and $C_2 = \pm 1$. Substituting these values of C_1 and C_2 in equation 2.4, we get two possible wave functions as

$$\Psi_s = \Psi_A(1)\,\Psi_B(2) + \Psi_A(2)\,\Psi_B(1) \qquad .....2.5$$

and $$\Psi_a = \Psi_A(1)\,\Psi_B(2) - \Psi_A(2)\,\Psi_B(1) \qquad .....2.6$$

The function Ψ_s represents the symmetric combination of the two hydrogen atomic orbitals and remains unaltered by the exchange of electrons 1 and 2, whereas Ψ_a represents the antisymmetric combination, since Ψ_a changes its sign by exchange of electrons. In Fig. 2.2 we have plotted the energy, E, against the internuclear distance between the two hydrogen atoms of H_2 molecule. As in evident from the plot, curve '*a*' represents Ψ_a state which is a *non–bonding state* in which the two electrons have parallel spins. On the other hand curve '*b*' represents a *bonding state* in which the two electrons have opposite spins. It may be noted that the symmetric combination results in lowering of energy while increase in energy occurs when the combination is antisymmetric. The bonding energy calculated by using Ψs as the wave function comes out to be 301 kJmol^{-1}. The difference (301–25) = 276 kJmol^{-1} is called the *exchange energy* because it arise from the concept of exchange of electrons between the two H–nuclei. The bond energy value 301 kJmol^{-1}, though significant, is still smaller than the experimental value of 435 kJmol^{-1}.

Linus Pauling has suggested that the calculations of energy made by Heitler–London method can be improved by considering *screening effect* and polarization of atomic orbitals. Screening effect is to be considered due to the fact that electrons 1 and 2 shield each other, consequently the effective nuclear charge z' will be less than the actual nuclear charge Z'. The polarization of atomic orbitals gives rise to the consideration of ionic configurations. Hence there is a possibility that both the electrons will be simultaneously near to one of the nuclei so that we must also consider the ionic wave functions. These ionic configurations can be shown as

$$H_A^-\,H_B^+ \text{ or } H_A{}^{(1)}_{(2)}\,H_B \qquad\qquad H_A^+\,H_B^- \text{ or } H_A\,H_B{}^{(1)}_{(2)}$$

(III) (IV)

Let these structures be represented by wave functions Ψ_{III} and Ψ_{IV} which are given by

$$\Psi_{III} = \Psi_A(1)\,\Psi_A(2) \qquad .....2.6$$

$$\Psi_{IV} = \Psi_B(1)\,\Psi_B(2) \qquad .....2.7$$

Obviously, the existence of such ionic structures would increase the force of attraction and hence the bond energy. Taking into account the contribution of ionic configuration, the wave function of the actual hydrogen molecule should be represented as

$$\Psi_{VB} = \Psi_A(1)\,\Psi_B(2) + \Psi_A(2)\,\Psi_B(1) + \lambda(\Psi_{III} + \Psi_{IV})$$

$$\Psi_{VB} = \Psi_A(1)\,\Psi_B(2) + \Psi_A(2)\,\Psi_B(1) + \lambda[\Psi_A(1)\,\Psi_A(2) + \Psi_B(1)\,\Psi_B(2)]$$

$$\Psi_{VB} = \Psi_{cov} + \lambda\Psi_{ion} \qquad .....2.8$$

Where λ is called the mixing coefficient and represents how much the ionic wave function is mixed with the covalent wave function. The value of λ for H_2 has been found to be 0.17. Equation 2.8 then can be written as

$$\Psi_{VB} = \Psi_{cov} + 0.17\,\Psi_{ion} \qquad .....2.9$$

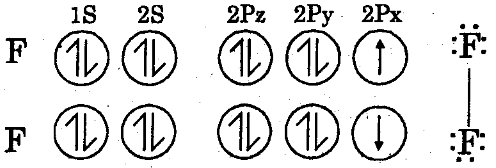
The calculated bond energy from the wave function Ψ_{VB} given by equation 2.9 works out to be 397.5 kJmol^{-1}. This bond energy value being very close to the experimental value (435 kJmol$^{-1)}$ suggests that H–H bond is partly covalent and partly ionic. The energy difference (397–301) = 96 kJmol^{-1} due to the contribution of ionic states to the actual state of the hydrogen molecule is called the *ionic covalent resonance energy*.

Applying further refinements and corrections due to *(i)* screening and *(ii)* polarization effects in calculations, the computed value for bond energy comes out to be 433 kJmol^{-1}, which is very close to the experimental value.

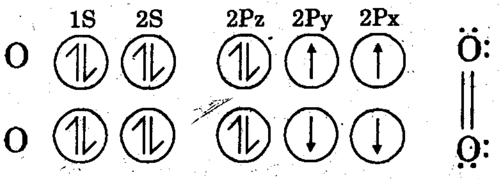
Applications of VBT

Valence bond theory follows the logical quantum mechanical extension of the Lewis theory of the electron pair formation. Since pairing of two electron spins takes place, VBT is, therefore, also called *electron pair theory*. This theory pictures the bond as forming from pair of electrons having opposite spins. Thus, it is necessary that atoms involved in bond formation should have unpaired electrons in them. The number of unpaired electrons would give rise to equal number of bonds. The isolated number of paired electrons is considered to be the *lone pair* in this theory. Let us apply this approach to various molecules.

1. **F_2 molecule.** This molecule is formed from two F–atoms. The electronic configuration of each F–atom is $1s^2$, $2s^2$, $2p_x^1$ $2p_y^2$ $2p_z^2$. The formation of F_2 molecule is shown below:

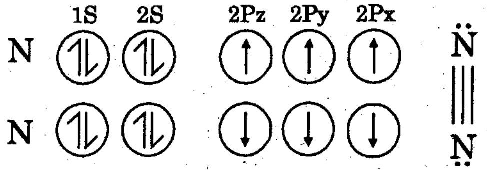


2. **O_2 molecule.** This molecule is formed by the combination of two O–atoms. Each O–atom has electronic configuration $1s^2$, $2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^2$ and the formation of O_2 molecule would involve two unpaired electrons resulting in the formation of a double bond.



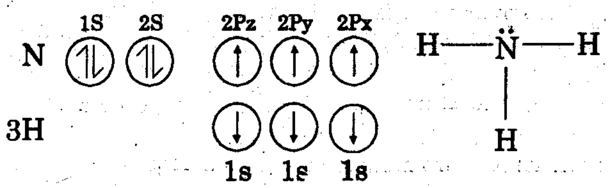
In O_2 molecule all the electrons are paired. Therefore, O_2 molecule should be diamagnetic in its behaviour. But in actual practice it is paramagnetic. Thus VBT fails to explain the paramagnetic behaviour of O_2 molecule.

3. **N_2 molecule.** There are three unpaired electrons in nitrogen atom with electronic configuration $1s^2$, $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. A N_2 molecule is formed by the interaction of these three unpaired electrons from each N–atom to form electron pairs resulting in the formation of three bonds.



4. **NH_3 molecule.** This molecule consists of one N–atom and three H–atoms. Nitrogen atom has electronic configuration $1s^2$, $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ whereas H–atom has $1s^1$ configuration. Thus the three unpaired electrons of N–atom undergo interaction with $1s^1$ electron of three H–atoms resulting in the formation of three bonds.

The model for NH_3 molecule leads to three valence bonds at right angles to each other. But NH_3 molecule in fact has H–N–H bond angles of 107.3°.



Limitations of VBT

1. This theory is unable to explain the paramagnetic behaviour of O_2–molecule.
2. This theory cannot properly describe the shape and geometry of molecules (e.g., unable to differentiate between square planar and tetrahedral geometry).

3. It does not provide explanation to the formation of co–ordinate bond in which one of the bonded atoms gives both the electrons.
4. This does not account for the formation of odd electron molecules (e.g., NO) or such as H_2^+ ion where no pairing of electrons occurs.
5. It cannot explain the non–existence of noble gas molecules.
6. It does not provide explanation for the presence of fractional bonds in many molecules, e.g., benzene, CO_3^{-2} ion etc.
7. This theory is also unable to explain bonding in electron deficient molecules.

2.5 SIGMA (σ) AND Pi (π) BONDS

According to valence bond approach, a covalent bond is set up due to overlap of atomic orbitals of the two combining atoms. Depending on the type or manner of atomic orbitals involved in bond formation, two main types of covalent bonds are obtained. These are:

1. Sigma (σ) bond
2. Pi (π) bond

1. Sigma (σ) Bond

A covalent bond which is formed between two atoms by the overlap of atomic orbitals along their axes (end–to–end or head to head overlap) is called a *sigma bond.* All the sigma bonds have axial symmetry. Since the overlap of two orbitals along their axes is maximum, sigma bonds are strong bonds.

If z–axis is assumed to be the molecular axis, sigma bond is given by s–s, s–p_z and p_z–p_z overlaps. For reasons of space and convenience, a pictorial representation of the formation of a sigma bond is not always possible. Therefore, in actual practice, a single horizontal line (–) between the two linked atoms is used to depict a sigma bond.

2. Pi (π) Bond

A covalent bond which is formed between two atoms by the overlap of atomic orbitals along a line perpendicular to the molecular axis (side to side or lateral overlap) is called a *pi bond.* If z–axis is assumed to be the *molecular axis,* then p_i bond is given by p_x–p_x and p_y–p_y overlaps. Since a pi bond results from side–on overlap of atomic orbitals, the regions of electron sharing are above and below the imaginary line connecting the bonded atoms; therefore it is a weaker bond than sigma bond. The various types of overlap and formation of sigma and pi bonds are shown in Fig. 2.3.

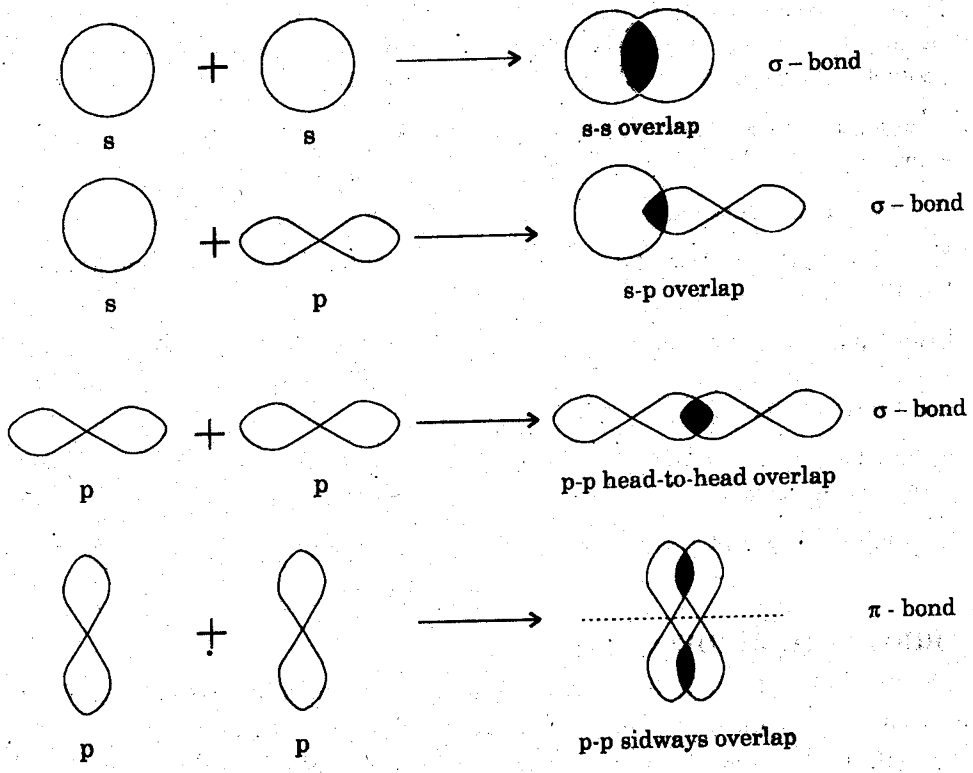


Fig. 2.3 Different types of overlap and formation of sigma (σ) and Pi (π) bonds.

Comparison of Sigma and Pi Bonds

	Sigma Bond		Pi Bond
1.	A sigma bond is formed by head–to head overlap of orbitals.	1.	A pi bond is formed from lateral or side–to–side overlap of orbitals.
2.	It is formed by the overlapping of s–s, s–p and p–p orbitals.	2.	It is always formed by the overlapping of p–p orbitals.
3.	The extent of overlapping of orbitals in sigma bond is greater, hence it is a stronger bond.	3.	The extent of overlapping of orbitals in pi bond is lesser; hence it is a weaker bond.
4.	Electron density of a sigma bond is symmetrical about the line joining the two nuclei.	4.	Electron density of a pi bond is unsymmetrical.
5.	It has only one region of electron density between the two nuclei.	5.	It has two regions of electron density, above and below the internuclear axis.
6.	A sigma bond can be present alone.	6.	A pi bond is always formed in addition to sigma bond.

7.	There can be free rotation of atoms around the sigma bond and no geometric isomers are possible.	7.	There is no free rotation about pi bond and geometrical isomers are possible.
8.	A sigma bond possesses high bond energy.	8.	A pi bond possesses low bond energy.
9.	A sigma bond is less reactive.	9.	A pi bond is more reactive.
10.	A sigma bond has greater bond length.	10.	A pi bond has lesser bond length.
11.	Compounds containing sigma bonds generally undergo substitution reactions.	11.	Compounds containing pi bonds usually undergo addition reactions.
12.	A sigma bond influences the geometry of the molecule.	12.	A pi bond generally has no effect on the geometry.
13.	Examples: CH_4, H_2, Cl_2 etc.	13.	Examples: $CH_2=CH_2$, $N\equiv N$, $O=O$ etc.

2.6 ORBITAL HYBRIDIZATION

The formation of different molecules comprising covalent bonds (e.g., H_2, N_2, O_2, HCl etc.) can be explained by simple valence–bond theory in terms of sharing of unpaired electrons. However, this theory does not account for the geometry of various molecules of elements such as Be, B and C are as follows:

$_4B_e = 1s^2, 2s^2$

$_5B = 1s^2, 2s^2 2p_x^1$

$_6C = 1s^2, 2s^2 2p_x^1 2p_y^1$

As per configuration, Be has no unpaired electron in the ground state, as both 1*s* and 2*s* orbitals are completely filled. Hence Be should not form any covalent bond and must behave as an inert element like helium. But in reality it forms compounds like BeH_2, $BeCl_2$ etc., in which it is bivalent. Similarly boron possesses only one–half–filled 2*p* orbital and, therefore, it should be monovalent. But boron has been found to form BH_3, BCl_3 etc. compounds in which it exhibits trivalency. Carbon also, according to its electronic configuration is expected to behave as divalent since it contains two, half–filled *p*–orbitals. But as we know carbon forms a very large number of compounds such as CH_4, C_2H_6, CCl_4 etc. in which it is tetravalent.

Evidently, it is not possible to explain the valency of these elements on the basis of the number of unpaired electrons in the atoms and the overlap of atomic orbitals. It is possible to do so, however, with the concept of *orbital hybridization* according to which different orbitals (say s and p), before overlapping and bond formation, mix and pool their energy and form new orbitals known as *hybrid orbitals* which are identical in directional character and have the same shape and energy. Moreover, the hybrid orbitals have higher electron densities in specified regions resulting in greater overlap and are entirely different properties than either type of orbitals

Thus, the hypothetical process of the mixing of two or more pure atomic orbitals on an atom of nearly equal energy to give equal number of hybrid orbitals is termed as *orbital hybridization.* The process of hybridization consists of the following steps:

1. Formation of excited states which may involve unpairing and promotion of the electrons to the next available orbital of higher energy.
2. Orbitals in the excited state on hybridization give hybrid orbitals with greater electron density along definite directions in the space.
3. Bond formation occurs on account of overlap of the hybrid orbitals with suitable orbitals of other atoms.

Types of Hybridization and Shapes of Molecules

Here six important types of hybridization *sp*, sp^2, sp^3 dsp^3, dsp^2 and d^2sp^3 are discussed with examples. The type of hybridization depends upon the kinds of orbitals involved in it and hence they differ in characteristics too.

1. *sp* Hybridization

sp hybridization involves the mixing of one *s* and one *p*–orbital on the same atom to form two identical sp hybrids. The *sp* hybrids lie in one plane and point an angle of 180° from each other. The formation of two sp hybrid orbitals in case of Be–atom is shown in figure 2.4. Each of the two hybrid orbitals has one electron.

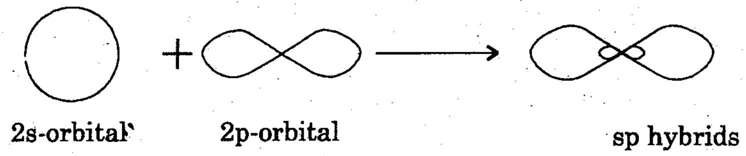


Fig. 2.4 Formation of sp hybrids

Let us explain the formation of $BeCl_2$ on the basis of sp hybridization. Each of the hybrid orbital of Be atom overlaps along the axis with partially filled *p*–orbital of Cl–atom and forms two Be–Cl sigma bonds. Both these bonds are σ–bonds, since the electron density is symmetrically distributed between the two atoms. Both the bonds are directed in opposite directions from the centre of Be–atom. Thus Cl–Be–Cl bond angle is 180° and both the bonds have the same bond length and bond energy. Thus $BeCl_2$ molecule has linear shape.

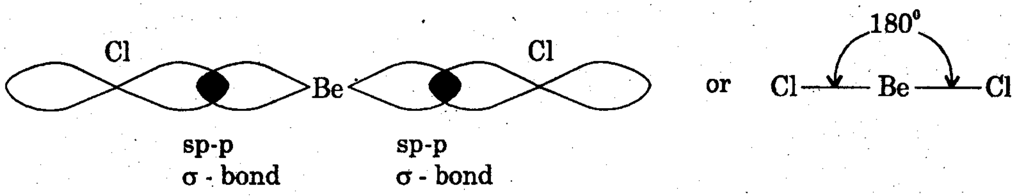


Fig. 2.5 Bond formation in $BeCl_2$ molecule

2. *sp*^{2} Hybridization

sp^2 hybridization involves the mixing of one *s* and two *p*–orbitals on the same atom to form three identical *sp*^{2} hybrids. All the hybrids lie in one plane and point at an angle of 120° from each other. They have trigonal planar symmetry. The formation of three *sp*^{2} hybrid orbitals in case of B–atom is shown in figure 2.6. Each of three hybrid orbitals contains one electron.

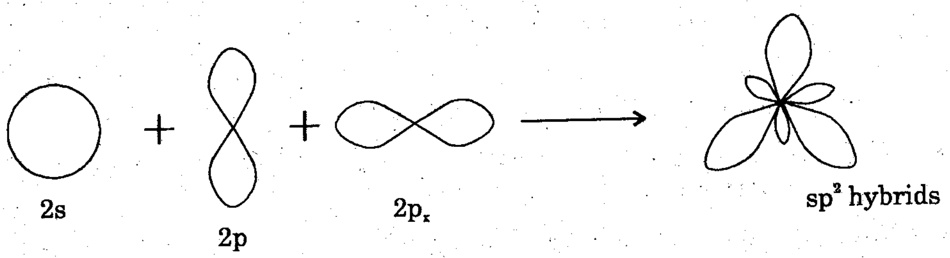


Fig. 2.6 Formation of sp^2 hybrids.

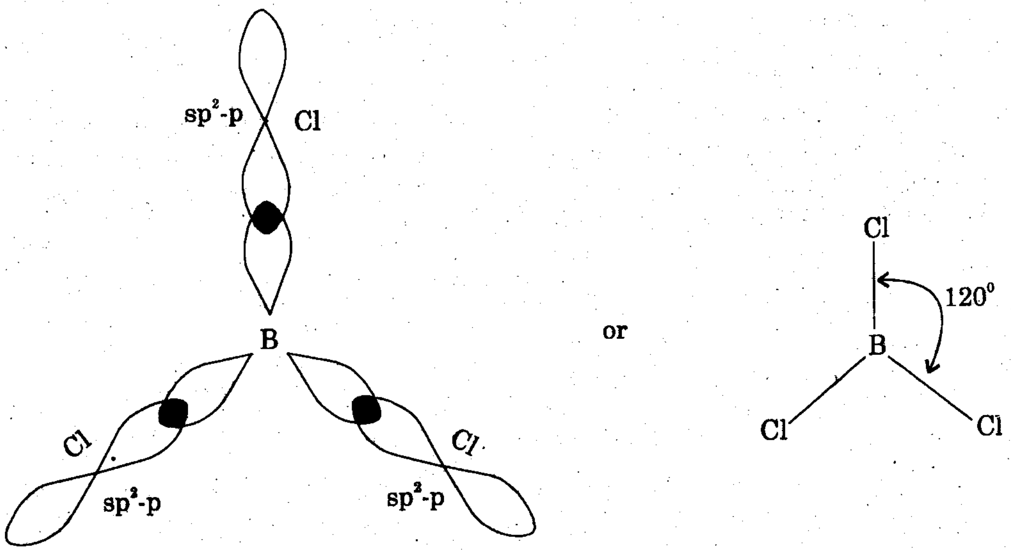


Fig. 2.7 Bond formation in BCl_3 molecule

Let us explain the formation of BCl_3 molecule on the basis of *sp*^{2} hybridization. Each of the three hybrid orbitals of B overlaps along the axis with partially filled *p*–orbital of Cl–atom and forms three B–Cl sigma bonds. All the bonds are directed towards the corners of a triangular plane and hence each Cl–B–Cl bond angle is 120° and all the bonds have same bond length and bond energy. Thus BCl_3 molecule has triangular shape with all the three B–Cl bonds identical in shape.

3. *sp*^{3} Hybridization

sp^3 hybridization involves the mixing of one *s* and three *p*–orbitals on the same atom to form four identical *sp*^{3} hybrids. All the *sp*^{3} hybrids point at the corners of a regular tetrahedron with an angle of 109.5°. The formation of four *sp*^{3} hybrids in case of C–atom is shown in figure 2.8, Each of the four hybrids contains a single electron.

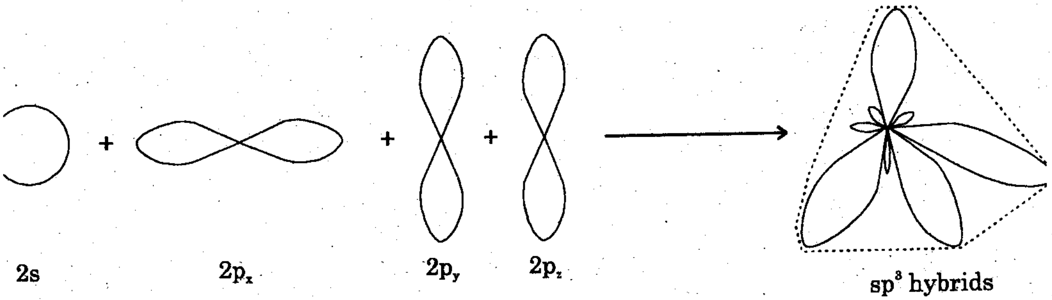


Fig. 2.8. Formation of sp^3 *hybrids*

The structure of CH_4 molecule can be explained on the basis of sp^3 hybridization. Each of these hybrid orbitals overlaps along the axis with the partially filled 1s–orbital of H–atom and form C–H sigma bond. In this way four C–H sigma bonds are formed due to sp^3–s overlap having bond angle of 109.5°. Thus the molecule of CH_4 has tetrahedral geometry.

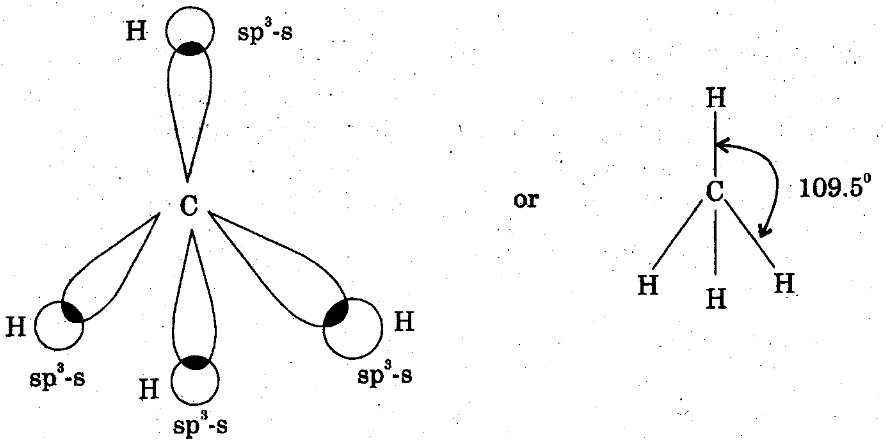


Fig. 2.9. Bond formation in CH_4 *molecule*

4. dsp^2 Hybridization

dsp^2 hybridization involves the mixing of one s, two p and one d orbitals on the same atom to form four identical dsp^2 hybrids. These four hybrid orbitals are directed to the corners of a square giving a square planar structure. The formation of XeF_4 molecule can be explained on dsp^2 hybridization. This molecule has square planar geometry as shown in figure 2.10.

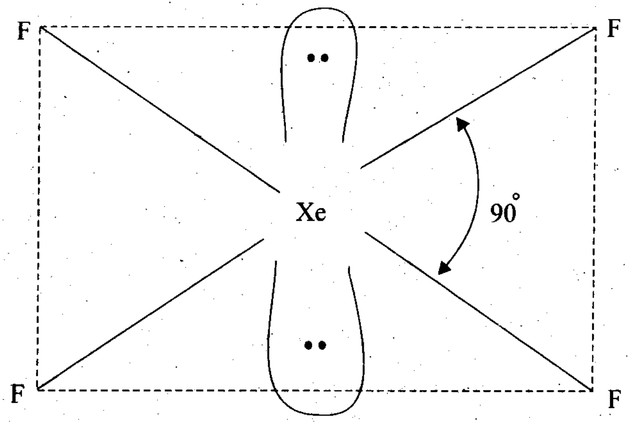


Fig. 2.10. Bond formation in XeF_4 *molecule*

5. *dsp³* Hybridization

This type of hybridization involves the mixing of one *s*, three *p* and one *d*–orbitals on the same atom to form five *dsp³* hybrid orbitals. All the five hybrid orbitals arrange themselves in a trigonal bipyramidal manner. The formation of PCl_5 molecule can be explained on *dsp³* hybridization. This molecule has trigonal bipyramidal geometry as shown in figure 2.11.

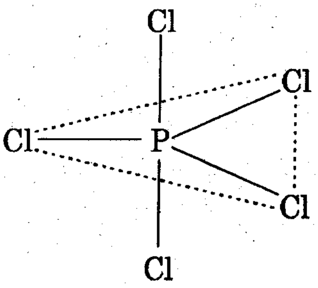


Fig. 2.11. Formation of PCl_5 *molecule*

6. *d²sp³* hybridization

This type involves the mixing of one *s*, three *p* and two *d*–orbitals on the same atom to give six *d²sp³* hybrid orbitals which arrange themselves in an octahedral manner. The formation of SF_6 molecule can be explained on the basis of *d²sp³* hybridization. This molecule has octahedral geometry as shown in figure 2.12.

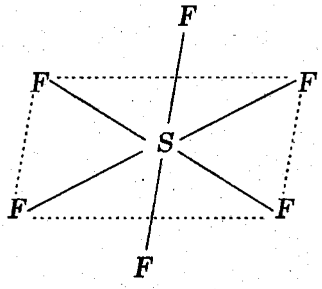


Fig. 2.12. Formation of SF_6 molecule

Rules for Hybridization

Following are the rules for orbital hybridization:

1. Only orbitals of similar energies belonging to the same atom or ion can hybridize together.
2. Number of hybrid orbitals produced, is equal to the number of orbitals undergoing hybridization.
3. Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They differ from one another in their orientation in space.
4. For equivalent hybrids, the orientation in space is determined by (a) the number of orbitals mixed and consequently the number of hybrids obtained, and (b) which of *x*, *y* and *z*–axes are preferred by the orbitals when pure.
5. From the type of hybridization one can predict the geometry and bond angles of a molecule.
6. An orbital which has been used to build up a hybrid orbital is no longer available to hold electron in its pure form.

Relationship between hybrid orbitals and the structure of the molecules formed are shown in Table 2.1.

Table 2.1. Hybrid orbitals and structure

No. of bonds	Atomic orbitals	Hybrid	Orientation	Examples
2	*s*, *p*	sp	Linear	$BeCl_2$, C_2H_2
3	*s*, two *p*	sp^2	Trigonal Planar	BCl_3, BF_3
4	*s*, three *p*	sp^3	Tetrahedral	CH_4, CCl_4
	s, two *p* and one *d*	dsp^2	Square planar	ICl_4^-, $[PtCl_4]^{2-}$
5	s, three p and one *d*	dsp^3	Trigonal bipyramidal	PCl_5, PF_5
6	*s*, three *p* and two *d*	d^2sp^3	Octahedral	SF_6, $W(CO)_6$

Limitations of Hybridization Concept

The following are some limitations of the concept of hybridization:

(i) Although promotion and hybridization are necessary for formation of hybrid orbitals, a promotion of electron need not necessarily lead to the formation of hybrid orbitals, e.g. in multiple bonding.

(ii) The driving force for hybridization is the energy released due to the bond formation involving hybrid orbitals. Methane is tetrahedral because the energy of the molecule in this configuration is the lowest. The carbon atom (ground state $2s^2\ 2p^2$) after promotion of $2s$ electron to $2\ p$ orbital, can use the sp^3, sp^2 or sp hybrid orbitals for bond formation, depending upon the number of bonds to be formed in a particular situation.

(iii) A set of hybrid orbitals need not be equivalent. A trigonal bipyramidal hybridization gives two axial orbitals perpendicular to the three equatorial orbitals. Thus PCl_5 has two chlorine atoms different from the other three.

2.7 CONCEPT OF RESONANCE

Sometimes it is not possible to represent a molecule by a single valence bond structure which can correctly account for the properties of the molecule. In such cases valence bond method introduces the concept of *resonance* according to which if two or more alternate valence bond structures are written for a molecule, the actual structure of the molecule is said to be *resonance* or *mesomeric hybrid* of all these alternate structures. The various structures of which the molecule is said to be a resonance hybrid are known as *canonical* or *contributing resonance forms*. For example, hydrogen molecule is considered to be a resonance hybrid of the following contributing structures. The resonance between the various canonical forms is represented by putting a double headed arrow (↔) between the various structures. Thus

$$\underset{\text{(covalent)}}{H_a - H_b} \leftrightarrow \underset{\text{(ionic)}}{H_a^+ H_b^-} \leftrightarrow \underset{\text{(ionic)}}{H_a^- H_b^+}$$

The canonical forms have no physical significance. They are merely convenient representations of a molecule in terms of Lewis structures. Resonance is the convenient way or choice of picturing a molecule in terms of different familiar Lewis or VB structures, even though the actual molecule does not belong to any one of these. There is no theoretical basis for it.

Resonance is the description of the electronic structures of a molecule or an ion by means of several schemes of pairing of electrons, with the features of each scheme contributing in the description.

Rules for Writing Resonating Structures

For resonance to be possible the different canonical or contributing structures must obey the following rules:

1. Contributing structures should have the same relative positions of atoms. They should differ only in the position of electrons.

2. Contributing structures should have the same number of unpaired electrons.
3. Contributing structures should not differ much in energy.
4. Contributing structures should be so written that the negative charge resides on electronegative atom and positive charge on electropositive atom.
5. Contributing structures should be so written that opposite charges reside on adjacent atoms.
6. Contributing structures with the greater number of covalent bonds contribute more towards the real structure.
7. The more is the number of contributing structures; the higher is the stability of the molecule.

Resonance Energy

Resonance energy is defined as the difference between the actual bond energy of the molecule and that of the most stable resonating structure.

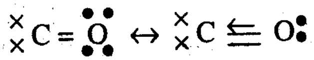
In a molecule which exhibits resonance it has been found that in every case the experimental heat of formation of the molecule is greater than the calculated heat of formation i.e., the actual molecule is more stable than the resonating structure considered for calculating the heat of formation. The resonating structure being used as the basis for calculating the heat of formation must be the most stable of all the resonating structures among which resonance occurs. The difference between observed and calculated heat of formation is usually called *resonance energy*. Resonance energy represents the extent to which the actual structure is more stable than the most stable resonating structure. Due to resonance phenomenon, stability of molecule increases and bond lengths decrease. This extra stability is attributed to resonance energy. Sometimes it is also known as *exchange energy*.

Resonance Structures of Some Species

1. Hydrogen molecule (H_2): Hydrogen molecule is considered to be resonance hybrid of the following three structures:

$$\underset{\text{(I)}}{H_a - H_b} \leftrightarrow \underset{\text{(II)}}{H_a^+ H_b^-} \leftrightarrow \underset{\text{(III)}}{H_a^- H_b^+}$$

2. Carbon monoxide molecule (CO): It is considered to be resonance hybrid of following two structures:



$${}^{\times}_{\times}C = \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \leftrightarrow {}^{\times}_{\times}C \overset{\leftarrow}{\equiv} O{:}$$

(I) (II)

The calculated bond lengths of C=O and C≡O bonds are 1.22Å and 1.10Å respectively while the experimental value is 1.15Å. This indicates that the experimental value is intermediate between these two values and thus CO molecule is resonance hybrid of the above two structures.

3. Nitric oxide molecule (NO): This molecule is supposed to be a resonance hybrid of the following structures:

$$\underset{\text{(I)}}{{}^{\times}_{\times}\overset{\times}{N} = \ddot{O}:} \longleftrightarrow \underset{\text{(II)}}{{}^{\times}_{\times}\overset{\overline{\times\cdot}}{N} = \overset{+}{\dot{O}}:}$$

Evidently NO molecule is an odd electron molecule. Thus it has effectively a structure, ${}^{\times}_{\times}N \overset{\times\cdot\cdot}{=} O:$ with one three electron bond and two two–electron bonds between N and O. The observed N–O bond distance of 1.14Å is intermediate between N=O (1.15Å) and N≡O (1.05Å).

4. Carbon dioxide molecule (CO_2): This molecule is considered to be resonance hybrid of the following structures:

$$\underset{\text{(I)}}{O=C=O} \leftrightarrow \underset{\text{(II)}}{\overset{+}{O}\equiv C-\overset{-}{O}} \leftrightarrow \underset{\text{(III)}}{\overset{-}{O}-C\equiv\overset{+}{O}}$$

The experimental value of C=O bond distance (1.15Å) is intermediate between the calculated values of C=O (1.22Å) and C≡O (1.10Å). This show that the structure (I) is inadequate to explain the properties of CO_2 molecule.

Example 2.1

Calculate the resonance energy of CO_2 molecule. The experimental value of heat of formation of CO_2 is 1602.8 kJmole^{-1}.

Solution

$\Delta E = E_{EXP.} — E_{Calc.}$

$= 1602.8$ — Energy of C=O (in kJmo^{-1})

$= 1602.8 — 2 \times 732.3$

$= 1602.8 — 1464.6$

$= 138.2$ kJmol^{-1}

2.8 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

There is a very natural correlation between the orientation of the bonds to an atom and the spatial requirements of the bonding and non-bonding (lone pair) electrons that reside at, and hence occupy the space surrounding, that atom. Sidgwick and Powell (1940) suggested that the shapes of polyatomic molecules and ions are determined by the total number of bonding and nonbonding electron pairs present in the valence shell of the central atom. Since then several workers including Gillespie have been emphasizing the importance of lone pairs of electrons in stereochemistry. Gillespie and Nyholm in 1957, proposed that the stereochemistry of an atom in a molecule is mainly determined by the repulsive interactions among all electron pairs in its valence shell. They named this theory *Valence Shell Electron Pair Repulsion Theory.* (VSEPR).

VSEPR theory has since been considerably developed largely through the efforts of Gillespie. According to this theory the bonding and nonbonding electron pairs in the valence shell of the central atom arrange themselves in such a manner that there is minimum repulsion between them. Hence electron pair orbitals adopt arrangements in space that provide maximum separation among electron pairs. Since there can only be one orientation of orbitals corresponding to minimum energy, the molecule or ion has a definite shape and geometry. For explaining the shapes of some covalent molecules of non–transition metals, the following rules are followed:

Rule 1. The preferred arrangement of a given number of electron pairs in the valence shell of an atom is that which maximizes their distance apart.

Rule 2. A nonbonding pair of electrons takes up more room on the surface of an atom than a bonding pair.

Rule 3. The size of a bonding electron pair decreases with increasing electronegativity of the ligand forming a molecule.

Rule 4. The two electron pairs of a double bond (or the three electron pairs of a triple bond) take up more room than does the one electron pair of a single bond.

Rule 5. Multiple bonds do not affect the geometry of the molecule. They merely strengthen the bond and decrease the bond length.

Rule 6. Repulsions between the lone pair electrons are greater than those between bond pairs. The repulsion follows the order:

(lp – lp) repulsion > (lp –bp) repulsion > (bp – bp) repulsion

Applications of VSEPR Theory

Let us now apply the valence shell electron pair repulsion concept to explain the geometries of the molecules and ions of non–transition elements. First, before applying VSEPR arguments to explain the geometries of the molecules and polyatomic ions, it will be convenient to define a quantity known as the "*occupancy*". Second, once we know many groups are needed to occupy the space around an atom, then we can deduce the best prototype geometrical arrangement of those groups. Finally, starting from the prototype geometry, we can analyse electron repulsions to explain small deviations in angles from those of prototype. For accounting purposes, it is convenient to define a quantity known as the occupancy for an atom. For structures AB_xE_y (where A is the central atom), x is the number of other atoms B bound to A. The sum (x+ y) is called the occupancy of atom A. The space surrounding atom A is said to be occupied by (x + y) other atoms or lone pairs. The occupancy for an atom is defined so that it is independent of the presence of multiple bonds; whether atoms B are singly or multiply bonded to atom A, each B still occupies only one position in the space surrounding atom A.

Table 2.2 lists the occupancies (atoms + lone pairs) and the corresponding geometries that best minimize electron pair repulsions for each situation. Those hybridizations of the central atom that separately give a particular geometry are also listed in Table 2.2, although it should be remembered that VSEPR should be applied without reference to hybridization. (It is only convenient to list two together in the table because of the close correspondence in result that is often seen when applying the two theories.

In the following examples, the three localized bonding theories have been applied in roughly the following fashion. . First determine the proper Lewis diagram for the molecule or the polyatomic ion. Next, having determined the occupancy value for the atom of interest, deduce the atom's hybridization. Multiple bonds are then invoked in the electronically unsaturated systems, using unhybridized *p* or *d* orbitals. Also, once occupancy has been determined, prototype geometry can be chosen, and VSEPR theory can be used to explain deviations from prototype.

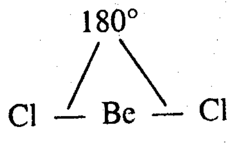
Table 2.2. The Separate Correspondence between Occupancy (x + y) and Prototype Geometry or Hybridization of the Central atom (A) in the Structures AB_xE_y

Occupancy	Prototype Geometry	Hybridization
Two	Linear	sp
Three	Triangular	sp^2
Four	Tetrahedral Square (planar)	sp^3 dsp^2
Five	Square pyramidal Trigonal bipyramidal	dsp^3 dsp^3
Six	Octahedral	d^2sp^3

1. **Species of AB_2type.** The following examples are considered.

(*a*) *$BeCl_2$ molecule in the vapor phase*. The Lewis structure of this molecule is Cl— Be— Cl in which the central atom (Be- atom) is surrounded by two *σ-bps* and no *lp*. These two *σ-bps* will occupy their positions as far apart as possible so that the electrostatic repulsion between them is reduced to minimum. This is possible only when these bonding electron pairs are at 180° about the central atom, i.e., the bonding electron pairs occupy positions on the opposite sides of Be-atom forming Cl— Be— Cl angle equal to 180°.

Thus $BeCl_2$ molecule in the vapor phase has linear geometry.



(*b*) *CO_2 molecule*. Lewis structure of this molecule is O = C = O. Since the central atom (C-atom) in this molecule is surrounded by two σ-*bps* and no *lp* (π-*bps* have not been considered).

Other examples of linear molecules are hydrogen cyanide (H— C ≡N) and acetylene (H—C≡C—H)

2. **Species of AB_3 Type:** The following examples may be considered.

(*a*) *BCl_3 molecule*. Lewis structure of this molecule shows that B-atom central atom) is surrounded by three σ-*bps* and no *lp*. These three *bps* arrange themselves in such a way the repulsion between them is minimum. This is most probable if the bind angle between them is 120°. Consequently in trigonal structure the repulsive forces between the electron pairs are reduced to minimum and hence this structure is the most probable structure of BCl_3 molecule.BF_3, $GaCl_3$ and BH_3 molecules also have trigonal planar geometry.

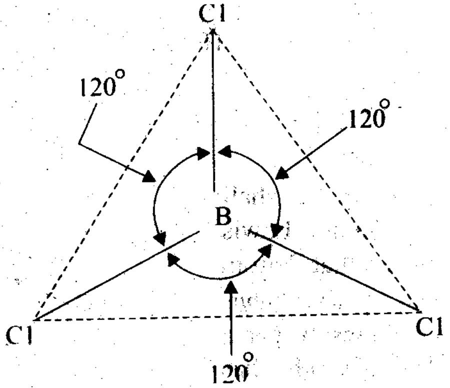


Fig. 2.13(a). Trigonal planar geometry of BCl_3 molecule.

(*b*) *SO_3 molecule*. **Lewis structure of this molecule suggests that S-atom (central atom) is linked with one O-atom by a double bond and with two O-atoms by coordinate (covalent) bonds.** Now since S-atom is surrounded by three σ-*bps* and no *lp* (π-bonds have not been considered), SO_3 molecule, like BCl_3 molecule, has trigonal geometry as shown in Fig. 2.13

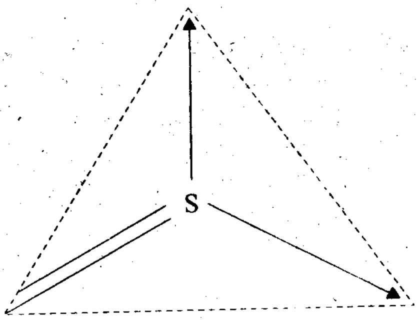


Fig. 2.13(b). Trigonal planner geometry of SO_3 molecule.

3. Species of AB_4 type: The following examples may be considered:

CH_4 molecule. Lewis structure of this molecule shows that C-atom (central atom) is surrounded by four *σ-bps* and no *lp*. These bps arrange themselves in such a way that they are at minimum repulsion. Clearly, since the repulsive interaction in tetrahedral shape is minimum; this shape is the most probable shape of CH_4 molecule. A tetrahedron is a solid figure which contains four faces each of which is an equilateral triangle. Each of the four H—C—H bond angles is equal to 109.5°.CCl_4 and $SiCl_4$ molecules and NH_4^+ and SO_4^{2-} ions also have tetrahedral geometry. The tetrahedral structure of CH_4 is shown in Fig. 2.14.

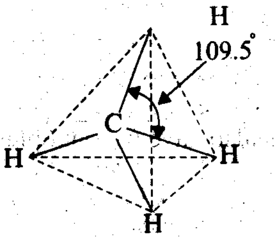
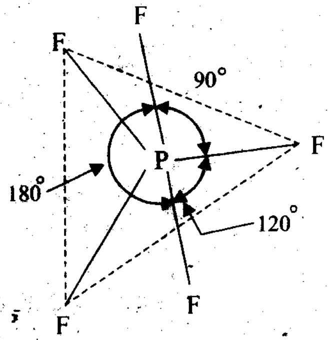


Fig 2.14 Tetrahedral shape of CH_4 molecule

4. Species of AB_5 Type: Here we shall consider the shape of PF_5 molecule. Lewis structure of PF_5 molecule shows that P-atom (central atom) is surrounded by five *σ-bps* and no *lp*. These *bps* arrange themselves in a trigonal bipyramidal shape which has minimum repulsions between the *bps*.PF_5 molecule geometry is shown in Fig. 2.15



In the molecule the three equatorial bonds are equal in length but shorter than the two axial bonds. Other molecules which have trigonal bipyramidal shape are PCl_5 (g), $SbCl_5$ etc.

5. Species of AB_6 Type: SF_6 and TeF_6 are the examples of molecules which have octahedral shape. Here we shall consider the geometry of SF_6 molecule. Lewis structure of this molecule shows that S-atom (central atom) is surrounded by six *σ-bps* and no *lp*. This molecule has octahedral geometry in which F-S-F bond angle is equal to 90° as shown in Fig. 2.16. This is the most probable geometry as all the *bps* are at minimum repulsions.

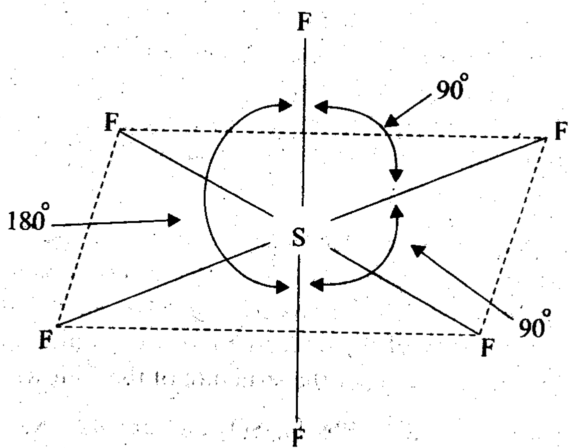


Fig. 2.16. Octahedral geometry of SF_6 molecule.

6. Species of AB_7 Type: IF_7 is an example of AB_7 type species. So here we shall consider the structure of this molecule. Lewis structure of this molecule shows that I-atom (central atom) is surrounded by seven *σ-bps* and no *lp*. Thus according to VSEPR theory this molecule has pentagonal bipyramidal geometry shown in Fig. 2.17. In this figure, F_a and F_b are the fluorine atoms lying in the pentagonal plane and at the axes of the pentagon respectively.

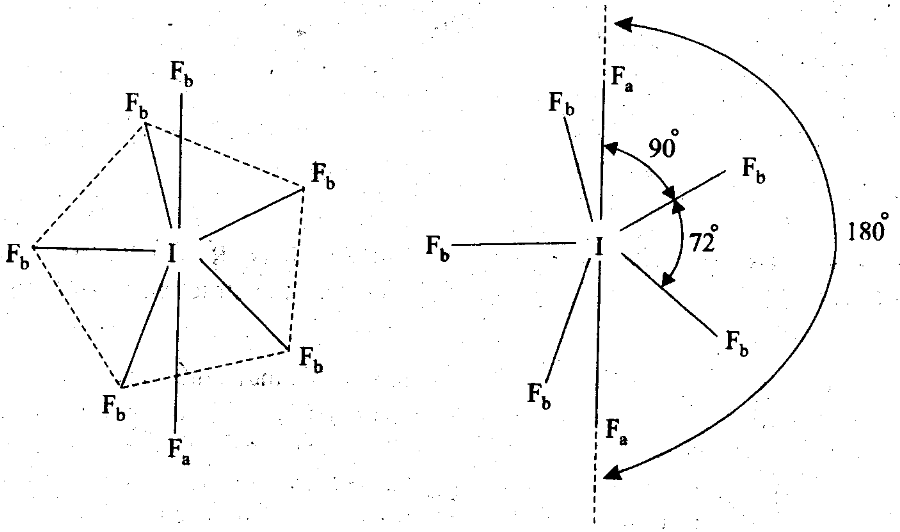


Fig. 2.17. Pentagonal bipyramidal geometry of IF_7 molecule.

Shape of molecules and ions whose central atom is surrounded by σ-*bps* as well as by one or more *lps*.

The molecules or ions whose central atom is surrounded by σ-*bps* as well as by one or more *lps* can be represented as $AB_m(lp)_n$ where A = central atom, B = atoms linked with the central atom (A), m = number of B-atoms or the number of σ-*bps* by which the central atom (A) is linked with m B-atoms (m also indicates the number of σ-*bps* by which the central atom is surrounded), lp = lone pair of electrons, n = number of *lps* by which the central atom is surrounded.

Thus total number of electron pairs which surrounded the central atom is equal to (m + n). While determining the geometry of the molecules or ions having one or more π-bonds, it should be remembered that the presence of π-bps surrounding the central atom does into influence the geometry of the molecule/ion, we should, therefore, not consider the presence of π-bonds. Let us consider the structure of the following types:

1. Species of AB_2 (*lp*) type. $SnCl_2$, $PbCl_2$, SO_2 etc. are the examples of this type of species. Here we shall consider the structure of SO_2 molecule. Lewis structure of this molecule is $O = S \rightarrow O$ which indicates that S-atom (central atom) is surrounded by two σ-*bps* and one *lp* (σ-*bps* = 2 and *lp* = 1). The spatial arrangement of these three electron pairs round the central atom is trigonal planar (according to VSEPR theory). Due to the presence of one *lp* which occupies one of the three vertices of the triangular plane, the shape of SO_2 molecule is not trigonal planar but it is angular with O—S—O bond angle equal to 120°. (See Fig. 2.18)

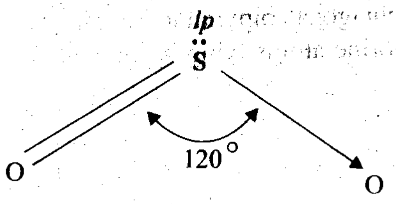


Fig. 2.18 Angular shape of SO_2 molecule.

2. Species of AB_3 (lp) type. NH_3, PH_3, PCl_3, RNH_2, R_2N, R_3N, ClO_3^-etc. , are the examples of this type of species. Here we shall consider the structure of NH_3 molecule only.

Structure of NH_3 molecule. Lewis structure of this molecule shows that since N-atom (central atom) is surrounded by 4 electron pairs (σ-*bps* = 3 and *lp* = 1), the spatial arrangement of these four electron pairs round N-atom (central atom) s tetrahedral (according to one of the postulates of VSEPR theory). Due to the presence of one *lp* at one of the four vertices of the tetrahedron, the shape of NH_3 molecule is not tetrahedral but it gets distorted and becomes trigonal pyramidal as shown in Fig. 2.19.Although the orientation of 4 electron pairs (σ-*bps* = 3, *lp* = 1) round N-atom is tetrahedral, H—N—H bond angle is not equal to the expected tetrahedral angle (109.5°) rather this angle is 107.5° which is less than 109.5°. Why H—N—H bond angle is less than 109.5° has been explained as follows:

We know that, according to VSEPR theory, repulsion between a *lp* and a *bp* is greater than that between a *bp* and a *bp*, i.e.,

$$(lp - bp) > (bp - bp)$$

It is due to the greater magnitude of (*lp* – *lp*) repulsion in comparison to that of (*bp* – *bp*) repulsion that the two N—H bonding electron pairs are pushed closer to each other and the result becomes 107.5°. Similarly the geometry of PCl_3 can be explained.

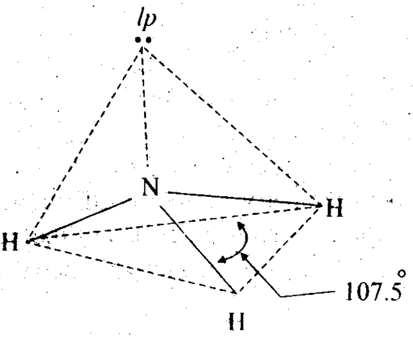


Fig. 2.19. Trigonal pyramidal shape of NH_3 molecule.

3. **Species for $AB_2 (lp)_2$ Type.** H_2O, SCl_2, $SeCl_2$, NH_2^-, ICl_2^+ etc. are the examples of such species. Here we shall consider the structure of H_2O molecule. Lewis structure of this molecule shows that since O-atom (central atom) is surrounded by 4 electron pairs (σ-*bps* = 2 and *lps* = 2), the spatial orientation of 4 electron pairs round O-atom is tetrahedral (according to VSEPR theory). Due to the presence of two *lps* located at the two tetrahedral positions, the shape of H_2O molecule gets distorted from tetrahedral shape and becomes angular (V-shape or bent) as shown in Fig. 2.20

H—O—H bond angle in H_2O molecule. Although the special orientation of 4 electron pairs (σ-*bps* = 2, *lps* = 2) round O-atom is tetrahedral, H—O—H bond angle is not equal to the expected tetrahedral angle (= 109.5°); rather this angle is equal to 105.5° which is less than 109.5°.

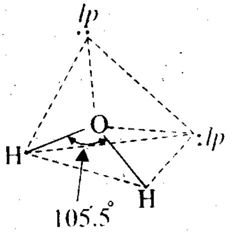


Fig. 2.20. Angular (v-shaped or bent) structure of H_2O

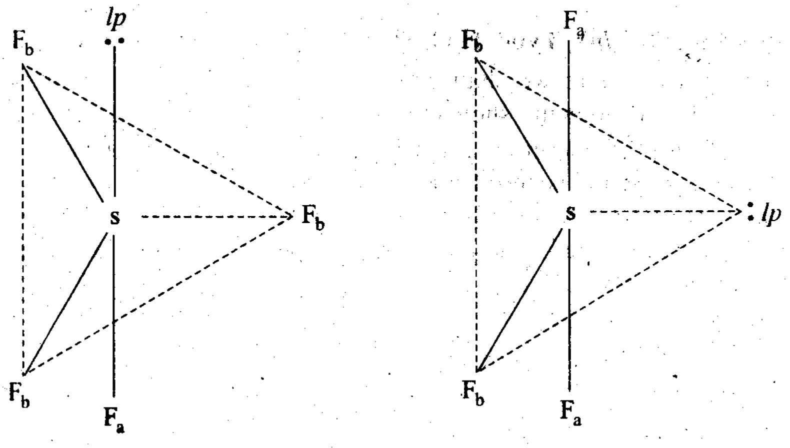
Explanation. We know that, according to VSEPR theory the magnitude of the repulsion between electron pairs is in the order:

$$(lp - lp) > (lp - bp) > (bp - bp)$$

The above order shows that (*lp* – *lp*) repulsion is the maximum, (*lp* – *lp*) repulsion is medium while (*bp* – *bp*) repulsion is minimum. The two *lps* on O-atom not only repel each other, but also repel the two *bps*. The repulsion between two *lps* pushes the two O—H bonding electron pairs closer to each other and this results in that H—O—H bond angle decreases from the expected tetrahedral bond angle (=109.5°) and becomes 105.5°. (See Fig. 2.20)

4. Species of AB_4 (*lp*) Type. SF_4, $TeCl_4$, $SeCl_4$ etc., are the examples of this type of species. Here we shall discuss the structure of SF_4 molecule.

Lewis structure of this molecule is shows that since S-atom (central atom) is surrounded by five electron pairs (σ-*bps* = 4 and *lp* = 1), the spatial arrangement of these electron pairs round S-atom is trigonal bipyramidal. Due to the presence of one *lp* of electrons, SF_4 molecule has irregular or distorted tetrahedral (also called see-saw) geometry in which the *lp* can occupy either one of the two axial position or one of the three equatorial (also called basal) positions. Thus theoretically SF_4 molecule can have any of the two distorted tetrahedral geometries shown in Fig. 2.21. In geometry (*a*), the *lp* occupies the axial position while in geometry (*b*) the *lp* has basal position. Rejecting the electron pair-electron pair repulsions where the angle between the electron-pairs is more than 100°, the (*lp* – *bp*) repulsions involved in geometry (*b*) are lesser, this geometry is more stable than geometry (a). Thus SF_4 molecule has see-saw geometry represented by (*b*) in which the *lp* is situated at one of the basal positions of the trigonal bipyramid. Thus the species of AB_4 (*lp*) type have geometry. (*b*).



(a) (b)

Fig. 2.21 Two possible geometries of SF_4 molecule, (a) Geometry of SF_4 molecule in which lp occupies the axial position of the trigonal bipyramid (wrong geometry). (b) Irregular or distorted tetrahedral (see-saw) geometry of SF_4 molecule in which the lp occupies the equatorial position of the trigonal bipyramid (correct geometry).

5. Species AB_3 $(lp)_2$ Type. Inter-halogen of XY3 type (e.g., ClF_3, BrF_3, ICl_3, IF_3 etc.) are the examples of AB_3 $(lp)_2$ type species. In XY_3 inter-halogens X is the bigger halogen atom and Y is the smaller halogen atom. X is the central atom in these molecules. As an example let us discuss the structure of ClF_3, molecule. Lewis structure of this molecule indicates that since Cl-atom (central atom) is surrounded by five electron pairs (σ-*bps* = 3 and *lps* = 2), the spatial orientation of these 5 electron pairs round Cl-atom is trigonal bipyramidal. Due to the presence of two *lps*, ClF_3 molecule has slightly bent T-shaped structure.

Theoretically, depending on the positions occupied by the two *lps*, ClF_3 molecule can have different geometries. If we do not consider the electron pair-electron pair repulsions where the angle between them is greater than 100°, we find that geometry in which both the *lps* occupy the equatorial positions of the trigonal bipyramid involves minimum repulsion. Thus the possible geometry which is called bent T-shaped geometry is the most stable geometry for ClF_3 molecule, i.e., ClF_3 molecule or any other molecule or ion of AB_3 $(lp)_2$ type has bent T-shaped geometry.

Each of the F—Cl—F (F_a—Cl—F_b) bond angles is equal to 87.5°. The basal Cl—F—F_b) bond lengths is equal to 1.60 Å(while each of the two axial Cl—F (Cl – F_a) bond lengths is equal to 1.70Å (See Fig. 2.22)

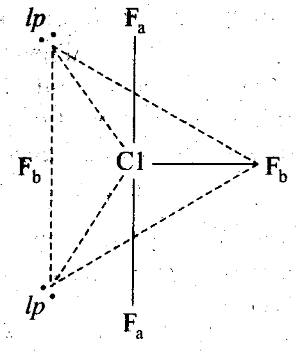


Fig. 2.22 T-shape bent geometry of ClF_3 molecule.

6. Species of AB_2 $(lp)_3$ type. XeF2, ICl_2^- etc. are the examples of AB_2 $(lp)_3$ type species. As an example let us consider the geometry of XeF_2 molecule.

Lewis structure of this molecule shows that since Xe—atom (central atom) is surrounded by five electron pairs (σ-*bps* = 2 and *lps* = 3), the spatial arrangement of 5 electron pairs round the central atom (Xe-atom) is trigonal bipyramidal. Due to the presence of three *lps*, XeF_2 molecule assumes linear shape with F—Xe—F bond angle equal to 180°.

Depending on the positions occupied by the three *lps*, XeF_2 molecule can have different structures. The number of electron pair-electron pair repulsions shown in geometry indicates that this repulsion in geometry is minimum and hence this geometry is the most stable. In other words we can say that all the three *lps* occupy the equatorial positions of the trigonal bipyramid and hence XeF_2 or any other species of $AB_2\ (lp)_3$ type has linear shape in which the length of each of Xe—F bonds is equal to 2.0Å.

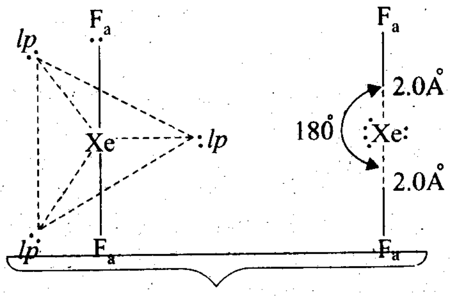


Fig. 2.23 Linear geometry of XeF_2 molecule.

7. **Species of AB_5 (*lp*) type.** IF_5, BrF_5, ClF_3, $[SbF_5]^{2-}$ etc., are the examples of AB_5 (*lp*) type species. As an example let us discuss the geometry of IF_5 molecule.Lewis structure of this molecule I-atom (central atom) is surround by six electron pairs (σ-*bps* = 5 and *lp* = 1) and hence the spatial arrangement of the six electron pairs round I-atom is octahedral. The lone pair of electrons may occupy either one of the four equatorial positions of the octahedron or any of the, two axial positions of the octahedron. Thus, depending on the position by the *lp*, IF5 molecule may have two geometries viz., (a) and (b) shown in Fig. 2.24.

It has been shown that the (*lp* – *lp*) repulsion in geometry (*b*) is minimum and hence IF_5 molecule assumes square pyramidal shape shown at (*b*) of Fig. 2.24. In this geometry the *lp* occupies the axial position.

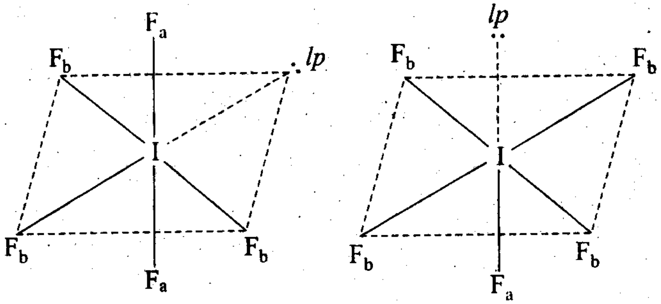


Fig. 2.24 Two possible geometries of IF_5 molecule. (a) In this geometry lp occupies the equatorial position of the octahedron (wrong geometry). (b) Square pyramidal geometry of IF_5 molecule in which the lp occupies the axial position (correct geometry).

8. Species of $AB_4 (lp)_2$ type. XeF_4, ICl_4^- etc. are the examples of this type of species. As an example let us consider the geometry of XeF_4 molecule. Lewis structure of this molecule shows that since Xe-atom (central atom) is surrounded by six electron pairs (σ-*bps* = 4 and *lps* = 2), spatial arrangement of these six electron pairs round Xe-atom is octahedral.

Depending on the positions occupied by the two *lps*, XeF_4 molecule can have different geometries. It has been observed that electron pair-electron pair repulsions in geometry in which the two *lps* occupy the axial positions of the octahedral are minimum and XeF_4 has square planar geometry in which each of the two F_b—Xe—F_b bond angles is equal to 90° and each of the four Xe—F_b bond lengths is equal to 1.95Å.

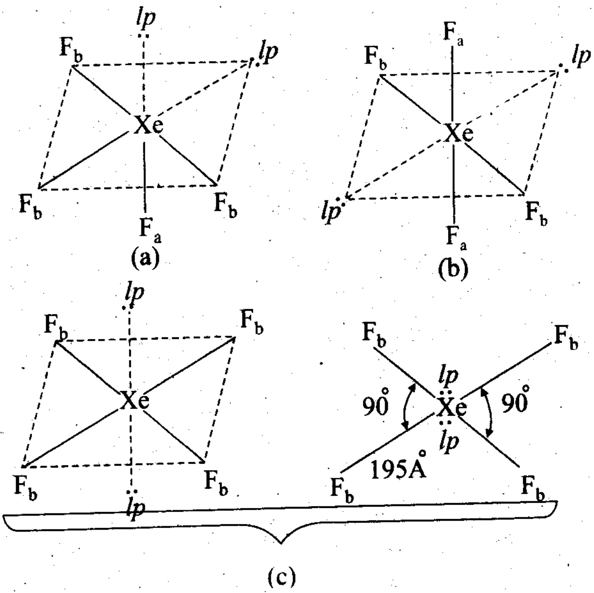


Fig. 2.25 The different geometries of XeF_4 molecule. (a) Geometry of XeF_4 molecule in which one lp is at the equatorial position and the other lp is at the axial position of the octahodron. (wrong geometry). Here (lp – lp) repulsions = 1, (lp – lp) repulsions = 6 and (bp – bp) repulsions = 5. (b) Geometry of XeF_4 molecule in which both lps occupy the axial positions (wrong geometry) (c) Square planner geometry of XeF_4 molecule in which both lps occupy the axial positions (correct geometry). Here (lp – lp) repulsions = 0, (lp – lp) repulsions = 8 and (bp – bp) repulsions = 4.

Limitations of VSEPR Theory

Although the VSEPR theory is very useful for explaining the geometries of a large number of molecules and ions, yet it has following limitations:

1. This theory cannot explain the shapes of molecules having very polar bonds, e.g., Li_2O should have the same structure as H_2O but in fact it is linear.
2. This theory is unable to explain the shapes of molecules having extensive delocalized π–electron systems.

3. This theory is unable to predict the shapes of certain transition metal complexes.
4. This theory also cannot explain the shapes of certain molecules which have an inert pair of electrons.

2.8. MOLECULAR ORBITAL THEORY

According to the valence bond theory, a covalent bond is formed between two atoms by the overlapping of atomic orbitals which are half-filled. These half-filled orbitals merge into one another and give a bond which is responsible for the stability of the resulted molecule. All other orbitals which are completely filled do not take part in bond formation. However, this seems to be an exaggeration because the nucleus of an approaching atom is bound to affect the electron waves of nearly all the orbitals. Apart from this, VBT fails to explain some of the properties of some molecules like O_2.

The method of molecular orbital theory was developed in 1927–28 by Hund and Mulliken, and in 1929 by Lennard–Jones. According to this theory:

(i) Each electron in a molecule is described by a wavefunction, known as the *molecular orbital.* These molecular orbitals extend over the entire region of the molecule.

(ii) A molecular orbital has the same significance as an atomic orbital. Hence $\Psi^2 d\tau$ represents the probability of finding an electron in the volume element $d\tau$.

(iii) The molecular orbitals are obtained by the linear combination of the atomic orbitals of the combining atoms.

(iv) Each molecular orbital is associated with a definite energy just like an atomic orbital and the total energy of the molecule is the sum of the energies of all the occupied molecular orbitals.

(v) The electrons occupy the molecular orbitals following the Aufbau and Pauli Exclusion principles in much the same manner as atomic orbitals do.

Linear Combination of Atomic Orbital (LCAO)

Molecular orbitals of a molecule are obtained by the linear combination of atomic orbitals of the combining atoms. The linear combination of the atomic orbitals is brought about either by adding or by subtracting the two wave functions of the two atomic orbitals. Let us consider the formation of diatomic hydrogen molecule. In case of hydrogen molecule, the atomic orbitals are 1s. Let the wave functions for describing the two 1s atomic orbitals be $\Psi_A(1s)$ for H_A and $\Psi_B(1s)$ for H_B. (Although the two atoms are identical but it will be convenient to distinguish the two atoms by writing H_A and H_B). Linear combination of these atomic orbitals produces two molecular orbitals:

$$\Psi_g = \Psi_b = N_b[\Psi_A(1s) + \Psi_B(1s)] \qquad .....2.10$$

and

$$\Psi_u = \Psi_a = N_a[\Psi_A(1s) - \Psi_B(1s)] \qquad .....2.11$$

Where N_b and N_a are the normalization constants. The wave function Ψ_g is symmetric, i.e., its sign or magnitude remains unchanged by inverting through the mid-point of the two nuclei. This wave function is therefore denoted by 'g' which stands for German word *gerade* (even or symmetrical). The second wave function is unsymmetrical, i.e., its sign changes by inverting through the mid-points of the two nuclei. It is denoted by 'u' means *ungerade* (odd or unsymmetrical). In Ψ_g the two orbitals that overlap are in the same phase in the region between the nuclei which corresponds to the concentration of the electron density between them. This leads to an attractive interaction. Such orbitals are called ***bonding molecular orbitals*** and are designated by σ_g (1*s*) or simply σ(1*s*). On the other hand, Ψ_u results if the two atomic orbitals are in opposite phase. It leads to a depletion of electron density between the two nuclei resulting in a strong repulsion between them. Such orbitals are called ***antibonding molecular orbitals*** and are denoted as σ_u (1s) or simply by $\sigma^*(1s)$. Both of these orbitals are shown in figure 2.26.

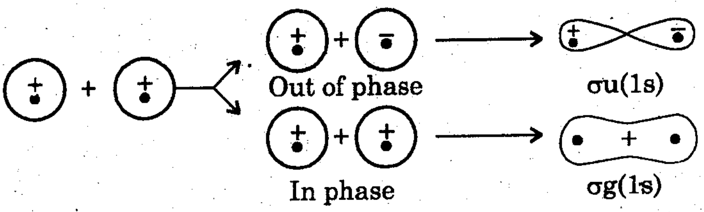


Fig. 2.26. Formation of MO's by linear combination of 1s orbitals.

The energy of bonding orbital is always lower (more stable) than the energies of combining orbitals while the energy of an antibonding orbital is higher (less stable) than the energies of the combining orbitals (Fig. 2.27)

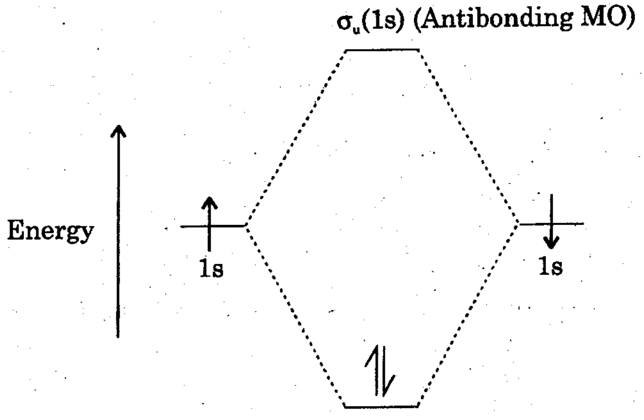


Fig. 2.27. Molecular orbital energy diagram

The values of N_b and N_a are fixed by the normalization conditions, i.e.,

$$\int \Psi^2 d\tau = 1 \qquad \text{.....2.12}$$

Let us first calculate the value of N_b. On substituting Ψ_g into equation 2.18, we get

$$\int \Psi_g^2 d\tau = \int N_b [(N_b[\Psi_A(1s) + \Psi_B(1s)]^2 \, d\tau = 1 \qquad .....2.13$$

or $$N_b^2[\int \Psi^2_A(1s) \, d\tau + \int \Psi^2_B(1s) d\tau + 2\int \Psi_A(1s) . \Psi_B(1s) d\tau = 1 \qquad .....2.14$$

If the atomic orbitals are already normalised, i.e.,

$$\int \Psi(1s) \, \Psi_A(1s) \, d\tau = \int \Psi_B(1s) \, \Psi_B(1s) \, d\tau = 1$$

The integral involving both $\Psi_A(1s)$ and $\Psi_B(1s)$ is called the overlap integral and is denoted by S.

$$S = \int \Psi_A(1s) \, \Psi_B(1s) \, d\tau$$

Overlap integral is the measure of the degree to which the atomic orbitals overlap, i.e., it determines the strength of any bond. Thus equation 2.20 reduces to

$$N_b^2 \, [2 + 2S] = 1 \qquad .....2.15$$

or $$N_b^2 = \frac{1}{2(1+S)}$$

or $$N_b = \pm\sqrt{\frac{1}{2(1+S)}} \qquad .....2.16$$

Neglecting the overlap integral to a first approximation and arbitrarily picking the positive sign, we get

$$N_b = \frac{1}{\sqrt{2}} \qquad .....2.17$$

Similarly $$N_a = \frac{1}{\sqrt{2}} \qquad .....2.18$$

The approximate molecular orbitals for H_2 – molecule are therefore,

$$\Psi_g = \Psi_b = \frac{1}{\sqrt{2}} \; \Psi_A(1s) + \Psi_B(1s)] \qquad .....2.19$$

$$\Psi_u = \Psi_a = \frac{1}{\sqrt{2}} \; [\Psi_A(1s) - \Psi_B(1s)] \qquad .....2.20$$

Now the charge density is proportional to the square of the wave function,

$$\Psi_g^2 = \Psi_b^2 = \frac{1}{\sqrt{2}} \; [\Psi_A^2 \, (1s) + \Psi_B^2 \, (1s) + 2\Psi_A(1s) \, \Psi_B(1s)] \qquad .....2.21$$

and $$\Psi_u^2 = \Psi_a^2 = \frac{1}{\sqrt{2}} \; [\Psi_A^2 \, (1s) - \Psi_B^2 \, (1s) - 2\Psi_A(1s) \, \Psi_B(1s)] \qquad .....2.22$$

In Fig. 2.31 the charge density is plotted against the internuclear distance of two states. It is clear that the charge density calculated using the wave function Ψ_g is higher in the region between the two nuclei, whereas the electron cloud is found to be very thin when Ψ_u is used. Thus the build up of charge density between the nuclei is the characteristics of bonding while depletion of charge density between the nuclei corresponds to an antibonding or a repulsive state.

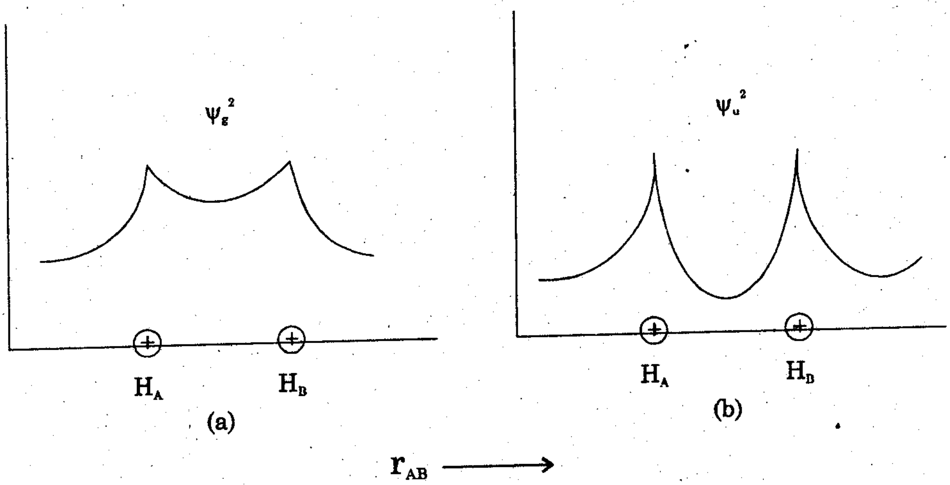


Fig. 2.28. Probability densities of (a) bonding and (b) antibonding states of H_2-molecule

Molecular Orbitals from *P*-Atomic Orbitals

We now consider how *p*-orbitals may combine in terms of LCAO to form molecular orbitals in homonuclear diatomic molecules. The three 2*p*-orbitals are directed along the three axes x, y and z. The line connecting the nuclei in a diatomic molecule is known as internuclear axis and is generally chosen as the z-axis. The other two axes x and y are perpendicular to each other. There are two different ways of overlapping of *p*-orbitals as shown in figure 2.29. When the two $2p_z$ orbitals are directed towards each other and overlap along the z-axis, it results in the formation of two molecular orbitals. In one case there is constructive interference that results in a high accumulation of electron density between the two nuclei. This gives a strongly bonding molecular orbital. In the other case the atomic orbitals interfere destructively, thereby reducing the electron density, yielding a nodal plane bisecting the molecular orbital. The bonding orbital is denoted by $\sigma_g\ (2p_z)$ or $\sigma(2p_z)$ while the antibonding orbital by $\sigma_u\ (2p_z)$ or $\sigma(2p_z)$. The two $2p_x$ and $2p_y$ orbitals do not overlap along the z-axis, rather they overlap above and below it as shown in figure 2.29.

As they are not cylindrically symmetrical about the internuclear axis, the electron density represented by these orbitals is thus quantitatively different from those of σ orbitals. The molecular orbitals so formed by the sideways overlap. The bonding orbital is antisymmetric because there is electron density that tends to draw the nuclei together, even though it is not on the internuclear axis and is denoted by $\pi_u\,(2p_y)$ or $\pi\ (2p_y)$. The antibonding molecular orbital is symmetrical and is designated by $\pi_g\,(2p_y)$ or $\pi^*(2p_y)$. There are two bonding and two antibonding molecular orbitals, because there are two p_y and p_x orbitals on the two nuclei. The basic difference, between the bonding and antibonding molecular orbitals is:

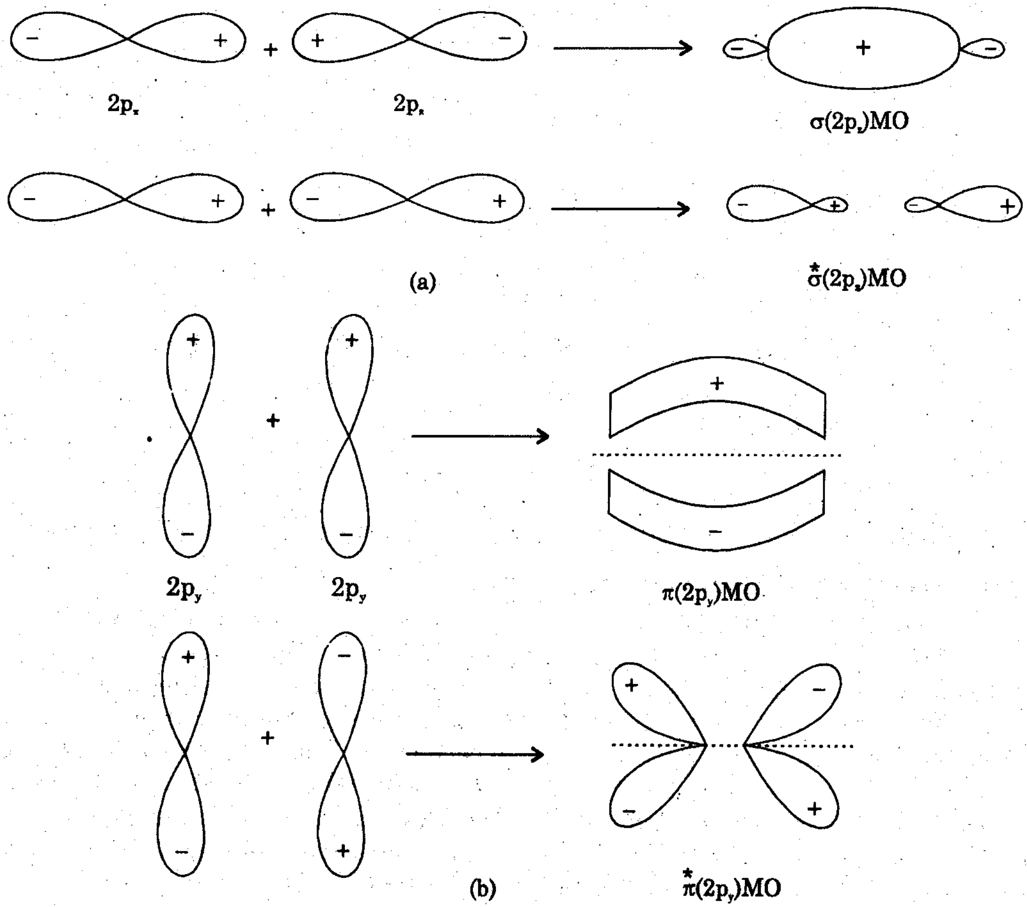


Fig. 2.29. Formation of MO's from linear combination of s and p-orbitals.

Bonding MO	**Antibonding MO**
1. It is formed by the constructive overlap of the atomic orbitals.	1. It is formed by the destructive overlap of atomic orbitals.
2. It possesses lower energy than the atomic orbitals.	2. It possesses higher energy relative to the constituent atomic orbitals.
3. The electron density is high in the region between the nuclei of bonded atoms.	3. The electron density is low in the region between the nuclei of bonded atoms.
4. Its formation takes place when the lobes of atomic orbitals have same signs.	4. Its formation takes place when the lobes of atomic orbitals have different signs.
5. The wave function of bonding MO is given by $\Psi_g = \frac{1}{\sqrt{2}} [\Psi_A(1s) + \Psi_B(1s)]$	5. The wave function of antibonding MO is given by $\Psi_u = \frac{1}{\sqrt{2}} [\Psi_A(1s) - \Psi_B(1s)]$

Conditions for the Combination of Atomic Orbitals

Before the atomic orbitals should combine to give molecular orbitals, the following conditions must be satisfied:

(i) The atomic orbitals should be of comparable energy.

(ii) The atomic orbitals should have the same symmetry about the molecular axis.

(iii) The atomic orbitals should overlap to a considerable extent.

Conventional and Modified Diagrams of Energy Levels of Molecular Orbitals

The relative energy levels of the molecular orbitals are determined by two factors: the energies of the atomic orbitals used in forming a molecular orbital and the extent of overlap between these atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the antibonding orbital is raised in energy relative to the atomic orbitals which are combined. The energies of the atomic orbitals, increase in the sequence $1s < 2s < 2p$, and it might be expected that for molecular orbitals derived from the degenerate $2p$ orbitals the overlap would be greater for the σ than for the π orbitals, thus leading to the overall sequence of increasing energy:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2pz} < \pi_{2py} = \pi_{2px} < \pi^*_{2py} = \pi^*_{2px} < \sigma^*_{2pz}$$

And in gerade–ungerade terminologe the order is:

$$\sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \sigma_u 2s < \sigma_g 2p_z < \pi_u 2p_y = \pi_u 2p_x < \pi_g 2p_y = \pi_g 2p_x < \sigma_u p_z$$

In filling these orbitals, we must bear in mind two generalizations carried forward from atomic structure, Pauli,s principle and Hund's rule; according to latter two electrons in the degenerate orbitals occupy each orbital singly rather than one doubly.

The actual electronic configurations of molecules are nearly always determined experimentally, particularly by *photoelectron spectroscopy*, in which electrons in different orbitals are distinguished by their ionization energies and the effects of their removal on the vibrational spectrum. It is found that the above order of energy holds for O_2 and F_2, for B_2, C_2 and N_2 the π_{2p} orbitals are of slightly lower energy than σ_{2p} orbital. This is also true for Li_2 and Be_2, but in the ground states of these molecules the σ_{2p} and π_{2p} orbitals are, of course, all empty. The modified sequence of increasing energy is as follows;

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2py} = \pi_{2px} < \sigma_{2pz} < \pi^*_{2py} = \pi^*_{2px} < \sigma^*_{2pz}$$

The simplest picture of MO energy levels for a homonuclear diatomic molecule is shown in figure 2.33.

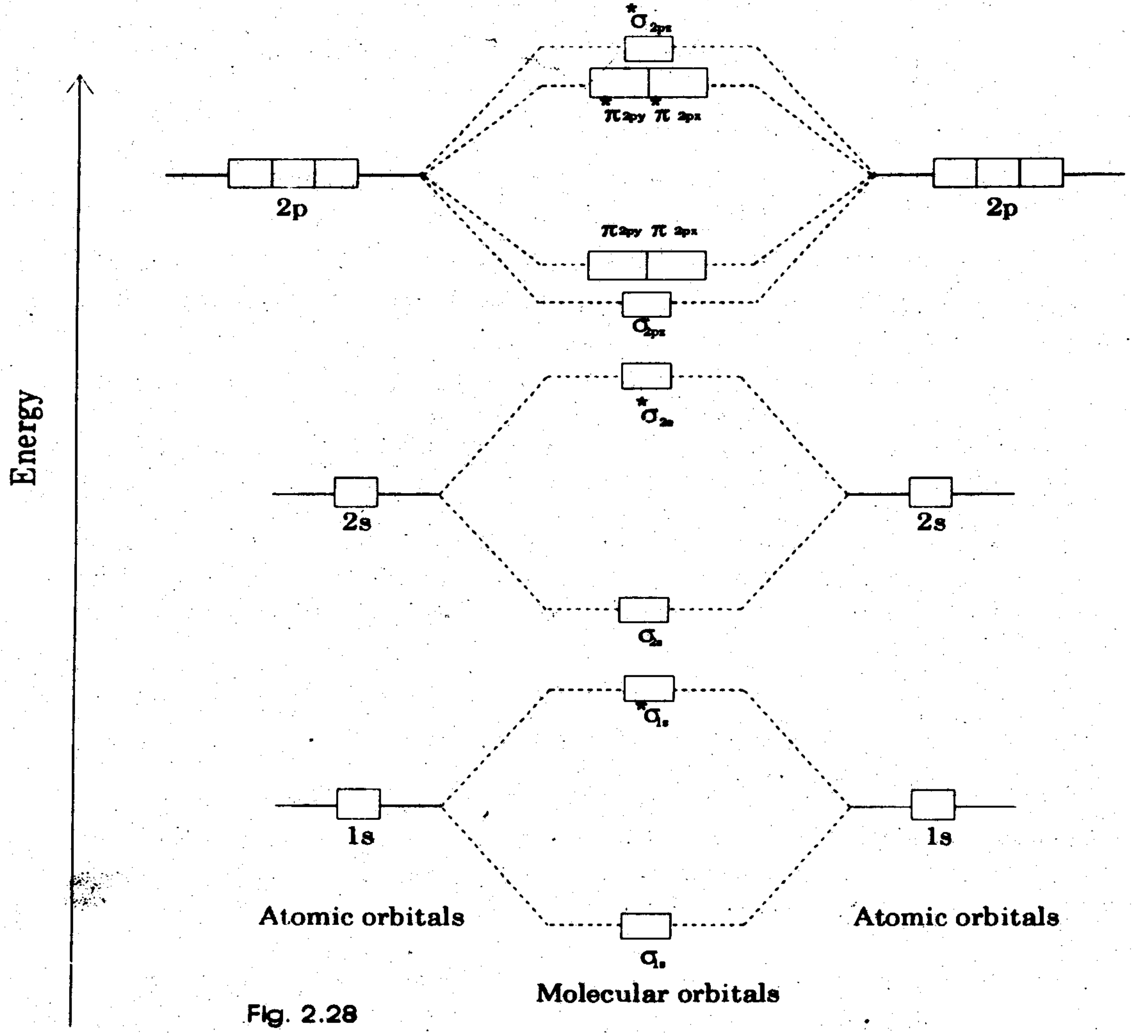


Fig. 2.30. Molecular orbital energy level diagram

Bond Order

A criterion to judge the stability of a molecule, (once its energy level diagram has been filled with appropriate number of electrons) is the bond order. It is defined as one–half of the difference of the number of electrons in the bonding molecular orbitals (N_b) and the number of electrons in the antibonding molecular orbitals (N_a). Mathematically,

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) \qquad .....2.23$$

In common practice, only MO's formed from valence orbitals are considered for determining bond order. The predicted bond orders are found to be in conformity with other methods of determining it. Thus molecular orbital theory helps in establishing whether the existence of a bond is feasible or not. The bond order as determined by the above formula is very useful as it gives the following valuable information:

(*i*) Stability of the molecules or ions
(*ii*) Bond dissociation energy
(*iii*) Bond length
(*iv*) Magnetic properties

Applications of MOT for Homonuclear Diatomic Molecules

After having discussed the basic principles of MOT, we are now able to take up the electronic structures and bonding properties of some homonuclear and heteronuclear diatomic molecules.

1. Hydrogen Molecule, H_2

Hydrogen molecule is formed from the overlap of 1*s* atomic orbitals of two hydrogen atoms. They give rise to two molecular orbitals σ_{1s} and σ^*_{1s}. The molecule has two electrons which occupy the lower energy σ_{1s} orbital as shown in figure 2.31. The electronic configuration of the molecule is represented by the equation:

$$2\text{H}\,(1\text{s}^1) \longrightarrow \text{H}_2\,[(\sigma_{1s})^2]$$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

Thus the two hydrogen atoms are bonded through only one bond in the molecule. We conclude that the H_2–molecule is stable, which indeed is. It has bond dissociation energy of 435 kJmol^{-1} and is diamagnetic in nature.

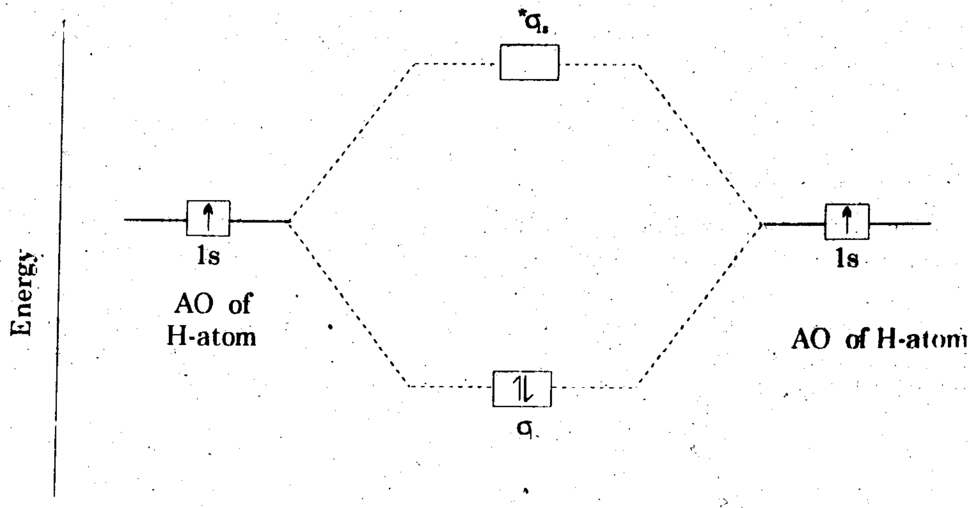


Fig. 2.31. Molecular orbital diagram for H_2 molecule

2. Helium Molecule (Hypothetical), He_2

The energy level diagram for He_2 is similar to that of H_2 except that it has two more electrons which occupy the antibonding σ^*_{1s} orbital (Fig. 2.32). Thus its bond order is zero, and we conclude that the molecule is not stable. In fact, He_2 is not known; helium exists only as monoatomic molecules.

$$\text{Bond order} = \frac{2-2}{2} = 0$$

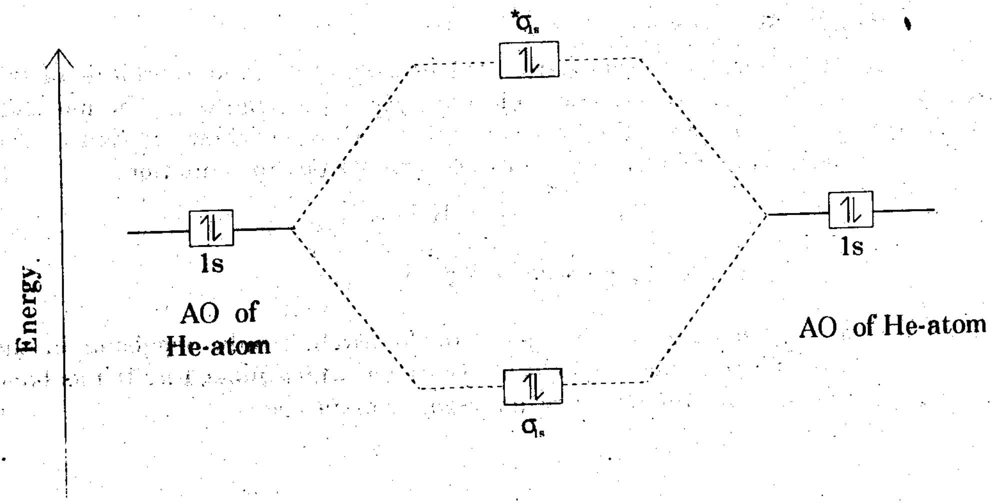


Fig. 2.32. Molecular orbital diagram for He_2 molecule

3. Lithium Molecule, Li_2

The electronic configuration for Li_2 has a total of six electrons, two each in σ_{1s}, σ^*_{1s} and σ_{2s} molecular orbitals. In shorthand notation this can be represented as σ_{1s}^2, $\sigma^*_{1s}{}^2$ and σ. There are two more electrons in the bonding orbitals than in antibonding orbitals, and the bond order is one.. We conclude that the molecule is stable, and it is indeed known to exist in the vapour phase. It possesses bond energy of 110 kJmol^{-1} which is more less than H_2 molecule.

$$2Li\,(1s^2) \longrightarrow Li_2\,[K\,K\,(\sigma_{2s})^2\}$$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

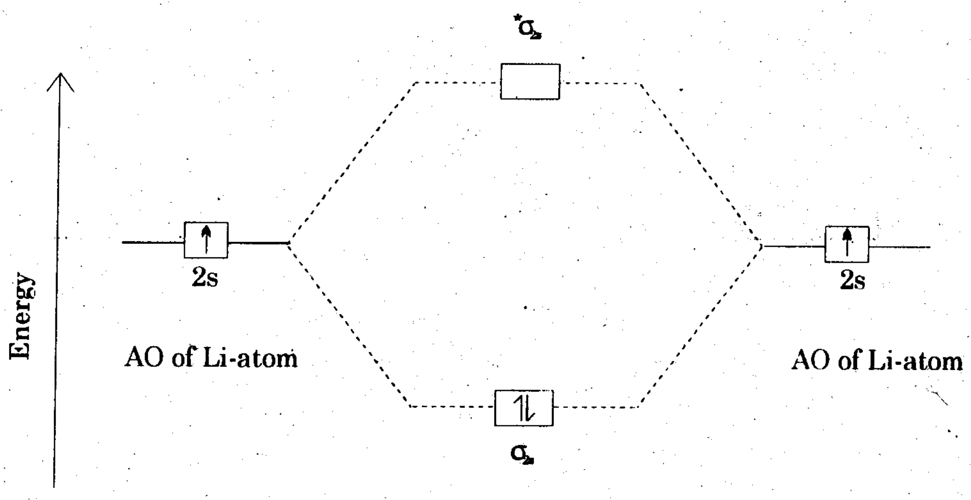


Fig. 2.33. Molecular orbital diagram for Li_2 molecule

4. Beryllium Molecule, Be_2

The situation for the Be_2 molecule is similar to that for He. Bonding and antibonding orbitals are equally populated and the bond order is zero. The electronic configuration is σ_{1s^2}, $\sigma^*_{1s^2}$, σ_{2s^2} $\sigma^*_{2s^2}$. The Be_2 molecule is known but is very unstable.

5. Boron Molecule, B_2

The boron atom has the configuration of $1s^2$, $2s^2$ $2p^1$ and is the first element with p–electrons to participate in bonding. Spectroscopic study has suggested that for B_2, C_2 and N_2 molecules, π_{2p} orbitals are lower in energy than σ_{2p} orbital. Thus the electronic configuration of B_2 is:

$$2B\,(1s^2 2s^2 2p^1) \xrightarrow{\qquad} B_2\,[KK\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\pi_{2py})^1\,(\pi_{2px})^1]$$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

Thus the two B–atoms are bonded through only one bond in the molecule. The experiments verify not only that the molecule exists in vapour phase but that it is paramagnetic with two unpaired electrons. The bond energy is 270 $kJmol^{-1}$.

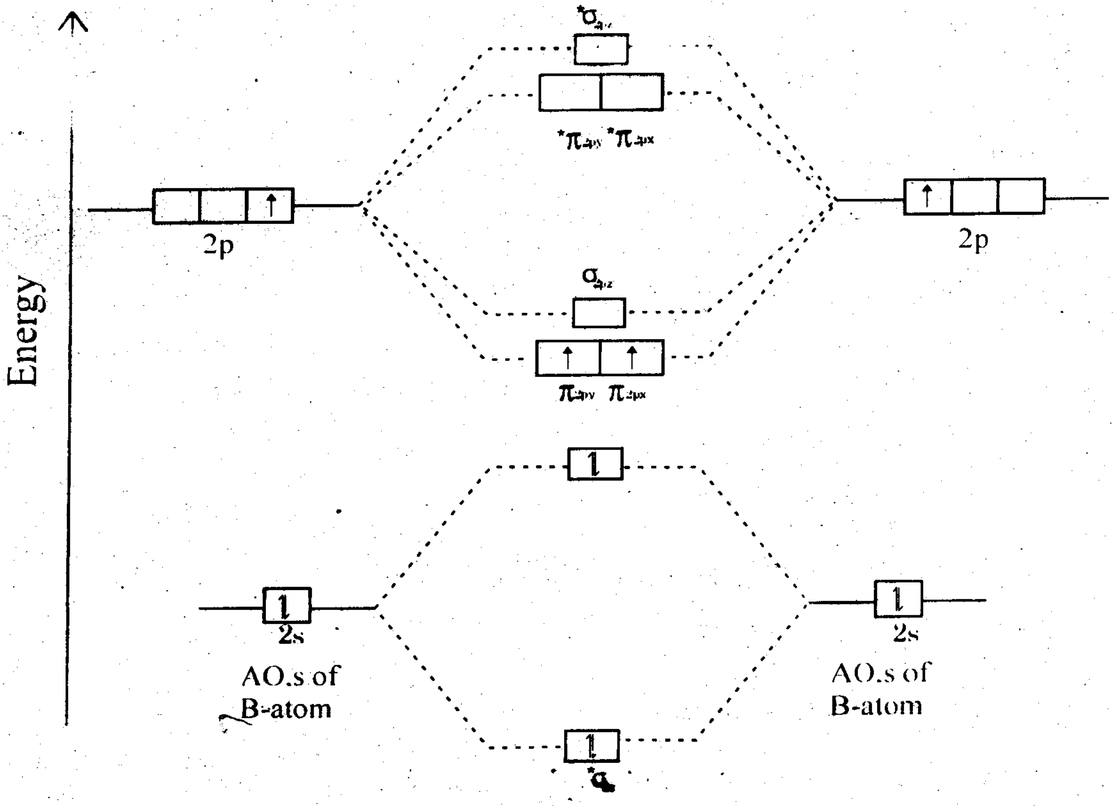


Fig. 2.34. Molecular orbital diagram for B_2 molecule

6. Nitrogen Molecule, N_2

Nitrogen atom has $1s^2$, $2s^2\ 2p^1_x\ 2p^1_y\ 2p^1_z$ electronic configuration. Only 2s and three 2p electrons from each N–atom are to be considered in the bond formation. Thus the electronic configuration of N_2 molecule is

$$2N\ (1s^2\,2s^2\,2p^1_x, 2p^1_y, 2p^1_z) \longrightarrow N_2\ [KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi_{2p_x})^2\ (\pi_{2p_y})^2\ (\sigma_{2p_z})^2]$$

$$\text{Bond order: } \frac{6-0}{2} = 3$$

It is obvious that the two N–atoms are bonded through a triple bond. N_2 molecule is very stable molecule and has very high bond energy, 946 kJmol^{-1}, which is consistent with MOT. It is diamagnetic in nature and possesses a very short bond length, 1.09Å.

(energy difference less than 100) Modified diagram
(Bond length increases)

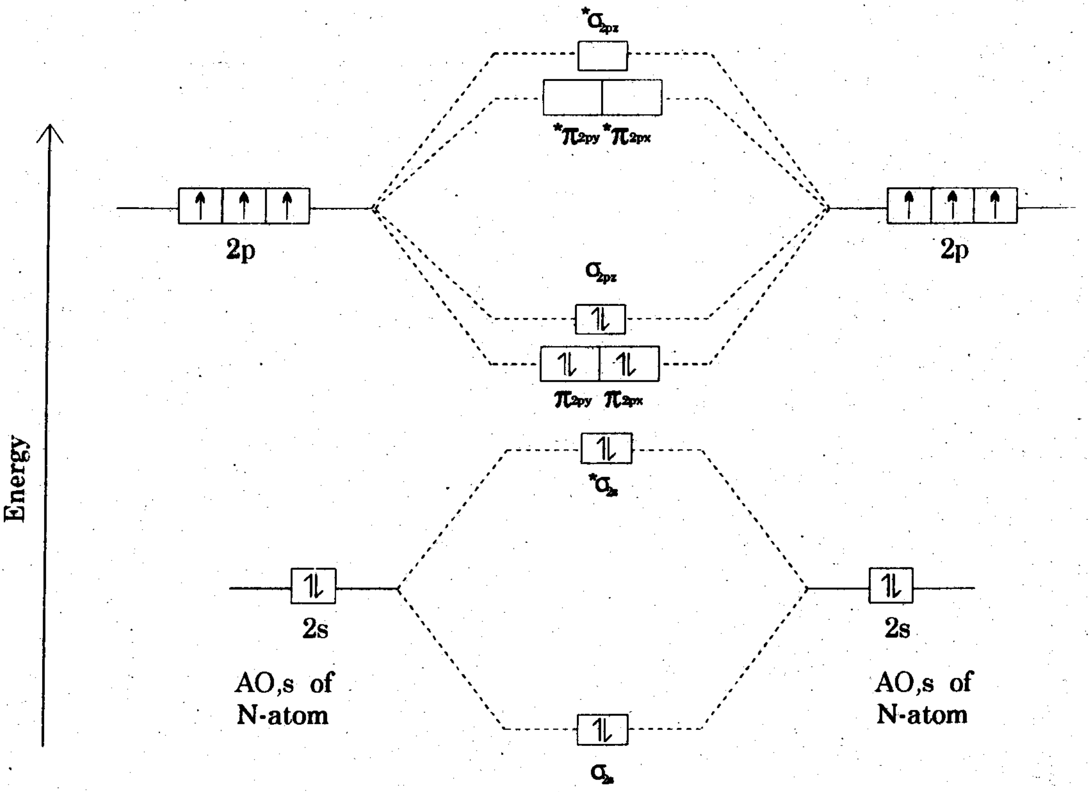


Fig. 2.35 Molecular Orbital diagram of N_2 molecule

7. Oxygen Molecule, O_2

The valence bond theory predicts that O_2 would be diamagnetic. However, experiments show that it is paramagnetic having two unpaired electrons. A structure consistent with this observation is predicted by MOT. Spectroscopic evidence indicates that for O_2, the σ_{2p} orbital is lower in energy than the π_{2p} orbitals. The electronic configuration of O_2 molecule is:

$$2O\,(1s^2\,2s^2\,2p^2_x,\,2p^1_y,\,2p^1_z) \longrightarrow O_2\,[K\,K\,(\sigma 2s)^2\,(\sigma 2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_y)^2\,(\pi 2p_x)^2\,(\pi^*{}_{2p_y})^1\,(\pi^*{}_{2p_x})^1]$$

conventional

σ 2p has large ener

$$\text{Bond order} = \frac{6-2}{2} = 2$$

It is obvious that the two O–atoms are bonded through a double bond. The two unpaired electrons reside in the degenerate antibonding orbitals $\pi^*{}_{2p_y}$ and $\pi^*{}_{2p_x}$, hence it is paramagnetic in nature. So we conclude that the molecule should be very stable, as it is. It possesses bond energy of 498 kJmol^{-1} with bond length 1.21Å

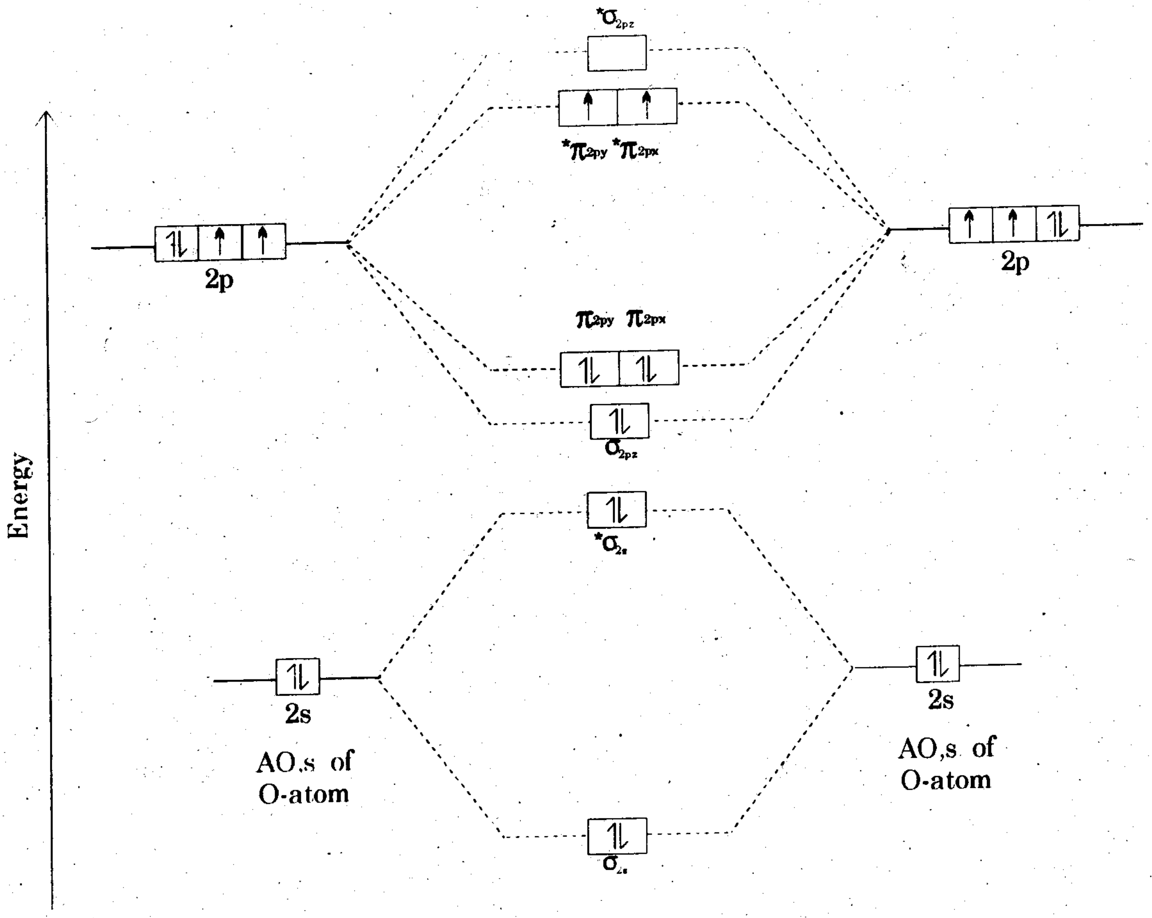


Fig. 2.36. Molecular orbital diagram of O_2 molecule

8. Fluorine Molecule, F_2

Each F–atom has the $1s^2 2s^2 2p^5$ configuration. The two participating F–atoms contribute a total of 14 Valence electrons and there are eight molecular orbitals towards F_2 molecule formed from two F–atoms having four atomic orbitals each. The electronic configuration of F_2 molecule is

$$F_2 = KK\,(\sigma 2s)^2\,(\sigma^* 2s)^2\,(\sigma 2p_x)^2\,(\pi 2p_y)^2\,(\pi 2p_x)^2\,(\pi^* 2p_y)^2\,(\pi^* 2p_x)^2$$

$$\text{Bond order} = \frac{6-4}{2} = 1$$

It is obvious that two F–atoms are bonded through a single bond. The F–F bond distance is longer (1.43Å) than the bond distance for larger O_2 (1.21Å) and N_2 (1.09Å) molecules. The bond energy of F_2 molecule is quite low (159 kJmol^{-1}). It is diamagnetic in nature.

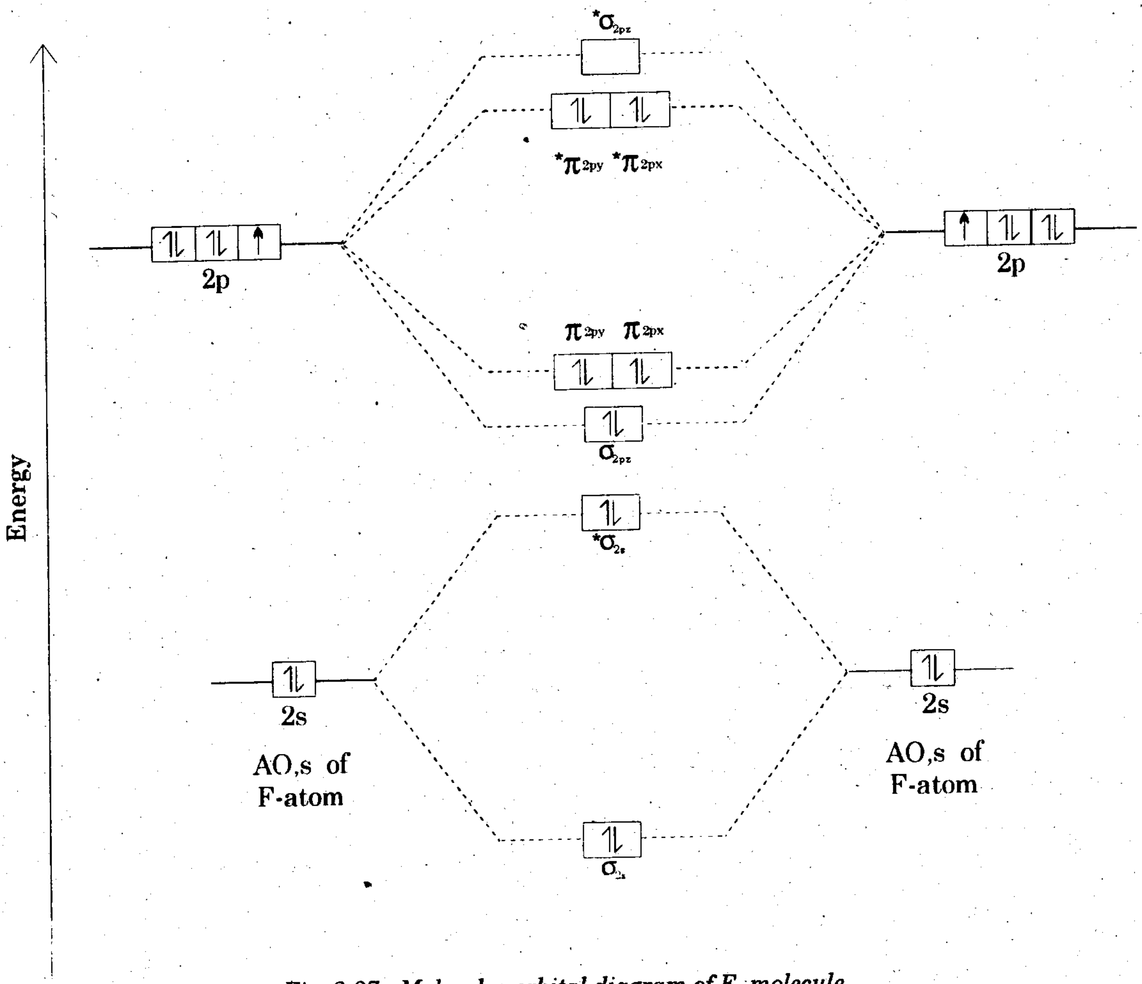


Fig. 2.37. Molecular orbital diagram of F_2 molecule

Applications of MOT for Heteronuclear Diatomic Molecules

In case of heteronuclear diatomic molecules, the corresponding atomic orbitals have different energies due to the different number of protons in the nuclei of atoms. As a result, molecular orbital diagrams such as figures 2.34 and 2.36 are inappropriate for heteronuclear diatomic molecules. However, if the two atoms are similar (as in CO, NO or CN molecules), we can simply modify the diagram by skewing it slightly. The atomic orbitals of the more electronegative element are lower in energy than the corresponding orbitals of the less electronegative element.

1. Carbon Monoxide Molecule, CO

The electronic configurations of participating C and O atoms are:

$C = 1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p_z$

$O = 1s^2\ 2s^2\ 2p^2_x\ 2p^1_y\ 2p^1_z$

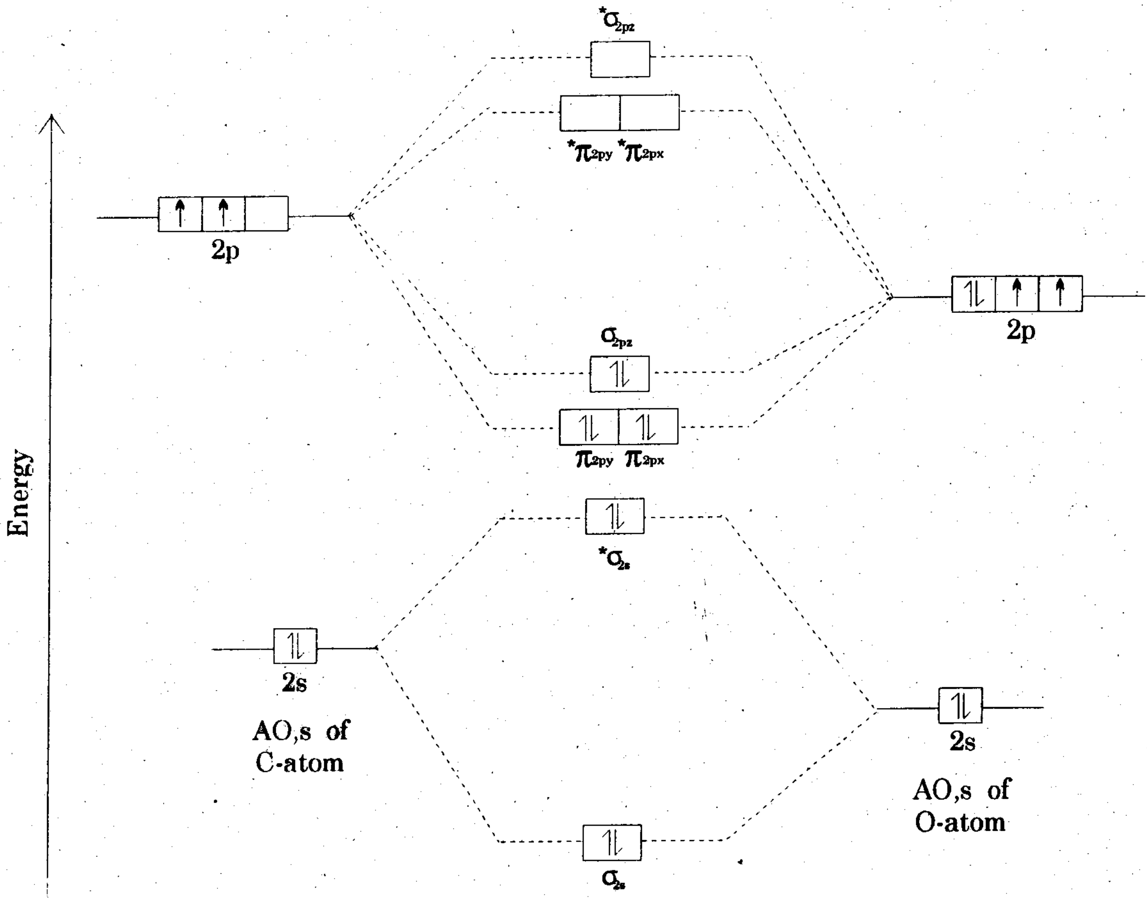


Fig. 2.38. Molecular orbital diagram of CO molecule

The total number of valence electron is 10 and the electronic configuration of CO molecule can be written as

$$CO = KK\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\pi 2p_y)^2\,(\pi 2p_x)^2\,(\pi 2p_z)^2$$

$$\text{Bond order} = \frac{6-0}{2} = 3$$

This shows that carbon and oxygen atom in CO are bonded to each other by a triple bond. There is no unpaired electron in CO molecule and hence it is diamagnetic.

2. Boron Oxide Molecule, BO

The electronic configuration of participating B and O atoms are:

$B = 1s^2\,2s^2\,2p^1_x$

$O = 1s^2\,2s^2\,2p^2_x\,2p^1_y\,2p^1_z$

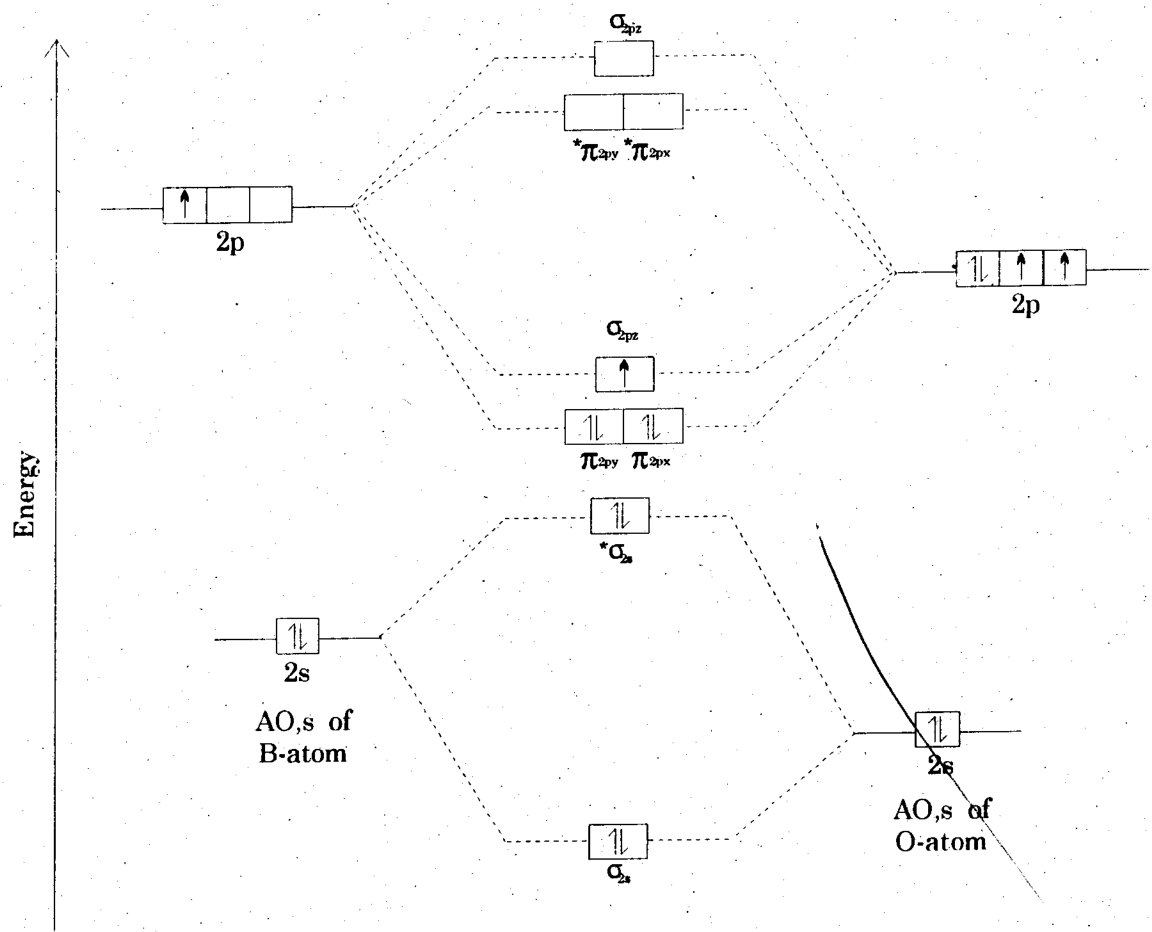


Fig. 2.39. Molecular orbital diagram of BO molecule

The total number of valence electrons is 9 and the electronic configuration of BO molecule can be written as

$$BO = KK\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\pi_{2p_y})^2\,(\pi_{2p_x})^2\,(\sigma_{2p_z})^1$$

$$\text{Bond order} = \frac{5-0}{2} = 2.5$$

This shows that boron and oxygen atom in BO are bonded to each other by a double and a half bond and the BO molecule is paramagnetic due to unpaired electron.

3. Hydrogen Fluoride Molecule, HF

The hydrogen fluoride molecule contains a very polar bond because the electronegativity difference between hydrogen (EN = 2.1) and fluorine (EN = 4.0) is very large (ΔEN = 1.9). The MO diagram of HF is shown in Fig. 2.40.

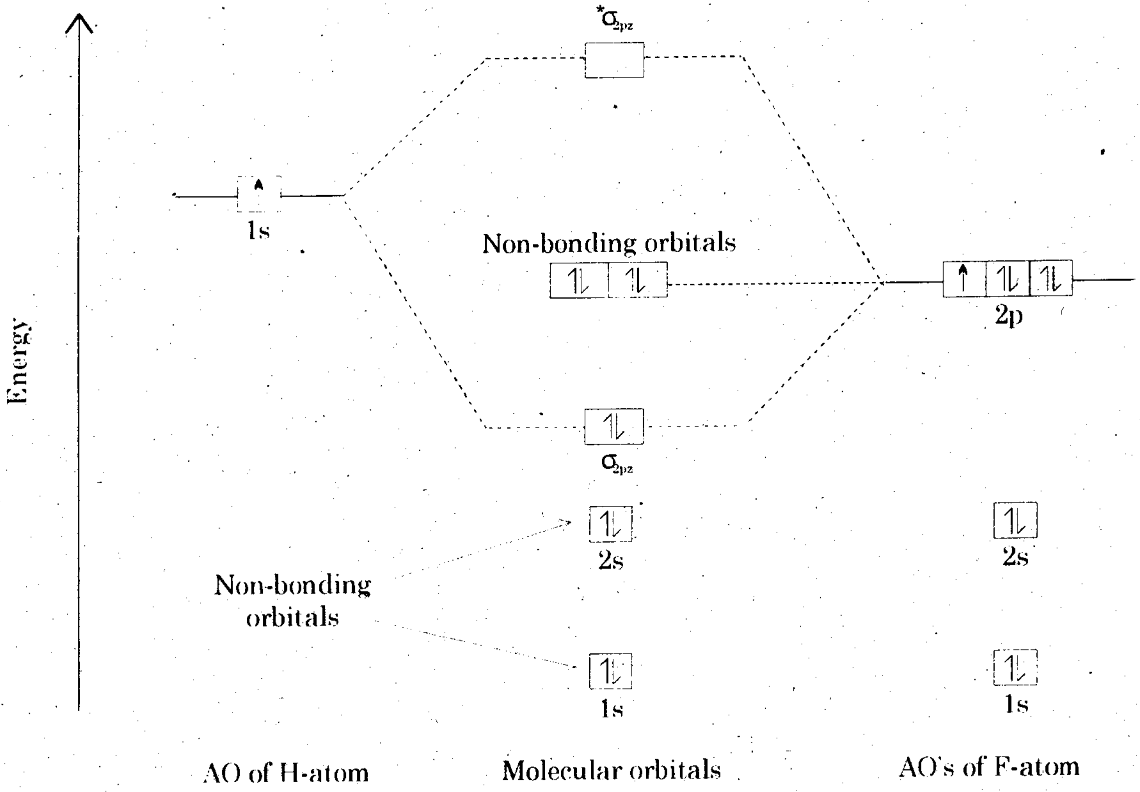


Fig. 2.40. Molecular orbital diagram of HF molecule

The bond in HF involves the 1*s* electron of hydrogen and an unpaired electron from a fluorine 2*p* orbital. Figure, 2.43 shows the overlap of the 1s orbital of hydrogen with a 2*p* orbital of fluorine to form σ_{sp} and σ^*_{sp} molecular orbitals. Since the remaining two fluorine 2*p* orbitals have no net overlap with hydrogen orbitals, they are called *non-bonding orbitals*. The same is true of the fluorine 2*s* and 1*s* orbitals. These nonbonding orbitals retain the characteristics of the fluorine atomic orbitals from which they are formed.

In general, the energy difference between the combining atomic orbitals reflects the difference in electronegativity between the two atoms. The greater this energy difference is the more polar is the bond joining the atoms and greater is the ionic character.

Applications of MOT for Polyatomic Molecules

In this section we illustrate the application of MO theory only to a couple of simple polyatomic molecules, $BeCl_2$ and BCl_3, assuming them to contain two and three single bonds respectively. The molecule $BeCl_2$ is linear, so the beryllium atom has two suitable atomic orbitals (2*s* and $2p_z$), and each chlorine atom has one ($3p_z$). We may represent the bonding and antibonding orbitals pictorially by figure 2.41, as shown below, in which we have omitted the $2p_x$ and $2p_y$ orbitals of beryllium atom and $3p_x$ and $3p_y$ orbitals of chlorine atoms. With two molecular bonding orbitals filled and no electron in antibonding orbitals, the Be— Cl bond order is unity and the molecule is diamagnetic in nature.

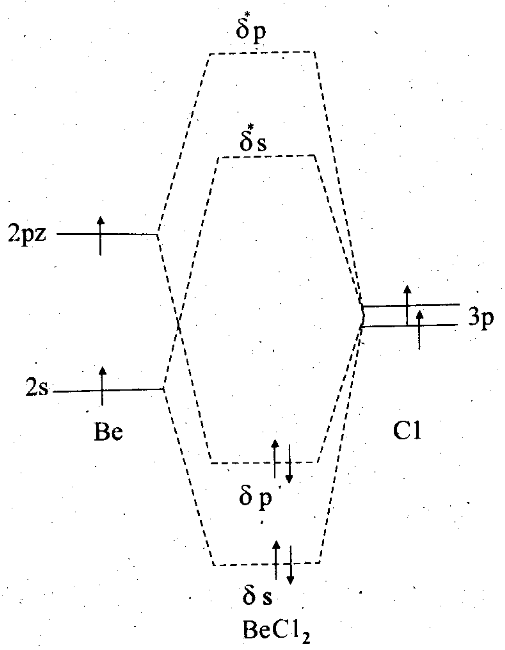


Fig. 2.41. Molecular orbital energy levels for $BeCl_2$

For the planar molecule BCl_3 we choose the z-axis as the axis of highest symmetry, i.e. the one through the boron atom and perpendicular to the plane containing the chlorine atoms. We now have four atoms and six suitable atomic orbitals (2*s*, $2p_x$ and $2p_y$ for the boron atom and 3*p* orbital for each chlorine atom). There are three bonding molecular orbitals (σ_s, σ_{px}, and σ_{py}) and three antibonding molecular orbitals (σ^*_s, σ^*_{px}, and σ^*_{py}). The formation of these orbitals is represented pictorially in figure 2.42. Thus for polyatomic molecules involving two different elements the quantitative aspects of MO theory become more complicated than for homonuclear diatomic molecules. With three molecular bonding orbitals filled and no electron in antibonding orbitals, the B— Cl bond order is unity and molecule is diamagnetic in nature.

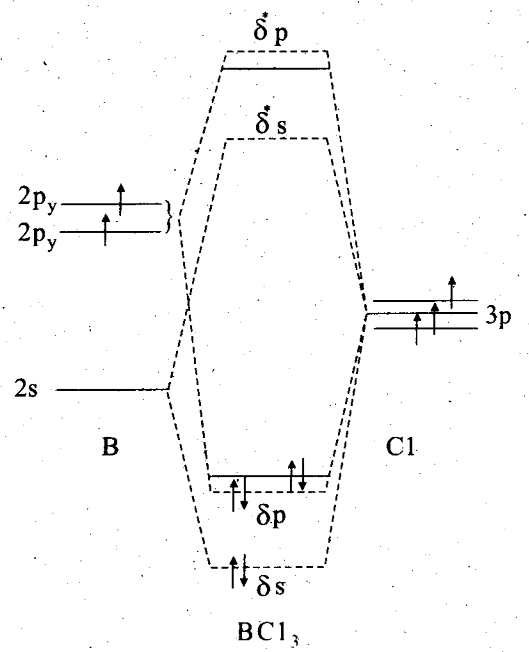


Fig. 2.42. Molecular orbital energy levels for BCl_3

2.10 COMPARISON OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

Similarities

The common features of the two theories are:

1. Both the theories explain the formation of covalent bonds.
2. In both the theories, a covalent bond is formed by the overlapping of atomic orbitals have appropriate symmetry about the molecular axis.
3. According to both, the electronic charge resides in the region between the atomic nuclei.
4. Both the methods lead to the formation of two types of bonds viz., σ and π bonds.
5. In both the methods, the atomic and molecular orbitals are filled up according to same principles.
6. Variation principle is utilized in both the methods.

Differences	
VBT	**MOT**
1. According to VB approach only valence electrons are involved in bond formation.	1. According to MO approach all the electrons of interacting atoms are involved in bond formation.
2. In VBT, the two concerned atoms do not lose their individual identity.	2. In MOT, the two atoms lose their individual identity.
3. It does not offer a simple method of excited states in molecules.	3. It offers a simple and more convenient description of excited states of molecules.
4. Resonance plays an important role in VBT.	4. Resonance plays no role in MOT.
5. It does not explain the paramagnetic behaviour of molecules like O_2 molecule.	5. It explains the paramagnetic behaviour of molecules like O_2 molecule.
6. It does not explain the non–existence of He_2 molecule.	6. It explains the non–existence of He_2 molecule.
7. It does not explain the formation of bonds between C_2, B_2 and Li_2 molecules.	7. It explains the formation of bonds between C_2, B_2 and Li_2 molecules.
8. It does not give better description of electron cloud distributions, bond energies and magnetic properties.	8. It gives better description of electron cloud distributions, bond energies and magnetic properties.
9. It does not give idea about the fractional bond order.	9. It gives idea about bond order by which we can determine that whether the bond is single, double, triple or fractional.
10. This theory rejects the ionic structure like A^-B^+ and A^+B^-.	10. This theory accepts the ionic structures like A^-B^+ and A^+B^-.
11. According to VBT, an electron moves in the field of one nucleus only.	11. According to this theory, an electron moves in the fields of more than one nucleus.

2.11. HYDROGEN BONDING

In order to understand the concept of hydrogen bond let us consider a molecule, say HA in which H–atom is linked with a strongly electronegative atom A (A may be N, O or F) by a normal covalent bond. The electron pair being shared between H and the strongly electronegative atom A will evidently lie far away from H–atom and thus partial positive and negative charges will be developed on H and A atoms respectively. Consequently HA molecule will behave as a dipole represented as $H^{\delta+}–A^{\delta-}$ with A as its negative end and H as its positive end. If another molecule H–B which also forms a dipole $H^{\delta+}–B^{\delta-}$ (B is a strongly electronegative atom like N, F or O) is brought near H–A dipole, these two dipoles will be linked together by a special type of bond which is called *hydrogen bond* and is represented by dotted lines. Thus the existence of hydrogen bond between A–H and B–H molecules can be shown as:

$$A^{\delta-} — H^{\delta+} \cdots\cdots\cdots B^{\delta-} — H^{\delta+}$$

H–atom acts as a bridge between electronegative atoms, A and B. Thus hydrogen bond can be defined as follows:

The attractive force that binds a hydrogen atom, which is already covalently attached with a strongly electronegative atom of a molecule with another electronegative atom of some other molecule is known as *hydrogen* bond. The atoms A and B may be same or different, i.e., the molecules AH and BH may be the same or different.

Hydrogen bond is electrostatic in nature and is a very weak bond with bond energies in the range of 2–10 kcal/mole. It is stronger than van der Waals forces but weaker than ionic or covalent bonds.

Necessary Conditions for Hydrogen Bonding

A hydrogen bonding is formed when

(i) a hydrogen atom is covalently bonded to an electronegative atom like F, O or N, so that due to the polarization of the bonded electron pair, it acquires a slightly positive charge, and

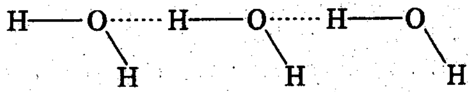
(ii) a lone pair of non–bonding electrons is available on one of the atoms so that it can be donated to the positive hydrogen atom. Again such atoms are F, O or N etc.

It is found that of all the electronegative donor atoms, only F, O and N–atoms enter into stable hydrogen bond formation. Other elements like Cl or S give extremely weak hydrogen bonds which have no significance. Their incapability is due to their large atomic size.

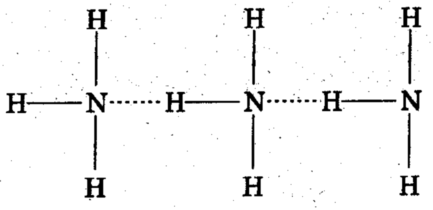
Types of Hydrogen Bonding

Hydrogen bonds have been classified into two major classes:

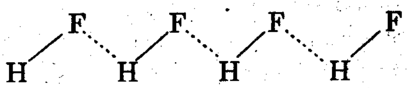
1. **Inter–molecular Hydrogen Bonding.** This type of H–bond occurs between two or more molecules of the same or different compounds. Thus NH_3, H_2O, HF and CH_3COOH are associated by intermolecular H–bond.



(H_2O)

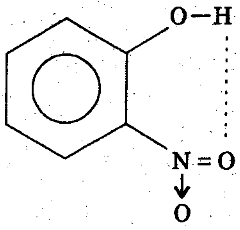


(NH_3)

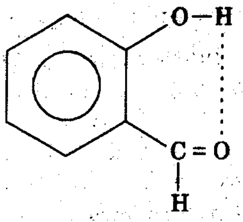


(HF)

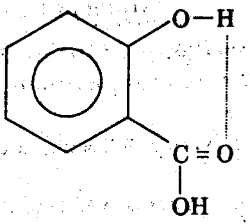
2. **Intra–molecular Hydrogen Bonding.** This type of H–bond is formed between a H–atom and an electronegative atom present in the same molecule. In intramolecular H–bonding the H–atom is bonded to two atoms of the same molecule. Examples of molecules showing intramolecular hydrogen bonding are provided by O–nitrophenol, O–hydroxy benzaldehyde and O–hydroxy benzoic acid.



O-nitrophenol



O-hydroxy benzaldehyde



O-hydroxy benzoic acid

Nature Of Hydrogen Bonding

A hydrogen bond is formed when a hydrogen atom is bonded to two or more atoms. This implies that the H–bonding is not an ordinary covalent bond as the hydrogen atom does not have more than one low energy orbital (1s) for use in covalent bond formation. The next orbital (2s) is at a very high energy level (962 $kJmol^{-1}$) and is not effective for bonding purposes. In order to understand the nature of H–bond, the following theories have been suggested.

1. **Electrostatic Approach.** According to this theory hydrogen bond is basically electrostatic in nature,

$$A^{\delta-}—H^{\delta+} \ldots\ldots\ldots B^{\delta-}—H^{\delta+}$$

As a result of covalent bond formation between H and strongly electronegative atom A, a strong dipole is produced with A as the negative end. A second electronegative atom Y, attached to another atom or molecule will also form the negative end of a dipole. The two dipoles approach each other because of the electrostatic attraction between the positive dipole on A–H and negative end of dipole on B–H. The closer Y approaches H, the stronger is this electrostatic link between them. This view is supported by the fact that a hydrogen bond is formed most readily if A and B have high electronegativity. The ability of A–H to form hydrogen bond increases from C–H through N–H and O–H to F–H.

2. Valence Bond Approach. According to valence bond theory hydrogen bond is not electrostatic in nature, but it involves the following resonating structures:

$$\underset{\text{(I)}}{A^{\delta-}\text{—}H^{\delta+}\ \ldots\ldots\ B^{\delta-}} \leftrightarrow \underset{\text{(II)}}{A\text{—}H:B} \leftrightarrow \underset{\text{(III)}}{A\text{—}H\leftarrow B}$$

Structure (III) shows that hydrogen atom is covalently linked with A and B. Thus in this structure H-atom is bicovalently linked. Structure (I) results from dipole interaction while structure (II) arises due to induced dipole interaction. Structure (III) does not make contribution to the overall bond energy of hydrogen bond while structures (I) and (II) make major contributions to the overall energy of bond. There are cases in which all the three forms make equal contributions. For example, HF_2^- ion.

$$\underset{\text{(I)}}{F^-\text{—}H^+\text{—}F^-} \leftrightarrow \underset{\text{(II)}}{F^-\text{—}H\text{—}F} \leftrightarrow \underset{\text{(III)}}{F\text{—}H\text{—}F^-}$$

3. Molecular Orbital Approach. Pimental (1951) has given a molecular orbital description of the hydrogen bonding using HF^-_2 ion as the model. From three

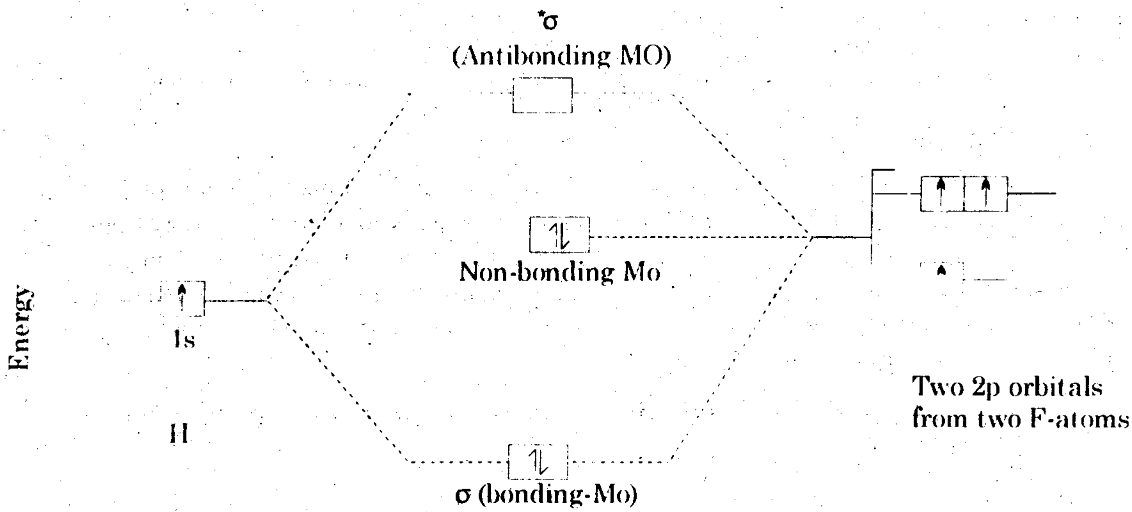


Fig. 2.43. Molecular orbital diagram for HF_2^- ion

atomic orbitals — 1s of hydrogen and 2p orbitals of two fluorines directed along the bond axis–three molecular orbitals (one bonding, one nonbonding and one antibonding) are constructed as shown in Fig. 2.43.

The two electron pairs involved in bonding occupy the lowest energy level (bonding MO) and the next lowest energy level (nonbonding MO). The molecular orbital treatment requires that the atoms A and B involved in hydrogen bonding have equal or nearly equal electronegativity.

Properties of Hydrogen Bond

Following are the important properties of hydrogen bond:

1. A hydrogen bond is a bond of hydrogen between two electronegative atoms only. It never involves more than two atoms (excluding H–atom).
2. Bond energy of a H–bond is in the range of 2–10 kcal/mole while that of a normal covalent bond is in the range of 50–100 kcal/mole. Thus a H–bond is much weaker and longer than a covalent bond.
3. H–bond has more energy than the van der Waals forces (1kcal/mole).
4. The formation of a H–bond does not involve any sharing of electron pairs. It is, therefore, quite different from a covalent bond.
5. Only N, F and O which have small size and high electronegativity, are capable of forming H–bonds.
6. H–bonding results in the formation of long chains or clusters of a large number of associated molecules like as many tiny magnets.
7. Like a covalent bond, H–bond has a preferred bonding direction.

Importance of Hydrogen Bonding

Apart from providing explanation for a number of abnormal properties of certain compounds containing H–bonding, it is also useful in explaining physiological and geological processes occurring around us. For example:

1. Water is a liquid at room temperature but H_2S is a gas because of the presence of H–bonding in water and absence of H–bonding in H_2S. Without H–bonding, H_2O would have existed as a gas like H_2S. In that case no life would have been possible without liquid water.
2. Due to directional character of H–bonding it helps in studying and establishing the structure of many compounds like ice (tetrahedral), solid hydrogen fluoride (zig zag), boric acid (sheet structure) etc.
3. H–bonding gives a satisfactory explanation for the mechanism of polymerization and hence of the formation of bigger aggregates of organic as well as inorganic molecules.

4. Many geological products such as organic compounds contained in petroleum, coal products and complex hydrates of minerals are formed and stabilized by means of H–bonding.
5. The adhesive action of glue, honey, dyes and paints is also due to the presence of H–bonding in them.
6. H–bond is of vital importance for our clothing. For example, the rigidity and tensile strength of cotton, silk or synthetic fibres is due to H–bonding in them.
7. Molecules of most of our food materials like sugars, carbohydrates etc. also consist of H–bonding.
8. H–bonding plays a significant role in making wood fibres more rigid so that they may be used to meet requirements of housing, furniture etc.
9. H–bonding is responsible for unexpected high solubilities of covalent compounds containing oxygen and nitrogen in solvents having one or more H–atoms.
10. Water shows maximum density at 4°C due to H–bonding. On further cooling to 0°C its density decreases due to expansion in volume. Ice floats on water surface. This has a great advantage as marine animals and fish etc. remain unaffected by ice formation.
11. H–bonding also exists in molecules of living systems like proteins, DNA etc.

2.12 METALLIC BONDING

The peculiar type of bonding which holds the metal atoms together in a metal crystal is called *metallic bonding*. The metal atoms are held together as a result of the attraction between the positive metal ions and surrounding freely mobile electrons.

Since all the atoms in a metal crystal are identical, these cannot be linked by ionic bonds as cations and anions are bonded together in ionic crystals. Moreover, ionic bond cannot be formed between the metal atoms, since the metal atoms have the same electronegativity. Also each atom in a metal crystal cannot be bonded to other 8 or 12 atoms (X–rays study of metal crystals has shown that each metal atom is surrounded by 8 or 12 other metal atoms) by the covalent bond (sharing of electrons), since in metals the number of valence electrons is insufficient for the formation of covalent bonds with all its 8 or 12 neighbouring metal atoms. For example, Na atom which has only one valence electron cannot be expected to form covalent bonds with 8 nearest neighbouring Na–atoms in its crystal.

Obviously, the metal atoms in a metal crystal are bonded together by a bond which is neither an ionic and nor a covalent bond, but it is a special type of bond which is called *metallic bond*. This bond binds the metal atoms together in a metal crystal and is of its own type.

Characteristics of Metals

Metals are characterized by a few physical properties. It should be kept in mind that though these are the properties of the metals in general, exception to almost all the properties exist. Examples can be found for the metals not obeying some of these properties, and of non–metals obeying them one by one in isolation.

(i) Metals have high electric conductivity which decreases with temperature.

(ii) Metals are good conductors of heat.

(iii) Metals have high melting and boiling points.

(iv) Metals possess a peculiar shine on their surface, called the metallic lustre and can take good polish.

(v) Metals have high density and are hard substances.

(vi) Metals are malleable and ductile, i.e., they can be hammered into sheets and can be drawn into thin wires.

(vii) Metals can withstand high stress – they have high elasticity.

(viii) Metals are opaque to light.

(ix) Metals crystallize in systems having high coordination number of 8, 12 or 14.

(x) Metals form solid solutions with each other, called alloys. These solutions also have metallic properties.

(xi) Metals tend to form non–stoichiometric compounds in which the other atoms (generally, hydrogen, boron, nitrogen) are trapped in the interstices of the metallic structure.

(xii) Metals are generally electropositive elements.

Theories of Metallic Bonding

Metals are good electrical and thermal conductors, they are opaque and have high refracting power, they have high melting and boiling points, and they crystallize with high coordination numbers. Such properties of metals cannot be explained on the basis of normal ionic or covalent bonding.

How the metal atoms in a metal crystal are bonded together has been answered by the following theories:

1. Electron Gas Theory

The first theory of metallic bonding, called electron pool or electron gas theory was proposed by Drude (1900) and extended by Lorentz (1923). According to Drude–Lorentz theory, each atom in a metal crystal loses all of its valence electrons which form a pool or gas. The resulting positively charged metal ions are believed to be held together by electron pool or gas. Positively charged metal ions do not float randomly in the sea of electrons. The ions occupy definite positions at measurable distances from each other in the crystal lattice. Since the valence electrons are not attached to any individual ions or pair of ions but belong to the crystal as a whole, they are free to move about from one part of the crystal to the other, hence the theory is also called *free electron theory*. The force that binds a metal cation to a number of electrons within its sphere of influence is known as *metallic bond*.

Though, this theory is able to explain most of the characteristic properties of the metals particularly metallic lustre, optical properties, malleability, ductility and high electrical and thermal conductivity, it fails to explain the following facts:

(i) Specific heats of metals.
(ii) The decrease in electrical and thermal conductivity with an increase in temperature.
(iii) Paramagnetic behaviour of metals.

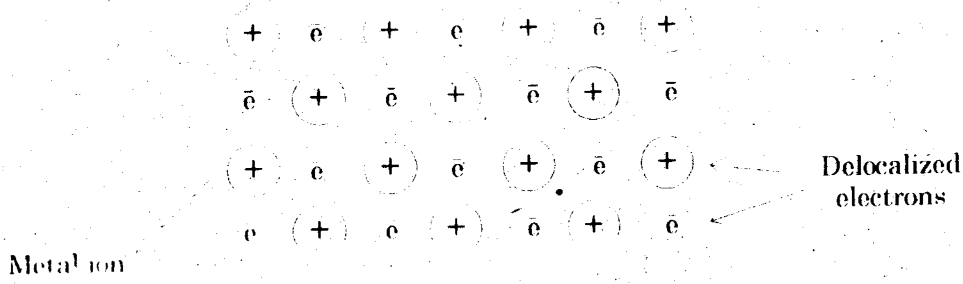


Fig. 2.44. The electron sea model of metallic bonding

2. Valence Bond Approach

The valence bond theory is due to Pauling. According to this theory the metallic bond is treated essentially as covalent in character. However, the number of valence electron is inadequate to form covalent bonds between each atom and its neighbors. It is therefore, assumed that the covalent bonds are not localized but are highly delocalized in the metal structure. The bonds resonate among alternate positions between each atom and its neighbors as shown below in lithium.

$$\begin{array}{c} \text{Li}-\text{Li} \\ \\ \text{Li}-\text{Li} \end{array} \leftrightarrow \begin{array}{cc} \text{Li} & \text{Li} \\ | & | \\ \text{Li} & \text{Li} \end{array}$$

The stabilization of the structure through this type of resonance would be expected to be relatively small, hence it is assumed that resonance involves ions, e.g.,

$$\begin{array}{c} \text{Li}-\text{Li} \\ \\ \text{Li}-\text{Li} \end{array} \leftrightarrow \begin{array}{cc} \text{Li}- & \text{Li}^- \\ & | \\ \text{Li}^+ & \text{Li} \end{array} \leftrightarrow \begin{array}{cc} \text{Li} & \text{Li}^+ \\ | & \\ \text{Li}^- & -\text{Li} \end{array}$$

For effective stabilization the metal atoms must possess vacant orbitals of low energy. Larger the number of such vacant orbitals greater will be the number of resonating structures and more effective will be the stabilization. Thus the contribution of ionic structures considerably strengthens the bond.

The characteristic properties of metals can be explained on this concept. Thus, the electrical conductivity of metals can be explained in presence of an electric field due to rearrangement of positive charges towards cathode and negative charges moving towards anode.

3. Molecular Orbital Approach (The Band Theory)

The molecular orbital theory, also known as the band theory, was proposed by Block and provides a more detailed account of the bonding in metals. It is assumed that electrons in the completely filled levels are essentially localized while atomic orbitals containing the valence electrons interact or overlap to form a set of delocalized orbitals (molecular orbital) extending over the entire crystal lattice. Such a combination of atomic orbitals produces a large number of closely spaced energy states known as *a band of energy*. Let us consider the formation of these bands in the case of lithium ($1s^2\,2s^1$). The molecular orbitals formed from 1s atomic orbitals are completely filled and hence do not contribute to bonding. 2s valence electrons of the individual atoms have the same energy. When two atoms are brought together, two molecular orbitals result. One of the molecular orbitals will be of higher energy and the other of lower energy. If a third lithium atom is introduced, three molecular orbitals will be possible; and for N atoms, N molecular orbitals can be formed. The building up of such molecular orbitals may be represented by Fig. 2.48. The energy difference between molecular orbitals decreases as

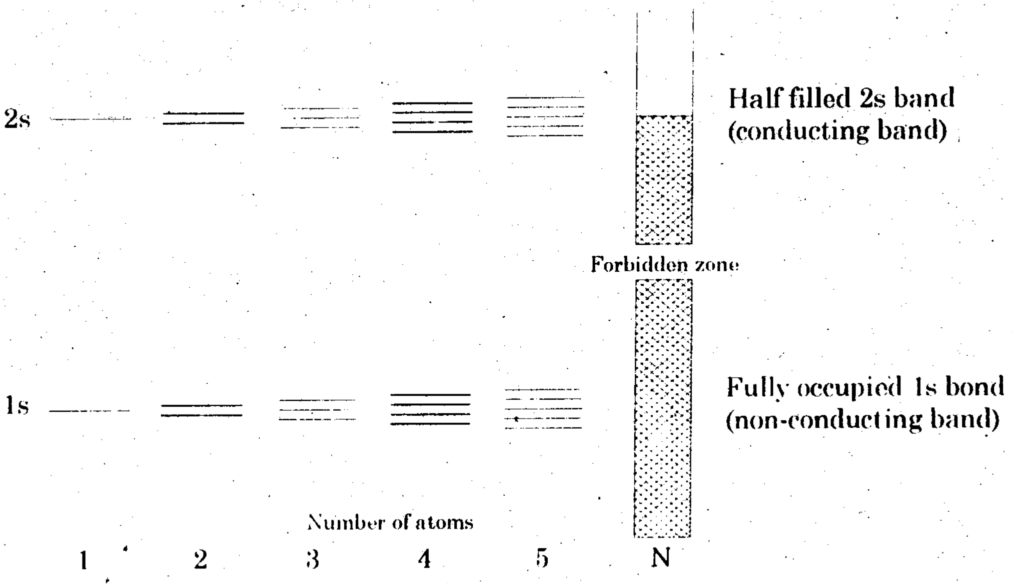


Fig. 2.45. Energy bands in lithium

the number of over–lapping atomic orbitals increases. For a large number of atoms the energy difference being so small that it can be regarded as continuous forming an energy band. In lithium, there are two energy bands, one of these bands originating from the 1s atomic orbitals is fully occupied; the other originating from the 2s atomic orbitals is only half occupied. The fully occupied band is known as *non-conducting* while the half occupied band is called the *conducting band.*

The energy gap between the two bands is so large that it effectively prevents the promotion of electrons from the lower to the higher band. Such energy gaps are called *forbidden zones*.

The energy bands belong to crystal as a whole and represent complete delocalization. They result from the interactions of a large number of atomic orbitals of right energy and right symmetry. Electrical conductivity in metals is due to the movement of electrons from lower occupied to higher accessible unoccupied orbitals under the influence of an applied field. In *nonmetals* all the accessible energy states are occupied so they are poor conductors of electricity. In *semiconductors* the gap between the occupied and the unoccupied orbitals is not very large and the conduction of electricity is negligible at lower temperatures and appreciable at higher temperatures. At low temperature, the electrons in the occupied orbitals do not have sufficient energy and unable to move to the higher energy states. As the temperature is raised, the electrons acquire sufficient energy and the transition to the higher unoccupied state is possible.

Questions

Q.1 What do you understand by the term chemical bond? Why do the atoms combine with each other? Explain.

Q.2 What are the various types of chemical bonds? Explain the formation of ionic, covalent and co–ordinate bonds with suitable examples.

Q.3 *(a)* Explain the phenomenon of variable covalency and electrovalency. Why do some of the elements show variable valences?

(b) Write some characteristic features of ionic compounds.

Q.4 *(a)* What types of elements would form ionic and covalent bonds. What conditions are necessary for such bond formations?

(b) Explain the general characteristics of covalent compounds.

Q.5 *(a)* What is co–ordinate covalent bond? Explain it with suitable examples.

(b) Compare the properties of ionic, covalent and co–ordinate compounds.

Q.6 *(a)* Describe valence bond theory of covalent bond for hydrogen molecule.

(b) How does VBT explain the structures of O_2, N_2, Cl_2 and NH_3 molecules?

Q.7 *(a)* Discuss the principles involved in VBT. How does this theory explain the formation of a chemical bond?

(b) Write down some limitations of VBT.

Q.8 Compare sigma bond with Pi bond. Explain why a sigma bond is stronger than a Pi bond.

Q.9 *(a)* What do you understand by orbital hybridization?

(b) Describe different types of hybrid orbitals that can be formed by an atom with *s*, *p* and *d*–orbitals in its valence shell.

Q.10 *(a)* Give the rules of hybridization.

(b) Discuss sp, sp^2, sp^3, dsp^3 and d^2sp^3 types of hybridization, give one example of each.

Q.11 *(a)* Indicate the different states of hybridization and deduce the geometry of following species:

$BeCl_2$, BF_3, NH_3, SF_6, IF_5, H_2O and CCl_4.

(b) Which of the following molecules is planar and why; BF_3, PCl_5 and NH_3?

Q.12 *(a)* Discuss the need of hybridization in the valence bond description of molecules.

(b) What are hybrid orbitals? Discuss their characteristics.

Q.13 *(a)* What do you understand by the term resonance? Why it is introduced?

(b) What do you understand by resonating structures? Give necessary conditions for writing these structures.

Q.14 *(a)* Explain the terms resonance hybrid and resonance energy.

(b) Write the resonating structures of CO_2, CO_2 and NO molecules and justify your answer on the basis of their physical properties.

(c) The calculated heat of formation for C=O bond is 732.3 $kJmol^{-1}$ whereas the observed heat of formation is 1071.3 $kJmol^{-1}$. Calculate the resonance energy for CO molecule.

(Ans: 339.0 $kJmol^{-1}$).

Q.15 *(a)* State in your own words the basic idea of VSEPR theory.

(b) Distinguish between "lone pairs" and "bonding pairs". Which has the greater spatial requirement?

(c) Predict the shape of the following molecules and ions on valence shell electron pair repulsion theory:

NH_4^+, PCl_3, $SnCl_4$, H_2O and IF_5

Q.16 *(a)* Discuss the principles underlying the valence shell electron pair repulsion theory. How does this theory explain the geometry of different species?

(b) The central atom in the molecules of CH_4, NH_3 and H_2O involves sp^3 hybridization in bonding. However, the bond angles in these molecules are 109.5°, 107° and 104.5° respectively. Comment.

Q.17 *(a)* Discuss the basic postulates of VSEPR theory.

(b) Predict the shapes of the following molecules on VSEPR concept:

$BeCl_2$, SF_6, XeF_2, XeF_4, PCl_5, $SnCl_2$ and BrF_3

(c) What are the limitations of VSEPR theory?

Q.18 *(a)* Discuss molecular orbital theory for the formation of H_2–molecule.

(b) Draw and explain the molecular structures of the following molecules:

H_2, O_2, N_2 and HF.

Q.19 *(a)* Write a note on molecular orbital theory.

(b) What is bond order? Briefly discuss its significance.

(c) Draw the molecular orbital energy level diagram of B_2, Li_2, N_2, N_2^+, O_2^+, O_2^-, O_2^{-2} and F_2. Calculate the bond order of each species and determine its magnetic behaviour.

Q.20 (a) How does molecular orbital theory differ from valence bond theory?

(b) Why is N_2 molecule diamagnetic in nature while O_2 is paramagnetic?

(c) How does the MOT explain the non–existence of He_2 molecule?

Q.21 (a) What do you understand by linear combination of atomic orbitals (LCAO)?

(b) Discuss the structure of CO, NO, BO, NO^+ and CN molecules on the basis of MOT.

(c) How does MOT resemble with VBT.

Q.22 (a) Explain the following with suitable examples.

(i) Bond order

(ii) Bonding molecular orbitals

(iii) Anti bonding molecular orbitals

(iv) Non–bonding molecular orbitals

(b) How does MOT explain the paramagnetic behaviour of O_2 molecule?

(c) What is the bond order of H_2^+ ion?

(d) Explain the relative stability of NO and NO^+ species.

Q.23 What is the nature of hydrogen bonding? Explain hydrogen bonding in various compounds and discuss its importance.

Q.24 (a) What is hydrogen bonding? What is the effect of H–bonding on the physical properties of the compounds in which this bond is present?

(b) Briefly discuss the significance of H–bonding.

Q.25 (a) Explain the difference between intermolecular and intramolecular H–bonding.

(b) H_2O is a liquid while H_2S is a gas, comment.

(c) O and Cl have the same electronegativity but Cl does not form H–bonding.

(d) O–nitrophenol has low m.p and b.p as compared to m.p and b.p. nitrophenol.

Q.26 (a) What is metallic bond? Why do metals not form ionic or covalent bonds?

(b) Name any four characteristics of metals and explain them on the basis of metallic bond.

Q.24 What is metallic bond? Name various theories which were put forward to explain the nature of metallic bond and explain band theory.

Q.28 Write short notes on the following.

- *(i)* H–bonding
- *(ii)* Metallic bonding
- *(iii)* LCAO approximation

Q.29 Justify/comment on the following statements.

- *(a)* H_2O boils at much higher temperature than H_2S.
- *(b)* Ionic compounds have high melting points than covalent compounds.
- *(c)* Ionic compounds are good conductor of electricity and heat.
- *(d)* NaCl is soluble in benzene.
- *(e)* H_2 is a non–polar molecule while HF is a polar molecule.
- *(f)* A sigma bond is stronger than a pi bond.
- *(g)* BF_3 has tetrahedral geometry.
- *(h)* CO_2 molecule has two types of bond lengths.
- *(i)* $PbCl_2$ has a linear geometry.
- *(j)* IF_5 has trigonal bipyramidal shape.
- *(k)* O_2 molecule is diamagnetic in nature.
- *(l)* The bond order of CO molecule is 2.
- *(m)* The bond order of H_2^+ ion is 1.
- *(n)* Ne_2 molecule exists in nature.
- *(o)* The geometry of SO_2 molecule is linear.
- *(p)* Metals are good conductor of electricity.
- *(q)* Iodine, sulphur and chlorine cannot form hydrogen bonds.
- *(r)* H_2O is a liquid while H_2S is a gas.
- *(s)* Ice floats on water surface.
- *(t)* The bond order of N_2 molecule is two.
- *(u)* CH_3OH and NH_3 are soluble in water.
- *(v)* Glycerol is more viscous than ethanol.
- *(w)* Sodium is a good conductor while silicon is a semi–conductor.

Chapter Three

ACID-BASE EQUILIBRIA

3.1 EARLY CONCEPTS

Different criteria for characterizing acids and bases used in the beginning were mainly experimental. Thus, Boyle in the sixteenth century, defined acids as substances whose aqueous solutions turned blue litmus red, neutralized bases, reacted with active metals evolving hydrogen, and tasted sour. Bases were similarly defined in 1774 by Rouelle as substances whose aqueous solutions turned red litmus blue, neutralized acids, tasted bitter, and gave soapy touch. The first departure from a strictly experimental definition of an acid came with the advent of Lavoisier's oxygen concept. Lavoisier (1783) proposed that the peculiar properties of an acid could be attributed to the presence of oxygen. The oxygen concept was abandoned when Davy (1811) showed that it was not necessary for an acid to contain oxygen (HCl, H_2S) ~~and further, many bin~~ary oxygen compounds (CaO, K_2O) did not possess acidic properties. Liebig (1838), the chief protagonist of this new concept, defined acids as substances possessing one or more hydrogen atoms replaced by metals.

3.2 ARRHENIUS CONCEPT OF ACIDS AND BASES

According to Arrhenius, an *acid* is any hydrogen-containing compound which yields hydrogen ions (H^+) in aqueous solution and a *base* is any hydrogen-containing compound which gives hydroxyl ions (OH^-) in aqueous solution. This concept is based on the ionic dissociation of substances in water. For example, HCl is an acid because it produces H^+ ions in water but C_2H_4 is not. Similarly, KOH is a base because it gives OH^- ions, whereas C_2H_5OH is not a base.

$$HCl \xrightarrow{H_2O} H^+ + Cl^-$$

$$KOH \xrightarrow{H_2O} K^+ + OH^-$$

The process of neutralization of an acid by a base can be represented as

$$H^+ + OH^- \longrightarrow H_2O$$

Advantages

1. This concept explained the constant heat of neutralization of any strong acid with any strong base as all these reactions involve only the combination of hydrogen and hydroxyl ions.

2. This concept leads to the quantitative determination of an acid or a base strengths from the equilibrium relations such as:

$$CH_3COOH \overset{H_2O}{\rightleftharpoons} CH_3COO^- + H^+$$

$$NH_4OH \overset{H_2O}{\rightleftharpoons} NH_4^+ + OH^-$$

The thermodynamic dissociation constants are given as:

$$K_a = \frac{a_{CH_3COO^-} \cdot a_{H^+}}{a_{CH_3COOH}} \qquad \text{..... 3.1}$$

And

$$K_b = \frac{a_{NH_4^+} \cdot a_{OH^-}}{a_{NH_4OH}} \qquad \text{..... 3.2}$$

3. One of the most significant achievements of Arrhenius concept was its ability to explain the catalytic properties of acids. Arrhenius theory of electrolytic dissociation correlated the catalytic actions of acids with concentration of hydrogen ion.

Limitations

In spite of the successes of Arrhenius definition, several shortcomings of this definition seen became apparent. The definition of acids and bases in terms of their behaviour in aqueous medium, limited the scope of acid-base concepts.

1. According to this concept, HCl is regarded as an acid only when dissolved in water and not in some other solvent such as benzene of when it exists in the gaseous form.
2. It cannot account for the acidic and basic character of the substances in non-aqueous solvents such as liquid ammonia and liquid sulphur dioxide.
3. Further, these concepts were not applicable to reactions in gas phase where no solvent is present.
4. The restriction of the term base to only hydroxyl compounds was another serious limitation of Arrhenius concept. Many substances such as ammonia and pyridine were known to exhibit basic properties although they contain no hydroxyl group.
5. It cannot explain the acidic character of certain salts such as $AlCl_3$ in aqueous solution.
6. The neutralization process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in many other solvents and even in the absence of solvents.

3.3 BRANSTED-LOWRY CONCEPT OF ACIDS AND BASES

In 1923 J.N. Bronsted (Denmark) and L.M. Lowry (England) independently proposed a new definition of acids and bases. They defined an *acid* as a substance which has a tendency to lose one or more protons, and a *base* as a substance which has a tendency to gain one or more protons. In short an acid is a proton-donor and a base is a proton-acceptor. Hence this concept is also known as *proton-donor acceptor system.* An acid qualifying Bronsted-Lowry concept is termed as Bronsted-Lowry acid or simply as a Bronsted acid; similarly a base qualifying Bronsted-Lowry definition is called Bronsted base. Bronsted-Lowry acids and bases are of the types given in Table 3.1.

Table 3.1. Bronsted-Lowry Acids and Bases

Type	**Acids**	**Bases**
Molecular	HCl, HBr, $HClO_4$, H_2SO_4, H_2O, H_2S, etc.	NH_3, H_2O, CH_3NH_2, N_2H_4, etc.
Cationic	H_3O^+, NH_4^+, $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$, etc.	$[Fe(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_5(OH)]^{2+}$, etc.
Anionic	HS^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$, etc.	Cl^-, Br^-, OH^-, CO_3^{2-}, SO_4^{2-}, etc.

Conjugate Acid-Base Pairs

In a typical acid-base reaction

$$HA + B \rightleftharpoons A^- + HB^+$$

HA proton-donor is an acid and B being a proton acceptor is a base. In the reverse reaction HB^+ being a proton donor is an acid and A^- being a proton acceptor is a base. In order to distinguish between the two acids and bases, those on the right-hand side of the equation are referred to as *conjugate acid* and the *conjugate base.* Thus HB^+ is a conjugate acid of the base B and A^- is a conjugate base of the acid HA. HA — A^- and HB^+ — B constitute two conjugate acid-base pairs. The acid and base in each conjugate differ by a proton. For an acid to exhibit acidic properties there must be a proton acceptor (base) present. Some examples of conjugate acid-base pairs are:

Acids$_1$		**Base$_2$**		**Conjugate acid$_2$**		**Conjugate base$_1$**
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
CH_3COOH	+	NH_3	$\rightleftharpoons$	NH_4^+	+	CH_3COO^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

$$HSO_4^- + NH_3 \rightleftharpoons NH_4^+ + SO_4^{2-}$$

Thus, according to Bronsted-Lowry concept *neutralization* is a process of transfer of a proton from an acid to a base. For example:

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

$$NH_4^+ + S^{2-} \rightleftharpoons HS^- + NH_3$$

An acid-base reaction always proceeds in the direction of formation of the weaker acid and the weaker base. Consider the equilibrium reaction

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Where HA is a strong acid; the fact that the equilibrium shifts to the right implies that A^- has a very little affinity for protons. Therefore, A^- must be a weak base. Thus we may infer that *the conjugate base of a strong acid is always a weak base and the conjugate base of a weak acid is always a strong base.*

Amphiprotic Species

A species that acts both as a proton donor and a proton acceptor is known as amphiprotic. For example, water can set both as an acid (proton donor) and as a base (proton acceptor). It acts as a base towards HCl and as an acid towards NH_3.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{Cl^-}$$

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_3} \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

Similarly HS^-, HCO_3^- and HSO_4^- also act as amphiprotic in nature.

$$\underset{\text{acid}}{HS^-} + \underset{\text{base}}{OH^-} \rightleftharpoons \underset{\text{base}}{S^{2-}} + \underset{\text{acid}}{H_2O}$$

$$\underset{\text{base}}{HS^-} + \underset{\text{acid}}{H_3O^+} \rightleftharpoons \underset{\text{acid}}{H_2S} + \underset{\text{base}}{H_2O}$$

The dual behaviour of water has been used to explain the alkaline, acidic and mentral behaviour of aqueous solution of salts. For example, aqueous solution of Na_2CO_3 is alkaline, that of $FeCl_3$ and $CuSO_4$ is acidic while that of NaCl and K_2SO_4 is neutral.

Polyprotic Acids and Bases

Acids which can donate one proton per molecule are called *monoprotic acids*, while those which can donate more than one protons per molecule are known as *polyprotic acids*. For example, HCl, HNO_3 and HCN are monoprotic, whereas H_2SO_4, H_3PO_3 and H_3PO_4 are polyprotic in nature. Similarly bases which can accept one proton only are called monoprotic bases, whereas those which can accept more than one proton are known as polyprotic bases. For example, H_2O and HS^- are monoprotic bases while SO_4^{2-} and PO_4^{3-} are polyprotic bases.

$$HCl \rightarrow H^+ + Cl^-$$

$$HCN \rightarrow H^+ + CN^-$$

$$SO_4^{2-} + 2H^+ \rightarrow H_2SO_4$$

$$PO_4^{3-} + 3H^+ \rightarrow H_3PO_4$$

Basic Strength of a Bronsted Base

According to Bronsted-Lowry concept, the basic strength of a molecule or ion that acts as a base is defined as its tendency to accept a proton (H^+) to form its conjugate acid. If the given molecule or ion accepts the proton quite readily, it is said to have high basicity. On the other hand, if the molecule or ion accepts the proton less readily, it has low basicity. For example, since F^- ion has greater power to accept a proton to form its conjugate acid, HF, while Cl^- ion has lesser power to do so to form HCl; F^- ion has greater basic power than Cl^- ion.

It has been found that the basicity of given anions decreases as we move from left to right in the period, i.e. the basicity is in the order

$$CH_3^- > NH_2^- > OH^- > F^-$$

We know that in the formation of the given anion, H-atom overlaps with the negatively charged central atom and hence some volume of the central atom is occupied by the H-atoms and remaining volume of the central atom is occupied by the electron due to which the central atom is carrying negative charge on it. Since the number of H-atoms overlapping the central atom is decreasing from CH_3^- to F^- ions and hence the volume occupied by the electron is increasing. In case of F^- ion, since no H-atom is present the whole volume of this ion is occupied by the electron. The increase in the volume occupied by the electron produces an increase in the delocalization of the electron and hence the electron density around the central atom decreases from CH_3^- to F^-. Thus we see that the basicity of the given anions decreases as $CH_3^- > NH_2^- > OH^- > F^-$. Moreover, it is also known that in a given conjugate acid – base pair, if the acid is strong, its conjugate base will be weak and *vice versa*. Since the acidic strength of CH_4, NH_3, H_2O and HF which are conjugate acids of CH_3^-, NH_2^-, OH^- and F^- ions respectively increases as $CH_4 < NH_3 < H_2O < HF$, the basis strength of the given bases should decrease in the same direction; $CH_3^- > NH_2^- > OH^- > F^-$

Acidic Strength of a Bronsted Acid

According to Bronsted-Lowry concept, the acidic strength of a molecule or ion that acts as an acid is defined as its tendency to lose a proton (H^+) to form its conjugate its base. If the given molecule or ion loses the proton quite readily, it is said to have high acidity. On the other hand, if the molecule or ion loses the proton less readily, it has low acidity. For example, since H_2S has greater power to lose a proton to form its conjugate acid, HS^- while H_2O has lesser power to do so to form OH^-; H_2S has greater acidic strength than H_2O molecule.

Experiments have shown that the acidic strength of CH_4, NH_3, H_2O and HF molecule increases as we move from left to right in the period, i.e. the acidity is in the following order:

$$CH_4 < NH_3 < H_2O < HF$$

We have already stated that the basicity of CH_3^-, NH_2^- , OH^- and F^- ions (which are conjugate bases of CH_4, NH_3, H_2O and HF respectively) decreases as $CH_3^- > NH_2^- > OH^- > F^-$. Again we know that , according to Bronsted- Lowry concept , in a given conjugate acid- base pair, if the acid is strong, its conjugate base would be weak and *vice versa*. Thus since the basicity of CH_3^-, NH_2^- , OH^- and F^- ions is in the decreasing order ($CH_3^- > NH_2^- > OH^- > F^-$), the acidity of their conjugate acids (viz., CH_4, NH_3, H_2O and HF) would be in the increasing order ($CH_4 < NH_3 < H_2O < HF$).

Advantages of Bronsted- Lowry Concept

(i) This concept is superior to Arrhenius concept, since Arrhenius concept can explain the acid/base character of a substance in aqueous medium while Bronsted-Lowry concept can explain this character in aqueous as well as in other protonic solvents like Liq. NH_3, liq. HF.

(ii) Acid – base reactions taking place in gas phase can also be explained by Bronsted-Lowry concept. For example, in the reaction between HCl (g) and NH_3 (g), HCl (g) acts as an acid and NH_3 (g) behaves as a base.

(iii) Bronsted-Lowry also classifies certain species as bases which are not classified by Arrhenius concept. For example, NH_3, $H_2PO_4^-$ etc

(iv) Moreover, any species that is classified as an acid by Arrhenius remains as acid in the Bronsted-Lowry. The same is true for bases.

Limitations of Bronsted-Lowry Concept

The most serious limitation of this concept is that it cannot explain the acid base reactions taking place in aprotic/ non -protonic solvents, like liq. SO_2, liq. BF_3, BrF3 etc., in which no transfer of proton takes place.

3.4 LEWIS CONCEPT OF ACIDS AND BASES

In 1923, Lewis proposed a new concept of acids and bases based on electronic theory of valency. According to him an *acid* in any species which can accept an electron pair while a *base* is any species which can donate an electron pair. Thus, in the Lewis system, *an acid is an electron pair acceptor*, where as *a base is an electron pair donor.* In other words an acid is an electrophile (electron loving) while a base is a nucleophile (nucleus loving).

According to Lewis concept the process of neutralization is simply the formation of coordinate covalent bond between an acid and the donor atom of a base. The product formed is called a neutralization product or an adduct. The neutralization reaction between a proton (Lewis acid) and ammonia (Lewis base) molecule takes place as,

$$\underset{\text{acid}}{H^+} + \underset{\text{base}}{\ddot{N}H_3} \longrightarrow \underset{\text{adduct}}{[H \leftarrow NH_3]^+ \text{ or } NH_4^+}$$

Similarly the other examples of acid-base reactions are given below:

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$HCl + C_5H_5\ddot{N} \longrightarrow [C_5H_5N \rightarrow H]^+ + Cl^-$$

$$BF_3 + \ddot{N}H_3 \longrightarrow [F_3B \leftarrow NH_3]$$

$$AlCl_3 + \ddot{N}H_3 \longrightarrow [Cl_3Al \leftarrow NH_3]$$

Lewis concept does not differ from Bronsted-Lowry concept with respect to substances classified as bases. A Lewis base is capable of donating electron pair to a proton. Being proton acceptor it is also a Bronsted base. Thus both definitions label the following species as bases:

$$OH^-, H_2O, Cl^-, Br^-, \ddot{N}H_3$$

However, many species which are acids in terms of Lewis definition cannot be termed so according to Bronsted definition. Some examples are sulphur trioxide and halides of boron, aluminium, iron and zinc.

Classification of Lewis Acids

Lewis acids may be classified as under:

1. All simple cation are Lewis acids. For example,

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$

$$Co^{2+} + 6H_2O \longrightarrow [Co(H_2O)_6]^{2+}$$

2. Molecules containing a central atom with an incomplete octet are Lewis acids. For example,

$$BF_3 + NH_3 \longrightarrow [F_3B \leftarrow NH_3]$$

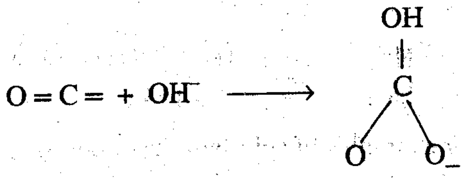
$$AlCl_3 + NH_3 \longrightarrow [Cl_3Al \leftarrow NH_3]$$

3. Molecules containing vacant d-orbitals as the central atom are Lewis acids. For example,

$$SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$$

$$SbF_3 + 2F^- \longrightarrow [SbF_5]^{2-}$$

4. Molecules with multiple bonds between dissimilar atoms also act as Lewis acids. Typical examples of this class are CO_2, SO_2 and SO_3.



Classification of Lewis Bases

Lewis bases include all anions, molecules having unshared pair of electrons such as water, alcohols, ether, and compounds like CO, NO etc., which can form the π-complexes with metals.

Advantages of Lewis Concept

1. Lewis concept is more general than the Bronsted-Lowry concept in that acid-base behaviour is not dependent on the presence of a particular element or on the presence or absence of a solvent.
2. This concept also includes those reactions in which no protons are involved.
3. It explains the basic properties of metallic oxides and acidic properties of non-metallic oxides.
4. This theory also includes many reactions such as gas phase, high temperature and non-solvent reactions as neutralization processes.

Limitations of Lewis Concept

1. Since the strength of Lewis acids and bases is found to depend on the type of the reaction and not on the absolute power of accepting or donating a pair of electrons, it is not possible to arrange the Lewis acids and bases in any order of their strength.
2. The conventional protonic acids *viz.*, HCl, H_2SO_4 are not covered under Lewis concept, as they do not establish a covalent bond by accepting a pair of electrons (which a Lewis acid ought to be).
3. The reactions catalyzed by Lewis acids are generally not catalyzed by the protonic acids.

3.5 SOLVENT SYSTEM CONCEPT OF ACIDS AND BASES

The protonic definition of acids and bases can be extended to reactions in non-aqueous solvents containing hydrogen, such as NH_3, N_2H_4, HF, H_2SO_4, CH_3COOH, NCN etc. This definition, however, cannot be applied to non-protonic solvents. Acid-base behaviour can be observed in systems where a proton plays no part in the reactions at all. It would, therefore, be desirable to have definition of acids and bases which is applicable to protonic and non-protonic solvents.

In an attempt to have more general definition of acids and bases applicable to protonic and non-protonic solvents, several definitions have been proposed. One of these is due to Cody and Elsey (1928). They proposed that substances which increase concentration of cation characteristic of the solvent are *acids,* whereas substances which increase the concentration of anion characteristic of the solvent are *bases.* Thus in water, substances providing protons are acids and those providing hydroxyl ions are bases. Similarly, in liquid ammonia, ammonium salts are acids because they provide ammonium ions, NH_4^+, and amides are bases, because they provide amide ions, NH_2^-.

The auto-ionization of some protonic and non-protonic solvents is shown below:

$$H_2O + H_2O \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{OH^-}$$

$$NH_3 + NH_3 \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{NH_2^-}$$

$$SO_2 + SO_2 \rightleftharpoons \underset{\text{acid}}{SO^{2+}} + \underset{\text{base}}{SO_3^{2-}}$$

Thio Thionyl ion

$$N_2O_4 + N_2O_4 \rightleftharpoons \underset{\text{acid}}{2NO^+} + \underset{\text{base}}{2NO_3^-}$$

Evidently this concept of solvent system can be used to explain the acid-base reactions occurring in aqueous and non-aqeuous solvents (i.e., protonic and non-protonic both).

Though the solvent system definition of acids and bases is useful, it has certain limitations. For instance, in a medium of low dielectric constant, the existence of ions cannot be conceived. Further more the concept lays too much emphasis on ionic mechanism of reactions.

Advantage of Solvent System Concept

The definition of acids and bases given by solvent concept can be used for protonic (*e.g.*, H_2O, NH_3, HF, CH_3COOH, HCN, etc) as well as non-protonic (*e.g.*, SO_2, $COCl_2$, BrF_3, N_2O_4, etc) solvents i.e., this definition is applicable to aqueous as well as non-aqueous solvents.

Disadvantages of Solvent System Concept

(i) According to this concept, the definition of acids and bases is based on the nature of solvent cation and solvent anion obtained by auto-ionization of the solvent.

(ii) According to this concept, acid base reactions taking place in the absence of a solvent cannot be explained.

(iii) This concept cannot account for the acid base reactions occurring in non-ionizing solvents like benzene chloroform etc.

3.6 LUX-FLOOD CONCEPT OF ACIDS AND BASES

Lux (1939) observed that the acid-base reactions are also feasible in oxide systems without the aid of protons. This concept was extended by Flood (1947) and applied to non-protonic systems which were not covered by Bronsted-Lowry concept. In terms of the Lux-Flood definitions, a *base* (CaO, MgO, or Na_2O) is an oxide ion donor and an *acid* (SiO_2, CO_2 or P_2O_5) is an oxide ion acceptor. Some acid-base reactions, in terms of Lux-Flood concept, may represented as:

Base		Acid		Salt
CaO	+	SiO_2	$\longrightarrow$	$CaSiO_3$
BaO	+	CO_2	$\longrightarrow$	$BaCO_3$
$6Na_2O$	+	P_4O_{10}	$\longrightarrow$	$4Na_3PO_4$
PbO	+	SO_3	$\longrightarrow$	$PbSO_4$

Substances may be classified as *amphoteric* in terms of this concept if they show a tendency both to take up and give up oxide ions. Thus:

$$ZnO \xrightarrow{+O^{2-}} ZnO_2^{2-} \qquad \text{(acid)}$$

$$ZnO \xrightarrow{-O^{2-}} Zn^{2+} + O^{2-} \qquad \text{(base)}$$

$$Al_2O_3 \xrightarrow{+O^{2-}} 2AlO_2^{-} \qquad \text{(acid)}$$

$$Al_2O_3 \xrightarrow{-3O^{2-}} 2Al^{3+} + 3O^{2-} \qquad \text{(base)}$$

This concept is particularly useful in explaining reactions which take place at high temperatures such as in metallurgical operations and during the manufacture of glass and ceramics.

3.7 USANOVICH CONCEPT OF ACIDS AND BASES

This is the most comprehensive concept of acid-base definition. This concept was proposed by Russian chemist, Urnovich in 1939. According to this concept an *acid* is any chemical species which reacts with a base, gives up cations, or accept anions or electrons. Conversely, a *base* is any chemical species which reacts with acids, gives up anions or electrons or combines with cations. This definition includes all Lewish acids and bases.

It also includes redox reactions which may consist of complete transfer of one or more electrons. Some examples of acid-base reactions in terms of Usanovich concept are given below:

	Acid		Base		Salt	Explanation
1.	SO_3	+	Na_2O	$\longrightarrow$	Na_2SO_4	Na_2O gives up O^{2-} ion (base) SO_3 combines with O^{2-} ion (acid)
2.	Cl_2	+	2Na	$\longrightarrow$	2NaCl	Na atom loses an electron (base) Cl gains this electron (acid)
3.	$Fe(CN)_2$	+	KCN	$\longrightarrow$	$K_4[Fe(CN)_6]$	KCN gives CN^- ion (base) $Fe(CN)_2$ combines with CN^- ion (base)
4.	HCl	+	NH_3	$\longrightarrow$	NH_4Cl	HCl gives H^+ ion (acid) NH_3 combines with H^+ ion (base)
5.	NH_4^+	+	OH^-	$\longrightarrow$	$NH_3 + H_2O$	NH_4^+ gives H^+ ion (acid) OH^- combines with H^+ ion (base)

It is apparent that Usanovich concept is a synthesis of all previous acid-base theories and in the process it has become too general. A comparison of the several concepts of acid-base reactions reveals that it is difficult to make an appropriate choice for the best. As a matter of fact, each concept has its own advantages and disadvantages and the knowledge of all the concepts is essential.

Limitation of the Concept

The only point that has been raised against this definition is that it is an extremely general concept, so general that almost all chemical reactions are considered as acid –base reactions in this concept.

3.8 SOFT AND HARD ACIDS AND BASE (SHAB) CONCEPT

The major drawback of Lewis concept is that it does not systematically the behaviour of acids and bases in terms of their relative strength. Moreover, this concept does not explain the stability of complexes and reaction kinetics of different reactions taking place between acids and bases.

Ahrland, Chatt and Davics (1958) divided metal ions into two classes, viz. Class (a) acceptors and Class (b) acceptors. Metal ions which form their most stable complexes with ligands containing nitrogen, oxygen, or flourine as donor atom are termed *Class (a) acceptors* (Lewis acids) and those which form their most stable complexes with ligands containing a heavier member of these families as donor atom (e.g., P, S, Br etc.) are termed *Class (b) acceptors* (Lewis acids).

Class (a) includes ions of alkali metals, alkaline earth metals, lighter transition metals in higher oxidation states such as Ti^{4+}, Cr^{3+}, Fe^{3+} and Co^{3+} and the hydrogen ion, H^+. Their outer electrons or orbitals are not easily distorted. The ligands which prefer to combine with these ions are placed in Class (b). The tendency of the ligands to form complexes with Class (a) metal ions is in the order

$$F >> Cl > Br > I$$

$$O >> S > Se > Te$$

$$N >> P > As > Sb$$

Class (b) includes ions of the heavier transition metals and those in lower oxidation states such as Cu^+, Ag^+, Pt^{2+}, etc. The ligands which exhibit preference towards these metal ions also belong to this category. The complexing ability of the ligands for the metal ions of Class (b) is in the order:

$$F << Cl < Br < I$$

$$O << S < Se \sim Te$$

$$N << P > As > Sb$$

The donor atoms and ions (Lewis bases) were classified on the basis of electron affinity, coordinating ability, effective charge, ionic size and polarization considerations.

Based on the polarization considerations, R.G. Pearson (1963) introduced the idea of HARD and SOFT acids and bases. He divided the acceptors (Lewis acids) and donors (Lewis bases) as defined below:

Soft Base

It is one in which the donor atom is highly polarizable, has low electronegativity and is easily oxidized is associated with empty low-lying orbitals.

Hard Base

It is defined as one with the opposite properties, viz. the donor is of low polarizability and high electronegativity, is hard to oxidize and is associated with empty orbitals of high energy.

Soft Acid

It is defined as the one in which the acceptor atom is of low positive charge, large size and has several outer electrons which can be easily excited.

Hard Acid

It is the one in which the acceptor atom is of high positive charge, small size and do not has outer electrons which can be easily excited.

Thus, metal ions of Class (a) become hard acids and the ligands of this class become hard bases. On the other hand, metal ions and ligands of Class (b) become soft acids and soft bases respectively. This classification is, however, not very rigid and there are borderline cases. A complete classification is given in Tables 3.2 and 3.3.

Table 3.2. Classification of Hard and Soft Acids

Hard Acids

H^+, Li^+, Na^+, K^+

Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}

Sc^{3+}, La^{3+}, Ce^{4+}, Gd^{3+}, Lu^{3+}, Th^{4+}, U^{4+}, Pu^{4+}

Ti^{4+}, Zr^{4+}, Hf^{4+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}, UO_2^{2+} , VO^{2+}, MoO^{3+}, Si^{4+}

$Be\,Me_2$, BF_3, BCl_3, $B\,(OR)_3$, Al^{3+}, $Al(CH_3)_3$, AlH_3, $AlCl_3$, Ga^{3+}

CO_2, RCO^+, NC^+,

SO_3, RPO^{2+}, $ROPO^{2+}$, AS^{3+}

Cl^{3+}, Cl^{7+}, I^{5+}, I^{7+}

RSO_2^+, $ROSO_2^+$,

HX (hydrogen bonding molecules)

Soft Acids

Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Hg^{2+}, CH_3Hg^+

Pd^{2+}, Cd^{2+}, Pt^{2+}, $Co\,(CN)_5^{2-}$, Pt^{4+}

BH_3, $Ga\,(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3, Tl^+

Te^{3+}, Pb^{4+}, Te^{4+}

CH_2, carbene, trinitribenzene , chloranil, quinone etc.

O, Cl, Br, I, N, RO, RO_2

M° (metal atom) and bulk metals

HO^+, RO^+, RS^+, Te^{4+}, RSe^+, RTe^+

Br_2, Br^+, I_2, I^+, ICN etc.

Borderline Acids

Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Rh^{3+}, Ir^{3+}, Ru^{3+}, OS^{2+}

$B(CH_3)_3$, GaH_3, R_3C+, $C_6H_5^+$, Sn^{2+}, Pb^{2+}

NO^+, Sb^{3+}, Bi^{3+}

SO_2

Table 3.3. Classification of Hard and Soft Bases

Hard Bases

NH_3, RNH_2, N_2H_4

H_2O, OH^-, O^{2-}, ROH, RO^-, SO_4^{2-}, R_2O

CH_3COO^-, CO_3^{2-}, NO_3^-, SO_4^{2-}, ClO_4^-

F^-

Soft Bases

H^-

R^-, C_2H_4, C_6H_6, CN^-, RNC, CO

SCN^-, R_3P, $(RO)_3P$, R_3As

R_2S, RSH, RS^-, SO_3^{2-}

I^-

Borderline Bases

$C_6H_5NH_2$, C_5H_5N, N_3^-, N_2

NO_2^-, SO_3^-

Br^-

Pearson's Principle or SHAB Principle

This is also known as the principle of Soft and Hard Acids and Bases (SHAB). It states that:

- *"Hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases".*

Thus, the complex A: B is the most stable when both A and B are either hard or soft. Pearson's principle provides the basis for an approximate qualitative prediction of the relative stability of the complexes, and is not an explanation of the observations.

Common Features of Hard and Soft Acids

(i) The hard acids coordinate to various donors mainly by the electrostatic interactions existing between charges of opposite signs. The higher the charge and smaller the radius of the acceptor and of the donor atom to be coordinated, the stronger are the complexes formed.

(ii) The coordination of uncharged ligand (soft base) such as CO, olefins and aromatic hydrocarbons is preferred with soft acids.

(iii) The rate of nucleophilic displacements depends much on polarizability.

Common Features of Hard and Soft Bases

(i) The hard or soft character of the base depends on the polarizability of the donor species. The more polarizable is the donor, the softest character it has.

(ii) Besides a high polarizability, a ligand must possess empty orbitals on suitable energy levels to accommodate *d*-electrons from the acceptors. The more available the orbitals, the softer the ligand.

(iii) The soft ligands like the hard ligands and tend to flock together.

Applications of SHAB Principle

1. *Thermodynamic stability of compounds*: Thermodynamic stability of simple compounds and complex ions can be rationalized in terms of hard and soft acid-base principle. For example, $[AgI_2]^-$ is stable but $[AgF_2]^-$ does not exist. The reverse is true for Cobalt (111); $[CoF_6]^{3-}$ is more stable than $[CoI_6]^{3-}$. Tables 3.2 and 3.3 show that Ag^+ is a soft acid and Co (111) a hard acid; F^- is a hard and I^- a soft base. Therefore, Ag^+ combines with I^- (soft and base) to form stable $[AgI_2]^-$ complex. Similarly, Co^{3+} acid and F^- base (both hard) combine to form stable $[C_6F_6]^{3-}$.

Short //

2. *Relative strength of halogen acids*: With the help of this principle we can explain the relative strength of halogen acids in aqueous solution. In the reaction:

$$HX + H_2O \longrightarrow H_3O^+ + \bar{X} \qquad (X = F, Cl, Br \text{ and } I)$$

the hard acid H^+ combines with the hardest base F^- to form the least dissociated or weak acid. Thus, the strengths of the halogen acids is in the order:

$$HF > HCl < BHr < HI$$

Hard solvents tend to dissolve hard solutes and soft solvents tend to dissolve soft solvents.

3. *Catalyst poisoning*: The SHAB principle has been used to explain the poisoning of metal catalysts. Certain soft metals such as platinum and palladium act as catalysts in certain reactions. Bases containing P, As, Sb and Se in low oxidation states (soft bases) poison these metallic catalysts. Thus soft metal catalysts are poisoned by impurities of soft bases, but remain unaffected by those of hard bases such as N, O and F.

4. *Prediction of rate of reaction*: The SHAB principle can be used to correlate the rates of certain chemical reactions. The speed of electrophilic and nucleophilic substitution reactions can be related to the hardness or softness of the acid and base centers. The reaction

$$H^+ + CH_3HgOH \longrightarrow H_2O + CH_3Hg^+$$

should produced towards the right hand side since it involves the combination of hard acid H^+ and hard base OH^-. On the other hand the reaction

$$H^+ + CH_3HgSH \longrightarrow H_2S + CH_3Hg^+$$

should proceed towards the left hand side as it involves the combination of soft acid CH_3Hg^+ and soft base S^{2-}

5. *Symbiosis* : Jorgenson (1968) has referred to the tendency of the soft ligand to combine with a centre having soft ligand and vice versa, as a *symbiosis*. He has, thus, explained that such compounds are symmetrically substituted and do not have mixed substituents.

$$BHF_3^- + BF3H^- \longrightarrow BH_4^- + BF_4^-$$

$$CH_3F + CHF_3 \longrightarrow CH_4 + CF_4$$

$$BF_3 + F^- \longrightarrow BF_4^-$$

6. *Prediction of sign of ΔH:* The principle of soft and hard acids and bases may be used to predict the sign of ΔH for the reaction of the type

$$AB + CD = AD + CB$$

7. *Choice of catalyst*: The SHAB principle is also useful to select a particular catalyst depending on the nature of the reactants (hard or soft acid or base).

Limitations of SHAB Concept

The chief limitation of the SHAB concept is its general nature without any quantitative measurement. Secondly, the arbitrariness permitted to break a compound to acid and base fragments in order to explain the observed phenomenon, is a convenience only when the reaction is known. Thirdly, as the hard-soft factors are independent the acidic or basic character of the compounds, they work independently.

3.9 RELATIVE STRENGTH OF ACIDS AND BASES

According to Bronsted-Lowry concept, the strength of an acid or a base is defined as its capacity to give H^+ and OH^- ions in equimolar solutions in water respectively. Thus relative strength of two acids or bases can be compared by comparing their H^+ or OH^- ions concentration in their equimolar solutions in water respectively.

Those acids and bases which ionize almost completely in solution are called strong acids and strong bases while those which are ionized only to a limited extent in solution are termed as weak acids and weak bases. Examples of strong acids are HNO_3, H_2SO_4, HCl, $HClO_4$ etc. and those of strong bases are NaOH, KOH, $(CH_3)_4NOH$ etc.

For an aqueous solution of an acid, HA, the equilibrium is shown as:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For the above equilibrium the value of equilibrium constant, *K* is given by

$$K = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]} \qquad \text{..... 3.3}$$

Now since water which is used as a solvent is present in large quantity, $[H_2O]$ = constant. Thus

$$K \times [H_2O] = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

or

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} \qquad \text{..... 3.4}$$

Here K_a is called *acid dissociation constant*. It represents the extent to which an acid is dissociated. Greater the value of K_a, stronger is the acid and vice versa.

Similarly for a weak base, B the corresponding equilibrium is:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

and the value of *base dissociation constant,* K_b is given by:

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]} \qquad \text{..... 3.5}$$

Equation 3.5 shows that the greater the value of K_b, higher the concentration of OH^- ions and consequently stronger the base.

It is generally more convenient to express K_a and K_b values in terms of their negative logarithms, i.e.; as pK_a and pK_b which are defined as:

$$pK_a = -\log K_a \qquad \text{..... 3.6}$$

and

$$pK_b = -\log K_b \qquad \text{..... 3.7}$$

A small value of pK_a means the acid is stronger similarly small value of pK_b indicates a stronger base.

The strength of an acid is also related to that of its conjugate base. If the acid is stronger its conjugate base is weak. For example, HCl is a strong acid as it has got a great tendency to lose a proton, its conjugate base Cl^- ion is a weak base as it has get a little tendency to accept a proton. Reverse is true, if the conjugate base is strong.

Values of dissociation constants (at 25°C) and relative strengths of some acids and bases are given in Table 3.4.

Table 3.4. Dissociation Constants of Some Acids and Bases at 25°C and their Relative Strengths

Acid or Base	K_a or K_b	Relative Strength
HCl	very large	very strong
NHO_3	very large	very strong
H_2SO_4	very large	very strong
HF	6.7×10^{-4}	weak
CH_3COOH	1.8×10^{-5}	weak
H_2S	1.0×10^{-7}	weak
H_2O	1.8×10^{-14}	very weak
NaOH	very high	very strong
KOH	very high	very strong
$Ca(OH)_2$	High	strong
NH_4OH	1.81×10^{-5}	weak
CH_3NH_2	4.38×10^{-4}	weak
$C_6H_5NH_2$	4.7×10^{10}	very weak

All the strong acids like HCl, HNO_3, H_2SO_4 have very close *Ka* values or *pKa* values. They appear to have nearly equal strengths in aqueous solutions. This phenomenon is called *Levelling effect* and water is known as *Levelling solvent.* Several ~~mineral acids are, however, only partially ionized in a~~ glacial acetic acid medium because acetic acid is a poor proton acceptor but rather a better proton donor. Acetic acid, therefore, acts as a *Differentiating solvent* towards mineral acids. The relative strengths of some mineral acids in acetic acid medium are:

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$$

Relative Order of Acidity of HF, HCl, HBr and HI Acids

To find the order of acidity of the halogen acids, let us find out the relative order of basicity of their conjugate bases, viz., F^-, Cl^-, Br^- and I^-

When we move from F^- to I^-, the volume available to electron increases from F^- to I^-. This results in an increase in electron delocalization and decrease in electron density from F^- to I^-. Consequently, the attraction for proton and basicity decrease in the order:

$$F^- > Cl^- > Br^- > I^-$$

It is obvious that F^- is the strongest base and its conjugate acid HF is the weakest acid. Similarly, I^- is the weakest base and its conjugate acid HI is the strongest acid among the halogen acids. The order of acidity of halogen acids is, therefore

$$HF \text{ (weakest acid } < HCl < HBr < HI \text{ (strongest acid))}.$$

Similarly the order of acidity of hydracids of group VIA is

$$H_2O < H_2S < H_2Se < H_2Te$$

Relative Order of Acidity of Oxyacids

The acidic character of oxyacids having the same central atom in different oxidation number increases with the increase in oxidation number of the central atom. For example:

(i) $HClO < HClO_2 < HClO_3 < HClO_4$

(ii) $H_2SO_3 < H_2SO_4$

(iii) $HNO_2 < HNO_3$ etc.

Let us explain the relative order of acidity of oxyacids of chlorine. In order to do so let us find out the relative order of the basicity of the conjugate bases viz; ClO^-, ClO_2^-, ClO_3^- and ClO_4^- of these acids. With the increase in the number of oxygen atoms in the conjugate bases, the delocalization of the π-bond becomes more and more extended. This results in decrease in electron density. Consequently, proton attraction and basisity also decrease in the order

$$ClO^- > ClO_2^- > ClO_3^- > Cl_4^-$$

It may now be inferred that ClO^- is the strongest base and its conjugate acid HClO is the weakest acid. Similarly ClO_4^- is the weakest base and its conjugate acid $HClO_4$ is the strongest acid among the oxyacids of chlorine. The relative order of acidity of oxyacids of chlorine is

$$HClO \text{ (weakest acid)} < HClO_2 < HClO_3 < HClO_4 \text{ (strongest acid)}$$

Relative Order of Basicity of NH_3, H_2O and HF

The base strength of the molecules NH_3, H_2O and HF increases with a decrease in electronegativity of the element. Thus the order is

$$NH_3 > H_2O > HF$$

A similar order is observed for negative ions of these molecules.

$$NH_2^- > OH^- > F^-$$

In these series, size differences are small and unimportant; the trend is set by decreasing electronegativity of the central atom. Both small size and low electronegativity are found in NH_2^- ion which is a powerful base. Another factor that influences the base strength of anions is the charge on the ion. Thus, the base strength of the monoatomic anions of the elements of the second period decreases with increasing electronegativity and with decreasing negative charge on the ion, hence

$$N^{2-} > O^{2-} > F^-$$

3.10 RELATIONSHIP BETWEEN ACID-BASE AND OXIDATION-REDUCTION REACTIONS

Oxidation is defined as a process which involves the loss of one or more electrons by an atom, ion or a molecule while reduction is a process in which one or more electrons are added to a substance. More broadly a chemical reaction resulting in a change in the electric charges on the reacting particles may be called a *reduction-oxidation* or *redox reaction* for short. The substance which furnishes the electrons is oxidized, and the substance receiving electron is reduced. Consequently those substances which donate electrons easily are called *reducing agents,* and those which accept electrons readily are termed *oxidizing agents.* The driving force of a redox reaction is the affinity of the oxidizing agent for electrons.

In a somewhat analogous fashion the G.N. Lewis concept of acids and bases describes a *base* as any substance having a pair of electrons which it can donate to establish a coordinate bond and an *acid* as any substance which may accept force of the reaction is the affinity of the acid for electrons. The close relationship between oxidation-reduction and acid-base reactions is clearly indicated. Both acids and oxidizing agents exhibit an affinity for electrons. To this extent they are both described as being *electrophilic* (electron loving) in their nature. In like manner, bases and reducing agents are designated as *electrodotic*, or electron-giving, agents.

The analogy between the two types of reactions leads to the expectation that a reactant may display either oxidation-reduction or acid-base properties depending upon the substance with which it reacts. An excellent example of behaviour of this kind is the action of silver ion as either an acid or an oxidizing agent. In its reaction with the hydroxide ion,

$$\underset{\text{acid}}{Ag^+} + \underset{\text{base}}{:OH^-} \rightleftharpoons Ag:OH$$

the silver ion acts as an acid in accepting a pair of electrons from the hydroxide ion. It reacts similarly with ammonia to form two coordinate bonds.

$$\underset{\text{acid}}{Ag^+} + \underset{\text{base}}{2\ddot{N}H3} \rightleftharpoons Ag(:NH_3)_2^+$$

Towards reducing agents the silver ion behaves as an oxidizing agent. For example

$$\underset{\text{oxidant}}{2Ag^+} + \underset{\text{reductant}}{Cu} \rightleftharpoons 2Ag + Cu^{2+}$$

Similarly the sulphide ion may behave as either a base or a reducing agent, depending upon its reaction partner.

$$\underset{\text{base}}{S^{2-}} + \underset{\text{acid}}{2H_2O} \rightleftharpoons H_2O + 2OH^-$$

$$\underset{\text{reductant}}{S^{2-}} + \underset{\text{oxidant}}{2Fe(CN)_6^{3-}} \rightleftharpoons S + 2Fe(CN)_6^{4-}$$

The difference between the two behaviors is that an electron pair is *shared* by the two reactants in the acid-base reactions, but get *transferred completely* from one reactant to the other in the redox reactions. Thus the distinction between the both types of behaviour is a matter of definitions, involving exists in the Usanovich treatment. This concept includes both types of reactions as acid-base systems, and no differentiation is made between them.

3.11 AUTOIONIZATION OF WATER

We know that water is most commonly used solvent. One of its special properties is its ability to act both as an acid and as a base-water function as a base in reactions with acids such as HCl and CH_3COOH, and it functions as an acid in reactions with bases such as HN_3. Water, too, has a tendency to ionize. The ionization of water can be represented as follows:

$$H—OH + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \text{..... 3.8}$$

The formula of the first water molecule was purposely written as H — OH to illustrate how ionization occurs. Expressing the hydrated proton as H^+ rather than H_3O^+, we can write the equilibrium constant for the autoionization of water.

$$Kc = \frac{[H^+][OH^-]}{[H_2O]} \qquad ..... 3.9$$

Since a very small fraction of water molecules are ionized, the concentration of water, that is, $[H_2O]$, remains virtually unchanged. Therefore

$$Kc\,[H_2O] = Kw = [H^+]\,[OH^-] \qquad ..... 3.10$$

The "new" equilibrium constant, Kw is called the ion-product constant, which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature. In pure water at 25°C, the concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M. Thus, from above equation 3.10

$$Kw = (1.0 \times 10^{-7})\,(1.0 \times 10^{-7})$$

$$= 1.0 \times 10^{-14} \text{ at } 25°C$$

Whenever $[H^+] = [OH^-]$, the aqueous solution is said to be neutral. In an acidic solution there is an excess of H^+ ions, or $[H^+] > [OH^-]$. In a basic solution there is an excess of hydroxide ions, or $[H^+] < [OH^-]$. In practice we can adjust the concentration of either H^+ or OH^- ions in solutions but we cannot vary both of them independently. If we adjust the solution so that $[H^+] = 1.0 \times 10^{-6}$ M, the OH^- concentration must change to

$$[OH^-] = \frac{Kw}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-6}} = 1.0 \times 10^{-8}\text{ M}$$

It is important to remember that, because Kw is an equilibrium constant, its value changes with temperature. Kw increases with temperature because the ionization of water is endothermic.

Thus, at 40°C, $Kw = 3.8 \times 10^{-14}$ and equation 3 becomes,

$$3.8 \times 10^{-14} = [H^+]\,[OH^-] = Kw$$

Since the solution is still neutral, $[H^+] = [OH^-]$. Therefore, at this temperature, the concentrations are

$$[H^+] = \sqrt{3.8 \times 10^{-14}} = 1.9 \times 10^{-7}\text{ M}$$

and $$[OH^-] = \sqrt{3.8 \times 10^{-14}} = 1.9 \times 10^{-7}\text{ M}$$

A neutral solution at 40°C will have a higher H^+ ions concentration (1.9×10^{-7} M) than a neutral solution at 25°C (1.0×10^{-7} M).

Example 3.1

The concentration of HO^- ions in a certain household ammonia cleaning solution is 0.0025 *M*. Calculate the concentrations of the H^+ ions.

Solution

We know that according to equation 3,

$$[H^+]\,[OH^-] = Kw$$

or

$$[H^+] = \frac{Kw}{[OH^-]}$$

$$= \frac{1.0 \times 10^{-14}}{0.0025} = 4.0 \times 10^{-12}\ M$$

Since $[H^+] < [OH^-]$, the solution is basic.

3.12 pH — A MEASURE OF ACIDITY

Since the concentrations of H^+ or OH^- ions are frequently very small numbers, it becomes essential to devise a scale which can express these concentrations in a convenient way. Soren Sorensen (Danish biochemist) in 1909 proposed a more practical measure called pH. The concept of pH provides a means of measuring the acid-base strength. By formal definition, the pH is equal to the negative logarithm of the hydrogen in concentration in moles per litre. Symbolically, this is written as

$$pH = -\log [H^+] \qquad \text{..... 3.11}$$

S.P.L. Şorensen originally wrote the symbol as pH and called P the "hydrogen ion exponent" (Wassertoffionexponent); it is the mitial letter of *Potenz* (German), *puissance* (French) and *power* (English). It is now customary to write the symbol as pH.

Keep in mind that equation 3.11 is simply a definition designed to give us convenient numbers to work with. Furthermore, the term $[H^+]$ in equation 4 pertains only to the numerical part of the expression for hydrogen ion concentration, for we cannot take the logarithm of units. Thus, like equilibrium constant, the pH of a solution is a dimensionless quantity.

Since pH is simply a way to express H^+ ion concentration, acidic and basic solutions at 25°C can be identified by their pH values, as follows:

Acidic solutions: $[H^+] > 1.0 \times 10^{-7}$ M, $pH < 7.00$

Basic solutions: $[H^+] < 1.0 \times 10^{-7}$ M, $pH < 7.00$

Neutral solutions: $[H^+] = 1.0 \times 10^{-7}$ M, $pH = 7.00$

A scale analogous to the pH scale can be devised using the negative logarithm of the OH^- ion concentration. Thus we define pOH as

$$pOH = -\log [OH^-] \qquad \text{..... 3.12}$$

Now consider again the ion-product constant for water:

$$[H^+] [OH^-] = Kw = 1.0 \times 10^{-14}$$

Taking logarithm of both sides

$$\log [H^+] + \log [OH^-] = \log Kw$$

or

$$-\log [H^+] - \log [OH^-] = -\log Kw$$

From the definition of pH and pOH we obtain

$$pH + pOH = 14 \qquad \text{..... 3.13}$$

Equation 3.13 provides us another way to express the relationship between the H^+ ion concentration and OH^- ion concentration.

Table 3.5. The pH Value of Some Common Fluids

Sample	**pH Value**
Gastric juice in stomach	1.0 — 3.0
Lemons	2.4
Vinegar	2.8
Soft drinks	3.0
Oranges	3.5
Urine	5.5 — 7.0
Water exposed to air	5.5
Saliva	6.4 —6.9
Milk	6.5
Pure water	7.0
Blood	7.35 — 7.45
Tears	7.4
Rainwater	6.2
Sea water	8.5
Tomatoes	4.2
Grapefruit juice	3.2

Table 3.6. The relationship between H^+ ion and OH^- ion Concentration

$[H^+]$	pH	$[OH^-]$
$10^0 = 1$	0	10^{-14}
$10^{-1} = 0.1$	1	10^{-13}
$10^{-2} = 0.01$	2	10^{-12}
$10^{-3} = 0.001$	3	10^{-11}
$10^{-4} = 0.0001$	4	10^{-10}
$10^{-5} = 0.00001$	5	10^{-9}
$10^{-6} = 0.000001$	6	10^{-8}
$10^{-7} = 0.0000001$	7	10^{-7}
$10^{-8} = 0.00000001$	8	10^{-6}
$10^{-9} = 0.000000001$	9	10^{-}
$10^{-10} = 0.0000000001$	10	10^{-4}
$10^{-11} = 0.00000000001$	11	10^{-3}
$10^{-12} = 0.000000000001$	12	10^{-2}
$10^{-13} = 0.0000000000001$	13	10^{-1}
$10^{-14} = 0.00000000000001$	14	10^0

Example 3.2

Calculate the pH of the following solutions.

(i) 1.3×10^{-4} *N* HCl

(ii) 0.0032 *M* H_2SO_4

(iii) 0.05 *N* HNO_3

(iv) 1.0×10^{-3} *N* NaOH

Solution

(i) $[H^+] = 1.3 \times 10^{-4}$ N

$pH = -\log [H^+]$

$$= -\log[1.3 \times 10^{-4}]$$

$$= 3.886$$

(ii) Since molecular mass of H_2SO_4 is twice its equivalent mass, therefore, 0.0032 *M* H_2SO_4 is same as 0.0064 *N* H_2SO_4.

$$[H^+] = 0.0064\ N = 6.4 \times 10^{-3}\ N$$

$$pH = -\log[6.4 \times 10^{-3}]$$

$$= 2.198$$

(iii)

$$[H^+] = 0.05 = 5 \times 10^{-2}\ N$$

$$pH = -\log[5 \times 10^{-2}]$$

$$= 1.301$$

(iv)

$$[OH^-] = 1.0 \times 10^{-3}\ N$$

$$[H^+][OH^-] = Kw$$

$$[H^+] = \frac{Kw}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}}$$

$$= 1.0 \times 10^{-11}\ N$$

$$pH = -\log[1.0 \times 10^{-11}]$$

$$= 11.0$$

Example 3.3

Calculate the pH of a 0.25 *N* formic acid solution which is 1.5% dissociated.

Solution

Since formic acid is 1.5% dissociated, the solution will have

$$[H^+] = \frac{1.5 \times 0.25}{100}$$

$$= 3.75 \times 10^{-3}\ N$$

$$pH = -\log[3.75 \times 10^{-3}]$$

$$= 2.42$$

Example 3.4

In a NaOH solution $[OH^-]$ is 2.9×10^{-4} *M*. Calculate the pH of the solution.

Solution

$$[OH^-] = 2.9 \times 10^{-4}\ M$$

$$pOH = -\log [2.9 \times 10^{-4}]$$

$$= 3.54$$

Since $pH + pOH = 14$

$$pH = 14 - pOH$$

$$= 14 - 3.54$$

$$= 10.46$$

Example 3.5

The pH of rain water collected in a certain area of University on a particular day was 4.82. Calculate the H^+ ion concentration of the rain water.

Solution

$$pH = -\log [H^+]$$

$$4.82 = -\log [H^+]$$

Taking the antilog on both sides, we have

or $[H^+] = 1.5 \times 10^{-5}$ M ($[H^+] = 10^{-pH}$)

Applications of pH value

The proper adjustment of pH values of different media is of great importance. There are four main applications of pH determinations.

1. Pharmaceutical Applications

The extraction stability and therapeutic efficacy of a large number of pharmaceutical preparations depend on their degree of acidity or alkalinity as shown by the following examples:

(*i*) In the preparation of injections of Pituatory, hot water containing acetic acid which gives a pH of 3—4 is used as this gives a maximum yield.

(ii) In the extraction of insulin form puncreas, alcohol whose pH is adjusted to 3.0—3.5 with HCl is ideally used.

(iii) Vitamin-B preparations are sensitive to a pH over 5. These are most stable at pH 3.5—4.5.

(iv) Lowering of pH value of many antiseptic solutions increases their efficacy.

2. Industrial Applications

The inversion of cane sugar is governed by the active acidity of a solution. If we hydrolyze a sugar solution by means of equal volumes of 0.1 *N* HCl and 0.1 *N* CH_3COOH solutions, we find that the efficiency of HCl as hydrolytic agent is much greater than that of CH_3COOH. This is due to the fact that inversion of cane sugar is so controlled by the pH of the solution which is different even for the same strength of different acids. This fact explains the significance of pH value in the sugar industry. In the same way regulation of pH is essential in the textile, leather, paint and other industries.

3. Analytical Applications

The increase of acidity or alkalinity by common ion effect control the preparation or precipitation of certain substances in qualitative and quantitative analysis. In volumetric as well as gravimetric analysis, proper adjustment of pH is of vital importance.

4. Physiological Applications

The pH of normal human blood is maintained at 7.35. Any marked deviation from this value shows adverse conditions like diabetic coma in which the pH of the blood may drop to 6.82. Thus lot of complications can set in if there is a slight deviation of pH from normal value.

The pH of gastric juice is less than 2. The increase of pH may cause vomiting. The control of the pH of various parts of digestive system is important, because the efficiency of the digestive enzymes is maximum only at a specific pH. The deviations from pH values will hinder or even stop the action of the enzymes.

It has also been found that eye drops having pH value more than or less than 7.35 cause much eye initiation of the eye.

3.13 DETERMINATION OF pH OF A SOLUTION

The pH of any solution may be determined by:

(a) Indicator Method, and

(b) The EMF Method.

These methods are discussed below:

(a) Indicator Method

In this method the principle of making pH measurements is based on the fact that various indicators change in colour when they are acted upon by solutions of different acidities or alkalinities. The solution to be examined is mixed with a suitable indicator and the colour obtained is compared with the colours of a series of mixtures of the same indicator with buffer solutions of known pH values. The buffer solution which gives the same colour as the test solution has the same pH value.

(b) The EMF Method

The pH of a solution is accurately measured from emf measurements. In principle, the activity of hydrogen ions or the concentration of hydrogen ions in a solution can be determined by setting a cell in which one of the electrodes is reversible to hydrogen ions. The electrode is dipped in the solution of unknown pH. The other electrode is a reference electrode such as SHE or SCE or other any reference electrode. The glass electrode is commonly used in the measurement of pH values of different solutions.

Glass Electrode

It is the universally employed electrode for pH measurement. It works on the principle that when two solutions of unknown pH values are separated by a glass membrane, an exchange of hydrogen ions between the solutions and glass takes place. Due to this exchange a potential develops across the membrane. The magnitude of this potential depends on the difference in pH values of the two solutions. If the pH of one of the solutions is maintained constant and other is varied, the potential of the electrode obeys the equation.

$$E_G = E_G{}^\circ - \frac{RT}{F} \ln a_{H^+} \qquad ..... 3.14$$

At 298 K, it becomes

$$E_G = E_G{}^\circ + 0.0591 \text{ pH} \qquad ..... 3.15$$

Where $E_G{}^\circ$ is a constant characteristic of each glass electrode and its value depends on the particular arrangement employed. Equation 12.65 suggests that the glass electrode can be conveniently employed for the determination of pH values of solutions.

The assembly of glass electrode (Fig. 3.1) consists of a thin glass bulb filled with 0.1 N HCl and a silver wire coated with silver chloride is immersed in it. The bulb is then placed in the solution of unknown pH and is combined with a reference electrode yielding the cell.

$$\text{Ag} \mid \text{AgCl} \mid 0.1 \text{ N HCl} \mid \text{glass} \mid \text{Solution (pH = x)} \parallel \text{SCE}$$

The emf of the cell at 298 K is given as:

$$E_{Cell} = E_R - E_L$$

$$E_{Cell} = E_{ref} - E_G^{o} - 0.0591\ \text{pH} \qquad \text{..... 3.16}$$

Thus the cell emf is a linear function of pH of the solution in which the glass electrode is dipped.

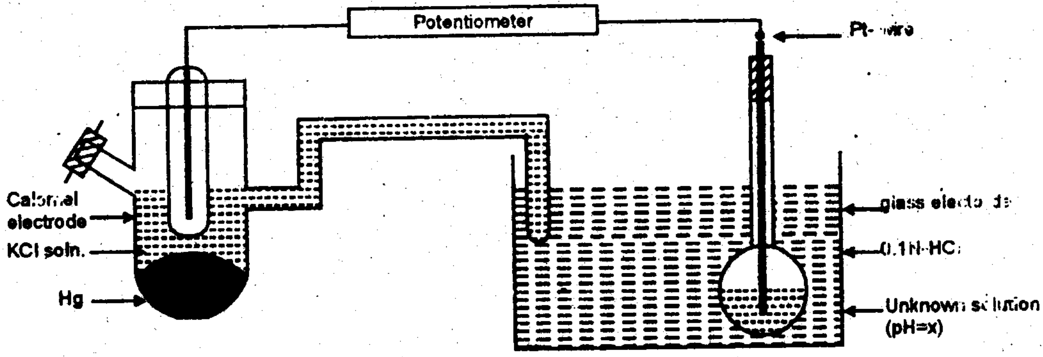


Fig. 3.1. Determination of pH by glass electrode.

To measure the pH of an unknown solution, E_G^{o} is first measured by dipping the glass electrode in a series of solutions of known pH values. Once E_G^{o} for a particular arrangement is determined, the electrode is then placed in the solution of unknown pH, the emf of the cell is measured and using equation 3.16 its pH can be calculated.

Glass electrode is the most convenient and has nearest approach to a universal pH electrode. It is not affected by oxidizing or reducing agents or by impurities in the solution. In strongly alkaline solutions, ordinary glass is attacked by alkali and electrode made of special quality glass should be used. Moreover, it cannot be used in pure CH_3COOH, C_2H_5OH and gelatin.

3.14 BUFFER SOLUTIONS

It has been observed that even the purest form of water does not retain a constant value of pH = 7 for a long time. This is due to the fact that the CO_2 from air or silicates from the glass containing water may dissolve in water thereby making the solution slightly acidic or basic respectively and pH will correspondingly be changed.

Since there are various chemical reactions and biochemical reactions in particular which can take place more rapidly in solution of specified pH values, therefore, it becomes essential to have solutions which can maintain constant pH values even if some little acid or base is added. *Such solutions which are resistant to change of pH when some acid or base is added to them are called Buffer solutions or simply Buffers.* This resistance to change in the pH value of a solution is known as the *buffer action.* Buffer solutions usually consists of:

(i) a mixture of weak acid and its salt (acidic buffer) such as acetic acid and sodium acetate, and

(ii) a mixture of weak base and its salt (alkaline buffer) like ammonium hydroxide and ammonium chloride.

Let us explain how a buffer solution acts and maintains its pH constant. In an acidic buffer, like acetic acid and sodium acetate, ionization of the weak acid is suppressed by the salt and the solution contains a large amount of unionized acetic acid (CH_3COOH), a large amount of acetate ions (CH_3COO^-) and a small amount of H_3O^+ ions. If a strong acid (HCl) is added to such a mixture, the equilibrium is disturbed, H_3O^+ ions added would combine with the acetate ions forming unionized acetic acid according to the following reaction:

$$H_3O^+ + CH_3COO^- \rightleftharpoons CH_3COOH + H_2O$$

Thus, acetate ions of the mixture, neutralize the added acid and thereby pH value of the buffer is almost maintained constant.

However, addition of hydroxyl ions in the form of a strong base (NaOH) neutralizes the acid forming salt and water.

$$OH^- + CH_3COOH \rightleftharpoons CH_3COO^- + H_2O$$

The pH of the solution remains very close to its original value. Similarly, addition of a strong acid or a strong base to an alkaline buffer ($NH_4OH + NH_4Cl$) causes the following reactions.

$$H_3O^+ + NH_4OH \rightleftharpoons NH_4^+ + 2H_2O$$

$$OH^- + NH_4^+ \rightleftharpoons NH_4OH$$

Thus in both cases, the solution will not change its pH. It should be remembered that the above considerations are applicable only when the amount of acid or base added to the buffer solution is small.

Addition of acids or alkalies to pure water or to aqueous solution of NaCl causes considerable changes in the pH values. Water and NaCl solutions are, therefore, highly unbuffered.

Calculation of pH Values of Buffers

pH of a buffer depends on the concentration of the buffer components. Consider a buffer containing a weak acid, HA and its salt Na^+A^-, ionization of weak acid may be represented as:

$$HA \rightleftharpoons H^+ + A^-$$

The ionization constant Ka, is given by

$$Ka = \frac{[H^+][A^-]}{[HA]}$$

or

$$[H^+] = Ka \, . \frac{[HA]}{[A^-]} \qquad \text{..... 3.17}$$

Now, since acid is a weak acid, it will undergo dissociation to a very small extent. In the presence of its salt which is completely dissociated, it can be assumed that the acid is not dissociated at all. Hence concentration of the ionized acid can be taken equal to the initial concentration of the acid. For the same reason, the concentration of the A^- ion can be taken approximately equal to the concentration of the salt. Thus hydrogen ion concentration from Eq. 3.17 with fair approximation is given by:

$$[H^+] = Ka \frac{[HA]}{[A^-]} \qquad \text{..... 3.18}$$

Where the terms in the brackets refer to the concentrations of the acid and the salt respectively. On taking the logarithms and reversing the signs throughout of Eq. 3.18, we get

$$-\log [H^+] = -\log Ka + \log \frac{[A^-]}{[HA]}$$

$$pH = pKa + \log \frac{[\text{conjugate base}]}{[\text{Acid}]} \qquad \text{..... 3.19}$$

This is known as *Henderson — Hasselbalch equation.* With the help of this equation, one can easily calculate the pH of the buffer solution by knowing ionization constant of the acid and the concentrations of the salt and acid. Alternatively, it can be employed to prepare solutions of desired pH values. As a rough rule, to prepare a buffer solution of given pH, we select an acid whose pKa value is very close to the pH of the buffer. We then calculate the ratio of concentration of the salt and acid to be used.

Uses of Buffer Solutions

Buffers are important in analytical chemistry and in general laboratory work. Biochemical reactions in particular require maintenance of definite pH values. Blood, milk and various animal fluids are highly buffered with bicarbonate ions and carbonic acid and with proteins. Normal human blood has a pH of about 7.4. Ordinarily variations are very small and an increase or decrease of as much as 0.4 pH unit is likely to be fatal and show pathological conditions such as diabetic, coma etc. Catalytic activity of an enzyme is maximum at a particular pH value. In the industrial field, buffers are used in the fermentation of alcohol where the pH of the solution is maintained around 6.0. Similarly they are used in electroplating, tanning of leather and manufacture of sugar where a constant pH of the medium is essential. For proper productivity of crops pH control of the soil is essential. To an acidic soil limestone is added while sulphur is added to a soil that is alkaline.

Preparing a Buffer Solution with a Specific pH

Now a question arises: How do we prepare a buffer solution with a specific pH? Henderson-Hasselbalch equation indicates that if the molar concentrations of the acid and its conjugate base are approximately equal, then

$$\log \frac{[\text{conjugate base}]}{[\text{acid}]} = 0$$

or

$$\text{pH} \approx \text{pKa}$$

Thus, to prepare a buffer solution, we choose a weak acid whose pKa is equal to or close to the desired pH. This choice not only gives the correct pH value of the buffer system, but also ensures that we have comparable amounts of the acid and its conjugate base present: both are prerequisites for the buffer system to function effectively.

Table 3.7. Ionization Constants of Some Diprotic Polyprotic and Monoprotic Acids in Water at 25°C.

Acid	Ka	Conjugate Base	Kb
H_2SO_4	very large	HSO_4^-	very small
HSO_4^-	1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
HPO_4^{2-}	4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
C_6H_5COOH	6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}

Example 3.6.

A buffer solution contains 1 mole dm^{-3} each of acetic acid and sodium acetate. Find the pH of the buffer solution. pKa of acetic acid is 4.74.

Solution

$$\text{pH} = \text{pKa} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} = 4.74 + \log \frac{1}{1}$$

$$\text{pH} = 4.74$$

Example 3.7.

How many moles of sodium acetate must be added to one dm^3 of 0.2 *M* CH_3COOH solution to make a buffer of pH 5?

(Ka for $CH_3COOH = 1.8 \times 10^{-5}$)

Solution

$$\text{pH} = \text{pKa} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$5 = -\log(1.8 \times 10^{-5}) + \log\frac{[\text{Salt}]}{2}$$

$$5 = 4.74 + \log\frac{[\text{Salt}]}{2}$$

$$5 - 4.74 = \log\frac{[\text{Salt}]}{2}$$

$$0.26 = \log\frac{[\text{Salt}]}{2}$$

$$[\text{Salt}] = 0.36 \text{ mole}$$

Example 3.8

Describe how you would prepare a "phosphate buffer" at a pH of about 7.40.

Solution

We write three stages of ionization of phosphoric acid as follows:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad pKa_1 = 2.12$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad pKa_2 = 7.21$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad pKa_3 = 12.32$$

The most suitable of the three buffer systems is $HPO_4^{2-} / H_2PO_4^-$, because the pKa of the acid is closest to the desired pH.

From the Henderson-Hasselbalch equation we write

$$\text{pH} = \text{pKa} + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$7.40 = 7.21 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.19$$

Taking the antilog we obtain

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.5$$

Thus, one way to prepare phosphate buffer with a pH of 7.40 is to dissolve dipotassium hydrogen phosphate (K_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4) in molar ratio f 1.5 : 1.0 in water. For example, we could dissolve 1.5 moles (261 g) of K_2HPO_4 and 1.0 mole (136 g) of KH_2PO_4 in enough water to make up a 1 litre solution.

Example 3.9

Describe the preparation of 100 ml of a 0.1 M phosphate buffer having pH 7.00 (pKa = 6.86).

Solution

$$\text{pH} = \text{pKa} + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$7 = 6.86 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.14$$

Taking antilog, we get

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{1.38}{1}$$

$$\text{Total} = 1.38 + 1 = 2.38$$

$$\text{Molarity of the salt } (HPO_4^{2-}) = \frac{1.38}{2.38} \times 0.1 = 0.058\ M$$

$$\text{Molarity of the acid } (H_2PO_4^-) = \frac{1}{2.38} \times 0.1 = 0.042\ M$$

$$\boxed{\text{Number of moles} = V(dm^3) \times M}$$

Number of moles of salt = 0.1 × 0.58 = 0.0058

Number of moles of acid = 0.1 × 0.042 = 0.0042

$$\boxed{\text{Weight in grams of substance} = \text{no. of moles} \times \text{molecular weight}}$$

Weight of salt = 0.0058 × 174 = 1.0092 g

Weight of acid = 0.0042 × 136 = 0.5712 g

Therefore, to prepare 100 ml of the phosphate buffer dissolve 1.0092 g of salt and 0.5712 g of acid per 100 ml of the solution.

Buffer Capacity

Buffer capacity is defined as the number of moles (b) of an acid or a base added to one litre of the solution to change the pH by unity.

$$\text{Buffer capacity} = \frac{db}{d[pH]}$$

i.e., it is absolute value of the slope of the curve between moles of the acid or base added to one litre of the solution and the pH of the solution.

Example 3.10

Calculate the pH of a buffer solution containing 0.1 *M* each of acetic acid and sodium acetate. What will be the change in pH on adding?

(*a*) 0.01 *M* of HCl to litre of solution?

(*b*) 0.01 *M* of NaOH to litre of solution?

(pKa of $CH_3COOH = 4.745$)

$$pH = pKa + \log\frac{[\text{sodium acetate}]}{[\text{acetic acid}]}$$

$$pH = 4.745 + \log\frac{0.1}{0.1}$$

$$pH = 4.745$$

(*a*) When we add 0.01 *M* of HCl to a litre of this solution, hydrogen ions from HCl will react with acetate ions to form unionized acetic acid. Therefore, the concentration of CH_3COO^- ions decreases by 0.01 *M* and that of CH_3COOH increases by 0.01 *M*. The concentrations become,

$$[CH_3COO^-] = 0.1 + 0.01 = 0.09 \text{ M}$$

$$[CH_3COOH] = 0.1 - 0.01 = 0.11 \text{ M}$$

$$pH = 4.745 + \log\frac{0.09}{0.11}$$

$$pH = 4.745 - 0.087 = 4.658$$

The change in pH is only -0.087

(*b*) On adding 0.01 *M* of NaOH to a litre of the solution, acetic acid will react with OH^- ions to give acetate ions. The concentrations are now

$$[CH_3COO^-] = 0.1 + 0.01 = 0.11\ M$$

$$[CH_3COOH] = 0.1 - 0.01 = 0.09\ M$$

$$pH = 4.745 + \log\frac{0.11}{0.09}$$

$$pH = 4.745 + 0.087 = 4.832$$

The change in pH is only 0.087

Example 3.11

When 0.01 moles of NaOH are added to a buffer solution, its pH changes from 4.745 to 4.832. What is its buffer capacity?

Solution

$$\text{Buffer capacity} = \frac{\text{No. of moles of alkali added per litre}}{\text{Change in pH}}$$

$$= \frac{0.01}{0.087} = 0.115$$

3.15 INDICATORS

Broadly defined, an indicator is a substance which is used for the visual detection and determination of a specific constituent present in any sample. The visual observation used is primarily that of color, but observation of fluorescence and turbidity are also used. Indicators under this general definition include all reagents which can be used in colorimetry, fluorimetry and turbidimetry. It is convenient, therefore, to define an indicator in a more limited way, as substance which is used for visual detection of the completion of a particular reaction that is for the end point of a titration. The choice of an indicator depends upon the nature of the reaction under observation. There are three different types of the indicators used:

1. Acid- base indicators
2. Redox indicators
3. Adsorption/Precipitation indicators

1. Acid – Base Indicators

Acid – base indicators are organic substances which have one color in acid solution while an altogether different color in alkaline solution. In acid – alkali titrations. the equivalence point is detected by the use of an acid-base indicator. The actual color that it produces in solution depends on the pH of the solution. The change in the color of the indicator is not sudden and abrupt but takes place in small pH range. This pH range is called the "color change interval" of the indicator. Let us examine briefly how acid-base indicators work.

(i) *Ostwald Theory*: The first attempt in the theory of indicators was made by Ostwald. The acid-base indicators are regarded as weak organic acids or bases. The unionized form of the acid indicator HIn or the basic indicator InOH had one color and the corresponding ionized form had another cooler. The ionization equilibrium in aqueous solutions may be written as

$$HIn + H_2O \longrightarrow H_3O^+ + In^-$$

And

$$InOH \xrightarrow{H_2O} OH^- + In^+$$

Let us apply the law of mass action to the ionization equilibrium of an acid indicator HIn. The ionization constant of the indicator is given by

$$K_{ind} = \frac{[H_3O^+]\,[In^-]}{[HIn]}$$

Or
$$[H_3O^+] = K_{ind}\frac{[HIn]}{[In^-]}$$

$$[H_3O^+] = K_{ind}\frac{[\text{unionized form}]}{[\text{ionized form}']} \qquad \text{-------3.20}$$

In acid solution presence of excess of H_3O^+ ions will suppress the ionization of the acid indicator and $[In^-]$ will be small. The cooler will therefore be mainly due to the unionized form HIn. ON the other hand, in alkaline solutions the ionization equilibrium is shifted to the right increasing the concentration of ionized form In^-. Hence in alkaline medium the indicator will exist mainly in the ionized form and the color of the ionized form becomes apparent.

The actual color of the indicator depends on the ratio of the concentration of the ionized and unionized forms, and is thus directly related to the hydrogen ion concentration of the medium. Equation (3.20) may be rewritten as

$$pH = pK_{ind} + \log\frac{[In^-]}{[HIn]} \qquad \text{.......3.21}$$

For a base indicator, an exactly analogous expression may be deduced and can be written as

$$pOH = K_{ind}\frac{[InOH]}{[In^+]} \qquad \text{.......3.22}$$

At any given pH of the solution, both forms of the indicators will be present. It is important to realize that the human eye has a limited ability to detect either of the two colors when one of the two predominates. In general, when $\frac{[HIn]}{[In^-]} = 10$, equation (3.20) reduces to

$$pH = pK_{ind}{}^{-1}$$

And the color of the solution will appear to be due to the unionized form. On the other hand, when the ratio of $\frac{[In^-]}{[HIn]} = 10$, equation (3.20) reduces to

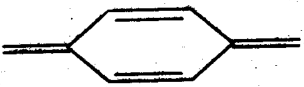
$$pH = pK_{ind} + 1$$

and the color in alkaline solution will be due to in$^-$. The color change interval is accordingly given by

$$pH = pK_{ind} \pm 1 \qquad \text{.......3.23}$$

and extends over approximately two pH units one above and one below the pK value of the indicator. Within this range, the indicator changes its color from one form to another. The change will be gradual as if depends on the logarithm of the ratio of the concentration of the two colored forms (unionized and ionized forms). When the pH of the solution is equal to the ionization constant of the indicator, $pK_{ind.}$ the ratio $\frac{[HIn]}{[In^-]}$ becomes unity and the indicator will have a color due to an equimolar mixture of the acid and base forms. This is sometimes called as the "*middle tint*" of the indicator. This applies strictly if the two colors are of equal intensity.

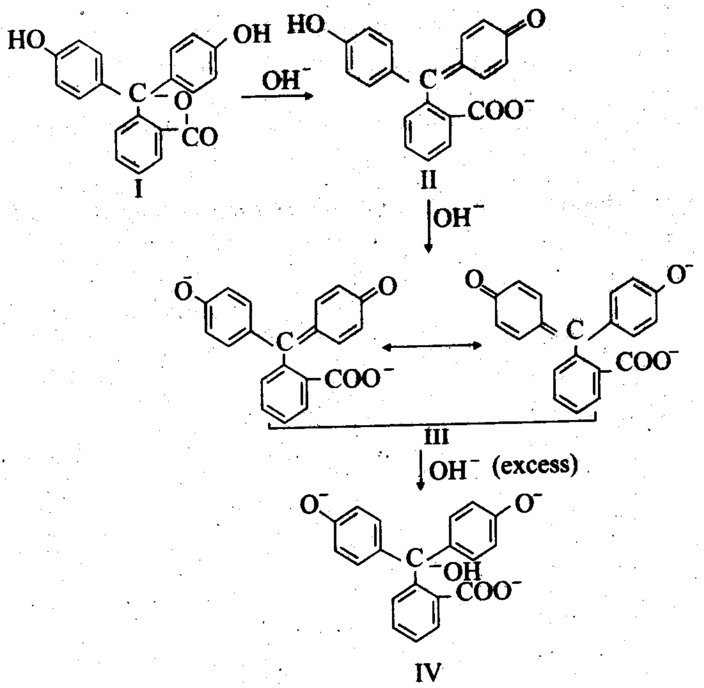
(ii) *Quinonoid Theory*. The color in most of the naturally occurring organic compounds has been attributed to be due to the presence of quinonoid structure.



Quinonoind structure

(Colored)

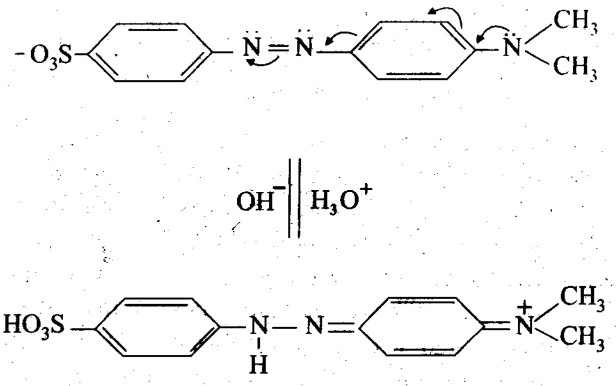
A theory called quinonoid theory based on this observation was put forward to explain the change in color of indicators with pH. According to this theory, the color changes are believed to be due to structural changes including the production of the quinonoid and resonating forms. This may be illustrated by reference to phenolphthalein where (I) represents the structure of phenolphthalein which in the presence of dilute alikali changes to structure (II),. This monoanion then yields a red resonating dianion (III). If phenolphthalein is treated with excess of concentrated alkali the red color first produced disappear owing to the formation of carbinol form (VI).



Similarly, the two forms of methyl orange are:

Methyl orange in presence of alkali

(Non quinonoid structure — yellow)



Methyl orange in presence of acids

(Quinonoid structure — red)

Table 3.8 contains a selected list of some indicators along with their colour change intervals.

Table 3.8 Some Indicators and their characteristic pH ranges

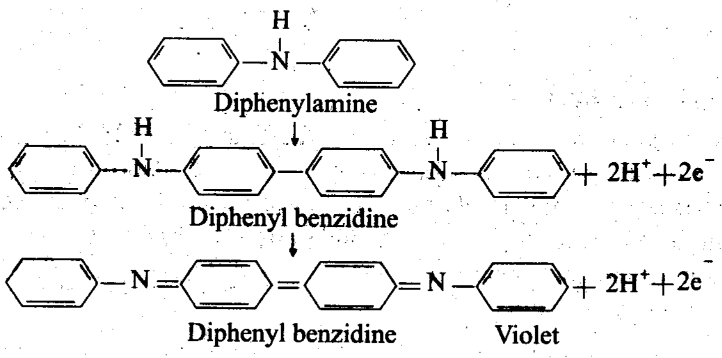
Indicator pH range		Color in	
		Acidic solution	Alkaline solution
Cresol red	0.2-1.8	Red	Yellow
m—cresol purple	1.2-2.8	Red	Yellow
Methyl orange	3.1-4.4	Red	Orange
Methyl red	4.2-6.3	Red	Yellow
Phenol red	6.8-8.4	Yellow	Red
Cresol red	7.2-8.8	Yellow	Red
Thymol blue	8.0-9.6	Yellow	Blue
Phenolphthalein	8.3-10.0	Colorless	Red
Alizarin yellow	10.1-12.1	Yellow	Orange red

By suitably mixing certain indicators the color change may be made to extend over a considerable pH range. Such a mixture is known as "*universal indicator*". These are mostly employed for determining the approximate pH of solutions. One such indicator is a mixture of methyl red, methyl orange, bromothymol blue and phenolphthalein. It covers a pH range of 3-11 and gives color changes at different pH values as shown below.

pH	3	4	5	6	7	8	9	10	11
Color	Red	Orange	Orange	Yellow	Yellowish green	Greenish blue	Blue	Violet	Reddish violet

2. Redox Indicators

A redox indicator is a substance which exhibits different colors in the oxidized and reduced forms. At any instant, the color intensity would depend upon the relative amounts of the two forms. Whenever a small amount of such indicator is placed in another redox system is comes to equilibrium in which its oxidation-reduction potential is the same as that of the system. The potential of the indicator can be estimated from its color and thus indirectly gives the potential of the system, For an indicator to be suitable for any oxidation-reduction reaction, its standard redox potential should coincide with the equivalence point of the titration or at least it should be somewhere in the region of the rapidly changing potential of the titration system. If it is not so, it is achieved by manipulating the reactions. One of the most common examples of such an indicator is the use of diphenylamine in the titration of Fe^{2+} by dichromate ion in the acidic solution. Diphenylamine, in the form of its soluble sulphonic acid, at first gets oxidized to diphenylbenzidine which ultimately gets oxidized to diphenylamine violet.



The color change from colorless to violet (with green as possible intermediate) occurs at a potential of about 0.75 volts. The standard redox potential for Fe^{2+} — Fe^{3+} and $Cr_2O_7^{2-}$ — Cr^{3+} couples in acidic medium are 0.78 and 1.2 volts respectively. Thus, a suitable indicator is expected to have standard potential of about 0.95 volts. It would thus appear that diphenylamine would not be a suitable indicator for the said titration. In actual practice, the titration is carried out in the presence of phosphoric acid or a fluoride; these substances form complex ions with the ferric ions with the result that the effective standard potential of ferrous-ferric pair gets lowered to about 0.5 volts. This results into a change of potential from 0.6 to 1.1 volts in the vicinity of equivalence point, and hence making diphenylamine to suffer a color change very near to the equivalence point at a potential of 0.75 volts.

For practical purposes, such indicators have been classified into two categories; those having low potentials viz 0.3 to — 0.5 volts in neutral solutions, and those having high positive values for standard pontentials. The former being useful in the biological work, while the latter one's are employed in the volumetric analysis. A few of the redox indicator used in the biological work are summarized in the following Table 3.9

Table 3.9 Redox indicators for biological work

Indictor	E° (volts)
m-Bromophenol indophenol	+0.248
Toluylene blue	+0.115
Cresyl blue	+0.047
Methylene blue	+0.011
Indigo trisulphonate	-0.081
Cresyl violet	-0.173
Neutral red	-0.325
Methyl viologen	-0.445

3. Adsoption Indicators

These indicators were introduced by K. Fajans in 1923-24 for the detection of end point, as a result of vigorous studies on the nature of adsorption. The action of these indicators is based upon the simple fact that at end point, the indicator gets adsorbed by the precipitate and during the process of adsorption; a change in color of the indicator will take place which may result in substance of different color. They are, therefore, termed as adsorption indicators.

Commonly used indicators for titrations of chloride against silver nitrate are:

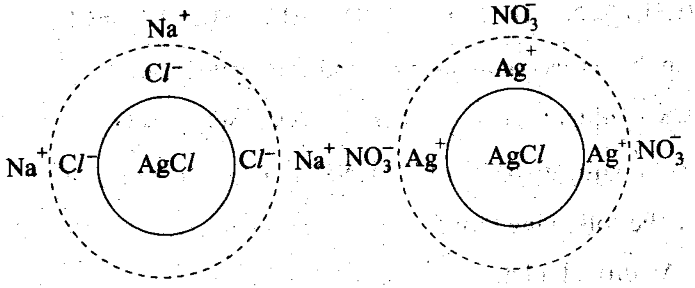
(i) **Fluorescein:** It is a suitable for very dilute solution of chloride with silver nitrate in neutral or fainty acidic solution. At the end point there is sudden change of white precipitate in greenish yellow medium to distinctly red.

(ii) **Dichlorofluorescein:** It is a suitable indicator for every dilute solution of chloride (say drinking water) and works even in the presence of acetic acid and weakly acid solution. The end point is from yellowish green to red.

(iii) **Eosin:** It is employed for titration of bromide and iodide with silver nitrate (from burette) in the presence of acetic acid. The end point is the change from pink `to reddish violet. The halide solution should be diluted to 100 ml.

(iv) **Di-iodo diethyfluorescein:** It is a better indicator for the determination of iodides. The solution of the iodide should be diluted to 100 ml before adding the indicator. It works in neutral or weakly acid medium. End point is change of orange red to blue red when an iodide is titrated with silver nitrate (from burette).

Theory of adsorption indicator: The theory is based upon the phenomenon of adsorption. When a chloride solution is treated with a solution of silver nitrate, the precipitated silver chloride adsorbs chloride ion (as they are in excess). This is called primary adsorbed layer. It will hold secondly adsorbed oppositely charged ions (say Na^+or K^- or NaCl or KCl) present in solution. As soon as the end point is reached, Ag^- ions are present which are now primarily adsorbed and NO_3^- ions will be held by secondary adsorption. Suppose sodium salt of fluorescein is used as an indicator, the negative fluoresceinate ion, which is now much more strongly adsorbed than the nitrate ion is immediately adsorbed which will show itself on the precipitate not by its own color, which is that of the solution, but by the formation of a pink complex of silver and a modified fluorescenate ion on the surface with the first traces of excess of silver ions.



Questions

Q.1. What is Arrhenius concept of an acid and a base? Illustrate your answer with examples. What are limitations of this concept?

Q.2. In spite of its limitations, the Arrhenius theory of acid-base behaviour satisfactorily explains the acid-base reactions in aqueous solutions. Why?

Q.3. Write a short note on Lowry-Bronsted acid-base theory.

Q.4. Give a comparative account of Lowery-Bronsted and Lewis concepts of acids and bases. Also discuss its merits and limitations.

Q.5.(*a*) Discuss the Lewis concept of acids and bases. Discuss its advantages and limitations.

(*b*) Classify the following giving reasons, as Lewis acids and Lewis bases:

BF_3, $(CH_3)_3N$, S^{2-}, H^+, NH_3, Al^{3+}, O^{2-}, $AlCl_3$, H_2O, F^-, $SnCl_4$.

Q.6.(*a*) Explain the terms conjugate acid and conjugate base.

(*b*) Give the conjugate acids of H_2O, Cl^-, NH_3, SO_4^{2-}, CO_3^{2-}, I^-, OH^- and HCO_3^-.

(*c*) Give the conjugate bases of H_2O, NHO_3, HI, HCl, NH_4^+, HCO_3^-, OH^- and HS^-.

Q.7.(*a*) Define the following terms:

(*i*) Acidity of a base

(*ii*) Basicity of an acid

(*iii*) Amphiprotic species

(*iv*) Conjugate acid and base pair

(*b*) Arrange the following ions in the increasing order of their basic nature.

CH_3^-, OH^-, NH_2^-, F^-

Q.8. What is meant of solvent system definition of the acid-base behaviour? Discuss its merits and limitations.

Q.9. What is the Lux-Flood system of acids and bases? How is it superior or inferior, to the Lowry-Bronsted concept?

Q.10. Write a short note on the Usanovich concept of acids and bases.

Q.11.(*a*) What is Pearson's hard and soft acid and base concept?

(*b*) What are the characteristics of a hard acid and a hard base? What are the characteristics of a soft acid and a soft base?

Q.12.*(a)* Define the following by giving suitable examples.

(i) Soft acid *(ii)* Soft base *(iii)* Hard acid *(iv)* Hard base.

(b) Discuss the principles underlying SHAB concept.

Q.13.*(a)* What are class (a) and class (b) metal ions and ligands. How are they related to hard and soft acids and bases?

(b) Discuss various applications of SHAB theory.

Q.14.*(a)* What is the hard and soft acid-base principle? How does this principle explain the stability of the complexes and reaction rates?

(b) Classify the following as hard or soft acid or base giving reasons.

Na^+, K^+, Cu^+, Ag^+, CO_3^{2-}, NO_3^-, ClO_4^-, NH_3, I, H^-

Q.15.*(a)* How are the relative strengths of acids and bases determined?

(b) What do you understand by "leveling effect" of solvent?

Q.16.*(a)* With the help of SHAB principle explain which is more stable and why?

(i) $[Cd(NH_3)_4]^{2+}$ or $[Cd(CN)_4]^{2-}$

(ii) $[AgF_2]^-$ or $[AgI_2]^-$

(iii) $[CoI_6]^{3-}$ or $[CoF_6]^{3-}$

(iv) $[Ag(CN)_2]^-$ or $[AgCl_2]^-$

(b) Arrange in the ascending order of acid strength

H_2SO_4, HCl, HBr, $HClO_4$, HNO_3

Q.17.*(a)* Arrange the species in the following groups in the order of decreasing basicity:

(i) F^-, OH^-, CH_3^- *(ii)* HF, H_2O, NH_3

(iii) H_2S, HS^-, S^{2-} *(iv)* F^-, Cl^-, Br^-, I^-

(v) NH_3, NH_2^- *(vi)* H_3O^+, H_2O, OH^-

Hint: The base strength decreases with *(i)* increasing size of the atom *(ii)* increasing electronegativity of the element and *(iii)* decreasing negative charge on the ion.

(b) Which is the stronger acid of each pair?

(i) H_3O+ or H_2O *(ii)* NH_4^+ or NH_3

(iii) H_2S or HS^- *(iv)* H_2O or OH^-

Q.18. Comment on the statement, "Usanovich concept of acids and bases is like a synthesis of many acid-base theories.

19. Arrange the following in order of increasing acidity:

(i) HF, HBr, HCl, HI

(ii) $HClO, HClO_2, HClO_3, HClO_4$

(iii) HIO, HIO_2, HIO_3, HIO_4

(iv) HOBr, HOCl, HOI

(v) $HClO_3, HBrO_3, HIO_3$

(vi) $HNO_3, HPO_3, HAsO_3$

(vii) $H_2SO_4, H_2SeO_4, H_2TcO_4$

(viii) $H_2SiO_4, H_3PO_4, H_2SO_4, HClO_4$

Hints: 1. For a series of oxyacids derived from the elements within a group, in which the central atoms have identical oxidation stacks, the first member is the strongest acid. As we move down a group the size of the central atom increases and the ratio of charge to size (ionic potential) decreases, resulting in less ready dissociation of the OH bonds in the oxyacids. In other words the acid strength increases with increase in electronegativity of the central atom

$$HOCl > HOBr > HOI^-$$

2.For a given element an increase in the oxidation number of the central atom X increases the acidity:

$$\begin{array}{cccccc} < & HOClO & < & HOClO_2 & < & HOClO_3 \\ & +3 & & +5 & & +7 \end{array}$$

3.The relative strength of an oxyacid can be predicted on the basis of the ratio of the oxidation number of the central atom to the number of atoms bonded to that element. the higher this ratio, the stronger is the acid.

$$\begin{array}{lccccccc} & H_2SiO_4 & < & H_3PO_4 & < & H_2SO_4 & < & HClO_4 \\ \text{Ratio:} & 4/4 & & 5/4 & & 6/4 & & 7/4 \end{array}$$

Q.20. Explain the relationship between acid-base equilibria and redox reactions.

Q.21.*(a)* Briefly discuss the significance of pH value. How is it accurately determined? Define negative pH.

(b) Calculate the pH of the following solutions:

(i) 0.002 *M* HCl

(ii) Pure water at 25°C, $Kw = 1 \times 10^{-14}$

(iii) 0.015 *M* NaOH

(iv) 0.1 *M* NH_4OH $(Kb = 1.8 \times 10^{-5})$

(*v*) 0.01 M CH_3COOH ($Ka = 1.8 \times 10^{-5}$)

(Ans: 2.699, 7, 12.85, 11.13, 3.37)

Q.22. A sample f blood has the pH value of 7.4. What is the hydrogen ion concentration in it? (Ans. 3.98×10^{-8} *M*)

Q.23.(*a*) What are buffers? How do they resist changes in their pH values?

(*b*) Write down some applications of buffers.

Q.24.(*a*) What is Henderson-Hasselbadch equation? Briefly discuss its significance.

(*b*) What is buffer capacity? Write some applications of pH value.

Q.25.(*a*) Find the pH of a buffer solution containing 0.20 mole per litre CH_3COONa and 0.15 mole per litre CH_3COOH. Ka for $CH_3COOH = 1.8 \times 10^{-5}$. (Ans. 4.86)

(*b*) Calculate pH, pOH, $[H_3O^+]$ and $[OH^-]$ for 0.01 M HNO_3 solution.

(Ans. pH = 2, pOH = 12, $[H_3O^+] = 1.9 \times 10^{-2}$, $[OH^-] = 1.9 \times 10^{-12}$)

Q.26. Describe the relationship between redox reactions and acid-base reaction.

Q.27. (*a*) What are indicators? Discuss various theories of acid-base indicators.

(*b*) Write a short note on redox and adsorption indicators.

Q.28. Justify / comment on the following statements:

(*a*) H_2O is an amphiprotic species.

(*b*) HCO_3^- is a Bronsted-Lowry acid.

(*c*) NH_4^+ is a conjugate acid of HSO_4^-.

(*d*) Cu^{2+} is a Lewis acid.

(*e*) Lewis concept is more general than Bronsted-Lowry concept.

(*f*) Usanovich concept is a synthesis of all acid-base theories.

(*g*) Ag^+ is a hard acid while K^+ is a soft acid.

(*h*) NH_3 is a soft base while H^- is a hard base.

(*i*) $[CoF_6]^{3-}$ is more stable than $[CoI_6]^{3-}$.

(*j*) The order of acidity of hydracids of group VIA is

$H_2S > H_2O > H_2Te > H_2Sc$

(*k*) Acid-base and redox reactions are the same thing.

(*l*) Buffers maintain their pH constant.

(*m*) The pH of 0.05 *M* HNO_3 is 5.6

(*n*) NH_4^+ is a stronger acid than NH_3.

(*o*) $HClO_3$ is stronger than $HClO_4$.

(*p*) HOCl is stronger than HOBr.

Chapter Four

ESSENTIALS OF CHEMICAL ANALYSIS AND EVALUATION OF ANALYTICAL DATA

4.1 THE LAW OF MASS ACTION

This law was first enunciated by C.M. Guldberg and P. Waage in 1864 and helps us to find the relations among the concentrations of reactants and products at equilibrium in chemical reactions. This law states that at constant temperature, the rate of a chemical reaction is proportional to the active masses of the reacting substances.

The term *active mass* of a reactant is the effective concentration of a reactant or its activity (a) which is related to concentration (c) as:

$$a = fc$$

The factor, f is called the activity coefficient of the substance. For ordinary systems like gases at low pressures or dilute solutions which do not deviate appreciably from ideal behaviour, $f = 1$ and hence $a = c$, i.e., the active mass may be replaced by molar concentration. It is generally represented by enclosing the formula of the reactant in square brackets. For example, [A] stands for the active mass of A.

To illustrate this law let us consider a simple reversible reaction occurring in a homogeneous system at a given temperature. Let one mole of A reacts with one mole of B to produce one mole each of L and M as indicated by the reaction.

$$A + B \rightleftharpoons L + M$$

According to the law of mass action, the rate of the forward reaction will be proportional to the molar concentration of A and B.

$$\text{Rate of forward reaction} \propto [A]\,[B]$$

or $$\text{Rate of forward reaction} = K_f\,[A]\,[B] \qquad \text{..... 4.1}$$

Where K_f is a proportionality constant and depends on temperature and nature of reactants. Similarly the rate of reverse reaction would be proportional to the molar concentration of L and M.

$$\text{Rate of reverse reaction} \propto [L]\,[M]$$

or $$\text{Rate of reverse reaction} = K_r\,[L]\,[M] \qquad \text{..... 4.2}$$

At equilibrium, the two rates must be equal. Hence,

$$K_f\,[A]\,[B] = K_r\,[L]\,[M]$$

$$\frac{K_f}{K_r} = \frac{[L]\,[M]}{[A]\,[B]}$$

or $$K_c = \frac{[L]\,[M]}{[A]\,[B]} \qquad \text{..... 4.3}$$

Where $K_c = \frac{K_f}{K_r}$ is known as *equilibrium constant* of the reaction and is defined as the ratio of the product of the molar concentration of the products to that of the reactants. The subscript c indicates that the equilibrium condition is expressed in terms of the concentration units, i.e., moles per dm^3 of the various species.

If we consider a process involving more than a single molecule of each of the reactants and products, then the rate is proportional to the product of the molar concentration of each reacting substance raised to a power equal to the number of molecules of the substance participating. Let us now consider a more general reaction of the type

$$aA + bB + \ldots.. \rightleftharpoons l\,L + mM + \ldots..$$

where a, b, ... represent the stoichiometric coefficients of the reactants A, B, ... and l, m, ... are the stoichiometric coefficients of the products L, M, ... etc.

At equilibrium

$$K_f\,[A]^a\,[B]^b \ldots.. = K_r\,[L]^l\,[M]^m \ldots..$$

or $$\frac{K_f}{K_r} = \frac{[L]^l\,[M]^m \ldots..}{[A]^a\,[B]^b \ldots..}$$

or $$K_c = \frac{[L]^l\,[M]^m \ldots..}{[A]^a\,[B]^b \ldots..} \qquad \text{..... 4.4}$$

The value of K_c is independent of the molar concentration of the reactants and products but changes only with changes in temperature. Equation 4.4 is a mathematical representation of Law of Chemical Equilibrium.

In case of reactions involving gases, it is sometimes more convenient to express the concentrations of gases in terms of their partial pressures at any given temperature. Let P_A, P_B, P_L and P_M etc. are the partial pressures of the gaseous species, then the equilibrium constant, K_p may be expressed as

$$K_p = \frac{P_L^{\,l} - P_M^{\,m} \ldots\ldots}{P_A^{\,a} - P_B^{\,b} \ldots\ldots} \qquad \ldots\ldots 4.5$$

If the concentrations are expressed in terms of mole fractions, then the equilibrium constant, K_X, is represented as

$$K_X = \frac{(X_L)^l \, (X_M)^m \ldots\ldots}{(X_A)^a \, (X_B)^b \ldots\ldots} \qquad \ldots\ldots 4.6$$

Significance of Equilibrium Constant

Knowledge of the equilibrium constant is a valuable asset to the chemist and chemical engineer chiefly for two reasons, viz.,

(i) It enables one to tell roughly, at a glance, the extent to which a reaction will proceed before equilibrium is reached.

(ii) It enables one to calculate equilibrium concentration if the starting concentrations are known.

Applications of Law of Mass Action

The law of mass action can be applied to

1. The dissociation of weak electrolytes
2. The solubility of sparingly soluble salts.

1. The Dissociation of Weak Electrolytes

Weak electrolytes are the substances that ionize to a very small extent in aqueous solution, *e.g.*, CH_3COOH, NH_4OH etc. The Arrhenius theory of electrolytic dissociation assumes a dynamic equilibrium between ions and unionized molecules. The law of mass action can also be applied to equilibrium involving ions in the same manner as was done in chemical equilibrium. The application of the law of mass action to the weak electrolytes was first attempted by Ostwald (1888) and the equation deduced by him is known as *Ostwald's dilution law.*

Consider a binary electrolyte AB which dissociates into charged ions A^+ and B^- according to the equation.

$$AB \rightleftharpoons A^+ + B^-$$

Applying the law of mass action we get

$$K_a = \frac{[A^+]\,[B^-]}{[AB]} \qquad \ldots\ldots 4.7$$

Let 'α' be the degree of ionization and 'c' the total concentration of the electrolyte in moles per dm^3. Then at equilibrium, the concentrations of the various species would be

$$[A^+] = \alpha c$$

$$[B^-] = \alpha c$$

$$[AB] = c(1 - \alpha)$$

Where [AB] represents the concentration of unionized molecule. On substituting these values in equation 4.7, we get

$$K_a = \frac{\alpha c \times \alpha c}{c(1 - \alpha)}$$

$$K_a = \frac{\alpha^2 c}{(1 - \alpha)} \qquad \ldots\ldots 4.8$$

Equation 4.8 is the mathematical representation of the Ostwald's dilution law. The equilibrium constant K_a for the reaction involving ions is called the *ionization constant* of the electrolyte. It is constant at a given temperature.

If one mole of the electrolyte is dissolved in a volume 'V' dm^3 of the solution, then

$$V = \frac{1}{c} \qquad \text{(V is called the dilution of the solution)}$$

Then equation 4.29 can also be written as

$$K_a = \frac{\alpha^2}{(1 - \alpha)V} \qquad \ldots\ldots 4.9$$

For weak electrolytes $\alpha << 1$ so that $1 - \alpha \approx 1$.

✧ $$K_a = \frac{\alpha^2}{V}$$

or $$\alpha = \sqrt{K_a \cdot V}$$

or $$\alpha \propto \sqrt{V}$$

In other words, the degree of ionization for weak electrolytes is proportional to the square root of dilution.

2. Solubility of a Sparingly Soluble Salt or Solubility Product

In a saturated solution of a sparingly soluble salt, a dynamic equilibrium exists between the insoluble salt and its dissociated ions. For example, a salt like

AgCl when added to water, a small amount of it goes into the solution yielding Ag^+ and Cl^- ions and the rest remains as excess solid. Solid AgCl is thus in equilibrium with Ag^+ and Cl^- ions. The equilibrium may be represented as

$$AgCl_{(solid)} \rightleftharpoons AgCl_{(solution)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

for which we can write

$$K = \frac{a_{Ag^+} \cdot a_{Cl^-}}{a_{AgCl}}$$

By convention the activity of solid AgCl is taken as unity and hence we can write

$$K \cdot a_{AgCl} = a_{Ag^+} \cdot a_{Cl^-}$$

or $$K_{sp} = a_{Ag^+} \cdot a_{Cl^-} \qquad \text{..... 4.10}$$

Where K_{sp} is known as the *solubility product* or *solubility product constant* of AgCl and is defined as the product of the activities of the ions in a saturated solution of a sparingly soluble salt. Since the salt is sparingly soluble and the solution is dilute, hence the activities of the ions may be replaced by the corresponding concentration terms. Equation 4.31 then can be written as

$$K_{sp} = [Ag^+]\,[Cl^-] \qquad \text{..... 4.11}$$

The value of K_{sp} for particular solubility equilibrium is constant at a given temperature. The product $[Ag^+]\,[Cl^-]$ in the above expression is also called the *ionic product.*

Now let us consider the dissolution of sparingly soluble CaF_2 in water

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

The K_{sp} for CaF_2 is given by .

$$K_{sp} = [Ca^{2+}]\,[F^-]^2 \qquad \text{..... 4.12}$$

Hence the solubility product constant is equal to the product of the concentration of the ions present in a saturated solution each raised to a power equal to its stoichiometric coefficient, in the balanced chemical equation.

A saturated solution exists only when the ionic product is equal to or greater than K_{sp}. When the ionic product is less than K_{sp}, the solution is unsaturated because more of the salt can be dissolved in order to raise the concentration of the ions to the point where the ionic product equals K_{sp}. When the ionic product exceeds K_{sp}, a supersaturated solution exists and hence the precipitation will occur.

4.2 SOLUBILITY PRODUCT PRINCIPLE

The solubility product principle states that the product of the ionic concentrations in a saturated solution of a sparingly soluble salt is constant at a given temperature.

As stated earlier that when a sparingly soluble salt is dissolved in water, it dissociates to give separate cations and anions. As the concentration of the ions increases in the solution, they collide and reform the solid phase. Ultimately, a dynamic equilibrium is established between the solid phase and the cations and anions in solution. At equilibrium the solute continues to dissolve at a rate that exactly matches the reverse process, the return of the solute from the solution. Now the solution is said to be saturated. A saturated solution is a solution in which the dissolved and undissolved solute is in equilibrium.

The solubility products of AgCl, Ag_2CrO_4, As_2S_3 and CaF_2 which dissociate as follows are:

$$AgCl \rightleftharpoons Ag^+ + Cl^- \qquad K_{sp} = [Ag^+][Cl^-]$$

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-} \qquad K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$As_2S_3 \rightleftharpoons 2As^{3+} + 3S^{2-}; \qquad K_{sp} = [As^{3+}]^2[S^{2-}]^3$$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-; \qquad K_{sp} = [Ca^{2+}][F^-]^2$$

where K_{sp} is called the ***solubility product constant*** or simply ***solubility product***. Solubility products of some salts are given in Table 4.1.

Table 4.1. Solubility Product for Some Sparingly Soluble Salts at 298K

Salt	K_{sp}	Salt	K_{sp}
$PbCl_2$	1.6×10^{-5}	$Fe(OH)_3$	4.5×10^{-37}
Hg_2Cl_2	2.0×10^{-18}	$Al(OH)_3$	2.0×10^{-33}
AgCl	1.6×10^{-10}	$Mn(OH)_3$	4.5×10^{-14}
AgBr	5.0×10^{-13}	$Mg(OH)_2$	1.2×10^{-11}
AgI	1.5×10^{-16}	$BaSO_4$	1.5×10^{-9}
CuS	8.6×10^{-36}	$PbSO_4$	1.7×10^{-8}
CdS	3.6×10^{-28}	$SrSO_4$	2.5×10^{-7}
AgS	1.6×10^{-54}	Ag_2CrO_4	9.0×10^{-12}
PbS	7.0×10^{-27}	$PbCrO_4$	1.8×10^{-14}
CoS	3.0×10^{-26}	PbC_2O_4	2.7×10^{-11}
NiS	2.0×10^{-21}	$ZnCO_3$	1.4×10^{-11}
ZnS	1.2×10^{-23}	PbI_2	7.1×10^{-7}

Relation between Solubility and Solubility Product

The solubility of a sparingly soluble salt such as AgCl may be defined as the moles of the solid AgCl which dissolve per litre of solution to reach the equilibrium with excess solid.

For a salt like AgCl, if S is the solubility expressed in moles per litre then the $[Ag^+]$ and $[Cl^-]$ ions are equal to S. hence the solubility product is given by

$$K_{sp} = [Ag^+]\,[Cl^-]$$

or $$K_{sp} = [S]\,[S] \qquad [Ag^+] = [Cl^-] = [S]$$

or $$K_{sp} = S^2$$

or $$S = \sqrt{K_{sp}} \qquad \text{..... 4.13}$$

Thus the solubility of a sparingly soluble salt like AgCl is always equal to the square root of solubility product.

For CaF_2,

$$[Ca^{++}] = S, \quad [F^-] = 2S \quad \text{and therefore}$$

$$K_{sp} = [S]\,[2S]^2$$

$$= 4S^3$$

or $$S^3 = \frac{K_{sp}}{4}$$

or $$S = \sqrt[3]{\frac{K_{sp}}{4}} \qquad \text{..... 4.14}$$

Determination of Solubility Product

Solubility product of a salt can be determined from the measurement of solubility. Solubilities of sparingly soluble salts can be measured from conductance potentiometric or colorimetric measurements.

Applications of Solubility Product

The concept of solubility product is helpful in explaining precipitation phenomenon in analytical chemistry. The important applications of solubility product are described as under:

1. Determination of Solubility

Knowing solubility product, the solubility of a sparingly soluble salt can be calculated using equation 4.34.

2. Precipitation of Salts

A substance will start precipitating as soon as the ionic product becomes greater than its solubility product. Knowing the solubility product of a salt, it is possible to predict whether, on mixing the solutions of its ions, precipitation will occur or not. This principle is of immense use in qualitative and gravimetric analysis, for the precipitation of cations or anions by adding sufficient amounts of the reagent. For example:

(a) In most of the industrial processes we get a mixture of soluble constituents which can not be separated in pure form by crystallization. In the saturated solutions of such mixtures, a salt having one ion common with the salt to be precipitated is added. Thereby the ionic product of the salt becomes greater than its solubility product. Hence it gets separated out. This process is known as *salting out.*

(b) Sodium chloride from aqueous solution is precipitated by passing HCl gas through it. HCl increases the Cl^{-} ion in the solution. Ionic product exceeds the solubility product of NaCl which precipitates out in the pure form.

The same principle is used in the precipitation of soaps. Soaps are sodium salts of higher fatty acids. Addition of NaCl increases the Na^+ ions concentration and hence the ionic product exceeds the solubility product of the soap which is separated out.

(c) In quantitative estimation of various ions by gravimetric method, e.g., of Ag^+ as AgCl the addition of excess of precipitating reagent (KCl) is recommended in order to keep the ionic product of the salt greater than its solubility product.

3. In Qualitative Analysis

The division of the cations in six groups in salt analysis is based on the principle of solubility product. In the first group solubility products of chlorides of Hg_2^{2+}, Ag^+ and Pb^{2+} are sufficiently low. On adding HCl in the mixture solution, the solubility products of AgCl, Hg_2Cl_2 and $PbCl_2$ are exceeded and they get precipitated while others remain in the solution.

In group II, cations are precipitated as sulphides by passing H_2S through their solutions containing dil. HCl (0.2 — 0.3N). In such a solution ionization of H_2S is suppressed by HCl, the concentration of sulphide ions is greatly reduced and only the sulphides of second group having low solubility products are precipitated out. Sulphides of Zn group are not precipitated because of their comparatively high solubility products. These are, therefore, precipitated by H_2S in alkaline medium.

Similarly the group III cations are precipitated as hydroxides by ammonium hydroxide in the presence of excess NH_4Cl because the solubility products of the hydroxides of Al^{3+}, Cr^{3+} and Fe^{3+} are very low. If NH_4OH is added without adding NH_4Cl, the ionic product of OH^- ions from NH_4OH and the metal ions in the solution exceeds the solubility products of hydroxides of metals other than 3rd group also. Therefore, hydroxides of these metals will also get precipitated in the 3rd group. In order to check the precipitation of metal hydroxides other than those of the 3rd group metals, NH_4Cl is added which furnishes large excess of NH_4^+ ions. These exert common ion effect on dissociation of NH_4OH and decrease the concentration of OH^- ions. As a result of this only the 3rd group cations are precipitated as hydroxides.

4. Fractional Precipitation

Sometimes a mixture of ions is separated by the same precipitating agent. Their separation is brought about by the fractional precipitation which is based on the solubility product principle. For example, to an aqueous solution of KI and KCl when a solution of $AgNO_3$ is added, precipitation of AgI and AgCl will take place. From solubility product principle, one can predict which salt will precipitate first and how much of the first salt would be precipitated out when the second start precipitating. The solubility product of AgI is 1.5×10^{-16} and that of AgCl is 1.6×10^{-10}. It is evident that AgI is less soluble and will precipitate first and AgCl will precipitate only when $[Ag^+]$ is greater than

$$[Ag^+] = \frac{K_{sp}\ AgCl}{[Cl^-]} = \frac{1.6 \times 10^{-10}}{[Cl^-]}$$

and then both the salts will precipitate simultaneously.

$$\frac{[I^-]}{[Cl^-]} = \frac{K_{sp}\ AgI}{K_{sp}\ AgCl} = \frac{1.5 \times 10^{-16}}{1.6 \times 10^{-10}} = 9.8 \times 10^{-7}$$

Hence AgCl will start precipitating out when $[I^-]$ is approximately one millionth part of $[Cl^-]$, or the precipitation of I^- ion as AgI will be almost complete.

Example 4.1

Determine the solubility product of the following:

(i) AgCl if the solubility of AgCl = 1.3×10^{-5} M

(ii) $PbCl_2$ if the solubility of $PbCl_2$ = 4.448 g dm^{-3}

(iii) Ag_2CrO_4 if the solubility of Ag_2CrO_4 = 8×10^{-5} M

Solution

(i)
$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

It is obvious that one Ag^+ ion and one Cl^- ion are formed from each molecule of AgCl.

$$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}\ M$$

$$\therefore \quad Ksp = [Ag^+]\,[Cl^-]$$

$$= (1.3 \times 10^{-5})\,(1.3 \times 10^{-5})$$

$$= 1.69 \times 10^{-10}$$

(ii)
$$PbCl_{2(s)} \rightleftharpoons Pb^{2+} + 2Cl^-$$

It is obvious that for each Pb^{2+} ion two Cl^- ions are formed from each molecule of $PbCl_2$.

The concentration of $PbCl_2$ = 4.448 g dm^{-3}

Molar mass of $PbCl_2$ = 207 + 71 = 278 g mol^{-1}

$$\text{Molar concentration of } PbCl_2 = \frac{4.448}{278} = 1.6 \times 10^{-2}\ M$$

Hence $[Pb^{2+}] = 1.6 \times 10^{-2}\ M$

and $[Cl^-] = 2 \times 1.6 \times 10^{-2} = 3.2 \times 10^{-2}\ M$

$$\therefore \quad K_{sp} = [Pb^{2+}]\,[Cl^-]^2$$
$$= (1.6 \times 10^{-2})\,(3.2 \times 10^{-2})^2$$
$$= 1.638 \times 10^{-5}$$

(iii) $$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

It is evident that each molecule of Ag_2CrO_4 on dissociation, gives Ag^+ ions and one CrO_4^{2-} ion.

$$\therefore \quad K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$$
$$= (8 \times 10^{-5})^2\,(8 \times 10^{-5})$$
$$= (64 \times 10^{-10})\,(8 \times 10^{-5})$$
$$= 5.12 \times 10^{-13}$$

Example 4.2

Calculate the solubility of Mg $(OH)_2$, in moles per litre if the solubility product of $Mg(OH)_2$ is 5×10^{-12}.

Solution

The solubility equilibrium is

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

Suppose the solubility of $Mg(OH)_2$ is x, then

$$[Mg^{2+}] = x, \quad [OH^-] = 2x$$
$$K_{sp} = [Mg^{2+}]\,[OH^-]^2$$
$$5.0 \times 10^{-12} = (x)\,(2x)^2$$

or $$4x^3 = 5.0 \times 10^{-12}$$

$$x^3 = \frac{5.0 \times 10^{-12}}{4}$$

$$x = \left(\frac{5.0 \times 10^{-12}}{4}\right)^{1/3}$$

$$x = 1.08 \times 10^{-4} \text{ mole per litre}$$

Hence the solubility of Mg $(OH)_2$ is 1.08×10^{-4} moles per litre.

Example 4.3

The solubility product of $BaSO_4$ is 1×10^{-10} at 18°C. What weight of $BaSO_4$ will be dissolved in 100 ml of pure water? [Molar mass of $BaSO_4$ = 233.5].

Solution

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$\therefore \quad [Ba^{2+}] = [SO_4^{2-}]$$

Let the solubility of $BaSO_4$ in pure water be x moles per litre, then at equilibrium

$$[Ba^{2+}] = [SO_4^{2-}] = x \text{ mol / litre}$$

$$\therefore \quad K_{sp} = x^2$$

$$1 \times 10^{-10} = x^2$$

$$x = \sqrt{1 \times 10^{-10}}$$

$$= 1 \times 10^{-5} \text{ moles per litre.}$$

(∴ Solubility is weight in g of the salt per 100 ml)

Hence $$x = \frac{1 \times 10^{-5} \times 100 \times 233.5}{1000}$$

$$x = 2.34 \times 10^{-4} \text{ g}$$

Example 4.4

Calculate $[Sr^{2+}]$ required to start the precipitation of SrF_2 ($K_{sp} = 7.9 \times 10^{-11}$) from a solution that contains 0.01 *M* F^- ions.

Solution

$$K_{sp} = [Sr^{2+}][F^-]^2$$

Precipitation will start when $[Sr^{2+}][F^-]^2$ becomes equal to K_{sp}. The $[Sr^{2+}]$ to start precipitation is

$$[Sr^{2+}][0.01]^2 = 7.9 \times 10^{-11}$$

$$[Sr^{2+}] = \frac{7.9 \times 10^{-11}}{(0.01)^2} = 7.9 \times 10^{-7}\,M$$

Hence $$[Sr^{2+}] = 7.9 \times 10^{-7}\,M$$

Example 4.5

Predict whether there will be any precipitation on mixing 50 ml of 0.001 *M* NaCl solution with 50 ml of 0.01 *M* $AgNO_3$ solution. K_{sp} (AgCl) = 1.5×10^{-10}.

Solution

On mixing, the total volume becomes 100 ml.

Thus, the concentration of NaCl and $AgNO_3$ are reduced to half their values, i.e.,

$$[AgNO_3] = \frac{0.01}{2} = 0.005\ M$$

and $$[NaCl] = \frac{0.001}{2} = 0.0005\ M$$

Now $AgNO_3$ ionizes as

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

$$[Ag^+] = 0.005\ M = 5.0 \times 10^{-3}\ M$$

and $$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$[Cl^-] = 0.0005\ M = 5.0 \times 10^{-4}\ M$$

The ionic product is

$$[Ag^+][Cl^-] = (5.0 \times 10^{-3})(5.0 \times 10^{-4})$$
$$= 2.5 \times 10^{-6}$$

Thus, the ionic product is greater than K_{sp} (1.5×10^{-10}), and, therefore, precipitation of AgCl will occur.

Example 4.6

The solubility products of silver halides are:

K_{sp} (AgCl) = 1.7×10^{-10}, K_{sp} (AgBr) = 5.0×10^{-13} and

K_{sp} (AgI) = 8.5×10^{-17}.

A solution containing 0.01 M each of Cl^-, Br^- and I^- ions. $AgNO_3$ is gradually added to the solution. Assume that the addition of $AgNO_3$ does not change the volume.

(i) Calculate the $[Ag^+]$ required to start precipitation of the three ions.

(ii) Which ion will precipitate first.

(iii) What will be the concentration of this ion when the second ion start precipitating?

(iv) What will be the concentrations of both the ions precipitated when the third ion starts precipitation?

Solution

(i) The concentration of Ag^+ ion required to start precipitation can be calculated from K_{sp} data.

For the Cl^- ion,

$$[Ag^+] = \frac{K_{sp}\,(AgCl)}{[Cl^-]} = \frac{1.7 \times 10^{-10}}{0.01} = 1.7 \times 10^{-8}\ M$$

For Br^- ion

$$[Ag^+] = \frac{K_{sp}\,(AgBr)}{[Br^-]} = \frac{5.0 \times 10^{-13}}{0.01} = 5 \times 10^{-11}\,M$$

For I^- ion

$$[Ag^+] = \frac{K_{sp}\,(AgI)}{[I^-]} = \frac{8.5 \times 10^{-17}}{0.01} = 8.5 \times 10^{-15}\,M$$

(ii) The $[Ag^+]$ required to precipitate I^- ion is minimum. Therefore AgI will be precipitated first.

(iii) After precipitation of AgI, the Br^- will be precipitated only when the $[Ag^+]$ becomes 5.0×10^{-11} M. Therefore the concentration of remaining I^- is

$$[I^-] = \frac{K_{sp}\,(AgI)}{[Ag^+]} = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-11}} = 1.7 \times 10^{-6}\,M$$

(iv) The chloride ion (Cl^-) will precipitate when the concentration of $[Ag^+]$ becomes 1.7×10^{-8} *M*. Therefore, the concentrations of Br^- and I^- remaining in solution are:

$$[I^-] = \frac{K_{sp}\,(AgI)}{[Ag^+]} = \frac{8.5 \times 10^{-17}}{1.7 \times 10^{-8}} = 5.0 \times 10^{-9}\,M$$

$$[Br^-] = \frac{K_{sp}\,(AgBr)}{[Ag^+]} = \frac{5 \times 10^{-13}}{1.7 \times 10^{-8}} = 2.94 \times 10^{-5}\,M$$

4.3. CO-PRECIPITATION

When a substance is precipitated from a solution it is not perfectly pure but contains various impurities depending n the nature of the precipitate and conditions of precipitation. The contamination of precipitate by substances normally soluble in the mother liquor is called *Co-precipitation.* The main reason for co-precipitation is adsorption of ions on the particles of the precipitate.

Contamination may be classified into two groups; those due to co-precipitation and those caused by post-precipitation. In co-precipitation, two types of contamination can be distinguished: adsorption and occlusion. In the case of adsorption, the precipitate particles carry the contaminant on their surface and can be removed by washing. In occlusion, the impurity is inside the primary precipitate particles, whether by mechanical trapping during crystal growth or by formation of solid solutions.

For example, in order to determine Cl^- ions in a given solution of NaCl, an excess of $AgNO_3$ solution is added to it and the resultant ppt of AgCl is washed, dried and weighed. In the mother liquor there are Ag^+, Na^+ and NO_3^- ions, Silver ions are the only ions that are common to those of AgCl (Ag^+ Cl^-), hence, Ag^+ ions will be preferentially absorbed on the particle surface forming the primary layer, the nitrate ions will form the secondary layer. Thus $AgNO_3$ which is ordinarliy a soluble salt is coprecipitated with AgCl.

Another type of coprecipitation can be understood by considering the process of growth of crystals of the ppt. If the rate of growth is rapid, some impurities are enclosed inside the growing crystals; this is known as *Occlusion*.

Following steps are taken to minimise coprecipitation:

(i) The solution from which precipitation is made should be dilute so that the concentration of foreign ions which may be adsorbed or occluded is small.

(ii) Stire the solution during precipitation so that larger crystals are formed, this will keep adsorption and occlusion at a minimum.

(iii) The precipitation should be done in hot so that the solubility of all the components present in the solution is increased and there are smaller chances of supersaturation.

In post-precipitation, the precipitation of another substance takes place on the primary ppt. The second substance is poorly soluble and forms a supersaturated solution. For example, when calcium is precipitated as calcium oxalate in the presence of magnesium, magnesium oxalate gets deposited over ppt of calcium oxalate (the primary ppt). Post-precipitation is minimized by bringing the ppt to a filterable conditions as soon as possible after its formation so that there is no time for the deposition on the primary ppt. In some cases a water-immiscible liquid is added as soon as the primary precipitation is complete. This liquid forms a protective layer and does not permit any other deposition on the primary ppt.

4.4. THE COMMON ION EFFECT

The dissociation of an acid or a base is much affected if one of the dissociated ions is added from a certain external source. For example, consider the dissociation of a weak acid such as CH_3COOH.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The dissociation constant of the acid,

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

has a constant value at any given temperature.

If we add a strong acid like HCl to acetic acid, the concentration of H_3O^+ ions will increase. To maintain value of K_a constant, the concentration of acetate ions will fall. In other words, the equilibrium will shift to the left hand side due to the large excess of H_3O^+ ions furnished by the dissociation of HCl (Le-Chatelier principle). The dissociation of acetic acid will be suppressed in a similar manner if large excess of common anion (i.e., CH_3COO^- ion) is furnished by adding a strong electrolyte like CH_3COONa which dissociates as

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Similarly the addition of NH_4Cl or NaOH in NH_4OH solution will result in suppression of dissociation of NH_4OH as

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

due to common ion, viz., NH_4^+ from NH_4^+ and OH^- ions from NaOH respectively.

The suppression of dissociation of a weak acid or a weak base by adding a solution of strong electrolyte having an ion common with the weak acid or weak base is called *common ion effect.*

Applications of Common Ion Effect

The principle of common effect has proved very useful in analytical chemistry. The following are some of its common applications:

1. Purification of Common Salt

The common salt (NaCl) is usually purified by passing dry HCl gas through its saturated solution. Sodium chloride in its saturated solution ionizes as

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

The equilibrium constant for the above reaction is given by

$$K_c = \frac{[Na^+]\,[Cl^-]}{[NaCl^-}$$

When dry HCl gas is passed through its saturated solution, it also ionizes to give H^+ and Cl^- ions as

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

It is obvious from the above expressions that Cl^- ion is the common ion in both the processes. After the ionization of HCl the concentration of Cl^- ions increases which alters the value of K_c. To keep K_c constant, the equilibrium is shifted to the left hand side of the equation. In other words, with the increase in the concentration of Cl^- ions the amount of NaCl is increased. Thus more and more NaCl molecules are formed and get precipitated. After the precipitation the salt is filtered and obtained in pure form.

2. Use of HCl in Group II of Salt Analysis

The cations of second group (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+} and Sn^{4+}) of salt analysis are precipitated by passing H_2S gas in the presence of HCl. The function of HCl is to suppress the ionization of H_2S gas due to common ion effect. The ionization of H_2S and HCl takes place as follows:

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

It is obvious that H^+ ions are common to H_2S and HCl. The equilibrium constant for the dissociation of H_2S is given by

$$K_c = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]}$$

With the increase in the concentration of H^+ ion (common ion), the equilibrium is shifted towards left hand side of the equation. In other words, more and more S^{2-} ions react with H^+ ions to form undissociated H_2S. Thus the ionization of H_2S is suppressed. Whatever the sulphide ions left ionized, these form metallic sulphides with the cations of second group. The cations of both the second and fourth groups are capable of forming sulphides. The sulphides of former group are sparingly soluble and those of latter are fairly soluble. That is why the sulphides of second group are precipitated by passing H_2S gas in acidic medium, and those of fourth group remain in solution and are not precipitated along with the sulphides of second group.

3. Use of NH_4Cl in Group III of Salt Analysis

NH_4Cl is added to the solution of the salt to be analysed after the second group. NH_4OH along with NH_4Cl is used as a group reagent for the precipitation of radicals of third group (Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}). NH_4OH is a weak base and hence ionizes in aqueous solution to a very small extent.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

In the presence of highly ionized NH_4Cl, there is an increase in the number of NH_4^+ ions, in the solution. Due to these NH_4^+ ions, ionization of NH_4OH is further suppressed (common ion effect) so that the concentrations of OH^- ions fall very low. Under these conditions the solubility product of the hydroxides of third group alone is reached and these precipitate out while the hydroxides of IV, V and VI groups (which possess a comparatively high value of solubility product) are not precipitated from their salt solutions and remain in solutions as ions.

4. Use of NH_4Cl in Group IV of Salt Analysis

The group reagent of this group is H_2S in the presence of NH_4Cl and NH_4OH. Due to the presence of NH_4Cl (which furnishes large number of NH_4^+ ions), the ionization of NH_4OH is restricted to the desired extent in which H_2S precipitated out radicals of this group such as Zn^{2+}, Ni^{2+}, Mn^{2+} and Co^{2+}.

5. Use of NH_4Cl in Group V of Salt Analysis

In Vth group NH_4Cl is used with $(NH_4)_2CO_3$ as a group reagent. If $(NH_4)_2CO_3$ alone is used as a group reagent, then Mg^{2+} of VI group will also precipitated as $MgCO_3$. To avoid this along with $(NH_4)_2CO_3$, ammonium chloride is used. The common NH_4^+ ions from highly ionized NH_4Cl suppresses the ionization of $(NH_4)_2CO_3$ to such an extent that the low concentration of Co_3^{2-} ions is only sufficient to increase the solubility product of the carbonates of Ca, Sr and Ba, but it is insufficient to exceed the solubility product of $MgCO_3$, hence it is thus not precipitated.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_4^+ + CO_3^{2-}$$

6. Use of NH_4OH in Group IV of Salt Analysis

The filtrate of third group contains OH^- ions and is basic. The function of NH_4OH is to provide OH^- ions which remove H^+ ions and thus enhances the ionization of H_2S. Thus more H_2S ionizes; the greater is the concentration of S^{2-} ions and more is the precipitation of sulphides.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$H^+ + OH^- \longrightarrow H_2O$$

4.5. THE MOLE

In biology a mole is a small furry animal, but in chemistry it has a very different meaning. A mole is a certain amount of substance. It is a general term to describe an amount of atoms, ions, or molecules, and it enables chemists to count these particles by weighing.

A mole is defined as the amount of substance which contains the Avogadro Number of particles.

This number is named after an Italian scientist, Amedeo Avogadro, and it is very large number indeed. Its value is 6.02×10^{23} or 602 000 000 000 000 000 000 000! It is such a large number that if all the people in the world started counting at a rate of one per second for the rest of their lifetime, in total, all the numbers counted would still not be large enough.

The Avogadro Number (or Avogadro Constant) is defined as the number of atoms in 12 g of the carbon-12 isotope.

Moles of Atoms: Relative Atomic Mass in Grams In the laboratory, if you weighted out 12 g of carbon, this would contain the Avogaddro Number of carbon atoms. In the same way, so would 23 g of sodium, or 27 g of aluminium, or 16 g of oxygen, or 1 g of hydrogen. All these contain the Avogadro Number of atoms. Accordingly for an element, the mass of one mole of atoms is its relative mass in grams.

Put another way, the relative atomic mass in grams of any element contains the same number of atoms: the Avogadro Number.

Element	Relative Atomic Mass	Mass of 1 mole	Number of atoms in 1 mole
hydrogen	1	1 g	6.02×10^{23}
carbon	12	12 g	6.02×10^{23}
oxygen	16	16 g	6.02×10^{23}
sodium	23	23 g	6.02×10^{23}
aluminium	27	27 g	6.02×10^{23}
iron	56	56 g	6.02×10^{23}
lead	207	207 g	6.02×10^{23}

Moles of Molecules: Relative Molecular Mass in Grams In the laboratory, if you weighted out 44 g of carbon dioxide (CO_2), this would contain the Avogadro Number of carbon dioxide molecules. In the same way, so would 18 g of water (H_2O) or 32 g of oxygen gas (O_2), or 2 g of hydrogen gas (H_2), etc. Accordingly for a compound, the mass of one mole of molecules is its relative molecular mass in grams. Put another way, the relative molecular mass in grams of any compound contains the same number of molecules: the Avodgadro Number.

Moles of Gases: Molar Gas Volume Gases are made up on particles. These are usually molecules, with the exception of the inert gases which are composed of atoms. Accordingly, a mole contains the same number of particles, one mole of different gases would, under the same temperatures and pressure, occupy identical volumes. In fact, one mole of any gas at room temperature and pressure occupies a volume of 24 000 cm^3 (24 dm^3). This is sometimes called the molar gas volume as it contains the Avogadro Number of particles. In more general terms, Avogadro's Law states that equal volumes of all gases at the same temperature and pressure contain the same number of particles.

It is important when measuring volumes of gases always to quote the temperature and pressure, because both affect volume. If the temperature increases, then so does the volume (Charles' Law). If the pressure increases, then the volume decreases (Boyle's Law). In all chemical calculations, gas volumes will be measured at room temperature and pressure (r.t.p.) Room temperature is taken as 25°C (298 K) and room pressure as one atmosphere (760 mm of mercury).

Therefore, assuming room temperature and pressure, 2 g of hydrogen gas (H_2) contains the same number of particles as 32 g of oxygen gas (O_2), or 44 g of carbon dioxide gas (CO_2), or 71 g of chlorine gas (Cl_2). These masses of different gases are all equivalent to one mole, and occupy a volume of 24 000 cm^3 at r.t.p.

Example 4.7. How many moles are there in

(a) 88 g of carbon dioxide?

(b) 64 g of oxygen molecules?

($A_r(C) = 12$, $A_r(O) = 16$)

Solution

$$\text{Number of Moles} = \frac{\text{mass in grams}}{A_r \text{ or } M_r \text{ of atom or molecule}}$$

(a) M_r of carbon dioxide molecules $CO_2 = 12 + (2 \times 16) = 44$

$$\text{Number of moles} = \frac{88}{44} = 2 \text{ moles}$$

(b) M_r of oxygen molecules $O_2 = 2 \times 16 = 32$

$$\text{Number of moles} = \frac{64}{32} = 2 \text{ moles}$$

Example 4.8. How many grams are there in?

(a) 10 moles of water?

(b) 0.25 moles of oxygen atoms?

$(A_r(H) = 1, A_r(O) = 16)$

Solution

Mass in grams = number of moles × A_r or M_r of substance.

(a) M_r of water molecules $H_2O = (2 \times 1) + 16 = 18$

Mass in grams = $10 \times 18 = 180$ g

(b) M_r of oxygen atoms $O = 16$

Mass in grams = $0.25 \times 16 = 4$ g

Example 4.9. How many particles are there in 16 g of oxygen molecules?

Solution

Number of particles = number of moles × Avogadro Number

(a) M_r of oxygen molecules $O_2 = 2 \times 16 = 32$

$$\text{Number of moles of oxygen molecules} = \frac{\text{mass}}{M_r} = \frac{16}{32} = 0.5 \text{ moles.}$$

$$\text{Number of particles} = 0.5 \times 6 \times 10^{23} = 3 \times 10^{23} \text{ molecules}$$

4.6. ACTIVITIES AND ACTIVITY COEFFICIENT

Equilibrium constants for gaseous equilibria and for non-ionic reactions in solution can be expressed in terms of concentrations to a fairly good approximation at relatively low pressure and concentrations. However in dealing with ionic equilibria, with certain aspects of kinetics in solution, and with emf studies, substitution of concentrations for activities is frequently not possible. For this reason it is essential to consider how ionic concentrations may be converted to activities, and how such activities can be evaluated.

It has generally observed that the inter-ionic attractions between the ions in the solution of an electrolyte have considerable influence as the mobility of ions. The ionic concentrations in case of weak electrolyte, being low, do not show appreciable deviation from the ideal behavior. But in solutions of strong electrolytes, the ionic concentrations are large, so inter-ionic forces cannot be neglected. Solutions of strong electrolytes therefore show appreciable deviation from ideal behavior. Ions in such solutions cannot be expected to behave like neutral or ideal molecules. The effect becomes more significant at higher concentrations and increasing value of ions. G. N. Lewis suggested that due to restricted mobility of ions in the solutions of strong electrolytes, the ions do not exert their full effect for showing their behavior. He proposed a term "activity" in place of concentrations term (molarity, molality or mole fraction) so as to explain the departure of electrolyte solution from ideal behaviour. The activities and concentrations are related as

$$\text{Activity} = \text{Concentration} \times \text{Activity Coefficient}$$

"So the real concentration of the ion which is available to take part in a chemical reaction is called activity". Total ionic concentration of an ion is not used or taking part in a chemical reaction, But there is some fraction of the concentration taking part in a chemical reaction.

Difference Between Activity and Concentration When $a = C$, then the solution is very dilute and interionic interactions can be neglected, then a and C can be considered the same thing.

But in case of concentrated solutions the interionic attractions become more stronger. If we know by some means the interionic attractions, then we relate the conc. and activity. For this purpose we need a parameter called coefficient of Activity.

$$a = f.\,C.$$

when a = activity $C = \text{mol/dm}^3$

C = concentration

f = activity coefficient (It is not a constant. It depends upon the total concentrated of the ions).

f-gives the extent of interionic attraction/departure from ideal behaviour.

For very much dilute solution the value of "f" becomes unity so interactions between the ions can be neglected

$$\therefore \quad f = 1 \text{ then } a = C$$

In electrochemical works, the concentration is expressed in molality (m) in moles for 1000 grams of solvent. The activity coefficient is then denoted by

$$a = \gamma m$$

The ionic activities can similarly be written as

$$a_+ = \gamma_+ m_+ \quad \text{and} \quad a_- = \gamma_- m_-$$

Since it is not possible to get only +ve ion or −ve ions in the solution, there is no experimental method available to determine the activity or activity coefficient of individual ionic species. Fortunately, for most purpose, it is sufficient to know the mean ionic activity ($a_\pm$) and mean activity coefficient ($f\pm$).

The reason is that the solutions are electrically neutral and we cannot increase the number of cations without an equal increase in the charge due to negative ion. For example, we can change the concentration of a solution of NaCl by adding an equal number of Na^+ and Cl^- ions. If we were to add Na^+ ions or Cl^- ions alone, the solution would acquire net electric charge, the properties of ions in such a solution would differ considerably from their properties in the normal uncharged solution. Since we cannot study separately the effects of cations/anions in the presence of each other in an uncharged solution, it is therefore not possible to measure the individual ion activities. However, an estimate of single ion activity can be made by an approximate method. For example, K^+ and Cl^- ions in KCl both have argon configuration and therefore nearly the same size. In a KCl solution, it should be good approximation to set.

$$a_{K^+} = a_{Cl^-}$$

so that $a_{\pm} = a_{K^+} = a_{Cl^-}$

4.7. CONCEPT OF MEAN

The mean $\overline{X}$, is the numerical average obtained by dividing the sum of the individual measurements by the number of measurements

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where X_i is the ith measurement, and n is the number of independent measurements.

Table 4.2 Masses of Seven United States Pennies in Circulation

Penny	Mass (g)
1	3.080
2	3.094
3	3.107
4	3.056
5	3.112
6	3.174
7	3.198

Example 4.10 What is the mean for the data in Table 4.2.

Solution

To calculate the mean, we add the results for all measurements

$$3.080 + 3.094 + 3.107 + 3.056 + 3.112 + 3.174 + 3.198 = 21.821$$

and divide by the number of measurements

$$\overline{X} = \frac{21.821}{7} = 3.117 \text{ g}$$

The mean is the most common estimator of central tendency. It is not considered a robust estimator, however, because extreme measurements, those much larger or smaller than the remainder of the data, strongly influence in the mean's value. For example, mistakenly recording the mass of the fourth penny as 31.07 g instead of 3.107 g, changes the mean from 3.117 g to 7.112 g.

4.8. MEDIAN

The median, X_{med}, is the middle value when data are ordered from the smallest to the largest value. When the data include an odd number of measurements, the median is the middle value. For an even number of measurements, the median is the average of the n/2 and the (n/2) + 1 measurements, where n is the number of measurements.

Example 4.11 What is the median for the data in Table 4.1?

Solution To determine the median, we order the data from the smallest to the largest value

3.056 3.080 3.094 3.107 3.112 3.174 3.198

Since there is a total of seven measurements, the median is the fourth value in the ordered data set; thus, the median is 3.107.

As shown by Example 4.13 and 4.14, the mean and median provide similar estimates of central tendency when all data are similar in magnitude. The median however, provides a more robust estimate of central tendency since it is less sensitive to measurements with extreme values. For example, introducing the transcription error discussed earlier for the mean only change the median's value from 3.107 g to 3.112g.

4.9. ACCURACY AND PRECISION

The numerical value obtained in every scientific measurement contains certain degree of uncertainty. In very accurate work the uncertainty may be very small, but it is still present. This uncertainty is called the error of the measurement. Accuracy relates to the closeness of approach of a single measurement, or of the average of a series of measurement, to the true value. *Accuracy* may also be defined as the concordance between the measured value and the true or most probable value. The true value cannot be measured exactly, however, in many cases it can be estimated very closely. By using calibrated equipment, performing the work very carefully, executing a very large number of measurements, and then applying statistics to the results, reasonable approximations of the true value can be obtained. Mostly, the true value is estimated from the results of different analysis in different laboratories.

Precision describes the closeness of approach of replicate results to a common value. Repeated measurements of the same quantity will usually not be identical, but will scatter around some common value. Precision describes the reproducibility or scatter of a series of measurements of result. Precision may also be defined as the concordance of a series of measurements of the same quantity.

Both accuracy and precision have specific meanings and implications, so they should not be used interchangeably or carelessly. To illustrate exactly what is meant by the two terms, accuracy and precision, let us examine two sets of data for he weight of a crucible. The data in set A were obtained by five different students each weighing the crucible on his own analytical balance, each using, therefore, a different set of weights. The second set B were obtained by weighing a sixth student weigh the crucible five times on his analytical balance, thus these data were obtained on the same equipment. The crucible is then weighted by a skilled analyst using ASTM-II-S-I weights, and applying all appropriate corrections to the weight obtained. He finds a value of 9.2474 g as the average of ten replicates, with no statistically significant trends or deviations in the individual weights or in the means. Thus, it is fairly safe to assume that this value is sufficiently close to the true value to be considered the correct weight of the crucible.

	Set A	Set B
Weight of the crucible	9.2463	9.2483
	9.2480	9.2481
	9.2477	9.2484
	9.2489	9.2480
	9.2455	9.2483
Average, weight, g	9.2473	9.2482

Let us now examine the data in sets A and B. The weights obtained in set B by the one operator using the same equipment are less scattered, much more closer to each other than those found in set A. The average of A weights obtained by the five students (Set A) is closer to the true value than is the average of weights in set B. These data reveal an interrelation between accuracy and precision that is very important. Precise data need not necessarily be accurate. A constant and reproducible error can be contained in each piece of data. The data in Set A are misleading, for it is highly unlikely that poor precision will accompany good accuracy. Precision always accompanies accuracy, but a high degree of precision does not imply accuracy.

Method for the expressing accuracy. The usual expression of accuracy is merely the difference between the piece of data (or the average of a set of data and the true value). This is known as the *absolute error or the mean error.* Generally, the absolute error by itself is of low information and of little use unless one knows the magnitude of the quantity being measured or calculated. Thus saying that there is 3.0 mg low error in weighing sample, while having some value, takes on a much greater significance if we know what the weight of the object is. It makes a difference whether the weight is 30 g or 30 mg. The error is usually negligible in 30 g, but is very significant in 30 mg.

Thus the accuracy of a measurement is usually expressed in relative terms, as a fraction of the true value. It is expressed in % or in parts per thousands (ppt).

Relative accuracy/Relative error = Absolute error/True value × 1000

Relative accuracy in the data A = $-0.0001/9.2474 \times 1000 = -0.01$ ppt

Relative accuracy in the data B = $+0.0008/9.2474 \times 1000 = +\ 2.086$ ppt

It should be pointed out that as a general rule, relative accuracy and relative precision expressions are rounded off to the first decimal place. Note that smaller the numerical value of the relative error (disregarding the sign) the more accurate the data. Thus the data in set B are less accurate than in set A.

Method of the expression of precision. There are many different ways to express the precision of a set of a data. Of these, only a few have any statistical basis, causing these expressions now to be recommended. Today these are the most frequently encountered terms. A couple of the terms below are listed for the historical purpose.

The Rang (W). This is merely the numerical difference between the highest and the lowest value of a set of results. For the data in Set A, W = 9.2489 − 9.2455 = 0.0034 g, use of the range is not particularly informative since it tells nothing about the distribution of the data. The data could be distributed uniformly between the two limits or they all could be clustered around one value, with just a single datum way off. The range is most frequently used for very small set of data, i.e., two or three items. The range becomes less informative as the number of pieces of data in a set increases. The range is more informative about the precision of a set of data than the average deviation when there are fewer than eight pieces in the set.

The other methods for expressing precision are based on the absolute difference between each particular piece of data and the average of the set. This difference is known as the *deviation* of a particular piece of data. A deviation has no sign, being obtained by subtracting the datum from the average of the set. Thus for any given measurement X_i, in a finite set of data whose average arithmetic mean is m, the deviation is = $[X_i - m]$.

The mean, of course is $\Sigma_i, X_i/n$,

Where n is the number of pieces of data in the set. The deviation in the sets A and B are given below:

Deviation for set A	Deviation for set B
0.0010	0.0001
0.0007	0.0001
0.0004	0.0002
0.0016	0.0002
0.0018	0.0001

4.10. SIGNIFICANT FIGURES

A number used to express the result of a physical measurement or a calculation should contain sufficient digits to express the accuracy of the measurement or calculation. The general rule used in chemistry states that the least digit of a number, has certain uncertainty in it, while all of the other digits in the number contains no uncertainty. To illustrate, a sample is weighed on an analytical balance that has accuracy ±0.1 mg. To report its weight as 1.4063 g is incorrect since the last decimal place is meaningless, because the balance is only capable of giving accurate information to the fourth decimal place. The weight should be properly written as 1.4064 g. Using the number of significant figures, the last digit, the 4 is uncertain by ±1 and this accuracy represents the capability of the balance. It is equally incorrect to express the sample weight as 1.406 g for in weighing the sample; there is no uncertainty about the number of milligrams taken. Full advantage of the accuracy and sensitivity of a measuring instrument should taken and the results obtained with it should reflect this accuracy.

Let us try to determine the correct number of significant figures in a number, 0.4060 g . How many significant figures does it have? Four, The zero to the left of the decimal point is merely to indicate the order of magnitude, to show that the weigh is less than one gram. In no way it is a part of the number. The other two zeros are significant figures. As a general rule for numbers smaller than one, zeros preceeding the first non-zero degit are not significant, but merely indicate order of magnitude of the number. Use of the exponential form for writing numbers eliminate confusion. Thus 0.004103 contains four significant figures, three zeros proceeding the 4 are non significant. This can be see more clearly when the number is written as 4.103×10^{-3} When writing numbers larger than one, the use of the exponential form is essential for clarity. Zeros to the right of the last non zero digit of a number larger than one, can be either significant or not; there is no way for the person reading the number to decide. Consider the number written as 4,510,000. How many significant figures does it contains? Three? Forth? Seven? When the number is written like this there is no way to judge. Some, perhaps all, of the zeros to the right of 1 may be merely to locate the decimal point. Some may be all, may be significant figures. In order to eliminate this confusion, the number should be written as say 4.510×10^{6}, which states clearly that there are four significant figures and still locate the decimal point.

It is customary at all intermediate stages of calculations to carry along one more significant figures than is proper. The calculation is rounded off to the correct number of significant figures only at the very end. This practice causes the error in the final result to be an accurate reflection of the final errors in the components. Only the final digit will contain a minimum of uncertainty.

In performing calculations one must be constantly alert so that the numerical result does not reflected an accuracy that is greatest or less than the least accurate number used in the calculation. When using computers, desk calculators or even with hand calculations, it is very easy to obtain long strings of digit. It is deceptive to believe these really reflect accuracy. In performing calculations we must be sure to dominate all meaningless, deceptive, excess digits form the results. The operational rules used for addition and subtraction are different from those used for multiplication and division. In addition and subtraction, the number of decimal place limit is the number of significant figures whereas in multiplication and division the number of decimal place is irrelevant. The result is restricted by the relative accuracy of the numbers involved in the calculation. The precision and accuracy of an experiment can never be increased by the computational process. Under certain conditions they may be decreased.

Addition and Subtraction

In addition and subtraction, the number of significant figures in the sum or difference can change from the number of significant figures of the components. Only the last digit of the sum or difference may contain any uncertainty. A sum or difference may contain no more decimal place than that component number having the fewest decimal place. Consider each of the following additions.

	1	2	3
	43.1	0.0025	10.414
	4.31	4.1167	0.0037
	0.431	5.9071	9.02
Sum	47.8	10.0263	19.43

In the first, all three numbers have identical significant figures, namely three, but 43.1 has the fewest decimal place and hence limit is the numbers of significant figures in the answer. Only one decimal place can be used, so that 47.8 is the correct sum. In the second sum, all three number have the same number of decimal places, even though the first one has the fewest significant figures. The result can be expressed to four decimal places. Note that in this case the sum has one more significant figures than any number. In the third sum, all three numbers have different numbers of significant figures the sum is limited to two decimal places by 9.02. The number 0.0037 cannot be included in the sum because it lies beyond the limit of the accuracy of the least accurate of the numbers. Nothing can be added beyond the second decimal place.

The same general consideration applies to subtraction.

	1	2	3
	44.341	19.4197	4.96
	–4.4432	–19.4153	–0.00321
Difference	39.898	0.0044	4.96

The first difference is limited to three decimal place by 44.341. Note that in the second subtraction, the difference has only two significant figures, whereas each of the two components has six-a tremendous decrease in significant figures and hence, in relative accuracy of the difference. In the third set a subtraction cannot be made because the limit is at the second decimal place.

Multiplication and Division. In many measurements, one estimated digit that is uncertain will be included. This is the last significant figures in the measurement; any digits beyond it are meaningless. In multiplication and division, the uncertainty of this digit is carried through the mathematical operations, thereby limiting the number of certain digits in the answers.

There are the same numbers of significant figures in the answer of multiplication or division as there are in the operator with the least number of significant figures. This is always the case, so you can say immediately how many significant figures will occur in the answer. We shall designate this limiting number as the key number. If there is more than one operator with the same lowest number of significant figures then the with the smallest absolute magnitude without regarded to the decimal point is the key number.

Example 4.12. Give the answer of the following operation to the maximum number of significant figures and indicate the key number.

$$35.63 \times 0.5481 \times 0.05300/1.1689 \times 100 = 88.5470578\%$$

Solution. The key number is 35.63. The answer is therefore, 85.55% and it is meaningless to carry the operation out to more than five figures (the fifth figure is used to round off the fourth). The 100% in this calculation is an absolute number, since it is used only to move the decimal point, and it has an infinite number of significant figures. Note that the key number has a relative uncertainty at best of 1 part in 3600 and so the answer has a relative uncertainty at least of this magnitude (i.e. about 2.5 parts in 8900). The objective in a calculation is to express the answer to at least the precision of the least certain number, but to recognize the magnitude of its uncertainty. (Similarly, in making a series of measurements, one should strive to make each to about the same degree of relative uncertainty).

If the magnitude of the answer with regard to decimal or sign is smaller than that of the key number, one additional figure may be carried in the answer in order to express the minimum degree of uncertainty, but it is written as a subscript to indicate that it is more doubtful.

Example 4.13. Give the answer of the following opinion to the maximum of significant figures and indicate the key number.

$$\frac{42.68 \times 891}{132.6 \times 0.5247} = 546.57$$

Solution The key number is 891. Since the absolute magnitude of the answer is less than the key number, it becomes 546.6. The last 6 is written as a subscript to indicate it is more doubtful. Again, the key number has a relative uncertainty of about 1 part in 900, so the answer has uncertainty of at least 6 parts a 5500 (0.6 parts in 550).

In multiplication and division, the answer from each step of a series of operation can statistically be rounded to the number of significant figures to be retained in the final answer. But for consistency in the final answer, it is convenient to carry one additional figure until the end and then round off.

Logarithms In changing from logarithms to antilogarithms and vice versa, the number being operated on and the logarithm mantissa have the same number of significant figures. All zeros in the mantissa are significant. Suppose, for example, we wish to calculate the pH of a 2.0×10^{-3} M solution of HCl from pH = $-\log [H^+]$. Then, pH = $-\log 2.0 + 10^{-3} = -(-3 + 0.30) = 2.70$. The -3 is the characteristic (from 10^{-3}), a pure number determined by the position of the decimal. The 0.30 is the mantissa for the logarithm of 2.0 and therefore has only two digits. So, even though we know the concentration to two figures, the pH (the logarithm) has three figures. If we wish to take the antilogarithm of a mantissa, the corresponding number will likewise have the same number of digits as the mentissa. The antilogarithm of 0.072 (contains three figures in mentissa 0.72) is 1.18, and the logarithm of 12.1 is 1.083 (1 is the characteristic, and mantissa has three digits .083).

Rounding off If the digit following the last significant figure is greater than 5, the number is rounded up to the next higher digit. If it is less than 5, the number is rounded to the present value of the last significant figure:

$$9.47 = 9.5$$

$$9.43 = 9.4$$

If the last digit is a 5, the number is rounded off to the nearest even digits:

$$8.65 = 8.6,$$

$$8.75 = 8.8,$$

$$8.55 = 8.6$$

4.11. THE STANDARD DEVIATION

It is a meaningful statistical term used to express precision. If one should happen to have a set of data that contains an infinite number of pieces, then a would be the parameter used to described the standard deviation of the members of the set. Normally, however, scientists have only finite set of data, and infact, in analytical chemistry, usually only a very small set of data (2, 3, 4 or 5 members). Thus the symbol used for the standard deviation is S, indicating that we are treating only a limited set of data. From the way that the standard deviation is formulated, more weight is given to pieces of data having large deviations. This is appropriate since they occur less frequently. The standard deviation is defined as the square root of the sum of the squares of the deviations divided by one less than the number of pieces of data in the set namely,

$$S = \sqrt{\Sigma_i(X_i - m)^2/n - 1}$$

The standard deviation for a finite set of data is obtained by dividing by one less than the number of piece of data since this denominator represent the number of degree of freedom the set of the data possesses which are available for asserting error. Since the mean rather than the true value is used in calculating the deviations, and it is property of the set that $\Sigma(X_i - m) = 0$, when one has selected n − 1 values of the deviation, the last deviation cannot be arbitrarily selected but is predetermined. Thus when calculating S for any set of the data possessing the mean, m, only n − 1 degrees of freedom, show the effect or error.

The square of the deviation for data in set A and B

	Set A	Set B
	$(X_i - m)^2$	$(X_i - m)^2$
	100×10^{-8}	1×10^{-8}
	49×10^{-8}	1×10^{-8}
	16×10^{-8}	4×10^{-8}
	256×10^{-8}	4×10^{-8}
	324×10^{-8}	1×10^{-8}
Sum =	745×10^{-8}	11×10^{-8}

Consequently the standard deviation for the data in set A

$$S = \sqrt{745 \times 10^{-8}/4}$$

$$= 1.4 \times 10^{-3} \text{ g} = 0.0014 \text{ g}$$

and the standard deviation for the data in set B.

$$S = \sqrt{\frac{11 \times 10^{-8}}{4}}$$

$$= 2 \times 10^{-4} = 0.0002 \text{ g}$$

The smaller the value of S, the more precise the is data. Note that the numerical value of the S is greater than of the average deviations for the data in both of the sets. This is due to the increased weight given to the values with larger deviations.

The variance S^2 . For certain statistical tests it is more convenient to use the square of the standard deviation, instead of the standard deviation. This term is called the variance, and it is defined as the sum of the square of the deviations divided by one less than the number of pieces of the data or

$$S^2 = \Sigma_i(X_i - m)^2/n - 1$$

The variance of the data in set A is 1.96×10^{-6}, and the variance of the set of the data in B = 4×10^{-8}.

4.12. RELATIVE STANDARD DEVIATION (COEFFICIENT OF VARIATION)

As pointed out above, when discussing accuracy, the absolute value of the standard deviation is of limited value. Usually the value of the mean of the data set is given along with the standard deviation which does enable one to estimate the relative magnitude of the S. When the S is expressed as a fraction of the mean of the set of data, a better feeling for the proportionality of the error is obtained. The relative S is nothing more than the S divided by the mean of the set. Again is it expressed in parts per thousand in order to avoid the possible confusion by the use of % values.

Relative Standard Deviation = $S/m \times 1000$

For the set A; $0.0014/9.2473 \times 1000 = 0.15$ ppt.

For the data in set B = $0.0002/9.2482 \times 1000 = 0.02$ ppt

Thus, once again it is found that the data in set B is more precise than those in the set A. The smaller the value of the relative standard deviation.

Questions

Q.1. What do you understand by law of mass action? How is it applied to the solubility of a sparingly soluble salt?

Q.2. Define solubility product. Discuss the relationship involved to get K_{sp}.

Q.3. What is solubility product principle? Discuss the use of this principle in analytical chemistry?

Q.4.(*a*) The solubility product of $Fe(OH)_3$ is 1.1×10^{-36}. What is the solubility of $Fe(OH)_3$ in moles per litre and gram per litre.

(Ans. 4.49×10^{-10} moles per litre, 4.80×10^{-8} g/litre)

(*b*) The solubility of CaF_2 in water is 1.6×10^{-2} g per litre at 20°C. Calculate the solubility product of CaF_2. (Molar mass of $CaF_2 = 78$) (Ans. 3.45×10^{-11})

Q.5. The solubility of AgCl at 25°C is 0.00179 g per litre. What will be its solubility product at this temperature? (Ans. 1.563×10^{-10})

Q.6. What is common ion effect? Justify with the help of suitable examples that it is a powerful tool in the hands of chemists to separate various cations and to purify salts.

Q.7. Define common ion effect. Discuss its applications in qualitative analysis.

Q.8. Justify the use of following in salt analysis:

(*i*) HCl in Group II cations.

(*ii*) NH_4Cl in Group III cations.

(*iii*) NH_4Cl and NH_4OH in Group V.

Q.9. (*a*) What is the function of HCl and NH_4OH in Group II and Group IV in basic radicals respectively in the mixture analysis?

(*b*) Write down the names of basic radicals of Group IIA and IIB.

Q.10. What do you understand by the term mole? Explain it with suitable examples.

Q.11. How many moles are there in (i) 20 gram of CO and (ii) 40 gram of NO_2?

Q.12. How many grams are there in 5 moles of oxygen atom and 20 mole of water molecule?

Q.13. What is difference between activity and concentration? How these are interrelated?

Q.14. Explain the term activity coefficient.

Q.15. Explain the mean and median with suitable examples.

Q.16. What is the difference between precision and accuracy? How these terms are expressed?

Q.17. What are significant figures? Discuss their importance in chemistry.

Q.18 What is standard deviation and relative standard deviation? Discuss their significance in data handling.

Q.19. Justify/Comment on the following statements:

(a) CH_3COOH is a weak electrolyte while HCl is a strong electrolyte.

(b) K_{sp} (AgCl) = $[Ag^+] [Cl^-]$

(c) Excess of KCl is recommended in the estimation of Ag^+ ion as AgCl.

(d) In a mixture of KI and KCl, iodide ion will be precipitated first with $AgNO_3$ as AgI.

(e) NaCl is purified by passing HCl gas through its solution.

(f) Hg_2^{2+}, Pb^{2+} and Ag^+ are placed in group I of cations.

(g) Cations of group III are precipitated as hydroxides while those of V group as carbonates.

(h) Cations of group II are precipitated as sulphides in acidic medium while those of group IV as sulphides in basic medium.

(i) There is no group reagent for cations like Mg^{2+}, Na^+ and K^+.

(j) NH_4Cl is an important reagent in salt analysis.

(k) Precision and accuracy go side by side.

(l) The absolute value of the standard deviation is of limited value.

(m) Standard deviation is a meaningful statistical term.

(n) Activity coefficient is a measure of non-ideal behavior.

(o) Activity is always equal to concentration.

Chapter Five

BORON AND ALUMINUM

5.1 INTRODUCTION

Group IIIA (13) of the periodic table comprises boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). Of these boron and aluminium are familiar elements, while the other three are rare. The two familiar elements, boron and aluminium have their individual peculiarities. Boron with its small size and highly concentrated charge possesses all the characteristics of a non-metal. Aluminium with its large size is highly electropositive. Other elements are all metals and show regular gradation in properties.

All the elements have three electrons in their outermost shell with two electrons in the s-orbital and one electron in the p-orbital ($ns^2 np^1$) as shown in Table 5.1

Table 5.1. Electronic Configuration of Group IIIA (13) Elements.

Element		At.No.	Electronic Configuration
Boron	(B)	5	$1s^2, 2s^2 2p^1$
Aluminium	(Al)	13	$1s^2, 2s^2 2p^6, 3s^2 3p^1$
Gallium	(Ga)	31	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^1$
Indium	(In)	49	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^1$
Thallium	(Tl)	81	$1s^2, 2s^2 sp^6, 3s^2 sp^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^{14}, 5s^2 5p^6 5d^{10}, 6s^2 6p^1$

On the basis of the electronic configuration of the penultimate shell, these elements can be divided into two sub-groups namely *(i)* Ist sub-group of the elements consists of B and Al elements whose penultimate shells have inert gas type configuration (s^2 or $s^2 p^6$) *(ii)*, 2nd sub-group consists of Ga, In and Tl whose penultimate shells have pseudo inert gas type configuration ($s^2 p^6 d^{10}$). This difference in electronic configuration is responsible for the difference in properties of the elements of both the sub-groups and also of boron and aluminium.

Some of the important physical properties of group IIIA (13) elements are summarized in Table 5.2.

Table 5.2. Physical Properties of Group IIIA(13) Elements

Property	B	Al	Ga	In	Tl
Atomic Number	5	13	31	49	81
Atomic Weight	10.81	26.98	69.72	114.82	204.37
Atomic Volume (cc)	4.62	10.0	11.8	15.1	17.2
Density (g/cm^3)	2.33	2.70	5.93	7.31	11.8
Melting point (°C)	2300	660	29.8	156	303
Boiling point (°C)	2550	2450	2237	2000	1457
Covalent radius (pm)	82	118	126	144	178
Ionic radius (pm) M^{3+}	20	50	62	81	95
Electronegativity	2.0	1.5	1.6	1.7	1.8
Ionization Energy (kJ/mol) Ist	801	572.4	479.0	559.7	588.7
2nd	2431.8	1283.5	1668.6	1282.5	1969
3rd	3657.4	2740.6	2952.9	2692.4	2806
Oxidation state	+3	+3	+3, +1	+3, +1	+3, +1
Electrode potential M^{3+}/M (V)	—	1.66	0.52	0.34	—
Crystal lattice	Complex	Close packed	Complex	Close packed (Distorted)	Close packed
Heat of sublimation (kJ/mol)	564.9	324.3	273.2	245.7	180.0

5.2 GRADATION OF THE CHARACTERISTIC PROPERTIES WITHIN GROUP IIIA (13) ELEMENTS

The gradation in the physical and chemical properties of the elements with the rise of atomic number is as follows:

(i) **Atomic Volume, Ionic Radius and Density.** Atomic volume, ionic radius (of M^{3+} ions) and density increase on moving from B to Tl.

(ii) **Melting Points, Boiling Points and Heat of Sublimation.** In the case of melting points, there is sudden fall down from aluminium to gallium followed by a gradual rise again to thallium. The melting point of boron is extremely high indicating strong bonding between individual atoms. The melting points of other elements especially gallium, indium and thallium, are significantly low indicating that the metallic lattices in them are much more readily ruptured. Boiling points and heats of sublimation show a continuous decrease with increasing atomic number. The successive decrease in heat of sublimation indicates that the atoms of these elements are held less and less closely as we move from boron to thallium.

(iii) **Ionization Energies.** First ionization energies of these elements correspond to the removal of np^1 electron from $ns^2\,p^1$ configuration, while the second and third ionization energies correspond to the removal of ns^2 electrons in succession. Because of the increase in size of Al, the ionization energy decreases from B to Al. But in going from Al to Ga the value of ionization energy increases. Thus increase in the case of gallium is due to the fact that the intervening *d*-electrons in Ga are not able to shield the nuclear charge effectively and hence the valence electrons in Ga are more firmly held to the nucleus and its ionization energy increases.

(iv) **Oxidation States.** Boron and aluminium show an oxidation state of +3 while other members show both +1 and +3 oxidation states. M^{3+} cations are obtained when all the three $ns^2\,p^1$ electrons are lost while M^+ cations are formed when only one np^1 electron is lost. In the formation of M^+ cations the electron pair in ns orbital remains inert. This is called *inert pair effect.* B and Al do not show inert pair effect and hence do not form M^+ cations. Since the inert pair effect increases from Ga to Tl, the stability of +3 oxidation state decreases while that of +1 state increases. Thus Ga(1) compounds are unstable, In(1) compounds are moderately stable whereas those of Tl(1) are the most stable. The relative stability order of M^{3+} and M^+ cations is shown below.

$$B^{3+} > Al^{3+} > Ga^{+3} > In^{+3} > Tl^{3+}$$

and

$$B^+ < Al^+ < Ga^+ < In^+ < Tl^+$$

(v) **Electropositive (Metallic) Character.** Electropositive character of the elements increases as we move from B to Tl. This is indicated from the ionization energies of these elements. Thus B is a semi-metal *i.e.*, it is closer to non-metals than to metals in its properties, while other members are metallic in nature. Al, Ga, In and Tl have almost equal electropositive character as is evident from their almost equal ionization energy values.

(vi) **Nature of M^{3+} Compounds.** From the electronic configurations of these elements it is clear that all of them would be expected to form M^{3+} ions. The nature of the compounds of M^{3+} ions is decided by Fajan's rule which states that the smaller the cation, the greater is its tendency to form covalent compounds. Thus with the increase of the size of M^{3+} ions from B^{3+} to Tl^{3+}, their tendency to form covalent compounds decreases.

(vii) **Reactivity.** Pure boron is almost unreactive at ordinary temperature. It reacts with air only when heated; it does not react with water. It is attacked only by hot conc. acids and alkalies.

Aluminium decomposes water and reacts readily in air at ordinary temperature to form a protective layer of its oxide which protects it from further action. Gallium and indium are not affected by air even when heated whereas thallium is a little more reactive and forms an oxide on its surface.

(viii) **Formation of Oxides and Hydroxides.** All the elements of this group form oxides and hydroxids. As we move from boron to thallium, the oxides and

hydroxides of these elements change from acidic through amphoteric to basic. Thus oxides and hydroxides of boron are acidic, those of Al and Ga are amphoteric while those of In and Tl are basic.

(*ix*) **Formation of Trihalides.** All the elements of this group react with halogens to form trihalides. The trihalides of boron are covalent and act as *Lewis acids.* The fluorides of Al, Ga, In and Tl are ionic while the other halide of these elements are covalent when anhydrous. For example, anhydrous $AlCl_3$ is covalent but in water it gets hydrolyzed to give Al^{3+} (aq) ions. This change is mainly due to high hydration energy of Al^{3+} ions. Some members of the group also form complex halides *e.g.*, $[AlF_6]^{3-}$ $[GaCl_6]^{3-}$ etc.

(*x*) **Formation of Hydrides.** Boron forms a large number of polymeric hydrides which are called *boranes, e.g.*, B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11} etc. These hydrides are covalent in nature. Aluminium forms only one high molecular weight polymeric hydride, $(AlH_3)_x$. Gallium gives GaH_4 which is called *gallanc*. It is an unstable and volatile liquid. Indium gives polymerised solid hydride, $(InH_3)_x$. The hydrides given by Tl are extremely unstable. The elements of this group also form the complex anionic hydrides like $Li^+[BH_4]^-$, $Li^+[AlH_4]^-$ etc.

(*xi*) **Flame.** Boron gives a green-edged flame. Aluminium does not give any colour. Gallium gives violet colour, indium, a dark blue, and thallium, a green coloured flame on heating.

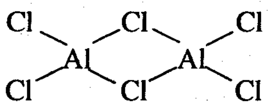
5.3 COMPARISON OF BORON AND ALUMINIUM

Both boron and aluminium are placed in the same group of the periodic table. They have many similarities and differences in their properties which are summarized below:

(*a*) Similarities

(*i*) Both elements have similar electronic configurations having three electrons in their outermost shells, *i.e.*, ns^2p^1.

(*ii*) Both elements form covalent compounds of valency 3. The covalency increases very rapidly to 4 either internally by polymerisation of molecules; e.g.



or by acting as acceptor, e.g;

$$H_3N \longrightarrow BF_3 \quad \text{and} \quad H_3N \longrightarrow AlCl_3$$

(*iii*) Both the elements have +3 common oxidation state.

(*iv*) Both elements form electron deficient compounds, *e.g.*, hydrides, B_2H_6, $(AlH_3)_n$, etc.

(*v*) Both form oxides when heated with oxygen at high temperature.

$$4B + 3O_2 \xrightarrow{700°C} 2B_2O_3$$

$$4Al + 3O_2 \xrightarrow{800°C} 2Al_2O_3$$

(vi) Both react with alkalies to form H_2 gas. (B only in fused alkali).

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2\uparrow$$

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow$$

(vii) Both, when heated with nitrogen or ammonia, form nitrides.

$$2B + N_2 \longrightarrow 2BN$$

$$2Al + N_2 \longrightarrow 2AlN$$

(viii) Both form trichlorides by direct combination with Cl_2. The trichlorides are covalent and are hydrolysed by water.

$$2B + 3Cl_2 \longrightarrow 2BCl_3$$

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

(ix) Both have no tendency to lose the three valence electrons to attain inert gas configuration.

(b) Differences

The difference in properties is due to the big difference in their size and ionization potential. The points showing dissimilarities between B and Al are given below:

(i) B has two electrons in the penultimate shell while Al has eight electrons in its penultimate shell.

(ii) B is typical non-metal while Al is metallic in nature.

(iii) B is a bad conductor of heat and electricity while Al is a good conductor of heat and electricity.

(iv) B has high melting point (2300°C) while Al has low melting point (660°C).

(v) B exhibits allotropy while Al does not exhibit allotropy.

(vi) B forms a number of hydrides like B_2H_6, B_4H_{10} etc. which are covalent in nature. Al does not form any stable and definite hydride.

(vii) B does not decompose water or steam Al decomposes steam to liberate H_2.

(viii) B does not react with dilute acids while Al reacts with dilute acids to form H_2.

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2\uparrow$$

(ix) The hydroxide and oxide of B is acidic in nature while that of Al are amphoteric in nature.

(x) B combines with metals to give borides, *e.g.*; Mg_3B_2. Al gives only alloys.

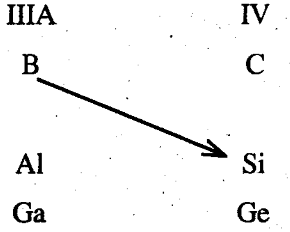
(xi) The maximum covalency of B is four while that of Al is six, e.g. $K[BF_4]$ and $Na_3[AlF_6]$.

(xii) Borates are more stable while aluminates are less stable.

(xiii) Boron forms different types of acids like H_3BO_3 (orthoboric acid) HBO_2 (metaboric acid) while Al does not form such acids.

5.4 DIAGONAL RELATIONSHIP BETWEEN BORON AND SILICON

We know that boron is present is group IIIA of the periodic table. The element lying below it is aluminium and the element which is diagonally related to boron is silicon which is present in group IVA as shown below:



Boron resembles silicon in many of its properties. Some common points showing the similarities between B and Si are given below:

(i) Both the elements are typical non-metals, bad conductors of electricity, have high melting points and low densities.

(ii) Both the elements show allotropy, *e.g.*, amorphous and crystalline forms.

(iii) Both the elements can be prepared by reducing their oxides.

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

(iv) Both the elements dissolve in alkalies (B only in fused while Si in fused as well as aqueous), forming metaborate (BO_2^-) and metasilicate (SiO_3^{2-}) and liberate H_2.

(v) Both B_2O_3 and SiO_2 are acidic and form salt with basic oxides. Complex borates resemble in some ways the complex silicates.

(vi) Boric acid and silicic acids are both weak acids. $B(OH)_3$ and $Si(OH)_4$ do not show any amphoteric behaviour.

(vii) The hydrides of boron and silicon are volatile and highly inflammable. They are heavily hydrolysed.

(viii) Both the elements form mainly covalent compounds like hydrides and halides, *e.g.*, B_2H_4, SiH_4, BX_3 SiX_4 etc.

(ix) None of these elements occurs in the free state. Both are found as oxy-compounds, *e.g.*, borates and silicates.

(x) Both the elements combine with metals like Mg and form borides and silicides.

$$2B + 3Mg \longrightarrow Mg_3B_2$$

$$Si + 2Mg \longrightarrow Mg_2Si$$

(xi) Certain oxo-salts of B and Si are structurally similar. Thus $(BO_2)_n$ and $(SiO_3)_n$ would form linear structure in metaborates and pyroxene silicates respectively.

(xii) B like Si is an electronegative element and never forms tripositive ion, B^{3+}.

(xiii) The halides of B (except BF_3) are readily hydrolysed as also the halides of Si giving boric and silicic acid respectively.

$$BX_3 + 3H_2O \text{ ——— } B(OH)_3 + 3HX$$

$$SiX_4 + 4H_2O \text{ ——— } Si(OH)_4 + 4HX$$

5.5 METALLURGY OF ALUMINIUM

Occurrence

Aluminium is the most abundant metallic element (7.3%) in the earth's crust. It does not occur free in nature. The chief minerals of aluminium are either silicates or oxides.

1. **Silicates**

Felspar	$K_2O.Al_2O_3.6SiO_2$
Kaolin	$Al_2O_3.2SiO_2.2H_2O$

2. **Oxides**

Corundum	Al_2O_3
Bauxite	$Al_2O_3.2H_2O$
Diaspore	$Al_2O_3.H_2O$

3. **Fluorides**

Cryolite	Na_3AlF_6

4. **Sulphates**

Alumite	$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

Extraction of Aluminium

The extraction of aluminium from bauxite consists of the following steps:

1. **Purification of Bauxite**

Bauxite is associated with silica, SiO_2 and ferric oxide, Fe_2O_3 and these impurities must be completely removed in order to get good quality of aluminium. A number of processes have been suggested for this purpose.

(a) **Baeyer's Process:** It is especially used for red bauxite containing ferric oxide as chief impurity. It is first roasted at low temperature to convert any ferrous oxide to ferric oxide and then digested at 150°C with a concentrated solution of caustic soda in an autoclave. The aluminium oxide present in the bauxite dissolves in caustic soda forming soluble sodium meta-aluminate, $NaAlO_2$, while the impurities are left behind.

$$Al_2O_3.2H_2O + 2NaOH \longrightarrow 2Na\,AlO_2 + 3H_2O$$

The solution is filtered and agitated with some freshly precipitated $Al(OH)_3$) which results in the precipitation of whole of the $NaAlO_2$ in the form of $Al(OH)_3$.

$$NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3\downarrow + NaOH$$

$Al(OH)_3$ is filtered off and washed. The filtrate containing caustic soda is concentrated and used again.

(b) **Hall's Process:** In this process, the ore is fused with sodium carbonate. Aluminium oxide being amphoteric dissolves to form sodium meta-aluminate while the insoluble iron oxide and silica are left as residue:

$$Al_2O_3.2H_2O + Na_2CO_3 \longrightarrow 2NaAlO_2 + 2H_2O + CO_2$$

The filtrate is warmed at a temperature of 50—60°C and a current of CO_2 is passed through it when aluminium hydroxide is precipitated.

$$2NaAlO_2 + 3H_2O + CO_2 \longrightarrow 2Al(OH)_3\downarrow + Na_2CO_3$$

(c) **Serpek's Process:** This is used chiefly for ores containing silica as the chief impurity. The ore is heated with carbon and nitrogen gas passed over the mixture. The aluminium nitride formed is hydrolysed by water to get $Al(OH)_3$.Silica (SiO_2) is reduced to silicon.

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

2. Conversion of $Al(OH_3)$ into Al_2O_3

The precipitate of $Al(OH)_3$ obtained by any of the above methods is washed, dried and ignited to get Al_2O_3.

$$2Al(OH)_3 \xrightarrow{1500°C} Al_2O_3 + 3H_2O$$

3. Reduction of Alumina (Al_2O_3)

Aluminium is obtained from alumina by an electrolytic process known as *Hall's process*. In this method a solution of Al_2O_3 in fused cryolite, Na_3AlF_6 is taken in an electrolytic cell in which it is electrolysed. The cell consists of a cast iron box (usually 8ft. × 6ft.) lined with blocks of carbon which serve as the cathode (Fig. 5.1). The anodes are rods of carbon hanging in the molten mass. The bath containing the electrolyte is maintained at a temperature of 900 – 1000°C. A glow lamp (control lamp) is connected in parallels with the electrolytic cell. This lamp begins to glow when the quantity of Al_2O_3 gets exhausted. Now more quantity of Al_2O_3 is added. Thus it is a continuous process. When electric current is passed, AlF_3 (from cryolite) ionises as

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

Al is liberated at the cathode and F_2 goes to anode where it reacts with Al_2O_3 to form AlF_3 and O_2 is liberated. The O_2 liberated at the anode reacts with carbon anodes to form CO and CO_2.

At Cathode $\quad Al^{3+} + 3e^- \longrightarrow Al$

At anode $\quad 3F^- \longrightarrow 3F + 3e^-$

$$3F + 3F \longrightarrow 3F_2$$

$$2Al_2O_3 + 6F_2 \longrightarrow 4AlF_3 + 3O_2$$

$$2C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

The process, however, is much more complex. Al metal produced by this method is 99% pure but contains trace impurities of Si, Fe, Al_2O_3 etc.

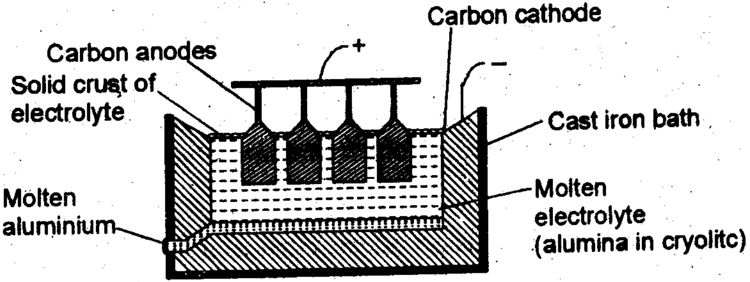


Fig 5.1. Extraction of Aluminium

4. Refining of Aluminium

The purification of aluminium is done by *Hoop's electrolytic process*. The cell used consists of a carbon-lined iron tank (Fig. 5.2). This tank contains the three liquid layers one over the other of different specific gravity. The top layer consists of pure molten aluminium which acts as cathode. The middle layer consists of fused mixture of fluorides of Na, Al (*i.e.*, cryolite Na_3AlF_6) and Ba. This layer acts as the electrolyte. The bottom layer consists of molten impure aluminium containing the impurities of Cu, Si, Fe etc. This layer acts as anode.

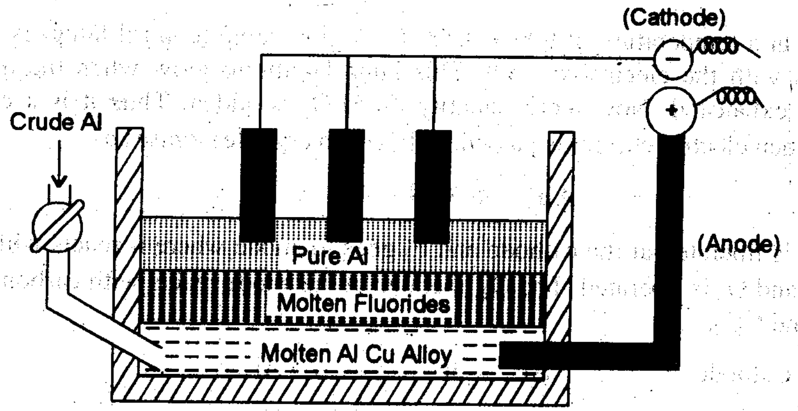


Fig 5.2. Refining of Aluminium

When electric current is passed, Al^{3+} ions from the middle layer go to the top layer and are discharged there as pure aluminium. At the same time an equivalent amount of Al from the bottom layer passes into the middle layer, while the impurities in the bottom layer do not pass, but remain below i.e., they do not dissolve into the electrolyte. Aluminium obtained in this way is 99.99% pure. It is periodically removed and impure Al containing the impurities of Cu, Fe, Si etc. are introduced into the bottom layer.

5.6 CHARACTERISTICS OF ALUMINIUM

(a) Physical

Aluminium is a bluish white metal with a brilliant lustre which is soon destroyed by the formation of a layer of oxide on it. It is a light metal, malleable, ductile and good conductor of heat and electricity. Density = 2.7; Melting point 652°C.

(b) Chemical

(*i*) **Action of Air:** Aluminium is not affected in dry air but in moist air a thin film of oxide is formed over its surface. It burns in oxygen producing brilliant light.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

(*ii*) **Action of Water:** Aluminium, if pure, is not affected by pure water but is corroded by water containing salts if some impurities are present in the metal. It decomposes boiling water.

$$\mathbf{2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2}$$

(*iii*) **Action of Acids:** Aluminium dissolves in HCl and dilute H_2SO_4 producing H_2.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2$$

Hot concentrated H_2SO_4 produces SO_2.

$$2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

Concentrated HNO_3 has no action on aluminium.

(iv) **Action of Alkalies:** Aluminium dissolves in alkalies with the evolution of H_2 and formation of soluble aluminates.

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

$$2Al + 6NaOH\,(\text{fused}) \longrightarrow 2Na_3AlO_3 + 3H_2$$

(v) **Action of Halogens:** Finely powdered heated aluminium combines with halogens, if the latter are passed over it.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

(vi) **Action of Nitrogen:** Aluminium combines with nitrogen forming aluminium nitride.

$$2Al + N_2 \longrightarrow 2AlN$$

(vii) **Reducing Properties:** Aluminium metal is a good reducing agent and reduces oxides of some metals.

$$2Al + Cr_2O_3 \longrightarrow 2Cr + Al_2O_3 + \text{Heat}$$

$$2Al + Fe_2O_3 \longrightarrow 2Fe + Al_2O_3 + \text{Heat}$$

(c) **Uses of Aluminium:**

(i) Aluminium is used for making utensils due to its lightness, resistance to corrosion and good conductivity.

(ii) It is used for making frames, coils for motors and wires for electrical transmission.

(iii) It gives foils of extreme thinness which are used as wrappers for chocolates and cigarettes.

(iv) The fine dust of metal is used in paints, lacquers, fireworks, flashlight powders and in thermit welding.

(v) Aluminium amalgum is used as reducing agent in the extraction of Cr and Mn.

(vi) It is also used for making alloys, e.g.,

Magnalium (Al = 94.5%, Mg 5.5%) which is used in scientific apparatus and machined articles.

Duralumin (Al = 95%, Cu = 4%, Mg = 0.5%, Mn = 0.5%) which is used in aircraft parts, railroad cars and boat machinery.

5.7 ELECTRON DEFICIENT MOLECULES

Electron deficient molecules are the compounds in which there are not enou electrons to form two electron bonds between the atoms. In these molecules the numb of usable orbitals is greater than the number of electrons, so they have strong tendency accept electrons from the donor atoms.

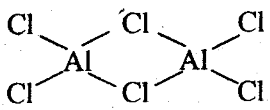
Some elements of group IIA and IIIA-namely beryllium, boron and aluminium – have a considerable tendency to accept electrons, and so acquire a tetrahedral configuration whenever possible. The molecules possessing `lone pair' of electrons would readily combine with the electron deficient molecules to remove their electron deficiency. This tendency to achieve a co-ordination number of four is so great that in the absence of suitable donor molecules, simple molecules of these elements may dimerize, e.g.,

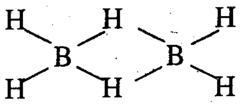
$$2BH_3 \longrightarrow B_2H_6$$

$$2AlCl_3 \longrightarrow Al_2Cl_6$$

Normal two-electron bonds are present in such dimers. It is more difficult to write down structural formulae for dimers such as diborane, B_2H_6 and alkyls of beryllium and aluminium, $Be_2(CH_3)_4$ and $Al_2(CH_3)_6$, since there are not enough electrons to provide two-electron bonds between the atoms in these molecules. Such molecules are, therefore, said to be electron deficient.

Examples





Sometimes adducts are formed by the interaction of electron deficient molecules with the donor atoms/molecules, e.g;

$$AlCl_3 + :NH_3 \longrightarrow H_3N : AlCl_3 \text{ or } H_3N \longrightarrow AlCl_3$$

$$BCl_3 + :NH_3 \longrightarrow H_3N : BCl_3 \text{ or } H_3N \longrightarrow BCl_3$$

$$BH_3 + :CO \longrightarrow H_3B : CO \text{ or } H_3B \longrightarrow CO$$

5.8 HYDRIDES OF BORON (BORANES)

Boron does not combine directly with hydrogen to form its hydrides. Nevertheless a number of interesting hydrides of boron are known. The hydrides of boron are also called *boranes* to establish an analogy with alkanes.

The boranes have been grouped into two classes namely B_nH_{n+4} (n = 2, 5, 6, 8, 10 and 18) and B_nH_{n+6} (n = 4, 5, 6, 9 and 10). The boranes of the former type are quite stable and have high melting point while those of the latter type are unstable and have low melting points.

Table 5.3. Physical Properties of Boranes

Formula	Name	m.p.°C	B.P.°C
B_2H_6	Diborane	-165.6	-92.5
B_4H_{10}	Tetraborane-10	-120	18
B_5H_9	Pentaborane-9	-46.6	48
B_6H_{10}	Hexaborane10	-62.5	110
B_8H_{12}	Octaborane-12	-20	—
$B_{10}H_{14}$	Decaborane-14	99.7	213

Of all the borones the most important one I the diborane, B_2H_6 which we shall study in detail.

Diborane, B_2H_6

Preparation

Diborane is prepared by the following methods:

(i) By the reduction of boron trichloride with $LiAlH_4$.

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

(ii) By the reduction of boron trifluoride with Lithium hydride

$$8BF_3 + 6LiH \longrightarrow B_2H_6 + LiBF_4$$

(iii) By the reduction of boron trifluoride with $NaBH_4$.

$$4BF_3 + 3NaBH_4 \longrightarrow 2B_2H_6 + 3NaBF_4$$

(iv) By reducing vapours of BCl_3 by molecular hydrogen.

$$2BCl_3 + 6H_2 \longrightarrow B_2H_6 + 6HCl$$

Properties

(i) It is an inflammable colourless gas (b.p. -92.5°C) with a sticky sweet odour and is extremely toxic.

(ii) It is stable only at lower temperature in the absence of moisture. At higher temperatures B_2H_6 gets decomposed into a number of higher boranes. For example:

$$5B_2H_6 \xrightarrow[\text{u-tube}]{115°C} 2B_5H_{11} + 5H_2$$

$$5B_2H_6 \xrightarrow[\text{u-tube}]{250°C} B_5H_9 + B_5H_{11} + 5H_2$$

(iii) It is readily decomposed by water into boric acid and hydrogen.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

(iv) It reacts with halogen (not iodine) under different conditions to give different products.

$$B_2H_6 + 6Cl_2 \xrightarrow{25°C} 2BCl_3 + 6HCl$$

$$B_2H_6 + Br_2 \xrightarrow{100°C} B_2H_5Br + HBr$$

(v) Pure B_2H_6 undergoes no change when mixed with dry air or O_2 at room temperature, but it may ignite (i.e. burn) if impure.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + 1976\ kJ$$

The production of large amount of heat in the above reaction makes B_2H_6 a useful rocket fuel

(vi) It reacts with halogen acids to form different substituted boranes.

$$B_2H_6 + HCl \xrightarrow{AlCl_3} B_2H_5Cl + H_2$$

$$B_2H_6 + HBr \xrightarrow[AlBr_3]{90°C} B_2H_5Br + H_2$$

(vii) When diborane is treated with alkalies or their concentrated solutions, a partial decomposition takes place and corresponding hypoborate is obtained.

$$B_2H_6 + 2KOH \xrightarrow{0°C} \underset{\text{Potassium hypoborate}}{K_2(B_2H_6O_6)_2}$$

(viii) When diborane is treated with sodium or potassium amalgum (reducing agent) in cold state, a crystalline product of the composition $B_2H_6.2Na$ or $B_2H_6 \bullet 2K$ is formed.

$$2Na\ (\text{amalgum}) + B_2H_6 \longrightarrow B_2H_6{\cdot}2Na$$

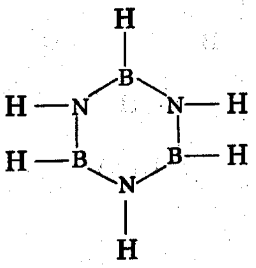
(ix) Diborane behaves as Lewis acid and would readily combine with Lewis bases such as $CO, NH_3, (CH_3)_2S$ etc.

$$B_2H_6 + 2NH_3 \xrightarrow[\text{temp.}]{\text{Low}} \underset{\text{Diammoniate of diborane}}{B_2H_6{\cdot}2NH_3}$$

When this substance is heated at 200°C, a stable cyclic compound $B_3N_3H_6$ (called *borazole* or *borazine*) is obtained which is an electronic isomer of benzene and is, therefore known as *inorganic benzene.*

$$3(B_2H_6{\cdot}2NH_3) \xrightarrow{200°C} \underset{\text{Borazole}}{2B_3N_3H_6} + 12H_2$$

The structure of borazole is

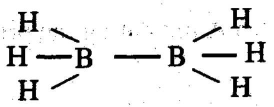


Uses of Diborane

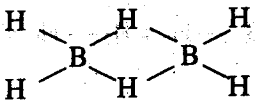
Diborane is used: *(i)* as rocket fuel for supersonic bombers, *(ii)* for the preparation of high energy fuels and propellants, *(iii)* for the preparation of higher boranes, organic boron compounds and metal boron hydrides like $LiBH_4$, $NaBH_4$ etc., *(iv)* as a reducing agent in organic reactions, *(v)* as a catalyst in polymerisation reactions *(vi)* for welding torches.

Structure and Bonding

Two main configurations have been put forward to explain the structure of diborane.



Ethane



Bridge

The 'ethane' structure is analogous to that of C_2H_6 and the 'bridge' structure is comparable with Al_2Cl_6. The essential difference between the two models is that whereas all six hydrogen atoms are equivalent in the ethane structure, two have a special position in the bridge model. Moreover, free rotation about the B-B axis should be possible for ethane model, but not for the bridge structure. It is significant that only four of the six hydrogen atoms in B_2H_6 can be replaced by methyl groups, giving $(CH_3)_4B_2H_2$, and that this tetramethyl molecule is symmetrical with two methyl groups attached to each boron atom. This suggests that two of the six hydrogen atoms in diborane are attached differently from the other four.

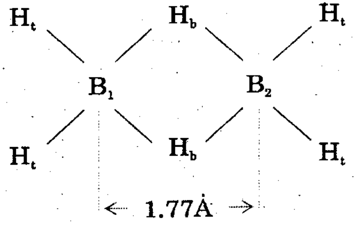


Fig. 5.3. Hydrogen bridge strucutre of B_2H_6

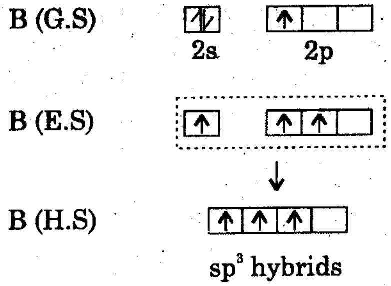
Electron diffration and IR studies of this molecule have shown that B_2H_6 has *hydrogen-bridge structure* as shown in (Fig. 5.3), in which two irregular BH_4 tetrahedrons have one edge in common. Thus two boron atoms (B_1 and B_2) and four hydrogen atoms (H_t – called terminal hydrogen atoms) lie in the plane of paper, while the remaining two hydrogen atoms (H_b – called bridging hydrogen atoms) are located centrally above and below the plane of paper.

From the figure it is evident that length of $B_1 — H_t$ bond = length of $B_2 - H_t$ which is equal to 1.19 Å. This bond length is almost equal to that expected for a single bond given by the sum of single bond normal covalent radii of B and H, *i.e.*,

$$r_B + r_H = 0.85 + 0.30 \approx 1.15 \text{ Å}$$

On the other an $B_1 — H_b = B_2 — H_b = 1.33$ Å > 1.15 Å indicating the presence of fractional bond.

The nature of bonding in diborane molecule has been established by molecular orbital theory (MOT). According to MOT, the hydrogen bridge, $B_1 — H_b — B_2$ in B_2H_6 is regarded as a three-centre two electron bond denoted as (3c — 2e) bond. This (3c — 2e) bond is a special type of bond which is formed by two electrons and binds three nuclei together, namely B_1, H_b and B_2.



Each of the B-atoms forms four sp^3 hybrid orbitals of which three are singly occupied and the fourth one is vacant. Singly occupied sp^3 hybrid orbital of B_1 atom and the vacant sp^3 hybrid orbital on B_2 atom overlap with the single filled is orbital of H_b

atom to form a *delocalized molecular orbital* containing two electrons and covering all the three nuclei viz. B_1, B_2 and H_b. This MO thus makes one of the bridges between two boron atoms. The delocalized molecular orbital is called three-centre two-electron molecular orbital and is, therefore, represented as 3c-2e. A second 3-centre MO also arises in a similar way. The formation of 3-centre MO is shown in Fig. 5.4

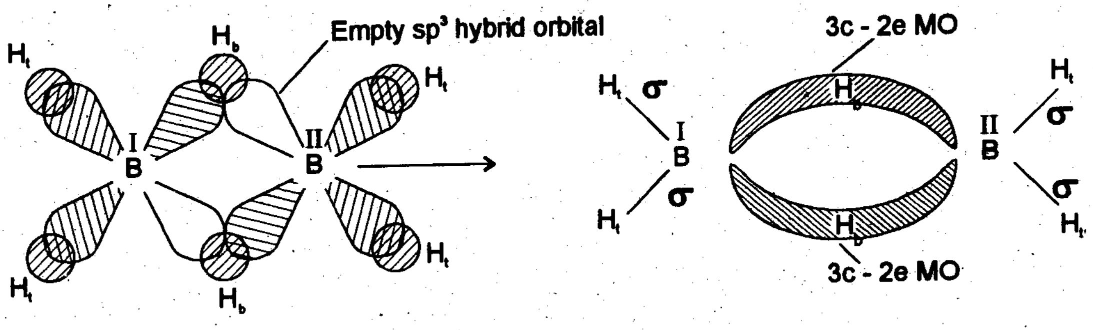


Fig. 5.4. Formation of two (3c-2e) MO's in B_2H_6

The two 3-centre MO's are indicated by two lobes (upper and lower) which are of *banana shape*. Clearly these two 3 centre MO's are formed by sp^3-s-sp^3 overlap. The four (2c-2e) B-H_t bonds arise from overlap of the remaining two sp^3-hybrids of each B-atom with IS-AO of H_t-atoms. Thus these four bonds are formed by sp^3-s overlap.

5.9 BORIC ACIDS AND BORATES

Several boric acids are known (either as such or in the form of salts). These are derived from boron trioxide with varying amounts of water, thus:

Orthoboric acid	H_3BO_3	or $B_2O_3{\cdot}3H_2O$
Metaboric acid	HBO_2	or $B_2O_3{\cdot}H_2O$
Tetraboric acid	$H_2B_4O_7$	or $2B_2O.H_2O$
Pyroboric acid	$H_6B_4O_9$	or $2B_2O_3{\cdot}3H_2O$

Salt corresponding to some condensed acids like $Ca_2B_6O_{11}$ and $Mg_3B_8O_{15}$ also exist. Of the free acids orthoboric acid or boric acid is the only important one, which is stable in solid as well as in solution form. The salts of boric acids are called borates. An important example is borax, $Na_2B_4O_7.10H_2O$.

Boric acid, H_3BO_3

Preparation

Boric acid is prepared by the following methods:

(i) By the action of concentrated sulphuric acid on concentrated solution of borax. Boric acid separates on cooling as white flaky crystals.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$$

(ii) **Hydrolysis of boron trihalides would yield boric acid.**

$$BX_3 + H_2O \longrightarrow H_3BO_3 + 3HX$$
$$(X = Cl, Br, I)$$

(iii) Colemanite mineral ($Ca_2B_6O_{11}\cdot 5H_2O$) is an important source of boric acid. It is powdered and dissolved in boiling water. Sulphur dioxide is passed through the solution when boric acid is formed along with calcium bisulphite. The crystals of acid separate on cooling while soluble calcium bisulphite remains in the solution.

$$Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$$

Properties

(i) Boric acid is fairly soluble in water and is slightly volatile in steam. It crystallizes out as white flaky crystals having soapy touch.

(ii) It decomposes on heating to form metaboric acid at 100°C, tetraboric acid at 140°C and a glassy mass of boric anhydride at red heat.

$$H_3BO_3 \xrightarrow{100°C} HBO_2 \xrightarrow{140°C} H_2B_4O_7 \xrightarrow{\text{red heat}} \underset{\text{Boric anhydride}}{B_2O_3}$$

(iii) It is a very weak acid and ionises mainly as a monobasic acid. It is not a proton donor but behaves as a Lewis acid, i.e., it can accept a lone pair of electrons from an OH^- ion.

$$B(OH)_3 \text{ or } H_3BO_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$$

(iv) **It reacts with alkalies to form salts.**

$$NaOH + H_3BO_3 \longrightarrow \underset{\text{Sod. Metaborate}}{NaBO_2} + 2H_2O$$

$$2NaOH + 4H_3BO_3 \longrightarrow \underset{\text{Sod. tetraborate}}{Na_2B_4O_7} + 7H_2O$$

(v) When it is heated with ethanol, it burns with green edge flame due to the formation of volatile ethyl borates.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Con. } H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

(vi) When treated with acetic anhydride, boron acetate is formed

$$2H_3BO_3 + 5(CH_3CO)_2O \longrightarrow (CH_3COO)_2BOB(OOCCH_3)_2 + 6CH_3COOH$$

(vii) With Na_2O_2, it gives sodium metaborate peroxyhydrate, $NaBO_2.H_2O_2.3H_2O$

(viii) When boric acid is neutralised with Na_2CO_2, borax is obtained.

$$2H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

Uses

It is used *(i)* in the manufacture of pottery glazes, glass and enamels, *(ii)* in medicine as an antiseptic and as an eye lotion, *(iii)* as preservative in food industry, *(iv)* in tanning industry, *(v)* in candle industry to stiffen wicks, *(vi)* in the manufacture of borax and pigments.

Sodium Tetraborate or Borax, $Na_2B_4O_7 \cdot 10H_2O$

Preparation

It is the sodium salt of tetraboric acid, $H_2B_4O_7$. It occurs naturally as tincal or suhaga. Tincal contains about 55% of borax, $Na_2B_4O_7.10H_2O$. It is prepared by the following methods:

(i) By boiling boric acid with soda-ash.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

(ii) It is also prepared from certain minerals such as Colemanite, $Ca_2B_6O_{11}$. The mineral is boiled with concentrated solution of sodium carbonate.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + \underset{\text{Borax}}{Na_2B_4O_7} + \underset{\text{Sod. metaborate}}{2NaBO_2}$$

Borax is crystallized from the filtrate. Carbon dioxide is passed through the mother liquor to convert the metaborate into borax.

$$4NaBO_2 + CO_2 \longrightarrow Na_2CO_3 + Na_2B_4O_7$$

Properties

(i) Borax exists in different forms:

(a) **Ordinary Borax** which is decahydrate or monoclinic, $Na_2B_4O_7.10H_2O$. This is the common form of borax and is obtained when a solution of the salt is crystallized at room temperature (i.e., below 60°C).

(b) **Octahedral Borax** which is pentahydrate, $Na_2B_4O_7.5H_2O$ and is obtained when the solution is crystallized above 60°C.

(c) **Borax Glass** which is the anhydrous from, NaB_4O_7 and is obtained by heating the ordinary borax above its melting point until all the water of crystallization is given off. It is a colourless glassy mass, absorbs moisture from air and is gradually converted into decahydrate form.

(ii) It is sparingly soluble in cold water and fairly soluble in hot water. The solution is alkaline in nature due to the formation of strong base, NaOH.

$$Na_2B_4O_7 + 7H_2O \longleftarrow 4H_3BO_3 + 2NaOH$$

(iii) It reacts with concentrated HCl or H_2SO_4 to form sparingly soluble boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

(iv) On heating above its melting point, it loses its water of crystallization and swells up to a white porous mass. On further heating, it melts to a liquid which then solidifies to a transparent glassy mass

$$Na_2B_4O_7 \xrightarrow{1000K} 2NaBO_2 + B_2O_3 \text{ (glassy bead)}$$

Boric anhydride, B_2O_3 produced as colourless glass combines with metal oxides to form metaborates with characteristic colours. This is the basis of *borax bead test.*

$$B_2O_3 + CoO \longrightarrow \underset{\text{Cobalt metaborate (blue)}}{Co(BO_2)_2}$$

$$B_2O_3 + CuO \longrightarrow \underset{\text{Cupric metaborate (blue in cold)}}{Cu(BO_2)_2}$$

Uses

It is used

(i) as an alkaline buffer in many dyeing and bleaching processes;

(ii) in qualitative analysis (borax bead test);

(iii) as a preservative;

(iv) as flame proofing agent for textile fabrics;

(v) in the manufacture of optical and borosilicate glasses;

(vi) as a flux in soldering, swelling and certain metallurgical operations;

(vii) in enamelling and making glazes for pottery and tiles;

(viii) in leather industry, both for soaking and cleaning hides and skins;

(ix) in the manufacture of washing powders and soaps.

5.10 ALUMINIUM HALIDES

Aluminium reacts with halogens to form the trihalides, AlX_3 (X = F, Cl, Br and I). The most important one is aluminium chloride.

Aluminium Chloride, $AlCl_3$.

Preparation

It is prepared by the following methods.

(i) By passing dry chlorine or hydrochloric acid gas over heated aluminium powder.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 2H_2$$

(ii) By heating alumina (Al_2O_3) and coke in a current of chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

(iii) By heating alumina in a current of S_2Cl_2 vapour and Cl_2.

$$4Al_2O_3 + 3S_2Cl_2 + 9Cl_2 \longrightarrow 8AlCl_3 + 6SO_2$$

Properties

(i) Anhydrous salt is a white crystalline solid. It is hygroscopic and sublimes at 180°C.

(ii) It is a typical covalent compound as is shown by its volatility, solubility in organic solvents like C_6H_6, CS_2 etc. and poor conductivity of the fused state.

(iii) An aqueous solution of the salt is acidic in nature because in water it undergoes hydrolysis and forms HCl.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

(iv) When NH_4OH is added to $AlCl_3$ solution, white precipitate of $Al(OH)_3$ is obtained

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow + 3NH_4Cl$$

(v) It forms addition compounds with a number of donor molecules like NH_3, PH_3 etc.

$$AlCl_3 + 6NH_3 \longrightarrow AlCl_3{\cdot}6NH_3 \text{ (Addition Compound)}$$

(vi) It reacts with reducing agents such as hydrides to form complex aluminium hydrides.

$$AlCl_3 + 4LiH \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl$$

(vii) It is used extensively in organic chemistry as a catalyst, e.g; in the Friedel-craft reaction:

$$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$$

It is believed that an intermediate complex ion $[AlCl_4]^-$ is formed thus:

$$C_2H_5Cl + AlCl_3 \rightleftharpoons C_2H_5^+ + AlCl_4^-$$

The $C_2H_5^+$ is a carbonium ion and reacts with the benzene:

$$C_6H_6 + C_2H_5^+ \longrightarrow C_6H_5C_2H_5 + H^+$$

and then HCl and $AlCl_3$ are formed.

$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

Uses

It is used

(i) in organic chemistry for introducing alkyl radicals originally linked with halogen into benzene nucleus;

(ii) in the manufacture of petrol by the cracking of mineral oils;

(iii) as a catalyst in the manufacture of drugs, dyes and perfumes.

Structure

The vapour density of the compound at 350 - 400°C corresponds to the dimeric formula, Al_2Cl_6, while at 750 - 800°C as well as in solution it corresponds to the monomeric formula, $AlCl_3$. Aluminium is tetrahedrally bonded to four chlorine atoms. One chlorine atom of an $AlCl_3$ molecule establishes coordinate bond with aluminium atom of the other aluminium chloride molecule (Fig. 5.5).

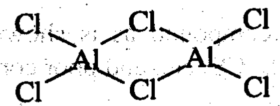


Fig. 5.5. Molecular structure of aluminium chloride.

5.11 ALUMINIUM HYDRIDES

Aluminium Hydride $(AlH_3)_n$

It is slowly formed as a white precipitate, when lithium hydride is allowed to react with excess of aluminium chloride in ethereal solution:

$$3LiH + AlCl_3 \longrightarrow AlH_3 + 3LiCl\downarrow$$

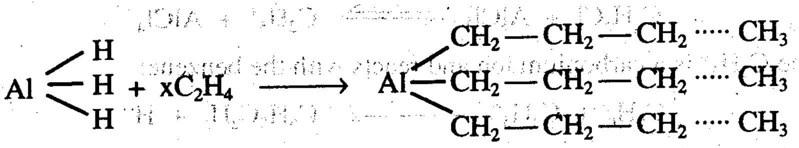
A more satisfactory method is to allow aluminium chloride to react with lithium aluminium hydride in ether:

$$AlCl_3 + 3LiAlH_4 \longrightarrow 4AlH_3 + 3LiCL\downarrow$$

The exact structure of polymer $(AlH_3)n$ is uncertain but it is electron deficient. It is a white solid and decomposes on heating, losing hydrogen. It reacts slowly with diborane to give aluminium borohydride.

$$2(AlH_3)_n + 3nB_2H_6 \longrightarrow 2nAl(BH_4)_3$$

Aluminium hydride undergoes a peculiar reaction with ethylene under pressure at 130°C:



The hydrocarbon chains may be many hundreds of thousands of CH_2 units long, and when the product is hydrolysed, *polyethylene* $(C_2H_4)_n$, is obtained.

Lithium Aluminium Hyride, $LiAlH_4$

It is obtained when excess of lithium hydride reacts with aluminium chloride in ether:

$$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl\downarrow$$

It is a colourless solid and soluble in ether. It reacts violently with water:

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3\downarrow + 4H_2\uparrow$$

It is a most useful reducing agent and is used extensively in organic and inorganic chemistry. It reduces aldhydes, ketones and carboxylic acids to alcohols. It reduces nonmetallic chlorides to corresponding hydrides, e.g.:

$$SiCl_4 + LiAlH_4 \longrightarrow SiH_4 + LiCl + AlCl_3$$

This is a general method for preparing many hydrides.

5.12 ALUMS

Originally the name *alum* was given to the double salt, potassium aluminium sulphate, $K_2SO_4.Al_2(SO_4)_3{\cdot}24H_2O$. But now the name is used for all double salts having the composition: $M^I_2\,SO_4.M^{III}_2\,(SO_4)_3{\cdot}24H_2O$, where M^I stands for univalent basic radical like Na^+, K^+, Rb^+, NH_4^+, Ag^+ and Tl^+ and M^{III} is a trivalent metal Al^{3+} Cr^{3+}, Fe^{3+}, Co^{3+} etc. The crystals of the alums are made up to $[M^I(H_2O)_6]^+$, $[M^{III}(H_2O)_6]^{3+}$ and two SO_4^{2-} ions. Some common examples of alums are:

(*i*) **Potash alum.** $K_2SO_4.Al_2(SO_4)_3.24H_2O$

(*ii*) **Sodium alum.** $Na_2SO_4.Al_2(SO_4)_3.24H_2O$

(*iii*) **Ammonium alum.** $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

(*iv*) **Potash Chrome alum.** $K_2SO_4.Cr_2(SO_4)_3.24H_2O$

All alums can be prepared by the general method for double salts by allowing a solution containing equimolar proportions of the two sulphates to crystallize. The alums separate from solution in octahedral crystals. They are isomorphous, form mixed crystals in all proportions and also layer crystals. They are usually much more soluble in hot water than in cold water. In solution they give the ions of the component salt.

Potash alum $K_2SO_4\ Al_2(SO_4)_3.24H_2O$ or $KAl(SO_4)_2.12H_2O$

Preparation

Commercially it is prepared from bauxite or alunite mineral. The bauxite is boiled with sulphuric acid and potassium sulphate in large reaction tanks. After reaction, the clarified liquor is evaporated and allowed to crystallize. Crystals thus obtained are purified by washing and centrifuging.

$$\text{Bauxite} + H_2SO_4 + K_2SO_4 \longrightarrow \underset{\text{(crystals)}}{K_2SO_4\ Al_2(SO_4)_3\cdot 24H_2O}$$

The mineral alunite or alum stone is calcined and treated with H_2SO_4 when $Al(OH)_3$ component is converted into $Al_2(SO_4)_3$. Now calculated quantity of K_2SO_4 is added to the solution which is then crystallized for alum. Finally it is purified by recrystallization.

$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3 + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$$

Properties

Potash alum is a white crystalline solid, soluble in water but insoluble in alcohol. The aqueous solution is acidic due to the hydrolysis of aluminium sulphate. When heated, it melts at 92°C and on further heating loses the whole of its water of crystallization and swells up. The swollen mass so produced is called *burnt alum (phul phatkiri).*

Uses

Alums are generally used:

(i) in water purification
(ii) in dyeing of fabrics
(iii) in water proofing of textiles
(iv) in dyeing and paper industry
(v) in tanning of hides
(vi) in arrest bleeding

Questions

Q.1*(a)* What are p-block elements? Write the electronic configuration of group IIIA elements.

(b) What are the general trends in the properties of group IIIA (13) elements?

Q.2*(a)* Compare and contrast the properties of boron and aluminium.

(b) Both boron and aluminium are in the same group of the periodic table. Which of them is likely to show more metallic properties and why?

Q.3*(a)* Discuss the diagonal relationship between boron and silicon.

(b) What are electron-deficient molecules? Explain with examples.

Q.4*(a)* What are the important minerals of aluminium? Describe the process used to extract aluminium from bauxite.

(b) How is aluminium refined?

Q.5*(a)* Outline the principle involved in the extraction of aluminium metal from alumina.

(b) Discuss some use of aluminium.

(c) What happens when?

(i) Al reacts with H_2O

(ii) Al reacts with H_2SO_4

(iii) Al reacts with NaOH

Q.6 What are boranes? Discuss the chemistry of boranes with special emphasis on their structure.

Q.7*(a)* What is diborane? How is it obtained? Discuss its structure.

(b) Write some uses of diborane.

Q.8*(a)* Discuss the structure and bonding of B_2H_6.

(b) What happens when

(i) B_2H_6 reacts with HCl

(ii) B_2H_6 reacts with O_2

(iii) B_2H_6 reacts with Cl_2

(iv) B_2H_6 heated at 250°C

Q.9 Give the preparation, properties in and uses of $AlCl_3$.

Q.10 Write the formulas of different boric acids. Discuss the preparation, properties and uses of orthoboric acid.

Q.11*(a)* What is borax? How is it prepared the laboratory. Briefly discuss the chemistry of borax bead test.

(*b*) Write done some uses of borax.

Q.12(*a*) What are alums? Give the formula of common alum and mention its uses.

(*b*) How do alums differ from double salts?

Q.13 Justify/comment on the following statements.

(*a*) The electron acceptor power of boron trihalides is

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

(*b*) BF_3 molecule acts as Lewis acid.

(c) $B(OH)_3$ is acidic while $Al(OH)_3$ is amphoteric in nature.

(d) BH_3 does not exist but BF_3 is quite stable.

(e) Aluminium halides exist as dimers while those of boron are monomers.

(f) Lewis acid strength of boron halides decreases in the order.

$$BBr_3 > BCl_3 > BF_3$$

(g) Aluminium forms the ion $[AlF_6]^{3-}$ but $[BF_6]^{3-}$ is not formed.

(h) Boron resembles with silicon.

(i) B–X bond distance in BX_3 type compounds is shorter than is expected theoretically.

(j) Boron has a tendency to form covalent compounds.

(k) B, Al, In and Tl are members of the same group.

(l) Boron differs from aluminium.

(m) B and Al show +3 oxidation states while other members show +1 and +3 oxidation states.

(n) Diborane has bridged structure.

Chapter Six

CARBON AND SILICON

6.1 INTRODUCTION

Group IVA (14) of the periodic table consists of carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Carbon is an essential constituent of all organic matter while silicon is the main constituent of inorganic matter. All the elements have four electrons in their outermost shell with two electrons in the *s*-orbital and two electrons in the *p*-orbital as shown in Table 6.1.

Table 6.1. Electronic configuration of Group IVA (14) Elements

Element	At. No.	Electronic Configuration
C	6	$1s^2, 2s^2\,2p^2$
Si	14	$1s^2, 2s^2\,2p^6, 3s^2\,3p^2$
Ge	32	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^2$
Sn	50	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6\,4d^{10}, 5s^2\,5p^2$
Pb	82	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6\,4d^{10}, 5s^2\,5p^6\,5d^{10}, 6s^2\,6p^2$

It is obvious that these elements possess s^2p^2 configuration in the valence shell. The penultimate shell of carbon contains s^2 electrons (saturated), of silicon contains s^2p^6 electrons (saturated), of germanium contains $s^2p^6d^{10}$ electrons (saturated) while tin and lead contain $s^2p^6d^{10}$ electrons (unsaturated). This shows why C differs from Si and these two (C and Si) from the other members of this group.

Some of the important physical properties of group IVA (14) elements are summarized in Table 6.2.

Table 6.2. Physical Properties of Group IVA (14) Elements

Property	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Atomic weight	12.01	28.08	72.60	118.69	207.19
Density (g/cm^3)	3.51 diamond 2.22 graphite	2.33	5.36	7.31 white	11.3
Ionization potential (eV)	11.2	8.1	7.8	7.3	7.4
Melting point (°C)	3570	1414	959	232	328
Boiling point (°C)	4827	2355	2830	2362	1755
Atomic radius (nm)	0.077	0.117	0.122	0.141	0.154
Electronegativity	2.5	1.8	1.7	1.7	1.6
Electrode potential	-	- 0.84	- 0.3	- 0.140	- 0.126
Atomic volume (cm^3/mol)	3.42	12.1	13.6	16.2	18.2

6.2. GRADATION OF THE CHARACTERISTIC PROPERTIES WITHIN GROUP IVA ELEMENTS

The gradation in the physical and chemical properties of the elements with the rise of atomic number is as follows:

(i) **Atomic Volume, Atomic Radius and Density.** Atomic volume, atomic radius and density show a regular increase on moving down the group from carbon to lead.

(ii) **Melting and Boiling Points.** As we move down the group from C to Pb, the melting and boiling points generally decrease, although the decrease is not in a regular order. This decrease in melting and boiling points indicates that interatomic forces also decrease in the same direction. The melting and boiling points of C and Si are notably high because of the tendencies of these elements to form giant molecules.

(iii) **Metallic and Non-metallic Character.** The change from non-metallic to metallic character with the increase of atomic number is best illustrated in this group. Thus C and Si are non-metals, Ge is a metalloid, while the last two elements viz, Sn and Pb are distinctly metals.

(iv) **Ionization Energies.** These values decrease gradually on moving from C to Sn. This value for Pb is slightly higher. The irregularity in the decrease of these values is due to the filling of intervening d-orbitals in the case of Ge and Sn and f-orbitals in the case of Pb which are not able to screen the valance electrons effectively in the elements following them.

(v) **Electronegativity.** Carbon is the most electronegative element of this group and the electronegativity values decrease with the rise of atomic number but not in a regular manner. This is probably due to the filling of the d-orbitals in case of Ge and Sn and f-orbitals in case of Pb.

(vi) **Allotropy.** All the elements except lead show allotropy and exist in various allotropic forms. For example, carbon — diamond, graphite, coal, coke et., tin — white tin, grey tin and rhombic tin.

(vii) **Oxidation States.** Carbon and silicon show +4 oxidation states while Ge, Sn and Pb show +2 as well as +4 oxidation states, but they prefer to exhibit +2 states due to the inert pair effect. Since the inert pair effect increases on moving down the group from Ge to Pb, the stability of M(+4) ions decreases and that of M(+2) ions increases. Thus the stability of M(+2) ions increases from Ge^{2+} to Pb^{2+} i.e.,

$$Ge^{2+} < Sn^{2+} < Pb^{2+}$$

Since the electronegativities of these elements are low, they do not have much tendency to form the negative ions. However, carbon forms C^{4-} and C_2^{2-} ions in certain compounds, e.g., Be_2C, Al_4C_3 and CaC_2.

(viii) **Catenation or Self-linkage.** The tendency of an element to form long chains of identical atoms is called catenation or self-linkage. This property decreases on moving down the group from C to Pb. Thus carbon has the maximum property of catenation, silicon has much lesser tendency, germanium has still lesser tendency whereas tin and lead hardly show this property.

It has been observed that the tendency of catenation of these elements decreases with the decrease of energy of M — M bond. Thus the M — M bond energy values (in kJ/mole) are:

C — C	Si — Si	Ge — Ge	Sn — Sn	Pb — Pb
348	222	167	155	-

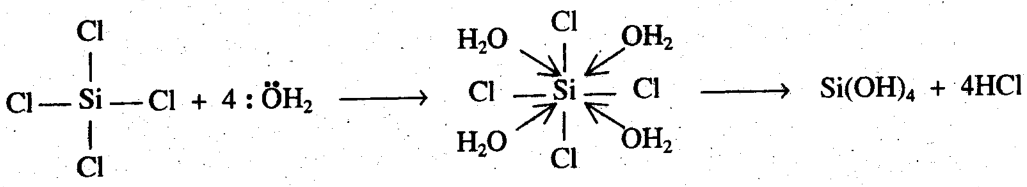
These values show that the tendency of these elements towards catenation is in the order:

$$C > Si > Ge > Sn > Pb$$

(ix) **Formation of hydrides.** All the elements of group IVA form the hydrides which are covalent in nature. Hydrides of MH_4 type are in the gaseous state and their volatility decreases with the increasing atomic number of the central atom. Thermal stability of these hydrides also decreases steadily from CH_4 to PbH_4 and this decrease is due to the decrease in M — H bond energy in going from C to Pb.

(x) **Formation of Halides.** All the elements of this group form halides like MX_4, MHX_3 (e.g., $CHCl_3$, $SiHF_3$ etc.) and MX_2 (e.g. $SiCl_2$ SiI_2 etc.). The stability of MX_4 halides decreases from CX_4 to PbX_4 (CF_4 is the most stable and unreactive). The tetrahalides of C are not hydrolysed by water while those of Si, Ge and Sn

get readily hydrolysed. Since C atom does not have d-orbitals in its valence shell to allow water molecules to get attach with the atom, its tetrahalides do no undergo hydrolysis. On the other hand, Si, Ge and Sn have vacant d-orbitals which accept the lone pair of oxygen of water and thus their tetrahalides get readily hydrolysed.



(xi) **Formation of Oxides.** Elements of group IVA form the oxides which are of three types viz. *(a)* monoxides (MO), *(b)* dioxides (MO_2) and *(c)* other oxides like C_3O_2, Pb_3O_4, Pb_2O etc.

(xii) **Formation of Acids.** All the elements give acids of H_2MO_3 type, e.g., H_2CO_3 (carbonic acid), H_2SiO_3 (silicic acid), H_2GeO_3 (germanic acid) etc. Sodium salts of these acids are stable.

6.3. COMPARISON OF CARBON AND SILICON

Both these elements belong to the same group of the periodic table and have the same number of electrons (= 4) in their valence shell. Due to this fact these have many similar properties. On the other hand, the number of electrons in the penultimate shells is different and because of this, these show much dissimilarity as well.

(a) Similarities

(i) Both the elements have ns^2p^2 valence shell configuration.

(ii) Both are widely distributed in nature. Carbon is an essential constituent of vegetable and animal kingdom i.e., of the organic compounds. Silicon is an essential constituent of mineral kingdom, i.e., of the inorganic compounds.

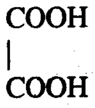
(iii) Both are tetravalent. These elements show a covalency of four and form compounds by sharing of electrons.

(iv) Both show allotropy, i.e., they exist in more than one form.

(v) Both burn in oxygen to form acidic oxides, i.e., CO_2 and SiO_2.

(vi) Both form a number of covalent hydrides like CH_4, C_2H_6, SiH_4, Si_2H_6, etc.

(vii) Both form similar types of acids, e.g.,



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

oxalic acid

$$\begin{array}{c} SiOOH \\ | \\ SiOOH \end{array}$$

silicon oxalic acid

(viii) Both form similar types of covalent halides, e.g.,

CF_4	CCl_4	$CHCl_3$
SiF_4	$SiCl_4$	$SiHCl_3$

(ix) The oxides of both the elements form same type of acids, e.g., H_2CO_3 and H_2SiO_3.

(b) **Dissimilarities**

(i) C has two electrons in the penultimate shell while Si has eight electrons in the penultimate shell.

(ii) C is a black solid (m.p. = 3500°C) while Si is a reddish brown solid (m.p. = 1410°C)

(iii) C is a good conductor of heat and electricity while Si is a bad conductor of heat and electricity.

(iv) C has a strong tendency for catenation while Si has lesser tendency to form chains and rings.

(v) C is unaffected by alkalies while Si reacts with aqueous and fused alkalies to liberate H_2.

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

(vi) The maximum covalency of C is 4 while that of Si is 6.

(vii) CO_2 is a gas while SiO_2 is a hard solid.

(viii) C does not form complex compounds while Si forms a number of complex compounds due to the availability of d-orbital in the valence shell.

(ix) CCl_4 is quite stable and is not hydrolysed by water. $SiCl_4$ is less stable and hence is hydrolysed by water.

(x) H_2CO_3 is unstable while H_2SiO_3 is stable.

(xi) C does not react with Cl_2 or Br_2 directly while Si reacts with both at 500 °C.

$$Si + Cl_2 \xrightarrow{500\ ^\circ C} SiCl_4$$

6.4. ALLOTROPES OF CARBON

Carbon occurs both as free element (graphite, diamond) and in combined form (mainly as carbonates of Ca, Mg and other electropositive elements. It also occurs as CO_2 a minor but crucially important constituent of the atmosphere. Estimates of the overall abundance of carbon in crystal rocks vary considerably, but a value of 180 ppm can be taken as typical; this places the element seventeenth in order of abundance after Ba, Sr and S but before Zr, V, Cl and Cr.

Carbon exists in many structural forms known as allotropes differing in spatial arrangement of atoms. These attoropic forms differ in physical properties but possess the same chemical properties as expected for the substances exhibiting allotropy. Following are the important allotropic forms of the carbon.

1. Graphite
2. Diamond
3. Fullerenes
4. Partially crystalline carbon

1, Graphite

Graphite is widely distributed throughout the world though much of it is of little economic importance. Large crystals occur in metamorphosed sedimentary silicate rocks such as quartz, mica, schists and gneisses. Average carbon content is 25% but can rise as high as 60%. Many forms of amorphous carbon (including charcoal, certain soots and lamp black are all actually micro crystalline forms of graphite. The physical properties of such materials are mainly determined by the nature and extent of their surface areas. The finely divided forms readily absorb large amount of gases and solutes from solution. Active forms of carbon impregnated with Pd, Pt or other metals are widely used as industrial catalysts. Graphite which has the layer structure is shown in the Fig. 6.1. The separation of the layers (3.35 Å) is approximately the sum of the van der Waals radii for C and indicates that the forces between the layers should be weak. This accounts for the softness and lubricity of graphite, since the layers can easily slip over one another. Each C atom is surrounded by only three neighbors; after forming one σ bond with each neighbor, each C atom still has one electron and these electrons are paired up into system of π bonds, as shown in structure 6.1 Resonance makes all bonds equivalent so that the C—C bond distances are all 1.415 Å.

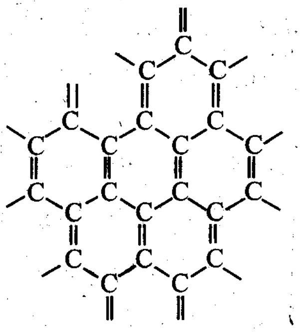


Fig. 6.1. The layer structure of Graphite.

This is a little longer than the C—C distance in benzene where the bond order is 1.5 and corresponds to a C— C bond order in graphite of about 1.33. Since pπ—pπ multiple bonding is clearly involved, the other Group IVA (14) elements cannot form this type of structure. The continuous π system in each layer makes possible good electrical conductance, especially in directions parallel to the layers. The conductance in these directions is 10^4 times greater than it is in the direction perpendicular to the layers. In diamond the conductance is only 10^{-18} of that in the graphite layers.

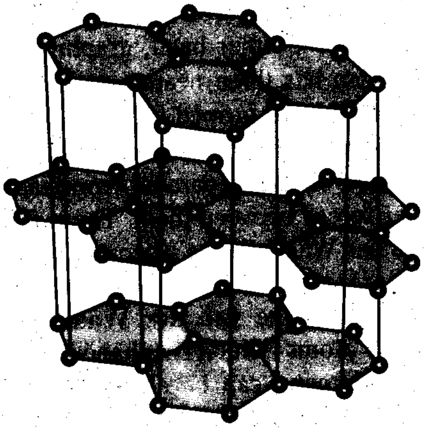


Fig.6.2. The structure of graphite as indicated by the vertical lines, the rings are in register in alternate planes, not adjacent planes.

Natural graphite is used in refractories (27%), lubricants (17%), foundries (14%), brake linings (12%), pencils (5.3%), crucibles, retorts, stoppers, sleeves and nozzles (4.0%) etc. Artificial graphite is manufactured on large scale by Acheson process. In this process coke is heated with silica at 2500°C for 25—35h.

$$SiO_2 + 2C \xrightarrow{-2Co} [SiC] \xrightarrow{2500°C} Si(g) + C(graphite)$$

It is mainly used for electrodes, crucibles, and vessels, and various un-machined shapes, specialist used include motor brushes and contacts and refractories of various sorts.

An important aspect of graphite technology is the production of very strong fibers by pyrolysis, at 1500°C or above, of oriented organic polymer fibers (e.g., those of polyacrylonitrile, polyacrylate esters, or cellulose). When incorporated into plastics the reinforced materials are light and of great strength. Other forms of graphite, such as foams, foils, or whiskers, can also be made.

(The loose layered structure of graphite allows many molecules and ions to penetrate the layers to form what are called intercalation or lamellar compounds). Some of these may be formed spontaneously when the reactant and graphite are brought together. The alkali metals, halogens, and metal halides and oxides (e.g., $FeCl_3$ and MoO_3) are examples of reactants.

2. Diamond. Diamond and graphite, the two common crystalline forms of elemental carbon, are strikingly different. Diamond is effectively an electrical insulator; graphite is a good conductor. Diamond is the hardest known substance and hence the ultimate abrasive; impure (partially oxidized) graphite is slippery and frequently used s a lubricant. Because of its durability, clarity, and high refractive index, diamond is one of the most highly prized gemstones; graphite is soft and black with a slightly metallic luster and is neither durable nor particularly attractive. The origin of these widely different physical properties can be traced to the very different structures and bonding in the two polymorphs.

In diamond, each C atom forms single bonds of length 1.54 Å with four adjacent C atoms at the corners of a regular tetrahedron (Fig. 6.3). The result is a rigid, covalent, three-dimensional framework. On the other hand, graphite consists of stacks of planar layers within which each C atom has three nearest-neighbors at 1.42 Å. The σ bonds between neighbors within the sheets are formed from the overlap of sp^2 hybrids, and the remaining perpendicular p orbitals overlap to form π- bonds that are delocalized over the plane. The planes themselves are widely separated from each other (at 3.35 Å), which indicates that there are weaker forces between them. These forces are sometimes, but not very appropriately, called van der Waals forces' (because in the common impure form of graphite, graphitic oxide, they are weak, like intermolecular forces), and consequently the region between the planes is called the **van der Waals gap**. The ready cleavage of graphite parallel to the planes of atoms (which is enhanced by the presence of impurities) accounts for its slipperiness. Diamond can be cleaved, but this ancient craft requires considerable expertise since the forces in the crystal are more symmetrical.

The conversion of diamond to graphite at room temperature and pressure is spontaneous ($\Delta_{trs}G^{\phi}$ = 2.90 kJ mol^{-1}) but does not occur at an observable rate under ordinary conditions. Diamond is the denser phase, so it is favored by high pressures, and large quantities of diamond abrasive are manufactured commercially by a d-metal catalyzed high-temperature, high-pressure process. The d-metal (typically nickel) dissolves the graphite at 1800°C and 70 kbar, and the less soluble diamond phase crystallizes from it. The synthesis of gem-quality diamonds is possible but not yet economical.

Because the high-pressure synthesis of diamond is costly and cumbersome, a low-pressure process would be highly attractive. It has in fact been known for a long time that microscopic diamond crystals mixed with graphite can be formed by depositing C atoms on a hot surface in the absence of air. The C atoms are produced by the pyrolysis of methane, and the atomic hydrogen also produced in the pyrolysis plays an important role in favoring diamond over graphite. The property of the atomic hydrogen is that it reacts more rapidly with the graphite than with diamond to produce volatile hydrocarbons, so the unwanted graphite is swept away. Although the process is not fully perfected, synthetic diamond films are already finding applications ranging from the hardening of surfaces subjected to wear to the construction of electronic devices.

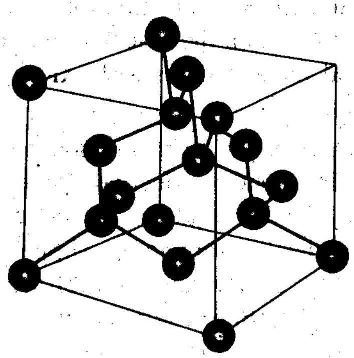


Fig 6.3 The cubic diamond structure

Diamond is the hardest and least perishable of all minerals, and these qualities coupled with its brilliant sparkle, which derives from its transparency and high refractive index, makes it the most priced of gemstones. By far the natural largest diamond ever found (25 January 1905) was the Cullinan (621.2g). Most naturally occurring diamonds, however, are of industrial rather than gem-stone quality. They are used as single point tools for engraving or cutting and for surgical knives, bearings and wire dies, as well as for industrial abrasives for grinding and polishing. Other uses are thermistors and radiation detectors and as optical windows for lasers etc.

3. Fullerenes

Recently, it has been found that carbon exists in a third allotropic form in which there are large, spheroidal C_n molecules, with $n = 60$ or more. Those with $n = 60, 70, 76,$ and 78 have structures that are more or less definitely established.The C_{60} molecules were first recognized and christened "buckminsterfullerence" after the American architect-enginner F. Buckminister (Bucky) Fuller, who was best known for designing hemispherical geodesic domes of pentagonal and hexagonal faces. Most commonly these molecules are now called fullerences and most informally, buckyballs. The C^{60} buckyball has the same form as a soccer ball.

Large scale preparation of fullerenes is achieved by vaporization of graphite in an electric arc or by a plasma discharge. However, these methods produce mixtures that are not easy to separate. The lower ones, especially C_{60} and C_{70}, can be separated from the many larger ones by extracting them into hexane, benzene, or toluene, when they form magenta solutions. The C_{100} to C_{250} fullerenes dissolve in high- boiling solvents, such as 1,2, 4,-$C_6H_3Cl_3$ (b.p. 214°C), while the completely insoluble residues are thought to contain fullerenes as large as C_{400}. Separation of C_{60} and C_{70} from each other is very difficult on more than a small (~30 mg) scale.

Because of their spheroidal shape, the fullerenes C_{60} and C_{70} form very disordered crystals and the determination of their structures was not easily accomplished. However, by use of derivatives and with the help of NMR and other spectroscopic data, the structures of the smaller fullerenes are well established. In all of them, each carbon atom has three neighboring carbon atoms and formsformally, two single and one double bond. C_{60} has 32 faces, 20 of which are hexagons and 12 of which are pentagons. C_{60} also seems to be the most stable for the fullerenes. This is, in part, due to the fact that there is considerable delocalization of the electrons in the formal double bonds, and in fact the two kinds of C—C distances are very close, with values of about 1.40 and 1.50 Å.

The fullerenes are the least stable of the carbon allotropes. Graphite, being the most stable, is assigned a standard heat of formation ($\Delta H^{o}_{f} = 2.9$ kJ mol^{-1} C_{60} has $\Delta H^{o}_{f} =$ 38.1 k Jmol^{-1}

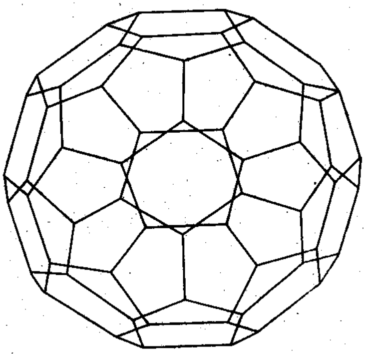


Fig.6.4 The structure of fullerene (C_{60})

The un-saturation of C_{60} is indicated by its reduction by Li in NH_3 (*l*) / t-BuOH (Birch reduction) to give a light cream solid composed of $C_{60}H_{36}$ and C_{60} H_{18}. Reaction with primary and secondary amines (e.g., n-$PrNH_2$, t-$BuNH_2$, ethylenediamine, morpholine, and n-dodecylamine) results in the multiple addition of H and NR_2 groups across the C==C double bonds to give $C_{60}H_6$(NR2)6. Each such addition results in the rehybridization of the carbon atoms from sp^2 to sp^3.

The first derivative structure of C_{60} was that of the remarkable osmium compound made as in given below.

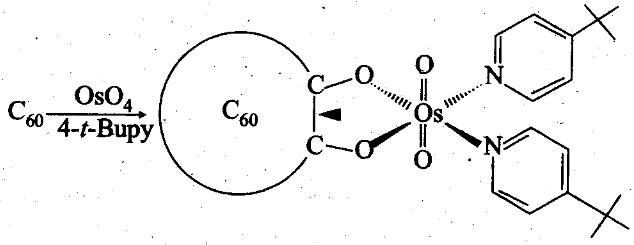


Fig.6.5(a). The first derivative structure of C_{60}

This reaction of OsO_4 is characteristic of the C==C double bonds of alkenes. Two similar pyridine (py) derivatives have been prepared by reacting either 2 equivalents of OsO_4 and 5 equivalents of py, or 1 equivalent of OsO_4 and 2.2 equivalent of py, with C_{60} in toluene, at 0°C, giving following two structures respectively.

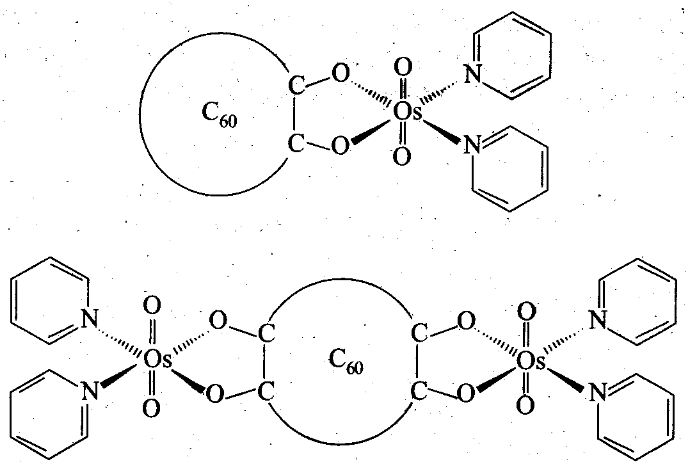


Fig.6.5(b). Pyridine derivative structure of C_{60}

Such osmylations are typical of pyridine-activated polycyclic aromatic hydrocarbons, and underscore the "aromaticity" of C_{60}. Nevertheless, certain facts are best interpreted by regarding the C_{60} structure as a series of isolated alkenes. This is consistent with the two distinct C—C bond lengths in C_{60}, and with the fact that only small ring currents are detectable in C_{60}. The high reactivity of C_{60} is attributable to the non-planarity of the C==C groups, which causes high-strain energy, and because each C==C double bond is attached to four electron-with-drawing groups.

Partial halogenation of C_{60} and C_{70} may be accomplished by reaction with Cl_2 or Br_2, although the extent of halogenation is sometimes uncertain. Reaction of C_{60} with Br_2 gives $C_{60}Br_2$ and $C_{60}Br_4$. In each case, the bromination can be reversed at 150°C, giving a quantitative recovery of bromine. Chlorination of C_{60} gives mixtures of $C_{60}Cl_n$ the average value of n being 24. The chloro-derivatives are dechlorinated only at temperatures above 400°C and are thus more stable than the bromo-derivatives. The chlorine atoms of $C_{60}Cl_n$ can be replaced by OCH_3 groups, using methanolic KOH, as well as by C_6H_5 groups, in a Friedel-Crafts reaction with benzene, catalyzed by $AlCl_3$. Partially fluorinated derivatives, $C_{60}F_6$ and $C_{60}F_{42}$, have been isolated, but prolonged (12 days) interaction with F_2 gives colorless $C_{60}F_{60}$.

Anions, known sa fullerides, are readily obtained, and these can be either diamagnetic or, like the radical C_{60}, paramagnetic. From bulk electrolysis, the salt $(Ph_4P)^+C_{60}^-(Ph_4PCl)_2$ has been obtained. The anion is also formed in THF solvent, using the tetraphenylporphyrin complex of Cr^{2+} as a reducing agent, as in the following reaction, where TPP = tetraphenylporphyrin.

$$Cr^{II}(TPP) + C_{60} \longrightarrow [Cr^{III}(TPP)]+C_{60}^-$$

Reduction of C_{60}/C_{70} mixtures by Li gives red-brown solutions which, on treatment with CH_3I, gives polymethylated fullerenes with 1-24 methyl groups. Direct interaction with other alkali metals gives black materials such as $(K^+)_3C_{60}^{3-}$. Also films of C_{60} doped with K, Rb, or Cs metal vapor can be prepared, which are super conducting and may be of value since the critical temperature for super conductivity is relatively high. For instance, T_c, for Rb_nC_{60} is 30 K.

Large metals atoms may be inserted into the center of certain fullerenes, giving compounds such as La_2C_{80} and LaC_{82}. These are obtained by the arc-vaporization of La_2O_3 and graphite, which yields solvent-extractable products.Reactions of C_{60} are listed in Fig. 6. 6

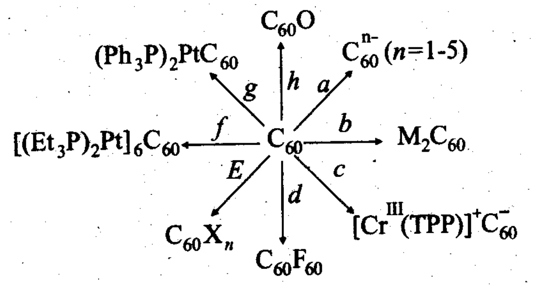


Figure 6.5(c). Some reactions of C_{60}: (a) electrochemical reduction (E^0 depends on the solvent); (b) alkali metals; (c) Cr^{II} (TPP); (d) F_2, 70^0C; (e) Cl_2, Br_2; (f) Pt $(Et_3P)_4$; (g) $Pt(C_2H_4)(PPh_3)_2$; and (h) C_6H_6, O_2, hv.

4. Partially crystalline carbon

There are many forms of carbon that have a low degree of crystallinity. These partially crystalline materials have considerable commercial importance; for they include carbon block activated carbon, and carbon fibers. Because single crystals suitable for complete X-ray analyses of these materials are not available, their structures are uncertain. However, what information there is suggests that their structures are similar to that of graphite, but the degree of crystallinity and shapes of the particles differ.

Carbon black is very finely divided form of the carbon. It is prepared on large scale (8×10^9 kg annually) by the combustion of hydrocarbons under oxygen-deficient conditions. Planar stacks, like those of graphite, and multiplayer balls, reminiscent of the fullerenes, have both been proposed for its structure. Carbon black is used on a huge scale as a pigment, in printer's ink (as on this page), and as a filler for rubber goods, including automobile tires, where it greatly improves the strength and wear resistance of the rubber and helps to protect it from degradation by sunlight.

'Activated carbon' is prepared from the controlled pyrolysis of organic material, including coconut shells. It has a high surface area (in some cases exceeding 1000 m^2g^{-1}), which arises from the small particle size. It is therefore a very efficient adsorbent for molecules, including organic pollutants from drinking water, noxious gases from the air, and impurities from reaction mixtures. There is evidence that the parts of the surface defined by the edges of the hexagonal sheets are covered with oxidation products, including carboxyl and hydroxyl groups (34). This structure may account for some of its surface activity.

Carbon fibers are made by the controlled pyrolysis of asphalt fibers or synthetic fibers and are incorporated into a variety of high-strength plastic products, such as tennis rackets and aircraft components. Their structure bears a resemblance to that of graphite, but in place of the extended sheets the layers consist of ribbons parallel to the axis of the fiber. The strong plane bonds (which resemble those in graphite) give the fiber its very high tensile strength. Amorphous and partially crystalline carbon in the form of small particles are used on a large scale as adsorbents and as strengthening agents for rubber; carbon fibers import strength to polymeric materials.

6.5. GREEN-HOUSE EFFECT (GLOBAL WARMING)

The earth receives radiant energy from the sun which is in a band of wavelengths from ultraviolet to infra-red. This radiation passes through the atmosphere of the earth with very little absorption and on reaching the earth, it warms the ground and sea. The warm surface of the earth radiates energy outwards as infra-red radiation (heat). However, some of the gases in the lower atmosphere, acting like glass in a green-house, allow the solar radiation (in the range 300 to 2500 nm, i.e., near U.V., visible and near I.R. region, while filtering the dangerous U.V. radiation) but do not allow the earth to re-radiate the heat into space. A part of the heat so trapped in these atmospheric gases is re-emitted to the earth's surface. This negative role of the atmospheric gases in absorbing the escaping infra-red radiation and directing some of it back to earth's surface results in the rise of temperature and is called *the green-house effect.* The gases that are responsible for this green-house effect are: CO_2, water vapors, CH_4, man-made chlorofluorocarbons (CFCs), ozone and nitrous oxide.

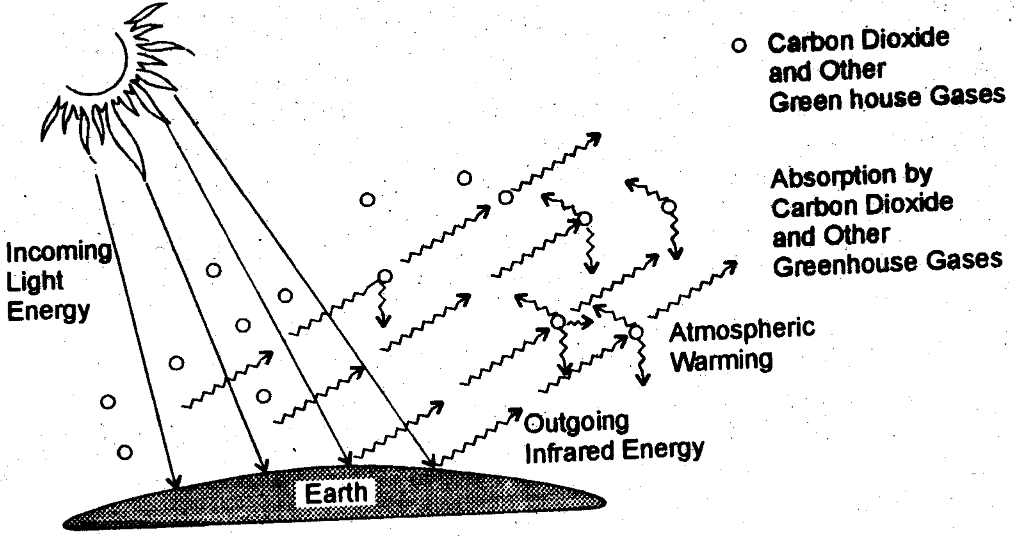


Fig. 6.6. The green-house effect phenomenon.

Green house gases (particularly CO_2 and water vapours) are responsible for keeping our planet warm and thus sustaining life on the earth. If the green-house gases are very less or totally absent in the earth's atmosphere, then the average temperature on the earth would have been at sub-zero levels. But, however, if the concentration of green-house gases is larger, they may trap too much of heat, which may threaten the very existence of life on the earth.

It is estimated that the atmospheric CO_2 content has increased by 25% during the last two centuries. This is mostly attributed to the industrial revolution over these two centuries. This is one of the reasons for the slight increase in the global temperature (about 0.5°C). Since the concentrations of the green-house gases have been continuously increasing because of deforestation, industrialization, increased burning of fossil fuels, mining, exhausts from increasing number of automobiles and other anthropogenic activities, there is an increasing concern about the possible "global warming". Some scientists fear that if proper precautions are not taken, the concentration of the green-house gases in the atmosphere may double within the next 50 – 100 years. If this happens, the average global temperature may increase by 3 to 5°C and plants and animals would face warming conditions than any felt in the past 100000 years. The rising world temperature will have serious repercussions on agriculture, animal production and human-being. Hot weathers may lead to dry conditions and agriculture is likely to see major shifts in its present pattern. Crop production may not be possible in some of the existing areas. Some other areas, now unsuitable, may become suitable. Rising temperature, however, will reduce crop yields and on the whole, food availability is expected to decline. Further, it will lead to melting of ice in lower ranges of high mountains and Polar Regions which would raise the sea level. As a consequence sea line would move further up affecting coastal regions. Low lying countries like Maldive and Bangladesh would be threatened, therefore.

Humanity is apparently heading for self destruction which can be avoided only through prudent policies. Some of the steps suggested to minimize the "green-house effect" include reduction in the use of fossil fuels, encouraging the use of alternative sources of energy (e.g., solar geothermal, wind, bio-gas etc.), conservation of forests, extensive afforestation, reduction in the use of automobiles, research in the development of more efficient automobile engines, ban on CFCs and nuclear explosions, development of environmentally compatible technologies with the help of intensive inter-disciplinary research, effective check on the growth of population and imparting of non-formal and formal environmental education. So it is high time to fight against pollution in order to make the word clean and safe for our future generations.

6.6. CARBIDES

The binary compounds of carbon with the elements which are more electropositive than carbon are called carbides. Thus this definition excludes the binary compounds of carbon with N, P, O, S and halogens. This is also usual to exclude the hydrides of carbon.

Carbides are classified into three types depending on the nature of bonding between carbon atoms and other elements. These three types are: *(a)* Ionic or salt like carbides *(b)* interstitial carbides, and *(c)* covalent carbides.

(a) Ionic Carbides

Ionic carbides are formed by the metals of groups IA, IIA and IIIA (except boron), coinage metals. Zn, Cd, and some lanthanides. These are obtained by heating the metal or its oxide with carbon or a hydrocarbon like acetylene.

$$2Be + C \longrightarrow Be_2C$$

$$4Al + 3C \longrightarrow Al_4C_3$$

$$2Ag_2O + C_2H_2 \longrightarrow Ag_2C_2 + H_2O$$

These carbides are colourless, crystalline solids, non-conductors of electricity in the solid state and hydrolysed to hydrocarbons by water or dilute acids. These may be sub-classified according to the hydrocarbon produced.

(*i*) **Methanides** such as BeC_2 and Al_4C_3 which liberate methane on hydrolysis.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$BeC_2 + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(*ii*) **Acetylides** such as CaC_2, MgC_2 which liberate acetyline on hydrolysis.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC \equiv CH$$

The ionic carbides possess ionic lattices in which the metallic cations are packed into the cavities between carbon anions, e.g., C^{4-}, C_2^{2-} and C_3^{4-}.

(*b*) Interstitial Carbides

These are formed by many transition metals and are similar to interstitial hydrides, i.e., they are non-stoichiometric. These are formed by those transition metals whose atomic radii are generally greater than 1.3 Å (R_M > 1.3 Å), since the radius ratio namely R_C /R_M must be either 1 : 041 or 1 : 059 to permit C-atoms to enter into octahedral holes of the cubic close packing of metal lattice without distorting it e.g., TiC, WC, Fe_3C, Mn_3C. etc.

These carbides possess a lustrous appearance high electrical conductance high melting points, hardness and chemical inertness. Some carbides are hydrolysed by water and dilute acids giving a variety of hydrocarbons.

(*c*) Covalent Carbides

The two typical examples of this type of carbides are silicon carbide (SiC) sold under the name carborundum and boron carbide (B_4C). Both are prepared by reducing their oxides with carbon in an electric furnace.

$$SiO_2 + 3C \longrightarrow SiC + 2CO\uparrow$$

$$2B_2O_3 + 7C \longrightarrow B_4C + 6CO\uparrow$$

These are not attacked by water and acids. These are extremely hard and decompose at high temperatures. Because of their hardness they are used for cutting and as abrasives.

6.7. SILICON AND ITS PRODUCTION FOR SOLAR ENERGY CELL

Occurrence

Silicon is our second most abundant element and is always found combined with the most abundant element, oxygen. It is estimated that silicon forms 27.6% by weight of

Earth's crust. Silicon dioxide, silica, SiO_2, is found comparatively pure as quartz, flint, agate and sand, and is formed by weathering of igneous rocks, which contain silicates.

Preparation

The appearance and properties of silicon prepared by different methods vary greatly, but all these forms have the same crystal structure, differing in particle size and content of impurities, e.g., silica and traces of metal. In the laboratory, silicon is prepared by heating together dry powdered quartz and magnesium powder:

$$SiO_2 + Mg \longrightarrow 2MgO + Si$$

On the industrial scale, silicon is prepared by reducing silica with carbon in an electric furnace:

$$SiO_2 + 2C \longrightarrow 2CO + Si$$

Usually, the silicon is to be used as an additive for iron, and hence a little iron is added in the above reaction to prevent the formation of silicon carbide, SiC (corborundum). The product, 'pure' silicon or 'metallic' silicon, therefore contains a small percentage of iron. The addition of silicon to steel or iron greatly increases resistance to attack by acids, and alloys such as silicon-bronze possess strength and hardness greater than bronze alone.

Pure silicon used in transistors and solar energy cells is prepared by reducing tetrahalides of silicon in vapour phase with an active metal such as magnesium or sodium. The tetrahalide is first obtained in pure state by distillation process to remove impurities.

$$SiCl_4 + 4Na \longrightarrow 4NaCl + Si$$

$$SiCl_4 + 2Mg \longrightarrow 2MgCl_2 + Si$$

Sodium chloride or magnesium chloride is dissolved in water leaving behind pure silicon which is melted and cast into bars. The silicon is further purified by zone-refining and allied techniques. In this method an induction heater surrounds a bar of the impure solid and passes slowly from one end to another. On repeated passing through the zone, silicon bar of high purity is obtained leaving behind impurities in the zone.

Silicon 'chips' are used in micro-electronic circuits. A single minute chip in a pocket calculator might contain over 30,000 transistors connected in a single integrated circuit.

Properties

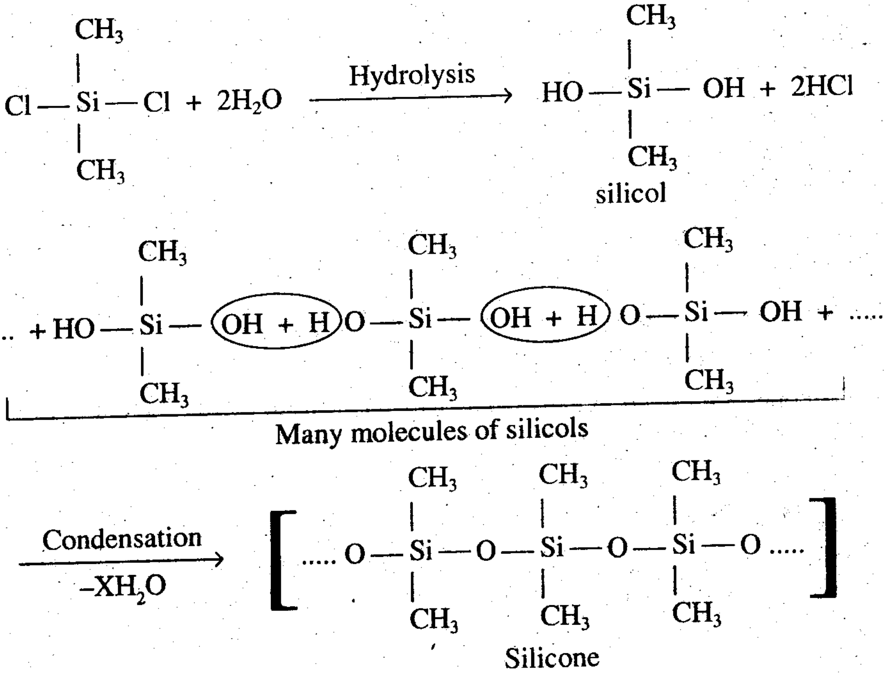
Silicon is a hard and brittle solid, with a high melting point (1413°C). All forms of silicon have a diamond-like crystal structure. Large crystals are chemically unreactive, e.g., they are not attacked by halogens or by hydrofluoric acid: but powdered silicon can be attacked by these reagents. All forms of silicon, are, however, easily attacked by even very dilute solutions of caustic alkali. For example, water which has been in contact with glass, will dissolve silicon on boiling:

$$Si + 2OH^- + H_2O \longrightarrow SiO_3^{2-} + 2H_2\uparrow$$

6.8. SILICONES

When an alkyl or aryl substituted silicon chloride such as $RSiCl_3$, R_2SiCl_2 (which can be obtained from $SiCl_4$ by Grignard reaction) is hydrolysed, we get *silicols* which condense together by intermolecular elimination of water to form the *organo-silicon polymers* which are called *silicones*. For example, $(CH_3)_2SiCl_2$ is obtained when CH_3Cl is passed over a copper-silicon mixture at 300°C, but it can be prepared by other methods.

$$Si + 2CH_3Cl \xrightarrow[Cu]{300°C} (CH_3)_2SiCl_2$$



$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl + 2H_2O \xrightarrow{\text{Hydrolysis}} HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH + 2HCl$$

$$\ldots + HO-\overset{CH_3}{\underset{CH_3}{Si}}-\boxed{OH + H}O-\overset{CH_3}{\underset{CH_3}{Si}}-\boxed{OH + H}O-\overset{CH_3}{\underset{CH_3}{Si}}-OH + \ldots$$

$$\xrightarrow[-XH_2O]{\text{Condensation}} \left[\ldots O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O\ldots\right]$$

Note that in the compound $(CH_3)_2Si(OH)_2$, the silicon atom can hold two —OH groups, unlike carbon. It is this property that makes the existence of silicones possible. By variation of the compounds and conditions of hydrolysis, straight chains, rings and cross-linked polymers are obtained.

For example, $RSiCl_3$ on hydrolysis gives a complex cross-linked polymer as shown in Fig. 6.7.

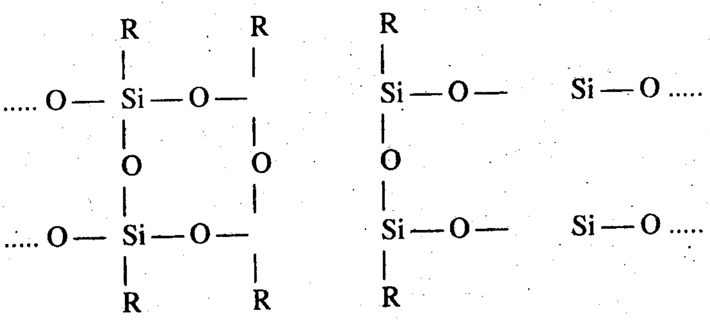


Fig. 6.7. Complex cross-linked polymer.

Properties and Uses

Depending on the length of chain and the nature of groups attached to the silicon atom the silicones can be obtained in the form of oils, viscous fluids, resins, or even rubber like solids and may possess high thermal stability, resistance to oxidation and chemical reagents, lubricating and water repellent properties. Some of the uses of silicones are given below:

(i) Silicon-oils are highly stable and non-volatile even on heating. They are, therefore, used for high temperature oil bath, high vacuum pumps etc.

(ii) They do not become too viscous on cooling and are, therefore, used for low temperature lubrication.

(iii) They are also used in making vaseline like greases which are used as lubricants in aeroplanes, since they do not freeze at low temperature as –40°C and do not melt at 200°C.

(iv) They are water-repellents and are, therefore, used in making water-proof cloth and paper by exposing cloth or paper to the silicone vapours.

(v) They are used as insulating materials for electric appliances since they can withstand high temperature without charring.

(vi) Silicones are mixed in paints and enamels to make them resistant to the effects of high temperatures, sunlight, chemicals and damp.

6.9. SILICATES

Silicates may be regarded as the metal derivatives of the silicic acid. Three silicic acids namely: meta silicic acid, (H_2SiO_3) ortho silicic acid (H_4SiO_4) and pyro-silicic acid ($H_6Si_2O_7$) are found to exist. The salts of these acids are well known.

Silicates can be prepared by fusing metal oxides or metal carbonates with sand (SiO_2). For example:

$$Na_2CO_3 + SiO_2 \xrightarrow{\text{Fuse}} Na_2SiO_4, (Na_2SiO_3)_n \text{ etc.}$$

Only some silicates of alkali metals are soluble in water while others are insoluble. The soluble silicates, e.g., sodium and potassium silicates, are known as soluble glass.

Structural Aspects and Classification

X-ray diffraction studies of various types of silicates have shown that all the silicates have SiO_4^{4-} anions which are formed by sp^3 hybridization of Si atom. Si atom in its excited state contains 4 unpaired electrons and hence forms 4 covalent bonds with four negatively charged O - atoms, resulting in the formation of SiO_4^{4-} anion. Each O - atom becomes negatively charged by picking up one electron from some metal. Since Si atom undergoes sp^3 hybridization, SiO_4^{4-} anion has tetrahedral geometry as shown in Fig. 6.3.

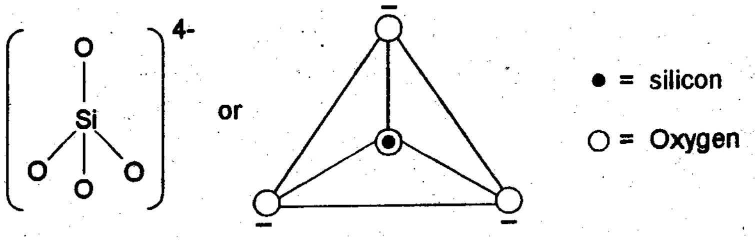


Figure. 6.8. SiO_4^{4-} *anion geometry.*

Silicates are classified according to the nature of linking between the tetrahedral anions (SiO_4^{4-}). This basis of classification gives the following types of silicates:

1. **Orthosilicates.** These silicates contain discrete SiO_4^{4-} tetrahedral anions. The O-atoms of each SiO_4^{4-} anion are also coordinated to the metal ion to impart electrical neutrality to the structure. Examples of such silicates are *phenacite* (Be_2SiO_4), *olivine* (Mg_2SiO_4), *zircon* ($ZrSiO_4$) etc. All these silicates have individual tetrahedra joined together by Be^{2+}, Mg^{2+} and Zr^{4+} cations respectively.
2. **Pyrosilicates.** These silicates contain the discrete $Si_2O_7^{6-}$ anion which is formed by joining two SiO_4 tetrahedral units through one oxygen atom (Fig. 6.9). Examples of silicates containing $Si_2O_7^{6-}$ anion are *thorteveitite* ($Se_2Si_2O_7$) and *hemimorphite* ($Zn_4(OH)_2Si_2O_7$).

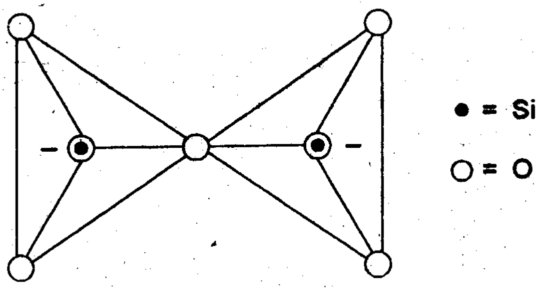


Fig. 6.9. $Si_2O_7^{6-}$ *anion geometry.*

3. **Ring or Cyclic Silicates.** Such silicates contain the cyclic or ring anions like $Si_3O_9^{6-}$ or $Si_6O_{18}^{12-}$. The structure of these anions is given in Fig. 6.10. These anions are obtained when each SiO_4 tetrahedral unit shares an O-atom with each of the two neighbouring SiO_4 units.

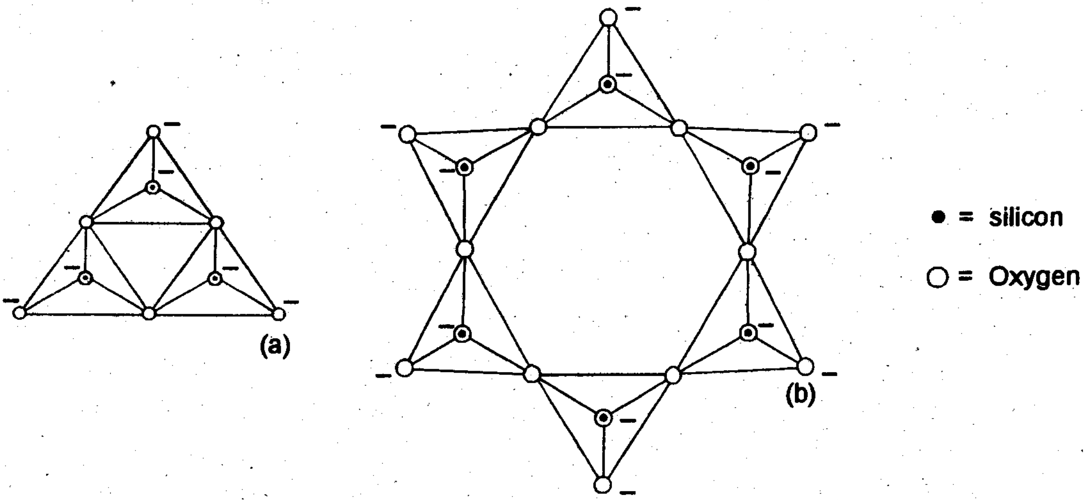


Fig. 6.10. Strcutres of $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ anions.

Examples of cyclic silicates containing $Si_3O_9^{6-}$ anion are *benitoite* ($BaTiSi_3O_9$) and *wollastonite* ($Ca_3Si_3O_9$) while the example containig $Si_6O_{18}^{12-}$ anion is *beryl* ($Be_2Al_2Si_6O_{18}$).

4. **Metasilicates or Chain Silicates.** Such silicates contain the anions which are formed by the sharing of two oxygen atoms by each tetrahedron. The anions may be one of the types *(a)* $(SiO_3^{2-})_n$ *(b)* $(Si_4O_{11}^{6-})$ whose structures are shown in Fig. 6.11.

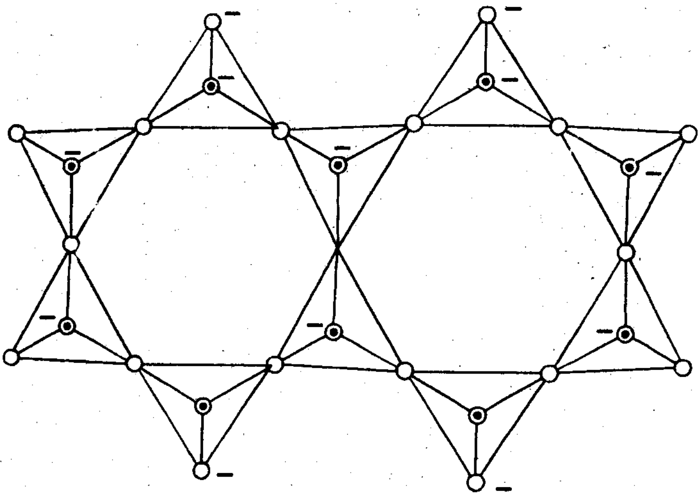


Fig. 6.11. Structures of $(Si_4O_{11}^{6-})$ anions.

The chains in the silicates containing $(SiO_3^{2-})_n$ anions lie parallel to each other and the cations lie between the chains and bind them together. Such silicates are represented by the *pyroxene* minerals and several synthetic silicates. Examples are: *(a) synthetic silicates, e.g.*, Li_2SiO_3, Na_2SiO_3

(b) pyroxene mineral, e.g., spodimene, $LiAl(SiO_3)_2$; enstatite, $MgSiO_3$; diopside, $CaMg(SiO_3)_2$.

The silicates containing $(Si_4O_{11}^{6-})^n$ anions have double chains in which the simple cations are held togetehr by shared oxygens. Such silicates are represented by the *amphibole minerals* which include most asbestos minerals. Structurally amphiboles are similar to pyroxenes though they contain some OH groups which are attached to the cations. *Tremolite,* $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$ is an example of amphibole.

5. **Sheet Silicates.** When all the SiO_4 tetrahedra share three corners with other tetrahedra, layer structures are formed which may be considered to be two-dimensional extensions of the network as shown in Fig. 6.7. The empirical formula for the anion is $(Si_2O_5^{2-})_n$. The metal ions present hold the layers together by weak electrostatic forces. As a result, the minerals containing $(Si_2O_5^{2-})_n$ anions are soft and cleave easily. Such sheet like anions are found in micas and different types of clay minerals. *Talc,* $Mg_2(Si_2O_5)Mg(OH)_2$ and *Kaolin,* $Al_2(OH)_4(Si_2O_5)$ are the common examples of clay minerals.

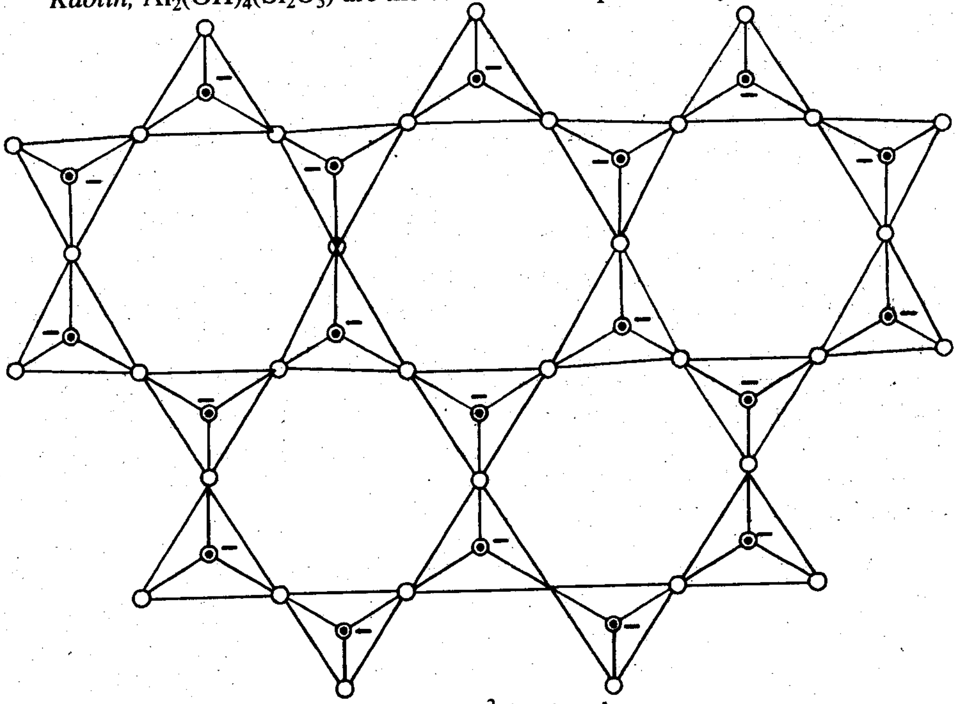


Fig. 6.12. $(Si_2O_5^{2-})$ anion sheet.

6. **Three Dimensional Silicates.** When all the four oxygens of a SiO_4 tetrahedron are shared with adjacent tetrahedra and the process is repeated, an infinite three-

dimensional structure results. Since all the oxygens are the bridge atoms, the silicate is neutral. This net-work is, in fact, the structure of silica (Fig. 6.13).

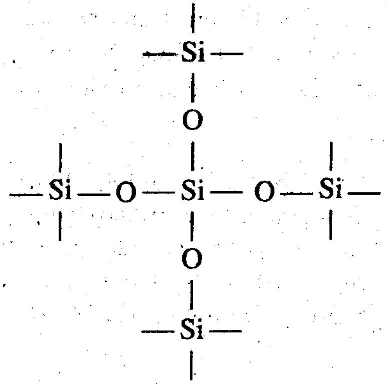


Fig. 6.13. $(SiO_2)_n$ *framework.*

However, if some Si^{4+} ions are replaced by Al^{3+} ions in the tetrahedral positions in the SiO_2 structure, in order to maintain electrical neutrality, some other monovalent cations (*e.g.*, K^+, Na^+, etc) must be introduced. Such a replacement of Si^{4+} cations by Al^{3+} and monovalent cations gives the minerals like *feldspars, zeolites* and *ultramarines.*

6.10. ZEOLITES

The zeolites are aluminosilicates, having large, open-structured anions and balancing cations. When some Si^{4+} ions are replaced by Al^{3+} ions in the tetrahedral positions in the SiO_2 structure, then negative charge develops on the basic framework.

$(Si^{4+}O_2^{4-})^{\circ}$	$(Al^{3+}O_2^{4-})^{-}$
neutral	negative charge

Thus aluminosilicate structures always carry negative charge which is counterbalanced by some cations such as Na^+ or K^+ ion. These ions can be replaced by Ca^{2+} or Mg^{2+} without changing the basic structure of silicates. Zeolite, therefore, acts as a base exchanger and is used in water softening where Ca^{2+} and Mg^{2+} cations are removed by zeolite through exchange reactions. Many artificial ion-exchange zeolites have been made, and used to remove cations from water, *e.g.*, the 'permutite', and more recently, ion exchange materials with a framework of an organic polymer have been made and used extensively in the purification of water.

Because of the open structure, zeolites can take up water molecules reversibly into the interstices of their structures. More importantly, they may be able to act as *molecular sieves,* by taking up from a gas mixture only molecules in a certain size range. The zeolite can then be taken out of the gas and the absorbed species pumped off. Thus the zeolite *mordenite* will acclude small molecules, e.g., nitrogen, argon, but not, for example, metahne or ethane. They also act as catalysts or catalyst-supporting materials for a vareity of heterogeneous reactions.

6.11. WATER GLASS

Water glass is the commercial name given to sodium silicate. This is a salt of metasilicic acid, H_2SiO_3 and is also called soluble glass.

Preparation

It is prepared by fusing together sodium carbonate with pure sand in a furnance composed of firebricks with arched silica roof *(reverberatory furnance).* The soda ash interacts with sand giving sodium silicate:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

The fused mass is drawn from the furnance at intervals and either fractured by a jet of cold water or allowed to solidify and then broken up. The fragments are placed in a boiler and heated with water and steam under pressure. The sodium silicate thus passes into the solution. The liquid is allowed to evaporate in special type of evaporators, and concentrated to a viscous fluid which is called *water glass.*

Properties

Water glass is soluble in water and the solution is strongly alkaline due to hydrolysis. Crystals of various soluble coloured salts like $CuSO_4$, $FeSO_4$, $MnCl_2$, $NiCl_2$ etc. when placed in a solution of water glass having a specific gravity of 1.1 produce beautiful growth which is called *silica garden* or *chemical garden.*

$$Na_2SiO_3 + 3H_2O \longrightarrow 2NaOH + H_4SiO_4$$

Uses

Sodium silicate is used:

(i) in fire-proofing of wood and textiles.

(ii) as a preservative of eggs.

(iii) as a furniture polish

(iv) as a adhesive along with other cementing materials or alone.

(v) in a soap industry as a filter for a cheaper variety of soap.

(vi) for fixing labels to glass.

(vii) in the paint industry.

6.12. PORTLAND CEMENT

Cement is a very important building material which was first of all introduced in 1824 by Joseph Aspidin, a mason of Leeds, England. He found that when a strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone-like mass resembling *Portland rock* which is a famous builidng stone of England. His cement was the prototype of the present Portland Cement.

Portland cement has been defined as "the product obtained by pulverizing clinker consisting of hydraulic calcium silicates usually containing one or more forms of calcium sulphate as an interground addition." Hydraulic calcium silicates possess the ability to harden without drying or by reaction with atmospheric carbon dioxide thus differentiating them from inorganic binders such as plaster of paris.

Composition of Cement

An average composition of a good sample of cement is:

Lime, CaO	61.5%
Silica, SiO_2	22.5%
Alumina, Al_2O_3	7.5%
Magnesia, MgO	2%
Iron oxide, Fe_2O_3	2%
Sulphur trioxide, SO_3	1%
Alkali, Na_2O, K_2O	1.5%

The proportions of lime, alumina or silica for a good cement satisfy the following ratios:

$$\frac{\% \, SiO_2}{\% \, Al_2O_3} = 2.5 \text{ to } 4.0 \qquad \frac{\% \, CaO}{\% \, SiO_2 + \% \, Al_2O_3 + \% \, Fe_2O_3} = 1.9 \text{ to } 2.5$$

Row Materials

The following substances are used as raw materials for the manufacture of cement.

1. **Lime stone.** It provides lime CaO, Marble, chalk and alkali wastes can also be used, since these also supply CaO.
2. **Clay.** Clay supplies silica (SiO_2) and alumina (Al_2O_3) to the cement.
3. **Gypsum.** It is found in very rich stones up to 95% purity. Its addition decreases the setting time of cement.

In addition to the above materials, a wide variety of other minerals, salts, and oxides are used, *e.g.*, Fe_2O_3, MgO, SO_3, Na_2O, K_2O, CO_2 and water.

Manufacture of Cement

The manufacture of cement consists of the following steps:

1. Treatment of Raw Materials

The raw materials are lime-stone and alumina which provide CaO and Al_2O_3 respectively. Generally huge deposits of these are present round the factory area. They are quarried and crushed separately in suitable machinery to a state of fine powder. There are two methods employed for this purpose.

(*a*) **Dry Process.** This process is employed when the raw materials viz. lime stone and clay are hard. In this process the lime stone is first broken into small pieces. It is then mixed with clay in the proper proportions and finally pulverised to such a fineness that 90–95% passes through a 100 mesh sieve. The mixture is made homogeneous to produce what is known as *raw meal.*

(*b*) **Wet Process.** This process is used when the raw materials viz. lime stone and clay are soft, the climate is fairly damp and the fuel is cheap. In this process, the lime stone is crushed to suitable size and the clay is washed with water in wash mills to remove foreign materials like flint. The powdered lime stone is then mixed with the clay paste in the proper proportions (lime stone 75%, clay 25%) and the mixture is finely ground and made homogeneous by means of a compressed air mixing arrangement. The resulting paste is known as *slurry*. The slurry contains about 40% water.

2. Burning of Raw Meal or Slurry

Raw meal or slurry prepared as above is introduced into the rotary kiln with the help of a screw conveyer. The rotary kiln consists of a long cylinder 6 to 8 feet in diameter and 100 to 250 feet in length. It is made of steel and is lined inside with fire bricks (Fig. 6.14). As the rotary kiln rotates, the charge slowly moves downwards due to the rotary motion of the kiln. Now the charge is heated by burning coal dust which enters at the lower end with the help of a blower. As the charge moves forward, it meets higher temperatures. When it reaches the lowest part of the kiln, the temperature is about 1500°C which is the maximum temperature in the kiln. The charge takes 2-3 hours to cover the journey in the kiln.

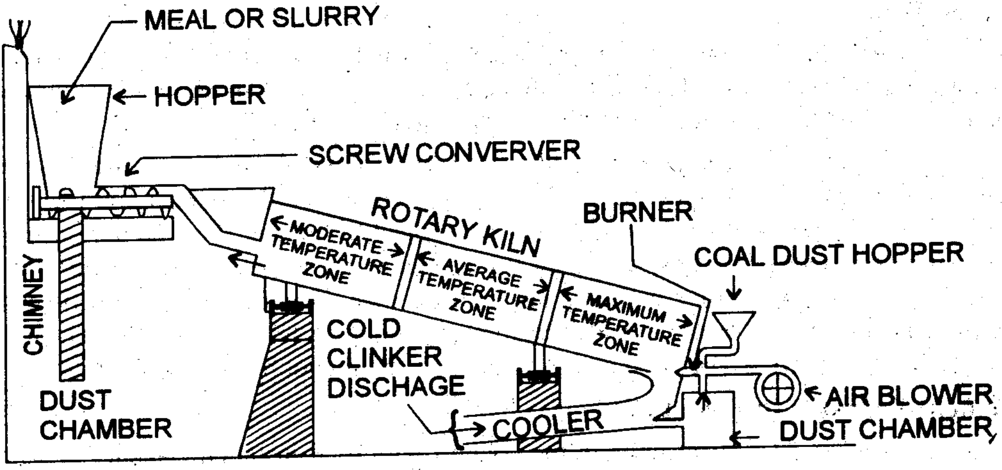


Fig. 6.14. Rotary kiln.

Reactions taking place in the kiln at various temperatures are:

(*a*) up to 100°C	Evaporation of free water.
(*b*) up to 500°C	Evolution of combined water from clay.
(*c*) 500°C to 800°C	Crystalization of amorphous dehydration products of clay.
(*d*) 900°C and above	Evolution of CO_2 gas from the decomposition of lime stone.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

(*e*)	900°C to 1200°C	Main reaction between lime and clay takes place $3CaO + SiO_2 \longrightarrow Ca_3SiO_5$ $2CaO + Al_2O_3 \longrightarrow Ca_2Al_2O_5$
(*f*)	1250°C to 1400°C	Commencement of liquid formation and formation of cement components into clinkers.

The resulting product is known as *cement clinker* and as it comes out into the cooler it has the appearance of small greenish black or grey-coloured balls varying in size.

3. Mixing the Cement Clinker with Gypsum

The burnt clinker is then mixed with 5-6% gypsum ($CaSO_4 \cdot 2H_2O$) to adjust solidification time in a ball mill. The ground material is sieved and packed in bags.

Setting of Cement

When cement is mixed with water, it absorbs water and the mass becomes hard and very resistant to pressure. This is known as the *setting of cement.* The cause of setting of cement is chiefly a hydration process, followed by the decomposition of calcium silicate and calcium aluminate and formation of new compounds.

Setting Time

Cement has a unique property by virtue of which it combines with water and the resulting mass is very hard. The time in which cement sets is known as *initial setting time* and the time in which it hardens is known as *final setting time.*

A paste of cement is made and placed on a glass plate. Vicat needle is then allowed to drop under its own weight. The needle will pierce the cement and touch the glass plate. After some time the needle will be stopped by cement slab and not reach the glass plate to touch. The time at which the needle is hindered by the cement slab is known as initial setting time, it should not be more than 45 minutes. The experiment is continued until cement hardens and it becomes difficult to take the needle out, this is called final setting time. For good quality cement, it should not be more than 10 hours.

Cement Industry in Pakistan

There are 23 cement units in the country with total installed capacity of 13029 thousand tonnes. Out of these 23 units, 4 units with installed capacity of 1831 thousand tonnes are in public sector and 19 units having capacity of 11,198 thousand tonnes are in private sector. Province wise break-up in given below:

Province	Units	Capcaity (000 tonnes)
Punjab	8	5343
Sindh	9	3441
NWFP	5	3495
Baluchistan	1	750
Total	23	13029

The total production of cement was 6676 thousand tonnes during July-March 1997-98 as compared to 6945 thousand tonnes during the same period last year, showing a shortfall of 3.87 percent in productin. The decline in production is attributed to partial closure of some plants and shrinkage in demand owing to low demand in market due to escalating prices of cement.

6.13. GLASS

Any substance which has solidified from the liquid state without crystallization is known as *glass*. Generally, however, the term glass refers to the product that is obtained by the fusion of mixture of silica, basic oxides and a few other compounds. Sometimes glass is called a 'super cooled' liquid as its ingredients cannot be identified.

Requisite qualities of glass are: (1) the material must liquefy at a conveniently feasible temperature, (2) on cooling the molten mass should not crystallize, (3) the molten glass should be such that it can be easily given the desired shape and form, and (4) the glas should be resistant to the conditions for which it is manufactured.

Raw Materials

The following substances are used as raw materials for the manufacture of glass.

1. **Silica.** Sand is used as the source of silica. The iron content of the sand must be as low as possible, as the presence of iron imparts colour to the glass.
2. **Soda Ash.** Sodium is introduced in the form of soda ash (Na_2CO_3), sodium nitrate or sodium sulphate. Sodium nitrate is useful in oxidizing iron and in accelerating the iron.
3. **Lime.** The important sources of lime are lime stone ($CaCO_3$) and burnt lime from dolomite ($CaCO_3 \cdot MgCO_3$), which also introduces MgO into the batch.
4. **Borax.** Borax is used as a flux. It also lowers the coefficient of expansion of the glass and increases its durabiltiy.
5. **Alumina.** Alumina makes the glass resistant to sudden changes of temperature. It is often used in the form of feldspar, $R_2O \cdot Al_2O_3 \cdot 6SiO_2$ where R_2O represents K_2O or Na_2O or a mixture of these two.
6. **Colouring Materials.** Certain metallic oxides or salts if added to the molten mass produce different shades of colours, and are used in the manufacture of coloured glasses.
7. **Oxide of Phosphorus.** P_2O_5 is introduced in the form of calcium phosphate. This as well as As_2O_3 which is added as such, produces glass which is opalescent.
8. **Cullets.** These are pieces of waste glass. Addition of these pieces to the charge facilitates melting and also helps to utilize the wastes.

Manufacture of Glass

The manufacture of glass consists of the following steps:

1. Melting

The raw materials to be used depend upon the variety of glass to be obtained. For ordinary soda-lime glass the raw materials are sand, washing soda and limestone. These are mixed in the proper proportion and ground together. The resulting mass known as "*batch*" is mixed with broken glass called "*cullet*" and introduced either into the pots of *pot furnance* or into the tank of a *tank furnance.*

(*a*) **Pot Furnace.** In this furnace the pots are placed in a circle around a central opening in its bottom. Hot gases and the flames come out of this opening. The roof over the pots is of refractory material which reflects the heat on the pots. Pots are of two types viz. open and closed. Clay rings are placed in pots which facilitate withdrawl of molten material (Fig. 6.15). The pot furnace is of batch type.

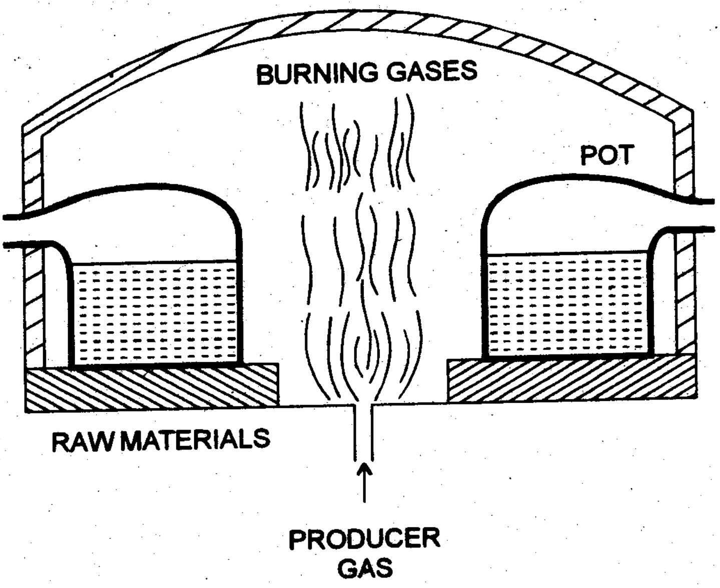


Fig. 6.15. A pot furnace.

(*b*) **Tank Furnace.** In this furnace the batch materials are charged at one end and the molten glass taken out at the other. Tank furnace is a type of reverberatory furnace in which the molten mass forms a pool over the hearth. Heating is done by means of producer gas which is burnt inside. (Fig. 6.16).

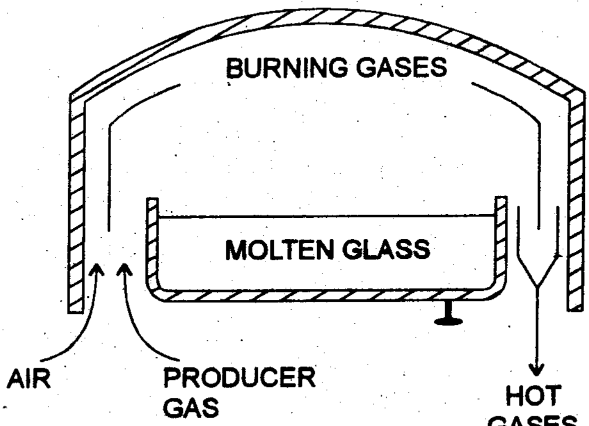


Fig. 6.16 A tank furnace.

During melting a good deal of frothing is caused owing to the evolution of gases like CO_2, SO_2, O_2 etc. When froth subsides, the temperature is raised and the molten glass is allowed to stand for some time. In this way a homogeneous mass free from gas bubbles is obtained. In tank furnace the products obtained may not be of a superior quality because the molten glass cannot be stirred and the glass is not of a uniform composition.

The chemical reactions taking place during the process are:

$$Na_2CO_3 + x{\cdot}SiO_2 \longrightarrow Na_2O{\cdot}xSiO_2 + CO_2$$

$$Na_2SO_4 + C \longrightarrow Na_2O + CO + SO_2$$

$$Na_2O + ySiO_2 \longrightarrow Na_2O{\cdot}ySiO_2$$

$$CaCO_3 + zSiO_2 \longrightarrow CaO{\cdot}zSiO_2 + CO_2$$

The mixture of $CaO{\cdot}zSiO_2$, $Na_2O{\cdot}ySiO_2$ and $Na_2O{\cdot}xSiO_2$ with some other compounds obtained is commercial glass.

2. Shaping

The articles to be made from glass are obtained by blowing the molten glass into definite shapes. The blowing or moulding is done by skilled workers or by machines. Whatever might be the technique of work, the whole process is to be done within a few seconds.

3. Annealing

It is the process by virtue of which the newly shaped articles are cooled slowly. If the articles are cooled quickly, they become brittle on account of high internal strain. During annealing the molecules of glass arrange themselves in such a way that there is no strain on them when the article is cooled.

4. Finishing

All types of glass articles require finishing after annealing. The finishing operations include cutting, grinding, polishing, enamelling, etc. It is only after the finishing operations that the glass aricles become ready for the market.

Varieties of Glass

Large varieties of glass are obtained by varying the composition of batch. Some important varieties are as follows:

1. **Soft Glass.** It is a mixture of sodium and clacium silicates and is the common variety employed for making ordinary glassware and glass plates.
2. **Hard Glass.** It is a mixture of potassium and sodium silicates and is used for making hard glass apparatus.
3. **Flint Glass.** It is a mixture of potassium and lead silicates. It has a high specific gravity, brighter lustre and greater refractive index. It is used in the manufacture of artificial gems, lenses, prisms, electric bulbs etc.
4. **Jena Glass.** It is a mixture of zinc and barium boro-silicates and is very resistant to heat, chemicals and shock. It has a high alumina content.
5. **Pyrex Glass.** It possess properties similar to Jena glass but it is a mixture of sodium aluminium borosilicates. It is rich in silica (SiO_2) but poor in alumina.
6. **Optical Glass.** It is generally made by fusing red lead, potassium carbonate and sand - special varieties contain B_2O_3 in place of silica and BaO and ZnO in place of red lead. Crooke's glass contians cerium oxide which cuts off UV light harmful to eyes.
7. **Safety Glass.** It is obtained by placing a layer of butyral plastic with a suitable adhesive between two layers of glass and cementing them by heat and pressure. It does not shatter and is used in making automobile wind screens.
8. **Glass Wool.** It is glass fibre obtained by forcing molten glass through tiny holes in the presence of a jet of high pressure system. Glass being a thermal insulator is wrapped round various articles in the form of glass wool. Glass fibres are used for making fire-proof cloths.
9. **Coloured Glass.** To produce glass of different colours, various mineral substances are mixed with it during the process of manufacture e.g., the following colours are obtained by substances noted against each:
   - *(a)* Red glass contains Cu_2O and selenium metal.
   - *(b)* Green glass contains CuO and Cr_2O_3
   - *(c)* Yellow glass contians CdS, carbon
   - *(d)* Blue glass contains CuO, CoO.
   - *(e)* Violet glass contains MnO_2.
   - *(f)* Milky glass contians SnO, $Ca_3(PO_4)_2$.
   - *(g)* Black glass contians oxides of cobalt, nickel manganese etc.

Questions

Q.1. Discuss the general group trends of group IV elements, compare the behaviour of carbon and silicon.

Q.2.*(a)* What is green-house effect? What substances are responsible for this phenomenon?

(b) What measures you suggest to minimize this phenomenon?

Q. 3.*(a)* What are different allotropic forms of carbon? Compare the structure of graphite with diamond.

(b) Write a short note on partially crystalline forms of carbon

Q. 4. What are fullerenes? How are these prepared? Discuss the chemistry of fullerenes in detail.

Q.5.*(a)* What is global warming? Discuss the role of CO_2 in global warming.

(b) What are the future predictions about global warming?

Q.6.*(a)* What are carbides? Discuss different types of carbides.

(b) How is pure silicon produced for solar energy cell?

Q.7. What are silicons? How are they prepared? Briefly discuss the properties and uses of silicones.

Q.8.*(a)* What are silicates? How are they classified? Discuss their structure and industrial applications.

(b) How does CO_2 differ from SiO_2?

Q.9. What are silicates? Discuss the structures of various silicates.

Q.10.*(a)* What is water glass? Discuss the preparation, properties and uses of water glass.

(b) What are zeolites? Discuss their uses.

Q.11.*(a)* What is Portland Cement? Discuss its composition.

(b) Discuss the wet process for the manufacture of cement.

(c) Discuss the prospects of cement industry in Pakistan.

Q.12.*(a)* What are the raw materials for cement industry?

(b) How it is prepared by wet process?

(c) What do you understand by "setting of cement"?

Q.13.*(a)* Give the detail of raw materials used for the production of glass industry.

How is glass manufactured on industrial scale?

(c) Discuss different types of glass.

(d) How are coloured glass produced?

Q.14.*(a)* What do you understand by the word "annealing"? Explain it with reference to glass.

(b) What are Pyrex glass, Flint glass and Jena glass?

(c) What are the future prospects of glass industry in Pakistan.

Q.15. Justify/comment on the following statements.

(a) Carbon and silicon form similar types of compounds.

(b) Carbon and silicon are always tetravalent but Ge, Sn and Pb show divalency.

(c) CCl_4 is resistant to hydrolysis but $SiCl_4$ is readily hydrolyzed.

(d) $[CF_6]^{2-}$ ion does not exist while $[SiF_6]^{2-}$ ion exists.

(e) Carbon possesses greater catenation property than other members of this group.

(f) CO_2 is a gas while SiO_2 is a solid.

(g) Silicon does not form multiple bonds like carbon.

(h) Carbon and tin show allotropy.

(i) Carbon, silicon and lead belong to the same group.

(j) Carbon is a non-metal while lead is a metal.

(k) Fullerenes are also known as buckyball.

(l) Fullerenes are also known as buckminsterfullerenes.

(m) Diamond is hard and graphite is soft.

Chapter Seven

NITROGEN AND PHOSPHORUS

7.1 INTRODUCTION

Group VA (15) of the periodic table consists of nitrogen (N), phosphorus (P), arsenic (As) antimony (Sb) and bismuth (Bi). They constitute a well defined series showing a regular change of properties with the atomic number. The gradual transition from non-metallic to metallic character within a group is no better illustrated than in this group. The first two elements, N and P, are typical non-metals, Sb and Bi are definitely metals, while As may be considered as a metalloid. All the elements have five electrons in their outer most shell with two electrons in the *s*-orbital and three electrons in the *p*-orbital as shown in Table 7.1.

Table 7.1. Electronic Configuration of Group VA (15) Elements

Element	At. No.	Electronic Configuration
N	7	$1s^2, 2s^2\,2p^3$
P	15	$1s^2, 2s^2\,2p^6, 3s^2\,3p^3$
As	33	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^3$
Sb	51	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6\,4d^{10}, 5s^2\,5p^3$
Bi	83	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6\,4d^{10}\,4f^{14}, 5s^2\,5p^6\,5d^{10}, 6s^2\,6p^3$

It is evident from the above configurations that all these elements possess s^2p^3 configuration in the valence shell. The three *p*-electrons are equally distributed in accordance with the *Hund's rule* amongst the three orbitals and since the orbitals are exactly half-filled, the elements are fairly stable and not so reactive, e.g., nitrogen behaves almost as an inert element. The penultimate shell of nitrogen contains s^2 electrons (saturated), of phosphorus s^2p^6 electrons (saturated), of arsenic $s^2p^6\,d^{10}$ electrons (saturated), while antimony and bismuth contain $s^2p^6d^{10}$ electrons (unsaturated). This shows why nitrogen differs from phosphorus and these two from the remaining members of this group.

Some of the important physical properties of group VA (15) elements are summarized in Table 7.2.

Table 7.2. Some Physical Properties of Group VA (15) Elements

Property	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic weight	14.00	30.97	74.92	121.75	208.98
Density (g/cm^3)	1.026 (solid)	1.82 to 2.31	4.7 to 5.7	6.7	9.6
Ionization potential I (eV)	14.48	10.9	10.5	9	8
Melting point (°C)	-209.8	44.1	814	631	271
Boiling point (°C)	-195.8	280	615	1380	1450
Atomic radius (nm)	0.074	0.110	0.121	0.141	0.146
Electronegativity	3.0	2.1	2.0	1.9	1.8

7.2 GRADATION OF THE CHARACTERISTIC PROPERTIES WITHIN GROUP VA ELEMENTS

The gradation in the physical and chemical properties of the elements with the rise of atomic number is as follows:

(i) **Physical State.** Nitrogen is a gas, phosphorus is a soft waxy solid, arsenic is hard but lustreless solid while antimony and bismuth are hard solids with metallic lustre.

(ii) **Atomic and Ionic Sizes.** The steady increase in size with increasing atomic number is apparent in the group. A comparison of the sizes of the atoms in different oxidation states is of special interest. The size of the radius for an atom in -3 oxidation state is very large and it is much smaller for +5 oxidation state. This is in accordance with gradual increase in the metallic character from top to bottom in the group.

(iii) **Ionization Potential and Electronegativity.** With increase in size, these elements have increasing tendency to lose valence electrons and their ionization potential shows a progressive decrease. The electronegativity decreases from nitrogen (= 3.0) to bismuth (= 1.9) nitrogen to bismuth 3 - 1.9.

(iv) **Density.** There is a pronounced increase in hardness and density in going from P to Bi.

(v) **Melting and Boiling Points.** The melting points (except for Sb and Bi) and the boiling points both increase as we move down the group. The melting point of Bi is usually low. Low melting point of Bi suggests that there is little possibility of the availability of the pair of electrons in s-orbital. The elements of this group are more volatile than their intermediate neighbours.

(vi) **Metallic Character.** Due to the decrease in the values of ionization energies from N to Bi, the metallic character of these elements increases in the same

direction. For example, the first two elements are exclusively non-metals, the next two elements viz. As and Sb are metalloids, while the last element namely Bi is typically a metal.

(vii) **Catenation.** Nitrogen and phosphorus have a tendency to form M-M links. For example, N-atoms are linked together in hydrazine ($H_2N—NH_2$) and azide ($(N — N — N)^-$) skeleton. In case of pohsphorus P — P links are limited only to two atoms (e.g., P_2H_4) while As has no tendency for catenation.

(viii) **Oxidation States.** The common oxidation states of these elements are -3, +3 and +5. This is in agreement with the number of electrons in the outer shell. The tendency to acquire three electrons and to be in -3 oxidation state is most pronounced in the case of nitrogen. It decreases with increasing atomic number until bismuth forms no stable compound in which its oxidation state is -3. In the +3 oxidation state, the inert pair, s^2, is of importance. This oxidation state becomes progressively more important from phosphorus to bismuth. Only Bi and Sb form simple cations Bi^{3+} and Sb^{3+} in aqueous solutions.

Some of the elements of this group also show other oxidation states, e.g., nitrogen shows +1, +2 and +4 and phosphorus shows +1 and +4, in addition to the normal states.

(ix) **Formation of Hydrides.** All the elements of this group form the hydrides like MH_3 (M = N, P, As, Sb, Bi), M_2H_4 (M = N, P). The stability of the hydrides decreases with the rise of atomic weight. Nitrogen forms the most stable ammonia (NH_3) while the existence of bismuth hydride is doubtful and it has been obtained only in traces.

(x) **Formation of Oxides.** All the elements form oxides of the general formulae X_2O_3, X_2O_4 and X_2O_5 in which the oxidation states are +3, +4 and +5 respectively. Their acidic character decreases with increasing atomic weight. The oxides of nitrogen (N_2O_3, N_2O_4 and N_2O_5) and phosphorus (P_2O_3, P_2O_4 and P_2O_5) are purely acidic in character; those of arsenic and antimony are amphoteric while that of bismuth (Bi_2O_3) is predominantly basic.

(xi) **Formation of Halides.** These elements form two types of halides namely trihalides (MX_3) and pentahalides (MX_5). With the exception of BiF_3, all other trihalides have covalent character which decreases down the group. Nitrogen and bismuth cannot form pentahalides, because nitrogen cannot expand its octet due to the non-availability of d-orbital and phosphorus has inert pair effect.

(xii) **Formation of Oxy-acids.** With the exception of bismuth, all other elements form oxy-acids in various oxidation states. Oxy-acids of nitrogen and phosphorus are quite common and useful. The strength and solubility of oxy-acids having the element in the same oxidation state (e.g., HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4) decreases gradually.

7.3. PECULIAR PROPERTIES OF NITROGEN

Nitrogen which is the first element of VA group differs considerably, like carbon (first element of IVA group), from the other elements of this group. This is because of the following inherent properties of nitrogen: *(a)* small size *(b)* high electronegativity, and *(c)* non-availability of *d*-orbitals. The main points of difference are:

(i) Nitrogen is a gas while other elements are solid.

(ii) Nitrogen molecule is diatomic (N_2) while other elements are tetra-atomic and are, therefore, represented as P_4, As_4 and Sb_4.

(iii) Nitrogen does not show allotropy while other elements (except Bi) show allotropy.

(iv) Nitrogen occurs in the free state while none of the other elements occurs in the free state.

(v) The covalency limit for nitrogen is 4 while the other elements can raise their covalency to 5 and 6 by expansion of outer shell.

(vi) Nitrogen cannot form complexes by accepting electrons but the other elements having suitable d-orbitals available can form complexes by accepting elements.

(vii) Nitrogen with its small size and high electronegativity can acquire three electrons to give the nitride ion N^{3-}. This tendency is very much suppressed in the subsequent elements.

(viii) Nitrogen is peculiar in showing a wide range of oxidation states, e.g., +1 in N_2O, +5 in HNO_3 and -3 in NH_3. Other elements do not show a variety of oxidation states.

(ix) The nitrogen molecule contains triply bonded nitrogen atoms ($N \equiv N$) and is very stable. The other elements which are found in different allotropic forms can form molecules of different complexity.

(x) Usually large number of binary compounds of nitrogen with oxygen are known, e.g., N_2O, NO, N_2O_3, NO_2, N_2O_4 and N_2O_5. Some of which, e.g., N_2O, NO and N_2O_4 have no counterparts in the other elements.

7.4. FIXATION OF NITROGEN

The conversion of atmospheric nitrogen into useful nitrogenous compounds by natural or artificial methods is called *fixation of nitrogen*. Nitrogen present in these nitrogenous compounds is called fixed or combined nitrogen.

Nitrogen present in the atmosphere is the source of various nitrogenous compounds such as proteins, amino acids, nucleic acids which are essential for animal and plant kingdom. Neither animals nor the plants can assimilate free nitrogen. Animals obtain the nitrogen supply from compounds present in plants, while plants secure the required nitrogen from nitrates present in the soil or from fertilizers. The nitrogenous compounds taken up by plants are converted into *proteins* in the presence of light. Proteins are essential for animal life. Thus, plants form a useful link between animals and soil substances.

The chief source of numerous nitrogen compounds is the atmospheric nitrogen. The atmospheric nitrogen is fixed by the following natural and artificial methods.

1. Natural Fixation

(a) By Electric Discharge

The nitrogen and oxygen present in air combine together to form nitric oxide under the influence of electric discharges. Nitric oxide is oxidized by excess of oxygen present in the atmosphere to form nitrogen dioxide which further combines with water to form nitric acid. This acid is washed down by rain into the soil, where it reacts with soil limestone or alkali to form calcium nitrate which is the food of plants.

$$N_2 + O_2 \xrightarrow{\text{lightning}} 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

$$2HNO_3 + CaCO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$

(b) By Symbiotic Bacteria

There are also some bacteria, known as *symbiotic bacteria* which grow in small nodules in the roots of plants of family *Leguminaceae* (pea gram etc). These bacteria can assimilate atmospheric nitrogen directly and convert it into products useful for plant growth.

Plants give out ammonical compounds to the earth on decay which under the action of *nitrosifying* and *nitrifying bacteria* form nitrites and nitrates. Most of the ammonia and ammonium compounds are produced, however, as a result of the decomposition of urea, amino acids etc., which are secreted by the animal body.

$$H_2N—CO—NH_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

These substances are formed in the animal body by the digestion of nitrogenous plant proteins taken by the animals as food. Again, there are some *denitrifying bacteria* also present, which break up these nitrites and nitrates and ammonical compounds to nitrogen which goes up to the atmosphere from where it started in the beginning and thus the cycle is complete. Ammonia to nitrite, and nitrite to nitrate and again nitrate to nitrogen are not only bacterial processes but photochemically too, and both these agencies help in the completion of the cycle. This whole phenomenon is known as *nitrogen cycle* (Fig. 7.1).

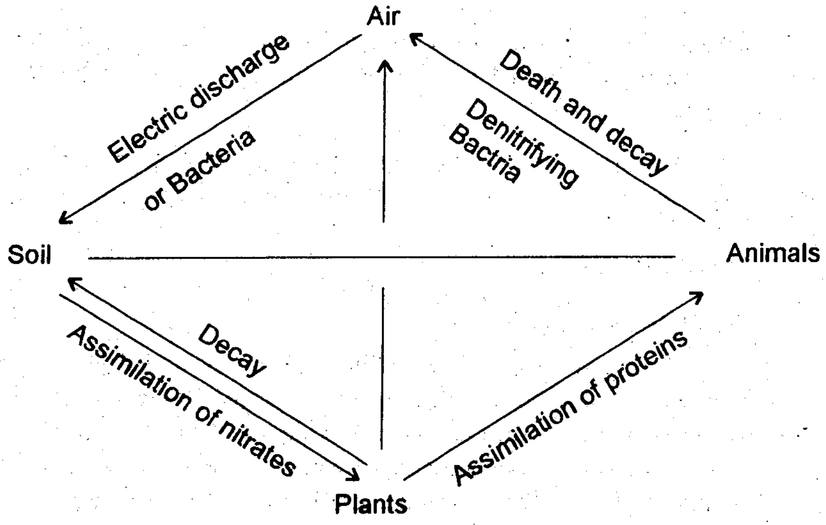


Fig. 7.1. Nitrogen Cyecle.

2. Artificial Fixation

(a) Fixation of Nitrogen as HNO_3

Under the influence of high tension electric arc, nitrogen of the air combines with oxygen to form nitric oxide. The equilibrium mixture is suddenly cooled when it combines with more of oxygen to form nitrogen peroxide. This may be absorbed in water in presence of excess air to get nitric acid which may be used for nitrogeneous fertilizers.

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

(b) Fixation of Nitrogen as NH_3

Under the influence of certain catalysts nitrogen combines with hydrogen to form ammonia. A mixture of nitrogen and hydrogen in the ratio 1: 3 is compressed to a pressure of 200 - 500 atmosphere and is passed over a catalyst heated to about 550°C. This is *Haber's process* for the manufacture of ammonia which can be converted into ammonium salts by treatment with suitable acids.

$$N_2 + 3H_2 \underset{\text{high pressure}}{\overset{\text{catalyst}}{\rightleftharpoons}} 2NH_3$$

(c) Fixation of Nitrogen as Nitrides

Nitrogen combines with Mg and Al at high temperature to give nitrides which are employed as a source of ammonia, since these nitrides are decomposed by H_2O and NH_3 is evolved.

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

$$2Al + N_2 \longrightarrow 2AlN$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

7.5. OXIDES OF NITROGEN

Nitrogen is unique in forming a number of oxides corresponding with the formal oxidation states for nitrogen of +1, +2, ±3, ±4 and +5 (N_2O, NO, N_2O_3, N_2O_4 and N_2O_5). Except N_2O_5, all are gases at ordinary temperature.

Nitrous Oxide, N_2O

Preparation

(i) It is prepared by heating a mixture of sodium nitrate and ammonium sulphate.

$$2NaNO_3 + (NH_4)_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + 2N_2O + 4H_2O$$

(ii) When hydroxylamine salts are oxidized by sodium nitrite, copper sulphate or permanganate, nitrous oxide is always evolved.

$$NH_2OH \bullet HCl + NaNO_2 \longrightarrow NaCl + N_2O + 2H_2O$$

(iii) When nitric acid is reduced by stannous chloride and hydrochloric acid, nitrous oxide is obtained.

$$4SnCl_2 + 8HCl + 2HNO_3 \longrightarrow 4SnCl_4 + 5H_2O + N_2O$$

Properties

(i) It is a colourless gas with pleasant odor and sweet taste. It is fairly soluble in water and alcohol. When inhaled with oxygen, it begets peculiar sort of consciousness with nervous excitement so that it has been named as *laughing gas.*

(ii) It is neutral to litmus.

(iii) It supports the combustion of substances like sulphur, phosphorus, sodium, magnesium etc. just as will as oxygen. This is because of its ready decomposition into its elements.

$$S + 2N_2O \longrightarrow SO_2 + 2N_2$$

$$C + 2N_2O \longrightarrow CO_2 + 2N_2$$

$$Mg + N_2O \longrightarrow MgO + N_2$$

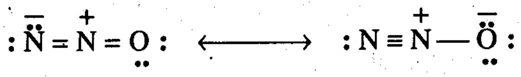
$$2Na + N_2O \longrightarrow Na_2O + N_2$$

(iv) A mixture of hydrogen and nitrous oxide (equal volume) explodes with violence

$$N_2O + H_2 \longrightarrow N_2 + H_2O$$

Structure

It is a linear and unsymmetrical molecule with a very small value of dipole moment (= 0.116D). Thus N_2O is a resonance hybrid of the following structures:



$$:\overset{-}{\ddot{\mathrm{N}}}=\overset{+}{\mathrm{N}}=\underset{\bullet\bullet}{\mathrm{O}}: \longleftrightarrow :\mathrm{N}\equiv\overset{+}{\mathrm{N}}-\underset{\bullet\bullet}{\overset{-}{\ddot{\mathrm{O}}}}:$$

(*a*) (*b*)

In structure (*a*) the central N^+ is sp hybridized. Each of the two linear sp hybrids orbitals has one electron. The remaining two 2p-orbitals which do not take part in hybridization also have one unpaired electron. The two sp hybrids overlap with suitable 2p orbitals of oxygen atom on one side and of nitrogen on the other side to give two σ-bonds. The remaining two 2p-orbitals of N^+ overlap with suitable 2p orbitals of oxygen and of nitrogen to form two π-bonds. The bond lengths in the molecule are as:

$$\mathrm{N}\overset{1.12\,\text{Å}}{\text{———}}\mathrm{N}\overset{1.19\,\text{Å}}{\text{———}}\mathrm{O}$$

Nitric Oxide, NO ✓

Preparation

(*i*) It is easily prepared by heating copper turnings with concentrated nitric acid.

$$3Cu + \underset{\text{(conc.)}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

The action of Ag, Zn and Hg metals on nitric acid is also similar.

(*ii*) It is also prepared when a mixture of N_2 and O_2 is passed through an electric arc:

$$N_2 + O_2 \rightleftharpoons 2NO$$

(*iii*) Pure nitric oxide is obtained when a mixture of ferrous sulphate and potassium nitrate is treated with conc. sulphuric acid

$$2KNO_3 + 6FeSO_4 + 4H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + 2NO + 4H_2O$$

Properties

(*i*) It is a colourless gas, heavier than air and very sparingly soluble in water. The gas is neutral to litmus solution.

(*ii*) It combines with O_2 to form brown fumes of nitrogen peroxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

(*iii*) It reacts with burning charcoal, S, P to give oxides.

$$2NO + S \longrightarrow SO_2 + N_2$$

$$2NO + C \longrightarrow CO_2 + N_2$$

(iv) It reacts with ferrous sulphate, potassium sulphate etc. to form addition products.

$$FeSO_4 + NO \longrightarrow FeSO_4{\cdot}NO$$

$$K_2SO_4 + 2NO \longrightarrow K_2SO_4{\cdot}2NO$$

(v) It reduces acidified solution of $KMnO_4$ to $MnSO_4$ and HNO_3 to NO_2.

$$6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 10HNO_3 + 4H_2O$$

$$2HNO_3 + NO \longrightarrow 3NO_2 + H_2O$$

(vi) It oxidizes SO_2 to H_2SO_4 and H_2S to S.

$$2NO + SO_2 + H_2O \longrightarrow H_2SO_4 + N_2O$$

$$H_2S + 2NO \longrightarrow H_2O + S + N_2O$$

(vii) It combines with Cl_2 and Br_2 to form nitrosyl chloride and nitrosyl bromide respectively.

$$2NO + Cl_2 \longrightarrow 2NOCl$$

$$2NO + Br_2 \longrightarrow 2NOBr$$

(viii) When passed through a strong solution of caustic potash it forms nitrite.

$$2KOH + 4NO \longrightarrow N_2O + 2KNO_2 + H_2O$$

Structure

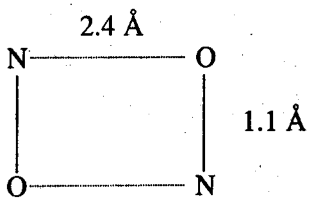
Valence bond theory says that NO molecule is a resonance hybrid of the following structures.

$$:\dot{N}=\ddot{O}: \longleftrightarrow :\underset{\cdot\cdot}{\dot{N}}=\overset{+}{\underset{\cdot}{O}}:$$

It is an *odd electron* molecule since it contains an odd number of electrons. NO molecule in the gaseous state has one unpaired electron which makes this molecule paramagnetic. According to magnetic evidence the odd electron in NO molecule spends half of its time on N-atom and half of its time on O-atom. This situation can be represented by assuming that NO molecule contains one *three-electron bond* and two *two electron bonds* as shown below:

$$:N\overset{\cdot\cdot\cdot\cdot}{=\!=}O:$$

In the solid state NO is known to form a loose *dimer*, N_2O_2 with structure as:



Dinitrogen Trioxide, N_2O_3

Preparation

(i) Nitrogen trioxide is prepared by the reduction of nitric acid with arsenious oxide.

$$As_2O_3 + 2HNO_3 \longrightarrow N_2O_3 + As_2O_5 + H_2O$$

(ii) It is also prepared by cooling a mixture of nitric oxide and nitrogen peroxide.

$$NO + NO_2 \xrightarrow{-21°C} N_2O_3$$

Properties

(i) It is a red colour gas. On condensing, it gives a dark blue liquid. On heating, it dissociates into NO and NO_2.

$$N_2O_3 \xrightarrow{\Delta} NO + NO_2$$

(ii) It is acidic in nature and reacts with sodium hydroxide to form sodium nitrite.

$$2NaOH + N_2O_3 \longrightarrow 2NaNO_2 + H_2O$$

(iii) It is also called nitrous anhydride, i.e., anhydride of HNO_2, since it gives HNO_2 when treated with H_2O.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

(iv) It reacts with sulphuric acid with the formation of nitrosonium hydrogen sulphate.

$$N_2O_3 + 2H_2SO_4 \longrightarrow 2NO^+(HSO_4^-) + H_2O$$

Structure

Since in liquid and gaseous state N_2O_3 dissociates to give NO and NO_2, it may be assumed that structure of N_2O_3 involves a link between NO and NO_2 via a π-bond. Thus the structure of N_2O_3 may be shown as:

$$\underset{\cdot\cdot}{\ddot{O}} = \ddot{N} \overset{\pi}{—} \underset{\cdot\cdot}{\ddot{O}} — \ddot{N} = \underset{\cdot\cdot}{\ddot{O}} \quad \text{or} \quad ON \overset{\pi}{—} ONO$$

This structure is confirmed by the tracer studies which have shown that when nitrogen dioxide labeled with N^{15} ($N^{15}O_2$) is mixed with $N^{14}O$, a rapid exchange between N^{15} and N^{14} takes place as shown below:

$$N^{14}O + N^{15}O_2 \rightleftharpoons N^{15}O + N^{14}O_2$$

N_2O_3 molecule is diamagnetic in spite of its intense blue colour and hence it is not an *odd electron molecule*.

Nitrogen Dioxide, NO_2 and Nitrogen Tetraoxide, N_2O_4

Preparation

(*i*) When nitric oxide mixes with air, it gives out ~~red~~ Brown fumes which are mainly of nitrogen dioxide.

$$2NO + O_2 \longrightarrow 2NO_2$$

(*ii*) In the laboratory, it is prepared by the action of heat on lead nitrate.

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$$

(*iii*) It is also prepared by the action of copper on conc. HNO_3.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Properties

(*i*) Nitrogen dioxide is a reddish brown gas with a pungent smell. This oxide is also called *nitrogen peroxide.* At 14°C it has a deep brown colour and a density which corresponds to the formula, NO_2. As the temperature falls, its colour goes on fading. On further cooling, it condenses to *pale yellow* liquid (b.p. = 22°C) which freezes to colourless crystals (m.p. = -9°C). The density of the solid corresponds to the formula, N_2O_4. Quite evidently, progressive association of molecules occurs with the decrease in temperature.

$$\underset{\text{(Dark brown)}}{2NO_2} \rightleftharpoons \underset{\text{(Colourless)}}{N_2O_4}$$

(*ii*) The colour of nitrogen dioxide begins to fade above 140°C also. This is due to its dissociation into NO and O_2.

$$2NO_2 \rightleftharpoons 2NO + O_2$$

(*iii*) It is soluble in water and acidic towards litmus. When dissolved in water, it forms a mixture of nitrous and nitric acids. It is, therefore, a *mixed anhydride.*

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$

(*iv*) It neutralizes alkali solution with the formation of mixture of nitrite and nitrate, thus proving its acidic nature.

$$2NaOH + 2NO_2 \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

(*v*) It acts as a strong oxidizing agent. Thus, it liberates iodine from potassium iodide and turns starch iodide paper blue.

$$KI + 2NO_2 \longrightarrow 2KNO_2 + I_2$$

Its reactions (as an oxidizing agent) with other inorganic compounds are given as:

$$NO_2 + H_2S \longrightarrow NO + H_2O + S$$

$$NO_2 + CO \longrightarrow CO_2 + NO$$

$$2FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO_4)_3 + H_2O + NO$$

$$NO_2 + 2Na \longrightarrow Na_2O + NO$$

$$2Cu + NO_2 \longrightarrow Cu_2O + NO$$

$$5NO_2 + 2P \xrightarrow{\Delta} P_2O_5 + 5NO$$

$$2NO_2 + S \xrightarrow{\Delta} SO_2 + 2NO$$

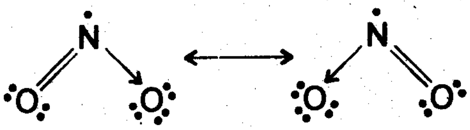
$$2NO_2 + C \xrightarrow{\Delta} CO_2 + 2NO$$

(vi) It also acts as a reducing agent. Thus it decolorizes permanganate.

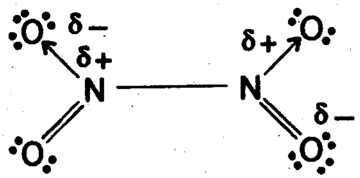
$$2MnO_4^- + 10NO_2 + 2H_2O \longrightarrow Mn^{2+} + 4H^+ + 10NO_3^-$$

Structure

NO_2 molecules has V-shaped structure with O — N — O bond angle = 132° and N — O distance = 1.19 Å. This structure shows that NO_2 has one unpaired electron and hence it is an *odd electron molecule.* Thus NO_2 is paramagnetic and can be regarded as resonance hybrid of the following structures.



The dimer N_2O_4 is planar with long N — N bond (= 1.75 Å) and O — N — O bond angle (= 132°). The planer structure of N_2O_4 admits some +δ charge on each N-atom. The repulsion between the adjacent +δ charges make N — N bond longer than a single bond.



Nitrogen Pentoxide, N_2O_5

Preparation

(i) It is prepared by the action of dry chlorine over dry silver nitrate at 90°C in the beginning and then at 60°C.

$$4AgNO_3 + 2Cl_2 \longrightarrow 4AgCl + 2N_2O_5 + O_2$$

(ii) It may be obtained by taking out water molecules from absolutely dry nitric acid by P_2O_5. The vapors of N_2O_5 so obtained are cooled in a U-tube which is cooled by solid CO_2 and ether.

$$2HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2HPO_3$$

Properties

(i) N_2O_5 forms colourless hard crystals which are deliquescent and melt at 30°C. It is very unstable and may explode even without heating.

(ii) It decomposes to give NO_2 and O_2.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

(iii) It dissolves in water giving nitric acid and is, therefore, called *nitric anhydride.*

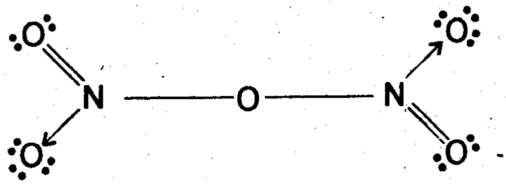
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

(iv) It reacts with iodine to from iodine pentoxide.

$$I_2 + N_2O_5 \longrightarrow I_2O_5 + N_2$$

Structure

X-ray studies of N_2O_5 suggest that it is an ionic solid and hence is *nitronium nitrate* $NO_2^+NO_3^-$. But in its vapour state it exists as a symmetrical molecule having the following structure.



N — O — N bond is almost linear i.e., N — O — N bond angle = 180°.

7.6. POLE OF NITROGEN OXIDES IN ENVIRONMENTAL POLLUTION

The atmosphere consists of a mixture of gases (e.g., N_2, O_2, CO_2, Ar, etc.) and it extends upto about 500 kms above the surface of the earth. These important gaseous constituents of the earth play important roles in sustaining life on earth. Oxygen supports life on earth, nitrogen is an essential macro-nutrient for plants (via nitrogen fixation and fertilizer manufacture) and carbon dioxide is essential for photosynthetic activity of plants. In addition to these, carbon monoxide, nitrogen oxides (N_2O, NO_2), sulphur dioxide and ozone are also present to small extent. Any major disturbance in the atmospheric composition either by extra-ordinary or anthropogenic activities, may lead to disastrous consequences or may even endanger the very survival of life on the earth. The latter gases if present in excessive amounts act as air pollutants. *Pollutants* are the substances that are present in excess amounts and have detrimental effects on the environment.

According to U.S. Public Health Service, "*air pollution* may be defined as the presence in the outdoor atmosphere of one or more contaminants in such quantities and of such duration as may be injurious to human, plant or animal life, or property."

The important air pollutants are:

(a)	Carbon monoxide	(CO)
(b)	Carbon dioxide	(CO_2)
(c)	Sulphur oxides	(SO_2, SO_3)
(d)	Nitrogen oxides	(NO_X)
(e)	Hydrocarbons	(HC)
(f)	Particulate matter	(sand, dust, etc.)

The above pollutants are continually released into the atmosphere through natural as well as anthropogenic activities. The magnitude of the problem of air pollution has increased alarmingly due to population explosion, industrialization, urbanization, automobiles and other human activities for great comfort. We shall discuss here only the role of nitrogen oxides in air pollution.

Oxides of Nitrogen

Out of the eight possible oxides of nitrogen, only N_2O, NO and NO_2 are the important constituents of the atmosphere. Although the concentration of N_2O is more in the atmosphere, NO and NO_2 are more significant from air pollution point of view and they are usually represented together as NO_X. Oxides of nitrogen may be formed either by natural or artificial fixation of nitrogen from the atmosphere or from nitrogen compounds present in organic matter. The annual global release of NO_X from man made sources is about 5×10^7 tonnes, which is only slightly less than that discharged by natural bacterial activity. Oxides of nitrogen are produced by combustion of coal, oil, natural gas and other organic matter. *Thus, NO_X is introduced into the atmosphere from automobile exhaust, incinerators, furance stacks, coal based power plants and other similar sources.*

When the fuels are burnt in air, some of the nitrogen in the air is oxidized to NO. The amount of NO formed depends on the temperature of the flame and the rate of cooling of the combustion products. Rapid cooling of the combustion products prevents the dissociation of NO. The oxidation of NO to NO_2 is also favored at higher temperatures (~ 1100°C) but the amount of NO_2 formed is usually not more than 0.5% of the total NO_X present. Some of the reactions involved are as follows:

$$N_2 + O_2 \xrightarrow{(1210-1750°C)} 2NO$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

$$2NO + O_2 \xrightarrow{(1100°C)} 2NO_2$$

$$NO_2 + h\nu \xrightarrow[(398\ nm)]{} NO + O$$

$$O_2 + h\nu \xrightarrow[(242\ nm)]{} O + O$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (M = \text{third body})$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

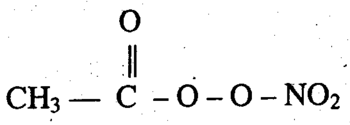
Photochemical Smog is initiated by the photochemical dissociation of NO_2 and the consequent secondary reactions involving unsaturated hydrocarbons, other organic compounds and free radicals, leading to the formation of organic peroxides and ozone. This phenomenon takes place during sunny days with low wind and low level inversion. The photochemical smog and the consequent formation of aerosols reduce the visibility, cause irritation to eyes and damage plant and rubber goods.

Photochemical Smog (Smoke + Fog)

Photochemical smog is characterized by brown, hazy fumes, which irritate eyes, lungs, leads to cracking of rubber and causes damage to vegetation.

The following steps are involved photochemical smog.

1. Emission of NO_x and hydrocarbons by vehicles and industry in the atmosphere.
2. Absortion of sunlight causing photodissociation of NO_x.
3. Consumption of NO_x and simultaneous build up of the oxidants such as O_3, O, O_2 and peroxides.
4. Oxidation of hydrocarbons to produce a vide variety of products aerosols.
5. Atmospheric oxidants include H_2O_2, organic peroxides (ROOR), organic hydroperoxides (ROOH) and peroxyacyl, nitrate or PAN.



$$CH_3 - \overset{\overset{O}{\|}}{C} - O - O - NO_2$$

PAN

Olefines and NO_x damage plants, leaves and causes bronzing of surfaces.

The following reactions are involved in photochemical SMOG formation:

(i) $NO_2 \xrightarrow{hu} NO + O$

(ii) $O_2 + O + M \longrightarrow O_3 + M$

$O_3 + NO \longrightarrow NO_2 + O_2$

(iii) $O + RH \longrightarrow R + \text{other products}$

$O_3 + RH \longrightarrow R + \text{other products}$

(iv) $NO + R + O \longrightarrow NO_2 + R$

A variety of sulphur compounds are also released into the atmosphere from both natural and anthropogenic sources. The most important of these are the sulphur oxides and hydrogen sulphides.

Among natural sources volcanoes provide 67% of the oxides of sulphur.

Sunligh plays an important role in smog formation. Hence this type of smog is referred to as photochemical smog. The eye irritation caused by smog is due to the formation of formaldehyde and acrolein from hydrocarbons.

Industrial smog consists primarily of ash and smoke, oxides of nitrogen, SO_2, oil and H_2SO_4 mist and is referred to as `acid rain'. Industrial operations such as coke refineries, smelters, etc., result in the liberation of SO_2 in atmosphere. Sulphur dioxide can undergo oxidation to SO_3 caused by air or NO_2. Sulphur trioxide reacts with water vapours to produce H_2SO_4 mist. The control of industrial smog can be made by passing SO_2 through scrubbers containing line or MgO when 83-85% SO_2 can be removed.

$$Ca(OH_2) + SO_2 \longrightarrow CaSO_3 + H_2O$$

$$MgO + SO_2 \longrightarrow MgSO_3$$

Biochemical effects of the Photochemical oxidants

Ozone and PAN are the major photochemical oxidants present in the smog. O3 and PAN are harmful to plants, animals and humans.

Oxidize cellular constituents. PAN and ozone toxicity is produced via generation of free radicals. The free radicals produced may damage DNA and thus alter cellular genetic integrity too. The toxic effects of ozone are manifested after inhalation and absorption in the lungs causing accumulation of fluids in the lungs (pulmonary edema), damaging lung capillaries and mortality if continued or high level exposures occur. Both O_3 and photochemical smog cause irritation of the eyes and respiratory tract. The free radicals produced by O3 and other photochemical oxidants attack the sulphydryl groups on the enzymes and also inactivate enzymes like isocitric dehydrogenase, malic dehydrogenase and glucose-6-phosophate dehydrogenase, which are so much involved and essential for citric acid cycle and generation of cellular energy. O3 may also inhibit the activity of some enzymes involved in synthesis of cellulose and lipids in plants. Among the sulphur containing amino-acids, cysteine is strongly attacked by PAN.

Control of NO_X Emissions

Control of NO_X emissions from the anthropogenic activities is completed on the following lines:

Use of two stage catalytic converters can minimize the NO_X from automobile emissions. NO_X are reduced to N_2 and NH_3 in the first converter at elevated temperature in the presence of catalysts such as Pt, Pd and Ruthenium.

Similarly, NO_X from power plant emissions can be reduced by 90% by using a two-state combustion process. The fuel can be first fired at a relatively high temperature using only about 90% of the stoichiometric air required so that only minimum quantity of NO is formed under these conditions. Then combustion of fuel may be completed at a relatively low temperature in excess of air. NO is not formed under these conditions.

7.7. OXYACIDS OF NITROGEN

Typical oxyacids of nitrogen are:

1. Hyponitrous acid, HNO, or $H_2N_2O_2$ (+1 oxidation state of N)
2. Nitrous acid, HNO_2 (+3 oxidation state of N)
3. Nitric acid, HNO_3 (+5 oxidation state of N)

In addition to these nitroxylic acid, H_2NO_2 and hyponitric acid $H_2N_2O_3$ are also known.

1. Hyponitrous Acid, HNO, $H_2N_2O_2$

Preparation

It can be prepared by the following methods:

(i) Free acid is prepared by treating silver hyponitrile with a solution of HCl in dry ether or with H_2S.

$$Ag_2N_2O_2 + 2HCl \longrightarrow H_2N_2O_2 + 2AgCl$$

$$Ag_2N_2O_2 + H_2S \longrightarrow H_2N_2O_2 + AgS$$

(ii) It can be obtained by the oxidation of hydroxylamine in the presence of CuO, Ag_2O or HgO.

$$2NH_2OH + 2Ag_2O \longrightarrow H_2N_2O_2 + 2Ag + 2H_2O$$

(iii) It can also be prepared by the alkali hydrolysis of sodium hydroxylamine sulphonate.

$$2(SO_3Na)NHOH + 4KOH \longrightarrow K_2N_2O_2 + 4H_2O + 2KNaSO_3$$

From the alkali hyponitrite solution, silver hyponitrite is obtained by adding silver nitrate solution.

Properties

(i) Hyponitrous acid yields hygroscopic crystals and in the pure state, white leaflets which explode, when rubbed.

(ii) It is soluble in water, alcohol, ether and benzene.

(iii) It is a weak dibasic acid and hence forms two types of salts viz. *acid salts* like $Ba(HN_2O_2)_2$ and *normal salts* (called hyponitrites) like BaN_2O_2.

(iv) In air, it decomposes to furnish a mixture of nitrous and nitric acids;

$$2H_2N_2O_2 + 3O_2 \longrightarrow 2HNO_2 + 2HNO_3$$

(v) It decomposes on warming to water and nitrous oxide

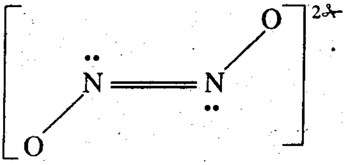
$$H_2N_2O_2 \longrightarrow H_2O + N_2O$$

(vi) It is a reducing agent and oxidized to nitrate by acidified $KMnO_4$.

$$5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 \longrightarrow 10HNO_3 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$$

Structure

The acid is dibasic one, since it gives both acidic and normal salts. The decomposition of its salts and esters gives N_2, showing that the acid has an azo —N═N— group. Infra-red spectra of silver, sodium and mercuric hyponitrite favour the following structure of anion.



2. Nitrous Acid, HNO_2

Preparation

The free existence of nitrous acid is not very definite because it is unstable and readily decomposes. However, it is prepared by the following methods:

(i) When nitrogen trioxide is dissolved in water at the ice temperature, a blue liquid thus obtained consists in main of this nitrous acid.

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2 \quad (\text{at } 0°C)$$

(ii) It can also be obtained when barium nitrite is treated with ice cold sulphuric acid.

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4\downarrow$$

The insoluble $BaSO_7$ is removed by filtration.

Properties

(i) Nitrous acid is not very stable and at lower temperature decomposes as:

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$$

On raising the temperature nitric oxide and nitrogen peroxide are formed:

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O$$

(ii) It decomposes ammonia, urea and other compounds with — HN_2 group.

$$CO(NH_2)_2 + HNO_2 \longrightarrow CO_2 + 2N_2 + 3H_2O$$

$$NH_3 + HNO_2 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

(iii) At lower temperatures, it acts on aromatic amines to give diazo-compounds.

$$C_6H_5NH_2\&HCl + HNO_2 \longrightarrow C_6H_5N_2Cl + 2H_2O$$

(iv) It is a good *oxidizing agent* on account of the ease with which it can take part with an atom of oxygen.

For example:

$$2HNO_2 + H_2S \longrightarrow 2H_2O + 2NO + S$$

$$2HNO_2 + 2KI \longrightarrow 2KOH + I_2 + NO$$

$$SnCl_2 + 2HCl + 2HNO_2 \longrightarrow SnCl_4 + 2NO + 2H_2O$$

$$2HNO_2 + SO_2 \longrightarrow 2NO + H_2SO_4$$

$$2FeSO_4 + H_2SO_4 + 4HNO_2 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$2HI + 3HNO_2 \longrightarrow I_2 + 2NO + 2H_2O$$

$$Na_3AsO_3 + 2HNO_2 \longrightarrow H_2O + 2NO + Na_3AsO_4$$

(v) It can be easily oxidized to nitric acid and as such reduces strong oxidizing agents.

$$HNO_2 + O \longrightarrow HNO_3$$

For example

$$HNO_2 + Br_2 + H_2O \longrightarrow 2HBr + HNO_3$$

$$KMnO_4 + 3H_2SO_4 + 5HNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$

$$HNO_2 + H_2O_2 \longrightarrow HNO_3 + H_2O$$

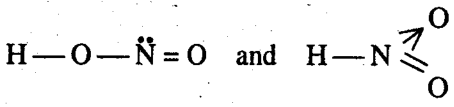
$$K_2Cr_2O_7 + 4H_2SO_4 + 5HNO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3HNO_3 + 4H_2O$$

(vi) It reacts with alkalies to form nitrites. Nitrites are much more stable than nitrous acid.

$$NaOH + HNO_2 \longrightarrow NaNO_2 + H_2O$$

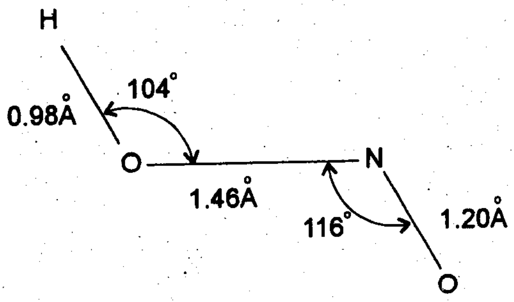
Structure

Nitrous acid gives two types of organic derivatives: the *nitrites* (*e.g.*, methyl nitrite, CH_3 — ONO) and *nitro compounds* (*e.g.*, nitro-methane, CH_3 — NO_2). On this basis two corresponding tautomeric forms of the acid are supposed to exist which are:

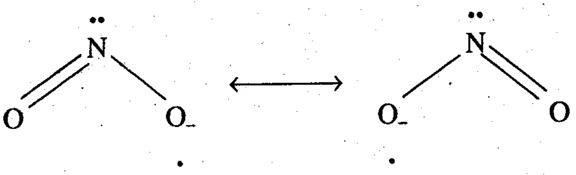


$$H-O-\ddot{N}=O \quad \text{and} \quad H-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$$

L.H. Jones, from 1R study of HNO_2 vapors came to the conclusion that the acid has a *trans* configuration with the dimensions shown below:



X-ray and Raman studies of crystalline $AgNO_2$ and $NaNO_2$ have shown that NO_2^- ion has an angular structure which is resonance hybrid of the following two structures.



3. Nitric Acid, HNO_3

Nitric acid is a chemical of great commercial importance because of its use in the manufacture of explosives like nitroglycerine, trinitrotoluene, gun cotton, picric acid etc., in the manufacture of nitrates which are used as fertilizers and in the manufacture of dyes, drugs and artificial silk.

Preparation

(*i*) **From Nitrates.** Nitric acid is prepared on large scale by heating *Chile saltpetre* ($NaNO_3$) with concentrated sulphuric acid. The mixture is placed in a cast iron retort and subjected to distillation at a temperature of about 200°C.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

Potassium nitrate has also been employed. The yellow colour of HNO_3 is due to the presence of NO_2 in it which can be removed by distillation in vacuum.

(*ii*) **From Air by Birkland Eyde Process.** Nitrogen and oxygen of the atmosphere can be made to combine by passing an electric discharge through air or the air may be passed through an electric arc (temp. 3500°C). This process at first gives nitric oxide, which is then quickly cooled to 500°C, when it further combines with oxygen to give about 2% nitrogen peroxide.

$$N_2 + O_2 \rightleftharpoons 2NO \qquad -43.2 \text{ k cals}$$

$$2NO + O_2 \longrightarrow 2NO_2$$

The vapours are then washed down by water trickling in absorption towers filled with quartz stones when nitric acid is produced:

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

Before the gases escape in air, they are led through towers containing lime or caustic alkali which recover all the oxides of nitrogen.

$$NO_2 + NO + 2NaOH \longrightarrow 2NaNO_3 + H_2O$$

$$Ca(OH)_2 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + 2H_2O$$

(iii) **From Ammonia (Ostwald's Process).** In this method a mixture of ammonia gas with air in the ratio 1: 8 is passed through a catalyst chamber packed with platinum gauze maintained at temperature of 800°C. The ammonia is oxidized to nitric oxide.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O + 215 \text{ k cals}$$

The exothermic reaction proceeds without supply of heat except the initial heating. About 90% NH_3 is converted to NO under these conditions.

NO is converted to NO_2 in the presence of air or oxygen and passed through the absorption tower as mentioned above in arc process.

$$2NO + O_2 \longrightarrow 2NO_2 + 27.8 \text{ k cals}$$

$$2NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

The acid so obtained is dilute which can be concentrated to 68% by distillation, when constant boiling mixture is formed. This constant boiling mixture of HNO_3 has a specific gravity of 1.42 and is the commercial concentrated HNO_3. More concentrated acid needed for certain uses is produced by distillation with conc. H_2SO_4 which holds back the water. The distillate is 98% HNO_3 having density 1.5.

Fuming nitric acid is made by distilling conc. HNO_3 with a little starch. The starch reduces some acid to NO_2 which dissolves in the remaining acid to form fuming nitric acid. It is yellow in colour due to NO_2. It is a much more powerful oxidizing agent and nitrating agent than conc. HNO_3.

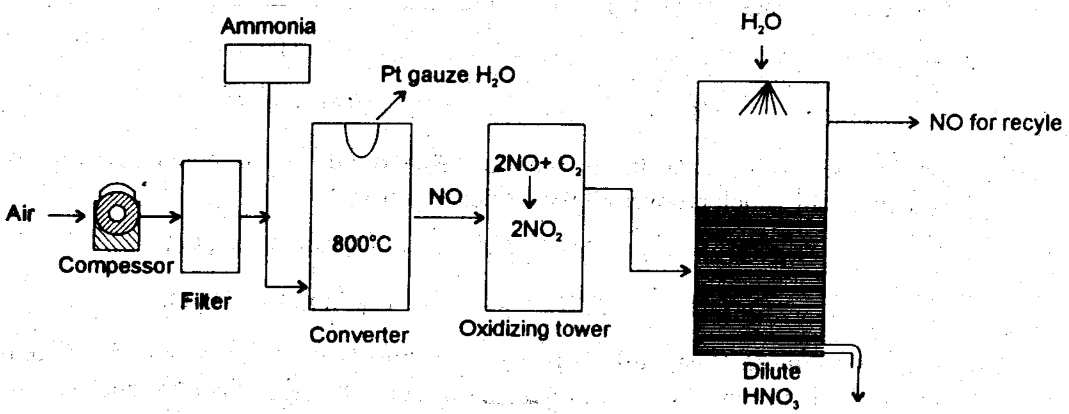


Fig. 7.2. Ostwald's process for manufacture of HNO_3.

Properties

Pure nitric acid is a colourless liquid with a characteristic choking smell. It boils at 86°C and freezes at -42°C into a transparent crystalline mass. It is soluble in water in all proportions.

1. *Oxidizing Property*

Nitric acid is a strong oxidizing agent because of the ease with which it decomposes to give nascent oxygen. The oxidizing properties of the acid are

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + O$$

indicated by its action on non-metals, metalloids, metals and on various compounds as shown below:

(i) It oxidizes non-metals like sulphur, phosphorus, carbon, and iodine to their corresponding oxy-acids.

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$$

$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + 4H_2O$$

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 10H_2O$$

(ii) Metalloids like arsenic and antimony are oxidized to corresponding oxy-acids.

$$As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$$

(iii) Most of the metals with the exception of gold and platinum are attacked by nitric acid. Some like tin and antimony gives *oxides* while the others form *nitrates.* During the reaction, a part of the acid is reduced to give products like NO_2, NO, N_2, H_2O or HN_3 and the nature of products depends upon the concentration of the acid, temperature and nature of the metal. For example;

(a) Copper with dilute nitric acid gives nitric oxide.

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

With concentrated nitric acid, it forms nitrogen peroxide.

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Silver, mercury and lead give similar reactions.

(b) Tin with dilute nitric acid forms stannous nitrate and ammonium nitrate.

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$$

With concentrated acid, it gives meta-stannic acid and nitrogen peroxide.

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + H_2O + 4NO_2$$

(c) Zinc with very dilute acid gives ammonium nitrate.

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$$

With dilute acid, it produces N_2O while concentrated acid gives NO_2.

(d) Magnesium and manganese are the only metals that liberate hydrogen from dilute acid.

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

(e) Gold and platinum dissolve in a mixture of 1 part HNO_3 and 3 parts HCl known as *aqua regia.* The dissolution occurs as a result of the action of nascent chlorine on the metals.

$$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2Cl$$

$$Au + HNO_3 + 3HCl \longrightarrow AuCl_3 + NO + 2H_2O$$

v) It also oxidizes a number of compounds. For example,

$$SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$$

$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + S$$

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

The nitric oxide formed gives a dark brown ring (*Ring test for nitrate*).

2. *Nitrating Property*

It reacts with organic compounds and forms their nitro-derivatives. The reaction takes place in the presence of stronger acids like conc. H_2SO_4. In the presence of an acid which is stronger than nitric acid, NO_2^+ (nitronium ions) ions are produced.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

When NO_2^+ ions replace the hydrogen ions in organic compounds, nitration is said to take place. Thus

$$\underset{\text{(benzene)}}{C_6H_6} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{(nitrobenzene)}}{C_6H_5NO_2} + H_2O$$

Trinitrotoluene (TNT) is also formed by nitrating toluene in presence of conc. H_2SO_4.

$$C_6H_5CH_3 + 3HNO_3 \xrightarrow{H_2SO_4} \underset{\text{(TNT)}}{(NO_2)_3C_6H_2CH_3} + 3H_2O$$

3. *Acidic Property*

Nitric acid is a strong acid. It ionizes in aqueous solution as:

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

It decomposes metal oxides, carbonates, bicarbonates, sulphides, sulphites, bisulphites and hydroxides forming metal nitrates.

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$

$$NaHCO_3 + HNO_3 \longrightarrow NaNO_3 + H_2O + CO_2$$

$$Na_2S + 2HNO_3 \longrightarrow NaNO_3 + H_2S$$

$$H_2S + 2HNO_3 \longrightarrow 2H_2O + 2NO_2 + S$$

$$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$$

$$NaHSO_3 + HNO_3 \longrightarrow NaNO_3 + SO_2 + H_2O$$

Uses

It is used:

(i) in the manufacture of nitrates which are important chemicals of commerce. Basic calcium nitrate is used as fertilizer. Silver nitrate is used in photography and sodium nitrate is used in the manufacture of gun powder.

(ii) in the manufacture of explosives like nitroglycerine, dynamite, trinitrotoluene, picric acid etc.

(iii) in the manufacture of artificial silk, dyes, medicines, and perfumes.

(iv) in the purification of gold and silver.

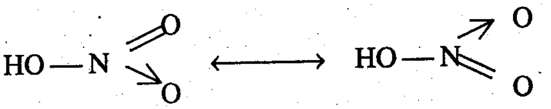
(v) as a important reagent in the laboratory.

(vi) in the manufacture of H_2SO_4.

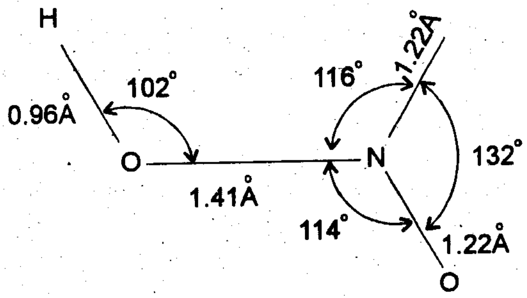
(vii) in the preparation of aqua regia.

Structure

HNO_3 is a monobasic acid and is supposed to exist in the following two resonating forms:



As indicated by electron diffraction studies, the molecule of nitric acid, in vapour state, possesses a planar structure as shown below:



7.8. ROLE OF OXYACIDS OF NITROGEN IN ENVIRONMENTAL POLLUTION

It has been stated in the earlier section that NO_X emission into the atmosphere is eventually converted into HNO_3 and HNO_2 due to a series of photochemical reactions and chemical reactions catalysed by other species present in the atmosphere. The reactions may take place in the following sequence:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_2$$

HNO_2 and HNO_3 may also undergo photochemical dissociation as follows:

$$HNO_2 + h\nu \longrightarrow NO_2 + H^{\bullet}$$

$$HNO_2 + h\nu \longrightarrow NO + HO^{\bullet}$$

$$HNO_3 + h\nu \longrightarrow NO_2 + HO^{\bullet}$$

In the stratosphere, NO_2 may react with the $HO^{\cdot}$ radicals forming HNO_3.

$$NO_2 + HO^{\bullet} \longrightarrow HNO_3$$

The acid droplets so formed are neutralized with bases e.g., particulate lime, NH_3 etc. These salts and the remaining HNO_3 droplets alongwith H_2SO_4 drops and HCl released into the atmosphere by man-made and natural emissions give rise to acidic precipitation, which is popularly known as **"Acid Rain."** (*H_2SO_4 is also an important constituent of acid rain which is formed by SO_x emission into atmosphere*).

Acid rain represents one of the major consequences of air pollution because of large SO_x and NO_x emissions from big industrial areas into the atmosphere. The longer the remain of SO_x and NO_x in the atmosphere, the greater the chances of their oxidation to H_2SO_4 and HNO_2 by the various photochemical and catalytic chemical reactions.

Effects of Acid Rain

Acid rain may cause extensive damage to materials and terrestrial ecosystems such as water, fish, vegetation, stone, steel, paint, soil and mankind as follows:

(i) Damage to building and structural materials as well as valuable ancient sculptures, carved from marbles, lime-stone, sand-stone etc., because of pitting and mechanical weakening due to attack by acidic components.

(ii) Potential effects on aquatic systems, such as acidification, decreased alkalinity and mobilization of metals like aluminium.

(iii) Foliar damage to crops and forests, leaching of nutrients from leaves and alteration of seed germination characteristics.

(iv) Corrosive damage to steel, zinc, oil-based paints and automobile coatings.

(v) Acidification of soils with the consequent effects on microbial and soil fauna and fixation of nitrogen.

(vi) Skin, hair and lungs of human beings may be affected. The heavy metals released by acid rain also may cause potential threat to human health. Acidification of drinking water reservoir and concurrent increase in heavy metals concentrations may cause injurious effects.

Remedial Measures

The phenomenon of acid rain is highly interactive problem and remedial measures to control it are very expensive. The only practical approach to counter the problem of acid rain is to reduce SO_x and NO_x emissions.

Reduction of NO_x emissions from stationary combustion sources can be achieved by modification of furnance and burner design and / or modification of operating conditions. The combustion modification techniques available now include using 2-stage combustion, precisely controlling air injecting system during combustion, recirculating flue gases, and / or by altering design of firing chambers. NO_x emissions from mobile combustion sources may be achieved by lowering the combustion temperatures in the engine and catalytic removal of NO_x from exhaust gases using devices such as a 3-way system that reduces CO, hydrocarbon and NO_x simultaneously.

7.9 OXYACIDS OF PHOSPHORUS

Typical oxyacids of phosphorus are:

1.	Hypophosphorus acid,	H_3PO_2	(+1 oxidation state of P)
2.	Orthophosphorus acid,	H_3PO_3	(+3 oxidation state of P)
3.	Pyrophosphorus acid,	$H_4P_2O_5$	(+3 oxidation state of P)
4.	Metaphosphorus acid,	$(HPO_2)_n$	(+3 oxidation state of P)
5.	Hypophosphoric acid,	$H_4P_2O_6$	(+4 oxidation state of P)
6.	Orthophosphoric acid,	H_3PO_4	(+5 oxidation state of P)
7.	Pyrophosphoric acid,	$H_4P_2O_7$	(+5 oxidation state of P)
8.	Metaphosphoric acid,	$(HPO_3)_n$	(+5 oxidation state of P)

The two series of phosphorus acids, phosphorus and phosphoric are derived from the lower, +1, +3 and higher +5 oxidation states of phosphorus respectively. All these acids have P — OH bonds where hydrogen is ionizable but the hydrogen atoms in R — H bonds (found in phosphorus acid) are not ionizable. The phosphorus acids are less well-known.

1. Hypophosphorus Acid, H_3PO_2

Preparation

(i) When white phosphorus is boiled with baryta solution, barium hypophosphite is formed which on treatment with sulphuric acid gives H_3PO_2.

$$2P_4 + 3Ba(OH)_2 + 6H_2O \longrightarrow 3Ba(H_2PO_2)_2 + 2PH_3$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow 2H_3PO_2 + BaSO_4 \downarrow$$

The solution is filtered and the filtrate is evaporated and cooled below 0°C to get crystals of H_3PO_2.

(ii) It can also be obtained by the oxidation of phosphine with iodine.

$$PH_3 + 2I_2 + 2H_2O \longrightarrow H_3PO_2 + 4HI$$

Properties

(i) It is a colourless crystalline solid having specific gravity = 1.492 and melting point 26°C. It is readily soluble in water and is monobasic acid.

(ii) When strongly heated, it is decomposed to phosphine.

$$3H_3PO_2 \longrightarrow PH_3 + 2H_3PO_3$$

(iii) The acid and its salts are powerful reducing agents. The potential equation for these reduction is

$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$$

For example:

$$4AgNO_3 + H_2O + H_3PO_2 \longrightarrow 4Ag\downarrow + 4HNO_3 + H_3PO_3$$

$$2Cl_2 + 2H_2O + H_3PO_2 \longrightarrow 4HCl + H_3PO_4$$

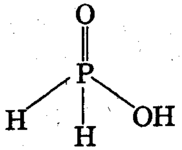
$$4CuSO_4 + 6H_2O + 3H_3PO_2 \longrightarrow 4CuH + 3H_3PO_4 + 4H_2SO_4$$

(iv) Active metals like Zn, Mg etc. dissolve in the acid and H_2 is evolved.

$$Zn + 2H_3PO_2 \longrightarrow Zn(H_2PO_2)_2 + H_2$$

Structure

H_3PO_2 is a monobasic acid, i.e., it has only one ionizable hydrogen atom. 1R spectrum shows the presence of P — H bonds. This is in accordance with the following tetrahedral structure.



2. Orthophosphorus Acid, H_3PO_3

Preparation

(i) It is prepared by the reaction of water on PCl_3 or phosphorus trioxide.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

(ii) It is also obtained by heating PCl_3 with oxalic acid.

$$PCl_3 + 3H_2C_2O_4 \longrightarrow H_3PO_3 + 3CO_2 + 3HCl$$

Properties

(i) It forms white deliquescent crystals (m.p. = 73.5°C) and is extremely soluble in water.

(ii) It is a dibasic acid and ionizes as

$$H_3PO_3 \rightleftharpoons H_2PO_3^- \qquad K_1 = 1 \times 10^{-2}$$

$$H_2PO_3^- \rightleftharpoons HPO_3^{2-} \qquad K_2 = 2 \times 10^{-7}$$

From the mode of its ionization shown above it is evident that the acid gives two types of salts viz.

primary phosphites (*e.g.*, MH_2PO_3) and *secondary phosphites* (*e.g.*, M_2HPO_3).

(iii) When heated to 200°C, it gives orthophosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{200°C} 3H_3PO_4 + PH_3$$

(iv) It is a strong reducing agent. The potential equation is:

$$H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2H$$

For example:

$$CuSO_4 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + Cu + H_2SO_4$$

$$I_2 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 3HI$$

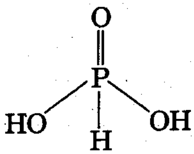
$$2HgCl_2 + H_3PO_3 + H_2O \longrightarrow Hg_2Cl_2 + 2HCl + H_3PO_4$$

$$2H_3PO_3 + SO_2 \longrightarrow 2H_3PO_4 + S$$

$$2AgNO_3 + H_3PO_3 + H_2O \longrightarrow 2Ag + 2HNO_3 + H_3PO_4$$

Structure

The diprotic nature and its reducing properties indicate the following tetrahedral structure for it.



3. Orthophosphoric Acid, H_3PO_4

Preparation

(i) Commercial orthophosphoric acid is prepared by treating bone ash (calcium phosphate) with sulphuric acid. After reaction, the precipitate of $CaSO_4$ is filtered and the solution is evaporated to get colourless crystals of H_3PO_4.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

(ii) It is prepared in the laboratory by dissolving red phosphorus in nitric acid diluted with equal volume of water.

$$P_4 + 10HNO_3 + H_2O \xrightarrow{180°C} 4H_3PO_4 + 5NO + 5NO_2$$

(iii) It may also be obtained by the hydrolysis of P_4O_{10} or PCl_5.

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

Properties

(i) Orthophosphoric acid forms hard, colourless, deliquescent, rhombic crystals. Commercial acid is 82.98% pure. It is soluble in all proportions. Its density is 1.87 and melts at 42°C.

(ii) It is tribasic acid and ionizes as follows:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \qquad K_1 = 8 \times 10^{-3}$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad K_2 = 6 \times 10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \qquad K_3 = 1 \times 10^{-12}$$

The acid therefore, forms three types of salts with alkalies.

For example,

$$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$$

$$H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + 2H_2O$$

$$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$$

(iii) When heated to 250°C, it gives pyrophosphoric acid, $H_4P_2O_7$

$$2H_3PO_4 \xrightarrow{250°C} H_4P_2O_7 + H_2O$$

(iv) It liberates hydrobromic and hydroiodic acids from bromides and iodides.

$$3NaBr + H_3PO_4 \longrightarrow Na_3PO_4 + 3HBr$$

$$3NaI + H_3PO_4 \longrightarrow Na_3PO_4 + 3HI$$

(v) It acts as a base in the presence of very strong acid, *e.g.*, $HClO_4$.

$$H_3PO_4 + HClO_4 \longrightarrow [P(OH)_4] [ClO_4]$$

(vi) It reacts with barium chloride to give a white precipitate of barium orthophosphate in neutral medium.

$$2BaCl_2 + 2H_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6HCl$$

(vii) It has no oxidizing properties below 400°C but at higher temperature it is fairly reactive towards metals and is reduced.

(viii) When phosphoric acid and phosphates are treated with ammonium molybdate and excess of conc. HNO_3, a yellow precipitate of ammonium phosphomolybdate is obtained on warming to about 60°C.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\text{(yellow ppt.)}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Uses

(i) Pure orthophosphoric acid has pharmaceutical applications and is used in the preparation of nervous tonics.

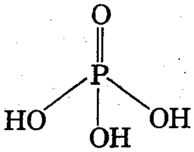
(ii) It serves as a stabilizer for H_2O_2.

(iii) It is used for the manufacture of fertilizers, dyes, enamels and porcelain cement.

(iv) It is used in the dental fillings..

Structure

It is a tribasic acid and has following tetrahedral structure.



7.10 HALIDES OF PHOSPHORUS

Phosphorus combines with halogens to give two series of halides in which it is trivalent and pentavalent. PX_3 and PX_5 are formed depending upon phosphorus or halogen being in excess. The existence of phosphorus pentaiodide PI_5, is, however, doubtful. Two additional halides, P_2Cl_4 and P_2I_4 are known which are presumably derived from P_2H_4. Stable mixed halides are also known in trivalent as well as in pentavalent states. All halides undergo hydrolysis forming halogen acids and oxoacids of phosphorus. The fluorides are less readily hydrolysed.

Important trihalides: PF_3, PF_2Cl, $PFCl_2$, PCl_3, PF_2Br, $PFBr_2$, PBr_3, PI_3.

Important pentahalides: PF_5, PBr_5, PCl_5, PF_3Cl_2, PF_2Br_3.

Here we shall discuss only PCl_3 and PCl_5.

1. Phosphorus Trichloride, PCl_3

Preparation

It is the most important trihalide. It is obtained by passing chlorine over white / red phosphorus. The phosphorus burns with a pale green flame and PCl_3 distills and is condensed as a colourless liquid. Since it is attacked by air and water, it is necessary to displace the air from the apparatus with a stream of CO_2.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

Properties

(i) PCl_3 is a colourless liquid boiling at 74°C. It can be frozen to a solid, m.p. −111.8°C.

(ii) It fumes strongly in air and is vigorously hydrolysed by water forming phosphorus acid and hydrochloric acid.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

(iii) It reacts with organic compounds containing a hydroxyl group.

$$C_2H_5OH + PCl_3 \longrightarrow H_3PO_3 + 3C_2H_5Cl$$

(iv) With excess of chlorine, it gives PCl_5.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

(v) It reacts with SO_3 forming phosphoryl chloride and sulphur dioxide.

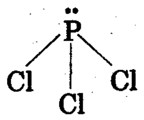
$$PCl_3 + SO_3 \longrightarrow POCl_3 + SO_2$$

(vi) It reacts with thionyl chloride forming phosphoryl chloride and PCl_5.

$$3PCl_3 + SOCl_2 \longrightarrow POCl_3 + PSCl_3 + PCl_5$$

Structure

PCl_3 molecule has a *pyramidal structure* as shown below:



2. Phosphorus Pentachloride, PCl_5

Preparation

(i) Phosphorus pentachloride is prepared by the action of dry chlorine (excess) on phosphorus trichloride.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

To push the equilibrium to the right, the temperature must be kept low and excess chloride must be present.

(ii) It can also be prepared by burning white phosphorus in excess of chlorine or by the action of sulphur monochloride on PCl_3.

$$3PCl_3 + S_2Cl_2 \longrightarrow PCl_5 + 2PSCl_3$$

Properties

(i) Phosphorus pentachloride is almost colourless crystalline solid with pungent odour in pure state.

(ii) It sublimes below 100°C and then dissociates on heating. Dissociation is completed above 300°C.

$$PCl_5 \longrightarrow PCl_3 + Cl_2$$

(iii) It reacts with water violently yielding first phosphorus oxychloride and then orthophosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 2H_2O \longrightarrow H_3PO_4 + 3HCl$$

(iv) It reacts with hydroxy compounds and replaces the —OH group by chlorine atoms. For example,

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

$$H_2SO_4 + PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

(v) Many metals like Zn, Cd, Pt, etc. are converted into chlorides when heated with PCl_5.

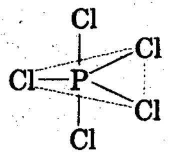
$$Zn + PCl_5 \longrightarrow ZnCl_2 + PCl_3$$

(vi) It reacts with SO_3 to give sulphuryl chloride.

$$SO_3 + PCl_5 \longrightarrow SO_2Cl_2 + POCl_3$$

Structure

Solid PCl_5 is ionic. Its crystal lattice contains positive tetrahedral PCl_4^+ ion and negative octahedral PCl_6^- ions. In the *vapor state*, it consists of discrete PCl_5 molecules which have a trigonal bipyramidal geometry. The axial P — Cl distance = 2.19 Å and equatorial P — Cl = 2.04 Å.



7.11 FERTILIZES

Definition

Chemical fertilizers are a class of substances which are added to the soil to make up and to provide the elements necessary for the growth of plants. These may include naturally occuring inorganic or organic substances or such substances prepared synthetically. These are in a way considered superior to the natural manures like decayed animal wastes and leaf and plant manures which cannot supply the various elements in correct and suitably adjusted proportions according to the needs of the plants.

Besides carbon, hydrogen and oxygen which the plants take from air and water, the other major requirements of growing plants are *nitrogen*, *phosphorus* and *potassium*. These elements are required by the plants for their normal growth, proper maintenance and high yield of produce, in bulk because they are not only the constitutents of plants enzymes, co-enzymes, harmones or activators but also make the very plant roots, stem, leaves, fruits, vegetables, grains, seeds etc. In addition to N, P and K, plants need a number of elements for their proper growth and maintenance, in very small quantities which act as activators for enzymes, e.g., Mn, Mg, Co, Zn, Cu, Fe etc. These are called *trace elements*. Their deficiency in the soil normally does not take place and are, therefore, not required to be regularly added to the soil except certain areas or region which may be deficient in one or more of these elements.

Besides the above mentioned elements, there are some elements and compounds such as gypsum which make the availability of fertilizers to the plants easier. These substances are known as *stimulants*.

Role of Fertilizers in Agriculture

Plants need the various substances such as water, nitrogen compounds, phosphorus compounds, potassium compounds etc., all in fair quantities, for their proper growth and maintenance. Iron, lime, magnesium and sulphur compounds are also required in small quantities. These substances stimulate the processes of metabolism in the plant cells, growth of plants and specially its fruits, increase the content of valuable materials (e.g. starch, proteins etc.) and increase resistance to frost, draught and various diseases. By consuming these elements, the soil becomes exhausted. Each year fertilizers (or manures), which are chemical substances serving as food materials to the soil, are added to the soil to replenish the loss suffered by it on account of growth of plants. The plants, so essential to our life, require food for nourishment. All these plant foods are supplied by nature. Plants draw their requirement from the soil by means of their roots.

Application of fertilizers to the soils increases the fertility of the soils - hence plants products have to be sustained on normal land by replenishing and can be increased above normal level by applying larger amounts of fertilizers. Fertilizers also help to maintain the pH of the soil near 7 to 8 which is optimal for plant health and growth. Today the increase of food production has become essential on account of the enormous growth of population. This is a problem of every country and the challenge of increased production is being met by larger and larger production of fertilizers.

Classification of Fertilizers

Fertilizers are classified according to the nature of the element/elements like N, P and K, they provide to the soil. This classification gives the following types of fertilizers:

(1) **Nitrogen Fertilizers.** These fertilizers mainly supply nitrogen to the plants of soil. Ammonium sulphate, calcium ammonium nitrate, urea etc. are the examples of nitrogenous fertilizers.

(2) **Phosphatic Fertilizers.** These fertilizers provide phosphorus to the soil. Superphosphate of lime, triple superphosphate and phosphate slag are the examples of phosphatic fertilizers.

(3) **Potash Fertilizers**. These fertilizers supply potassium to the plants. KCl, KNO_3, K_2SO_4 etc. are the important examples.

(4) **NP Fertilizers.** These fertilizers contain two elements namely nitrogen and phosphorus. These are obtained by mixing together nitrogenous and phosphatic fertilizers in suitable proportions. Examples of NP fertilizers are: dihydrogen ammoniated phosphate, $NH_4H_2PO_4$, calcium superphosphate nitrate, $Ca(H_2PO_4)_2.2Ca(NO_3)_2$.

(5) **Complete Fertilizers.** These fertilizers supply all the three essential elements namely nitrogen, phosphorus and potassium to the soil and are produced by mixing nitrogenous, phosphatic and potash fertilizers in suitable proportions. It is observed that these fertilizers produce much better results. These are also known as *mixed fertilizers or NPK fertilizers.*

Here we shall discuss only nitrogenous and phosphatic fertilizers.

1. Nitrogenous Fertilizers

These fertilizers mainly supply nitrogen to the plants or soils. Most of them are synthetic products and nitrogen is present in the fertilizers either as NO_3^- ion or amide or NH^+_4 ion. All the nitrogenous fertilizers are soluble in water and are readily available to plants. Typical nitrogenous fertilizers are:

1.	Ammonia	(82% N)
2.	Urea	(46% N)
3.	Ammonium nitrate	(33% N)
4.	Ammonium sulphate	(21% N)
5.	Ammonium chloride	(26% N)
6.	Ammonium sulphur nitrate	(26% N)
7.	Calcium ammonium nitrate	(26% N)
8.	Mono-ammonium phosphate	(11% N)
9.	Diammonium phosphate	(16% N)
10.	Nitrophosphate	(20%N)

1. Ammonia

Ammonia usually exists as a colourless gas but may be preserved as a colourless liquid or ice like solid. It can be obtained by either of the following methods.

(*i*) **From ammonium salts.** Ammonia is prepared in the laboratory by heating an ammonium salt with a base.

$$2NH_4^+ + OH \longrightarrow 2NH_3 + H_2O$$

$$\text{or} \quad 2NH_4^+ + CaO \longrightarrow Ca^{2+} + 2NH_3 + H_2O$$

(*ii*) **From ammonical liquor**. Coal contains about 1.5 percent of decayed nitrogen of ancient vegetables and when coal is carbonized, ammonia passes along with the coal gas in form of its compounds with H_2S, HCN, HCl, H_2SO_4 etc. and comes in the ammonical liquor. When this liquor is heated with lime in a current of steam, some of the ammonium salts are decomposed by the action of heat alone and the rest under the influence of lime to give out ammonia gas.

$$NH_4.HS \rightleftharpoons NH_3 + H_2S$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

(iii) **From air.** The nitrogen obtained from air is converted to ammonia by the *Haber's proess* or the *Cyanamide process.*

(a) **Haber's Process**

Most of the commercial ammonia is now prepared by fixing atmospheric nitrogen. When nitrogen and hydrogen are passed over an iron catalyst at 500°C under a pressure of about 200 atm; ammonia is formed.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H = 46\ kJmol^{-1}$$

In the actual process the required hydrogen is obtained from water gas and nitrogen from the fractional distillation of liquid air. The mixture of nitrogen and hydrogen (1:3 by volume) is also obtained from an appropriate mixture of water gas and producer gas by blowing steam and air over hot coke alternately. Steam is added to this mixture and the whole is passed over heated iron oxide at 500°C and 20-30 atmospheric pressure, carbon monoxide being converted to carbon dioxide.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

CO_2 is removed by water under pressure and residual CO by ammonical sodium formate (at 250 atm) or by ammonical cuprous chloride. By suitable adjustment of the process, a mixture of nitrogen and hydrogen in the required proportion of 1:3 is obtained.

The gas mixture is compressed and then passed into the catalytic chamber which consists of a steel tower containing thin walled steel tubes packed with the catalyst (Fig. 7.2). The incoming gases pass up in between these tubes so as to get heated and then enter down through them. The temperature of the catalytic tubes is maintained at 500°C by heating them electrically. The issuing gas containing about 10 per cent ammonia is cooled and liquid ammonia condenses. The unconverted nitrogen and hydrogen are returned to the inlet and passed again over the catlayst. According to Le-Chatelier's principle, the most favourable conditions for the synthesis of ammonia are:

(i) High pressure due to decrease in volume (200 atm).

(ii) Low temperature due to exothermic nature of the reaction. (500-600°C in the presence of suitable catalyst).

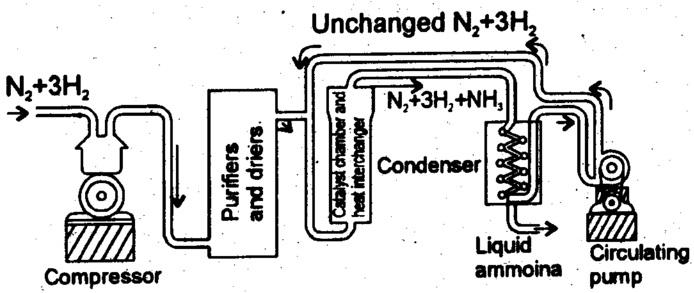


Fig. 7.3. Haber's process for the synthesis of ammonia

(b) Cyanamide Process

In this process the air is passed or calcium carbide heated to about 800^0C when nitrogen combines to form calcium cyanamide.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

Properties and Uses. Ammonia is a colourless gas with characteristic smell. It can be liquified in a bath maintained at -40^0C). The liquid boils at -33.2°C. Liquid ammonia resembles water in its physical behaviour, being highly associated because of the polar nature and strong H-bonding. Ammonia is utilized for

(i) manufacture of urea

(ii) manufacture of ammonium sulphate

(iii) manufacture of ammonium nitrate, and

(iv) oxidation to nitric acid

2. Urea

Urea (carbamide) is a high quality nitrogenous fertilizer with 46.6% nitrogen contents. It is also used as a nitrogen containing admixture to animal feed. It is synthesized from ammonia (NH_3) and carbon dioxide (CO_2). The manufacturing process consists of the following steps:

(i) Production of NH_3

(ii) Production of CO_2

(iii) Chemical reaction between NH_3 and CO_2

(iv) Distillation and processing to end product.

(i) **Production of NH_3**

(a) **Haber's Process.** N_2 is obtained from air by burning any combustible material which utilizes O_2 leaving N_2 or by liquefaction of air. H_2 gas is obtained by cracking of natural gas or by heating the natural gas with steam in the presence of Ni as catalyst.

$$(N_2 + O_2)\ \text{air} + C \longrightarrow CO_2 + N_2$$

$$CH_4 \longrightarrow C + 2H_2$$

$$CH_4 + 2H_2O \xrightarrow{Ni} CO_2 + 4H_2$$

CO_2 is obtained as a byeproduct which is used in the manufacture of urea. N_2 and H_2 gases obtained from above methods are mixed in the ratio 1:3 heated to optimal temperature 450-500^{0}C and pressure 200 atm. in the presence of Fe_2O_3 - Al_2O_3 as catalyst.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(b) **From Coal.** When coal is heated in closed retorts to red heat (1000^{0}C) in the absence of air or O_2, it produces coal gas, coal tar and coke as major fractions. Ammonium salts such as $(NH_4)_2CO_3$, $(NH_4)_2S$, $(NH_4)HS$, NH_4CN, $(NH_4)_2SO_4$ and NH_4Cl present in ammonical liquor, are obtained as byproducts, which on heating or treatment with lime produce NH_3 gas.

$$NH_4HS \xrightarrow{\Delta} NH_3 + H_2S$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

(ii) **Production of CO_2.** Carbon dioxide is obtained by igniting C obtained from natural gas.

$$C + O_2 \longrightarrow CO_2$$

(iii) **Reaction between NH_3 and CO_2.** NH_3 and CO_2 obtained are reacted with each other in reaction tower as under:

$$CO_2 + 2NH_3 \rightleftharpoons \underset{\text{ammonium carbamate}}{NH_2COONH_4}$$

On dehydration, ammonium carbamate produces liquid urea.

$$NH_2COONH_4 \xrightarrow{\Delta} \underset{\text{urea}}{NH_2CONH_2} + H_2O$$

The conversion ratio increases with temperature.

(iv) **Processing to end product.** According to *Solvay Process* 1 part compressed CO_2 is reacted with 2 parts liquid NH_3 at 180^{0}C and 200 atm pressure. The reaction between NH_3 and CO_2 results in a liquid mass known as ammonium carbamate. Dehydration of the carbamate takes place in tower made of alloy steel. This results in the formation of liquid urea. The conversion ratio increases with temperature. Since urea formed is in liquid state, hence high pressure is

needed. The urea solution is concentrated in an evaporator and the urea is produced in the form of crystals or it is granulated in prilling tower, where concentrated solution is allowed to fall from the top of a high tower while a hot blast of air is blown in a counter current way. This evaporates excess water and urea granules also called "prills" about 1/16 to 1/8 inches in diameter fall at the bottom where they are packed.

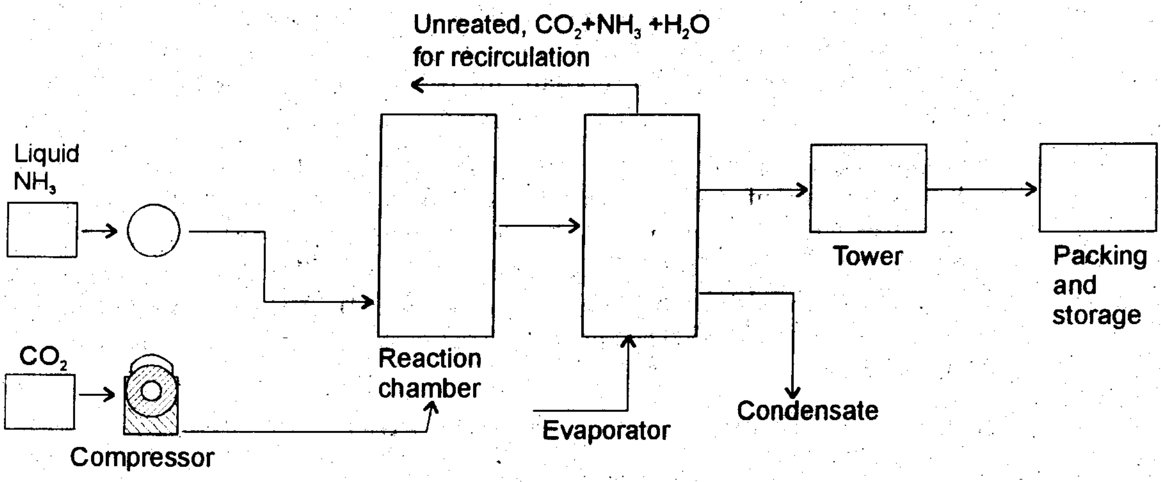


Fig. 7.4 Flow sheet diagram for urea manufacture

Uses of Urea

Urea has the highest nitrogen content equal to 46.6%. This percentage of nitrogen is much higher than any other fertilizer. It does not change the pH of the soil and can be used to all types of soils and crops, since after its assimilation by plants through the interaction of nitrifying bacteria, it leaves behind only CO_2 in the soil.

$$O=C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + H_2O \longrightarrow CO_2 + 2NH_3$$

Ammonia is then converted to nitrates by oxidation.

3. Ammonium Sulphate

(*i*) Ammonium sulphate, $(NH_4)_2SO_4$ is manufactured by passing ammonia gas into 60 percent sulphuric acid solution.

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

The mixture of ammonia and steam is bubbled through a lead lined tank containing 60% H_2SO_4. From this reaction, crystals of ammonium sulphate are obtained.

(ii) It may be made on large scale by passing NH_3 into a suspension of gypsum powder in water and then passing CO_2 through the liquid. CO_2 is obtained by heating $CaCO_3$.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$2NH_3 + H_2O + CO_2 + CaSO_4 \longrightarrow \underset{\text{(soluble)}}{(NH_4)_2SO_4} + \underset{\text{(ppt)}}{CaCO_3}$$

The precipitate of $CaCO_3$ is filtered off and the filtrate containing $(NH_4)_2SO_4$ is concentrated by evaporation under vacuum and cooled when crystals of $(NH_4)_2SO_4$ are obtained. These crystals are packed in bags and sold in the market.

(iii) It can also be obtained from ammonical liquor which is obtained as by-product in the manufacture of coke. Besides organic compounds, this liquor contains free NH_3 and ammonium salts such as $(NH_4)_2CO_3$, $(NH_4)_2S$, NH_4CN, $(NH_4)_2SO_4$, NH_4HS and NH_4Cl. Volatile salts are decomposed by boiling alone, while fixed salts are decomposed by lime water, $Ca(OH)_2$. The total ammonia in combination is about 17 g/l. The liquor is heated in stills, first by steam and then with Ca $(OH)_2$.

$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O$$

$$NH_4HS \longrightarrow NH_3 + H_2S$$

$$(NH_4)_2SO_4 + Ca\,(OH)_2 \longrightarrow 2NH_3 + CaSO_4 + 2H_2O$$

$$2NH_4Cl + Ca\,(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

The mixture of ammonia and steam so produced is passed through a lead-lined tank containing 60% H_2SO_4, when crystals of ammonium sulphate separate on cooling.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Properties and Uses

Ammonium sulphate forms large colorless transparent rhombic crystals of density 1.77 and highly soluble. Besides being a useful fertilizer it is used as a reagent in the laboratory, in the preparation of the other ammonium salts and in the preparation of alums. It contains 24-25% NH_3 which is converted to nitrates by nitrifying bacteria in the soil. It is less hygroscopic than urea and NH_4NO_3 and, therefore, has better storage properties. It can supply nitrogen to the soil and is particularly useful for potato and rice crops.

4. Ammonium Nitrate

Ammonium nitrate, NH_4NO_3 is an important nitrogenous fertilizer containing 33% nitrogen. It is manufactured by the neutralization reaction between NH_3 and HNO_3. The manufacturing process consists of the following steps:

(i) Production of NH_3

(ii) Production of HNO_3

(iii) Reaction between NH_3 and HNO_3

(i) **Production of NH_3.** N_2 (obtained from liquefaction of air) and H_2 (obtained by the electrolysis of water) are mixed together in the ratio of 1:3 and are converted into NH_3 by Haber's process in the presence of Fe_2O_3-Al_2O_3 as catalyst.

$$N_2 + 3H_2 \underset{200\text{ atm.}}{\overset{500°C}{\rightleftharpoons}} 2NH_3$$

(ii) **Production of HNO_3.** A part of NH_3 produced as above is used in the manufacture of HNO_3 by the Ostwald's process. In this process NH_3 and air are mixed together in the ratio of 1:10 by volume. The mixture is introduced into a converter having a cage of five platinum gauge (80 mesh) which is kept electrically heated between 800-900^{0}C. By this treatment NO is produced.

$$4NH_3 + 5O_2 \underset{\text{Pt gauge}}{\overset{800\text{-}900^0C}{\rightleftharpoons}} 4NO + 6\,H_2O$$

NO is cooled and mixed with air so that it is oxidized to nitrogen peroxide, NO_2. NO_2 is dissolved in water to get the solution of HNO_3.

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

NO produced in the above process is reoxidized to NO_2 which can be used to prepare HNO_3 by dissolving it into H_2O as shown above.

(iii) **Reaction between NH_3 and HNO_3.** Solution of HNO_3 obtained as above is concentrated and heated to about 75^{0}C and is then allowed to fall in the form of a fine spray from the top of a tower called neutralizer while NH_3 gas pre-heated to about 70^{0}C is introduced from the bottom of the neutralizer. This operation results in the neutralization of HNO_3 by NH_3 and formation of NH_4NO_3.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

NH_4NO_3 is obtained in the form of a liquor at the bottom of the neutralizer. This liquor contains about 84% NH_4NO_3. This liquor is taken to vacuum concentrator where this gets concentrated upto 94-96%. The solution of NH_4NO_3 is stirred with finely powdered lime stone ($CaCO_3$) in a granulator to make it a granulated product. Lime stone is added as a filler. Its function is to render NH_4NO_3 safe to handle, since it is an explosive substance.

Properties and Uses

NH_4NO_3 is an important nitrogenous fertilizer and contains about 33% nitrogen. It is simple and cheap in its manufacture. It is directly assimilated by plants and does not undergo any changes in soils. It is highly soluble in water and as such finds its way into the soil very easily.

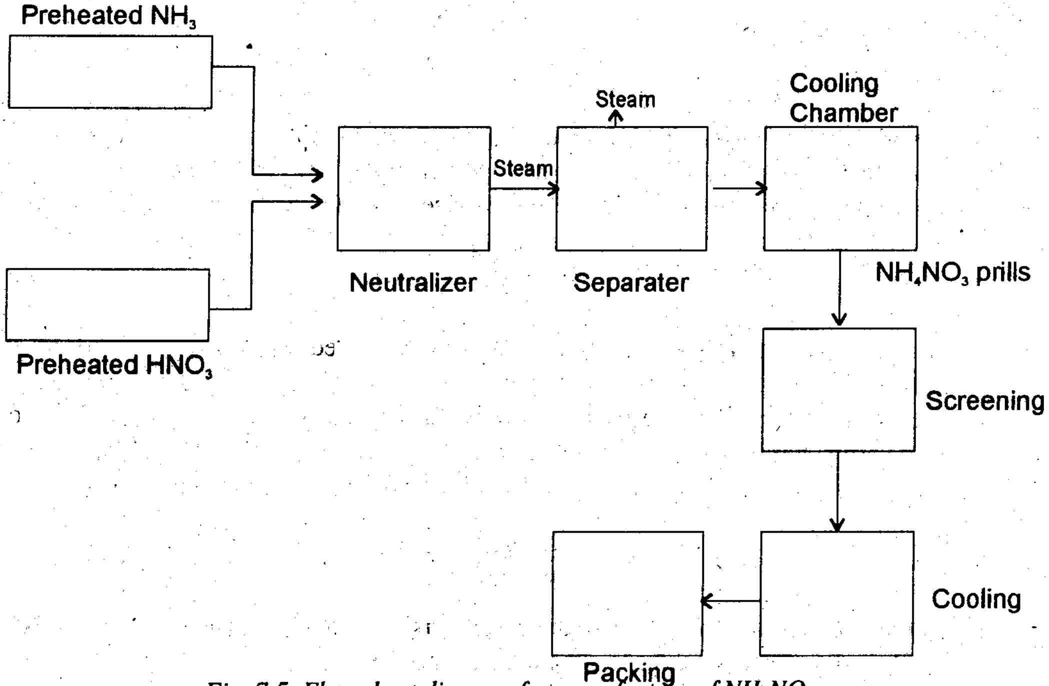


Fig. 7.5 Flow sheet diagram for manufacture of NH_4NO_3

2. Phosphatic Fertilizers

Phosphatic fertilizers provide phosphorus to the soil and plants. They come next to nitrogenous fertilizers keeping the deficiency status of Pakistani soils and requirement of principle crops. The two fertilizers therefore should be used in a mixture or in the form of compounds containing both components. Phosphorus is a constituent element of phosphatic enzymes which are responsible for energy metabolism.

It is generally considered that plants absorb most of the phosphorus in the primary orthophosphate ion $H_2PO_4^-$. Small amounts of secondary ortho-phosphate ion HPO_4^{-2} are also absorbed. Lower pH values favour the absorption of $H_2PO_4^-$ form. Phosphorus is associated with early maturing of crops, especially the shortage is accompanied by marked reduction in plant growth. It is considered essential to seed and fruit formation. Typical phosphatic fertilizers are:

1. Calcium superphosphate (16 - 20% P_2O_5)
2. Triple superphosphate (42-46% P_2O_5)
3. Phosphatic slag (14 - 22% P_2O_5 and 40% lime)

1. Calcium Superphosphate

Superphosphate is the soluble phosphate of calcium. It is a mixture of calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$ and gypsum, $CaSO_4.2H_2O$. It is manufactured by treating calcium phosphate or phosphate rock or bone ash with calculated quantity of commercial H_2SO_4. The manufacturing process consists of the following steps:

(i) Preparation of phosphate rock

(ii) Preparation of H_2SO_4

(iii) Mixing of H_2SO_4 with phosphate rock (processing)

(i) **Preparation of Phosphate rock**. Phosphate rock mainly consists of tricalcium phosphate, $Ca_3(PO_4)_2$ with varying amounts of impurities, chief of which include fluorine compounds and $CaCO_3$. Phosphate rock with more fluorine is called fluorapetite, $3Ca_3(PO_4)_2.CaF_2$. The mineral is crushed or powdered before its treatment with acid.

(ii) **Preparation of H_2SO_4**. 70% strong H_2SO_4 is needed. This can be manufactured from sulphur which is now abundantly available in Pakistan from desulphurization plants used in natural gas and petroleum industry.

(iii) **Processing**. The manufacturing process for superphosphate includes a chemical reaction between powdered phosphate rock and 70% H_2SO_4. The phosphate rock is well powdered and is placed in a cost iron mixer. Now a calculated quantity of chamber H_2SO_4 is added to it. The whole mass is stirred by means of paddles for 2 to 5 minutes and then dumped mechanically into one of the brick lined pits or dens D_1 or D_2 through the valves V_1 or V_2. Here the mixture is left for about 24 hours. The reaction which actually started in the mixture continues in the pot or den and the temperature gradually rises to 100-110°C because of the exothermic nature of the reaction.

$$\underset{\text{(insoluble)}}{Ca_3(PO_4)_2} + 2H_2SO_4 + 5H_2O \longrightarrow \underset{\text{(superphosphate)}}{Ca(H_2PO_4)_2H_2O + 2(CaSO_4.2H_2O)} + \text{Heat}$$

Since the phosphate rock invariably contains $CaCO_3$ and CaF_2 as impurities, they react with H_2SO_4 to evolve CO_2 and HF.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

Free HF reacts with silica (SiO_2) present as impurity in the phosphate rock to produce SiF_4 which at once gets decomposed in presence of H_2O, forming hydrofluosilic acid, H_2SiF_6.

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

$$3SiF_4 + 2H_2O \longrightarrow SiO_2 + 2H_2SiF_6$$

The evolution of these gases makes the whole mass of superphosphate porous due to their escape through the solid mass. The resulting porous mass is easier to be powdered subsequently, otherwise it is very difficult to grind and powder hard non-porous mass. However, these gases have important industrial and commercial uses. CO_2 is used in beverages and HF in glass making and cutting. This method is known as *Den's process.*

There is another continuous process known as ***Broad-feld process.*** In this process well grinded phosphate rock is mixed with the acid and is continuously and simultaneously introduced into cost iron cylinder with inside revolving blades. Then the well-mixed material is delivered mechanically into a mechanical den, then reaction time is 1.5 hours. The product has a granulated structure and is good for plant use.

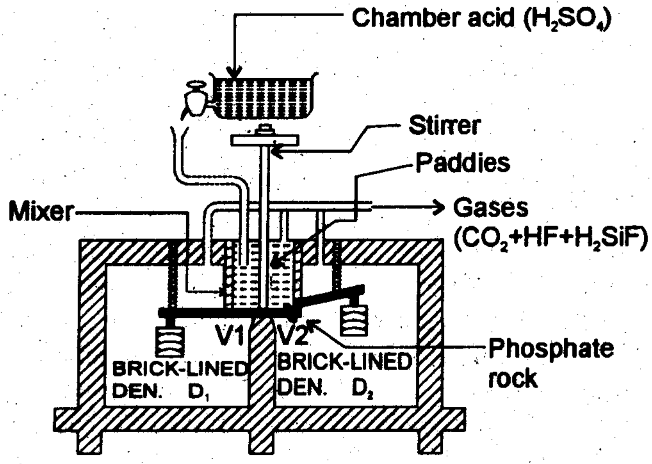


Fig. 7.6 Plant used for superphosphate

Properties and Uses

It contains about 16-20% of P_2O_5 depending on the purity of phosphate rock used in its manufacture. It active ingredient is calcium dihydrogen phosphate. Normal phosphate, $Ca_3(PO_4)_2$ being insoluble, cannot be assimilated by plants, while superphosphate, $Ca(H_2PO_4)_2.H_2O$ dissolves in soil moisture and is, thereby easily assimilated by plants. Thus its use as fertilizer is preferred over normal phosphate.

2. Triple Superphosphate

It is called triple superphosphate because it furnishes three times as much available phosphorus to the plant as compared to superphosphate per mole of phosphate rock, i.e., 46-48% P_2O_5. Normal superphosphate contains $CaSO_4$ in a quite high percentage along with active ingredient, $Ca(H_2PO_4)_2$, which decreases the percentage of phosphorus in the mixture. Triple superphosphte is prepared by reacting phosphatic rock with phosphoric acid in place of sulphuric acid, thus avoiding the formation of $CaSO_4$ and achieving 3 times the amount of available phosphorus.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow \underset{\text{triple superphosphate}}{3\,Ca(H_2PO_4)_2}$$

Granular triple superphosphate is prepared by mixing pulverized rock phosphate with phosphoric acid in a two stage reactor. The resultant slurry is sprayed into the granulator. The granules from the granulator are dried and screened. The final product is conveyed to bulk storage where the material is cured for 4-6 weeks during which a further reaction between phosphoric acid and rock phosphate takes place which increases the available P_2O_5 as plant food. During ageing, some amount of water evaporates. After the ageing period, the triple phosphate is dried by hot flue gases. The dried triple phosphate is screened by vibrating screens and then is made ready for sale.

Fertilizer Industry in Pakistan

There are 10 fertilizer units operating in the country (Punjab 6, Sindh 2, and NWFP 2) with an installed capacity of 45516 thousand tonnes. Out of these 10 units, four units having capacity of 2621 thousand tonnes are in the private sector and six units having 1930 thousand tonnes, capacity are in public sector. The overall production of fertilizers have declined to 3019478 MT during July-March 1997-98 as compared to 3089191 MT during the same period last year, depicting an overall decline of 2.26 percent over last year. The production of fertilizers like urea, nitrophosphate and ammonium sulphate increased by 1.09 percent, 13.51 percent and 0.36 percent respectively during July-March 1996-97 while the production of superphosphate and ammonium nitrate declined by 99.86 percent and 14.60 percent during the same period.

The overall domestic production during the year 1997-98 was about 3894 thousand product tonnes compared to 4017 thousand tonnes in 1996-97 showing a decrease of 3.1 percent. Domestic production met only 65.2 percent of the country's product requirements during 1997-98. The gap between fertilizer demand and domestic production is filled through imports. Fertilizer imports are, therefore, a regular activity of the fertilizer sector, which entains a burden on the country's foreign exchange. A total quantity of 1227 thousand tonnes of mainly six products were supplied through imports which represented a decrease of 22.2 percent, as compared to 1996-97.

Questions

Q.1 Justify the inclusion of N, P, As, Sb and Bi in the same group of the periodic table.

Q.2 Discuss the gradation in properties of nitrogen family elements in respect of oxidation states, stability and basic nature of hydrides, hydrolysis of chlorides and inert pair effect.

Q.3 (a) Discuss the general characteristics of group VA elements (nitrogen family) of the periodic table.

(b) How does nitrogen differ from the other members of this group?

Q.4 What do you mean by fixation of nitrogen. Discuss the various methods for the fixation of nitrogen.

Q.5 (a) Name the various oxides of nitrogen. Describe the preparation and properties of NO_2 and N_2O_5.

(b) Discuss the structure of various oxides of nitrogen.

(c) Explain why NO_2 readily forms the dimer, N_2O_4.

Q.6 (a) Discuss the role of oxides of nitrogen in environmental pollution. How can the production of these oxides are reduced?

(b) Write short note on photochemical smog describing various reactions involved.

Q.7 (a) Write down the names of oxyacids of nitrogen with formula; also describe the oxidation state of nitrogen in these compounds.

(b) Briefly discuss the role of nitric acid in environmental pollution.

Q.8 (a) How nitrogen acid is prepared in the laboratory?

(b) Complete and balance the following equations.

(i) $HNO_2 + H_2S \longrightarrow$

(ii) $HNO_2 + NH_3 \longrightarrow$

(iii) $HNO_2 + Br_2 + H_2O \longrightarrow$

(iv) $HNO_2 + NaOH \longrightarrow$

(v) $HNO_2 + HI \longrightarrow$

Q.9 (a) Discuss the various methods used for the manufacture of nitric acid.

(b) Discuss some reactions in which HNO_3 acts as oxidizing agents.

Q.10 (a) Discuss the uses of HNO_3.

(b) Complete and balance the following equations:

(*i*) $Zn + HNO_3 \longrightarrow$

(*ii*) $Mg + HNO_3 \longrightarrow$

(*iii*) $H_2S + HNO_3 \longrightarrow$

(*iv*) $Cu + HNO_3 \longrightarrow$

(*v*) $SO_2 + HNO_3 \longrightarrow$

(*vi*) $P + HNO_3 \longrightarrow$

(*vii*) $C + HNO_3 \longrightarrow$

(*viii*) $S + HNO_3 \longrightarrow$

(*ix*) $KOH + HNO_3 \longrightarrow$

(*x*) $CuO + HNO_3 \longrightarrow$

Q.11 What is acid rain? How is it produced? Discuss its effects on the environment.

Q.12 (a) Write down the names of various oxyacids of phosphorus. Also determine the oxidation state of phosphorous in these compounds.

(b) How phosphorous acid is prepared in the laboratory. Briefly discuss its structure and properties.

Q.13 (a) Write down the various methods for the preparation of phosphoric acid.

(b) Complete and balance the following equations:

(*i*) $H_3PO_4 \xrightarrow{250^\circ C}$

(*ii*) $NaBr + H_3PO_4 \longrightarrow$

(*iii*) $HClO_4 + H_3PO_4 \longrightarrow$

(*iv*) $NaOH + H_3PO_4 \longrightarrow$

(*v*) $PCl_5 + H_2O \longrightarrow$

Q.14 Discuss preparation, properties and structure of PCl_5.

Q.15 What are fertilizers? Why are they needed? Discuss the role of fertilizers in Agriculture.

Q.16 (a) Briefly discuss the classification of fertilizers.

(b) How are the urea and ammonium nitrate manufactured in Pakistan?

(c) What are the prospects of fertilzer industry in Pakistan.

Q.17 (a) How is ammonia prepared by different methods?

(b) Discuss some uses of ammonia.

Q.18 What are phosphatic fertilizers? Discuss in detail the manufacture of calcium superphosphate and triple superphosphate.

Q.19 Justily/comment on the following statements.

(a) Nitrogen is a gas while phosphorus is a solid at room temperature.

(b) Nitrogen molecule is diatomic (N_2) while phosphorus molecule is tetravalent (P_4).

(c) The basic character decreases on proceeding from NH_3 to BiH_3.

(d) PCl_5 exists while NCl_5 does not exist.

(e) N-atom shows a maximum coordination number of 4 but phosphorus shows a coordination number of 6.

(f) Fertilizers are added to soil.

(g) NO_2 causes environmental pollution.

(i) HNO_3 causes environmental pollution.

(j) Nitrogen is essential for plant growth.

(k) HNO_3 is stronger acid than HNO_2.

(l) NH_3 is basic in nature.

(m) Orthophosphoric acid (H_3PO_4) is tribasic while phosphorous acid (H_3PO_3) is dibasic.

Chapter Eight

OXYGEN AND SULPHUR

8.1 INTRODUCTION

Group VIA (16) of the periodic table consists of oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Oxygen and sulphur are the typical elements of this group. The elements O, S, Se and Te are often collectively called chalcogens i.e., the ore forming elements. All the elements have six electrons in their outer most shells with the two electrons in the S-orbital and four electrons in the P-orbital as shown in Table 8.1

Table 8.1. Electronic Configuration of Group VIA (16) Elements

Element	At. No.	Electronic Configuration
O	8	$1s^2, 2s^2\, 2p^4$
S	16	$1s^2, 2s^2\, 2p^6, 3s^2\, 3p^4$
Se	34	$1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^{10}, 4s^2\, 4p^4$
Te	52	$1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^{10}, 4s^2\, 4p^6\, 4d^{10}, 5s^2\, 5p^4$
Po	84	$1s^2, 2s^2\, 2p^6, 3s^2\, 3p^6\, 3d^{10}, 4s^2\, 4p^6\, 4d^{10}\, 4f^{14}, 5s^2\, 5p^6\, 5d^{10}, 6s^2\, 6p^4$

Table 8.2. Some Physical Properties of Group VIA(16) Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic weight	16.00	32.06	78.96	127.60	210
Density of solid (g/cm^3)	1.27 (solid)	2.06(rhmb)	4.82(grey)	6.25	9.196
Ionization potential I (kJmol^{-1})	14.10	10.70	1005	930	870
Melting point (°C)	-219	112	217	450	254
Boiling point (°C)	-183	444	685	990	962
Atomic radius (nm)	0.066	0.104	0.117	0.137	0.14
Electronegativity	3.5	2.5	2.4	2.1	1.9

It is evident from the above configurations that all elements have ns^2p^4 configuration in the outer most shell. The penultimate shell in the oxygen atom contains s^2 group (saturated), in sulphur s^2p^6 (saturated), in selenium $s^2p^6d^{10}$ whereas in tellurium and polonium $s^2p^6d^{10}$ (unsaturated). This shows that oxygen differs from sulphur and these two elements from remaining elements of this group.

Some of the important physical properties of group VIA (16) elements are summarized in Table 8.2

8.2 GRADATION OF CHARACTERISTIC PROPERTIES WITHIN THE GROUP

The gradation in the physical and chemical properties of the elements with the rise of atomic number is as follows:

(i) **Physical state:** Oxygen is a colourless gas, sulphur is a yellow solid existing in a number of allotropic forms, selenium also exists in two allotropic forms and tellurium and polonium are solid.

(ii) **Density, melting and boiling points:** With the rise of atomic number, the density, melting point and the boiling point all show a steady increase. Polonium shows exception to its melting and boiling points due to diminished availability of "*s*" electron pair.

(iii) **Ionization energy:** With the increase in the size of the atoms with atomic numbers, ionization energies show a regular decrease in this group.

(iv) **Metallic and non-metallic character:** Due to the decrease of ionization energy from O to Po, the metallic character of these elements increases down the group. Thus, oxygen and sulphur are non-metals, selenium and tellurium show some metallic properties and polonium is typical metal.

(v) **Electronegativity:** As expected from the position of these elements in the periodic table, the electronegativity values of these elements are high, and they decrease with increasing atomic number from oxygen to polonium in the group.

(vi) **Polymorphism:** All the elements are polymorphic, i.e., they show allotropy, e.g., oxygen exists in two allotropic forms, viz. O_2 and O_3. Sulphur has several allotropic forms all of which are non-metals, e.g., rhombic, monoclinic and plastic sulphur. Selenium, tellurium and polonium also exist in two forms.

(vii) **Catenation:** Oxygen and sulphur show the property of catenation i.e., they have a tendency to form chains of identical atoms. Chains of sulphur atoms are present in persulphides, polythionic acids and in S8 molecules. Oxygen gives polyoxides. Examples are: H_2O_2 (H-O-O-H), H_2S_2 (H-S-S-H) etc.

(viii) **Oxidation states:** Positive oxidation states are shown by these elements when they are bound to more electronegative elements. With oxygen, the positive oxidation states are found only in compounds containing fluorine which is more electronegative than oxygen; but such states become increasingly common as one proceed from S to Te. The most common oxidation states are +4 and +6. The higher oxidation states become less stable on descending the group.

(ix) **Formation of hydrides:** All the elements of this group form the hydrides of H_2M type, (where M=O, S, Se, Te and Po). H_2o H_2S, H_2Se, H_2Te and H_2Po. H_2O is a liquid, neutral and colourless while all others are gases which are feebly acidic and possess an unpleasant smell. The stability of these compounds decreases with increasing atomic number.

(x) **Formation of Oxides:** All the elements of this group form oxides. The lower oxides of sulphur, selenium and tellurium (So_2, SeO_2 and TeO_2) are acidic in nature. The oxides of the elements in the same oxidation state become less acidic as we go down the group. The higher oxide of tellurium, TeO_3 is more easily reduced than SO_3.

(xi) **Formation of halides:** All the elements of this group form halides of the type MF_6, MX_4 and MX_2 (where M represents element of the group and X represents Halogens). Except oxygen, all other elements for hexaflourides, viz. SF_6, SeF_6 and TeF_6. All these are colourless gases. They are highly volatile and hence have high degree of covlency. Other examples of halides are: SF_4, SeF_4 and TeF_4, OF_2, SCl_2, $SeCl_2$, PoCl, etc.

(xii) **Formation of oxy-acids:** Sulphur, selenium and tellurium form a number of oxy-acids, sulphuric, selenic and telluric show a rapid falling off in strength and also a decrease of stability as atomic number rises.

H_2SO_4	H_2SeO_4	H_2TeO_4
Sulphur acid	Selenic acid	Telluric acid

8.3 COMPARISON OF OXYGEN WITH SULPHUR

Both oxygen and sulphur are the typical elements of group VIA (16) of the periodic table and show many similar and dissimilar properties.

Similarities

(i) Both are non-metals.

(ii) Both have six electrons in their outer most shell

(iii) Both form similar types of compounds like

C_2H_5OH	C_2H_5SH
Ethyl alcohol	Ethyl mercaptan
$(C_2H_5)O$	$(C_2H_5)S$
Ether	Thio-ether
H_2O	H_2S
Water	Hydrogen sulphide

(iv) Both show the phenomenon of allotropy.

(v) Both of them exist in free and combined state.

(vi) They both form oxides of type RO_2, e.g., O_3 (O-O_2) and SO_2.

(vii) Both the elements combine with oxygen to form CO_2 and CS_2

(viii) Both the elements are obtained by heating their higher oxides and sulphides.

$$2BO_2 \xrightarrow{\Delta} 2BaO + O_2^-$$

$$FeS_2 \xrightarrow{\Delta} FeS + S^-$$

(ix) Both show catenation.

Dissimilarities

(i) Oxygen is a colourless and odorless gas while sulphur is a pale yellow solid with a faint odor.

(ii) Oxygen is more widely distributed in nature than sulphur.

(iii) Maximum covalency of oxygen is 2 while that of sulphur is 6.

(iv) Oxygen is stronger oxidizing agent than sulphur.

(v) Oxygen does not react with concentrated HNO_3 while sulphur is oxidized by conc. HNO_3.

(vi) Oxygen, due to non-availability of d-orbitals, does not form co-ordination compounds while sulphur gives a large number of co-ordination compounds.

(vii) Oxygen is the only element in the group which is sufficiently electronegative to form hydrogen bonds. For this reason the compounds containing H-bonds often differ considerably in their physical properties from the corresponding sulphur compounds. For example, H_2o is a neutral and stable associated liquid, whereas H_2S is a gas having acidic properties and unpleasant smell.

(viii) Molecule of oxygen is paramagnetic due to two unpaired electrons. Sulphur exists as a polymer S_8 at room temperature and therefore, has no unpaired electrons and is diamagnetic.

(ix) Oxygen forms only two and three atoms chains, (e.g., H_2O_2 and O_3) while sulphur can form molecules up to 6 atoms per chain in compounds.

8.4 OXIDES OF SULPHUR

Typical oxides of sulphur are:

1. Sulphur monoxide, SO
2. Sulphor dioxide, SO_2
3. Sulphur trioxide, SO_3
4. Sulphur resquioxide, S_2O_3
5. Sulphur tetraoxide, SO_4
6. Sulphur heptaoxide, S_2O_7.

Here we sha'l discuss the chemistry of SO_2 and SO_3 only.

1. Sulphur Dioxide, SO_2

Preparation

(i) It is obtained either (a) by burning sulphur in air or (b) by reducing concentrated sulphuric acid by a number of substances as:

$$2H_2SO_4 + Cu \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$2H_2SO_4 + C \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$2H_2SO_4 + 2Ag \longrightarrow Ag_2SO_4 + SO_2 + 2H_2O$$

$$2H_2SO_4 + S \longrightarrow 3SO_2 + 2H_2O$$

(ii) It may be obtained by the action of dilute acids on a sulphite or bisulphite.

$$Na_2SO_3 + 2HCl \longrightarrow SO_2 + 2NaCl + H_2O$$

(iii) It is also obtained by the roasting of pyrites.

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

Properties

(i) Sulphur dioxide is a colourless gas having a pungent suffocating odor. It can be condensed to a liquid (B.P = -10.0). It is readily soluble in water (1 volume of H_2O at 0^0C dissolves about 80 volumes of SO_2.

(ii) It possesses bleaching properties because it is oxidized in the presence of water liberating nascent hydrogen which unites with the coloring matter to give a colourless compound.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

(iii) It reacts with alkalies to form sulphites and hydrogen sulphites.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

(iv) It reacts with oxygen and chlorine giving sulphur trioxide and sulphuryl chloride.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$SO_2 + Cl_2 \xrightarrow{\text{Charcoal}} SO_2Cl_2$$

(v) It acts as a reducing agent and is itself oxidized to sulphuric acid. As a reducing agent, it liberates iodine from potassium iodate solution.

$$2KFO_3 + 5SO_2 + 4H_2O \longrightarrow 2KHSO_4 + 3H_2SO_4 + I_2$$

It also reduces potassium dichromate to chromium salt.

$$K_2CrO_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

It decolourizes a solution of potassium permanganate.

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(vi) In certain cases it can act as oxidizing agent and hence oxidizes H_2S to S, Fe to FeO, Mg to MgO etc.

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

$$4FeCl_2 + SO_2 + 4HCl \longrightarrow 4FeCl_3 + 2H_2O + S$$

$$6SnCl_2 + SO_2 + 8HCl \longrightarrow 5SnCl_4 + 4H_2O + SnS_2$$

(vii) With lead peroxide, it furnishes lead sulphate.

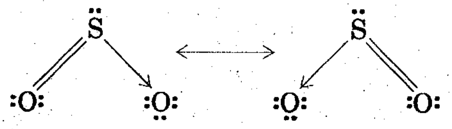
$$PbO_2 + SO_2 \longrightarrow PbSO_4$$

(viii) It also acts as a Lewis base due to the presence of lone pair of electron.

$$BF_3 + SO_2 \longrightarrow \underset{\text{(adduct)}}{BF_3SO_2}$$

Structure

The molecule of SO_2 is bent or V-shaped with OSO angle 119.5°, the bond length (S-O) is 1.43 Å. The S-O bond distance is shorter than expected for a single band (1.78 Å) suggesting that the following canonical forms are the major contributors.



2. Sulphur trioxide, SO_3

Preparation

(i) Sulphur trioxide is the anhydride of sulphuric acid and can be obtained from it by dehydration with P_2O_5.

$$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$$

(ii) It can be obtained by catalytic oxidation of SO_2 by air in the presence of heated platinized asbestos at 400°C.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

(iii) It can also be prepared by the thermal decomposition of certain metallic sulphates.

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$

$$CuSO_4 \xrightarrow{\Delta} CuO + SO_3$$

Properties

(i) Sulphur trioxide is a liquid at room temperature which strongly fumes in air. It exists in three modifications:

- –SO_3 is also silky asbestos like solid which melts at 62.2°C but sublimes without melting at ordinary temperature.

SO_3 as normally obtained melts at 16.85°C and boils at 44.52°C. The vapour density corresponds with the formula SO_3.

(ii) On heating it decomposes as

$$2SO_3 \longrightarrow 2SO_2 + O_2$$

(iii) It is a typical acidic oxide and combines with water with almost explosive violence, forming sulphuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

(iv) It is absorbed in concentrated sulphuric acid giving the pyrosulphuric cid, $H_2S_2O_7$ called *fuming sulphuric acid* or *oleum.*

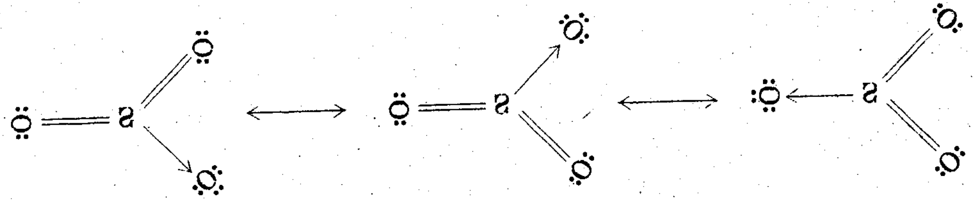
$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{(Oleum)}}{H_2S_2O_7}$$

(v) It also combines with basic oxides forming sulphates.

$$CaO + SO_3 \longrightarrow CaSO_4$$

Stucture

The molecule in the gaseous state has a planar triangular structure, S^{-O} distance being 1.43°A and OSO angle 120°. The structure may be regarded as resonance hybrid of the following three forms:



8.5 ROLE OF SULPHURIC DIOXIDE IN AIR POLLUTION

Sulphuric dioxide, present in the atmosphere, absorbs solar radiations in the range of 300-400nm and produce electronically excited states of SO_2. This undergo oxidation to SO_3 and in the presence of water vapors, this is converted to sulphuric acid. The overall reaction in the presence of sunlight may be represented as:

$$SO_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow H_2SO_4$$

Combustion of any sulphur-bearing materials also produces SO_2 accompanied by a small quantity of SO_3. This mixture is usually denoted s SOx. Nearly 67% of the global SO_2 pollution is due to volcanic activity and other natural sources, over which we have no control. The remaining 33% SO_2 emission is because of human activities such as combustion of fuels, coal fired power smelting transportation, refineries, metallurgical operations such as smelting of sulphide ores and chemical plants, e.g., manufacture of sulphuric acid. Most of the man-made pollution is concentrated in urban and industrial areas.

Almost all the sulphur present in liquid and gaseous fuels and about 80%of sulphur present in the solid fuels appears as SO_2 in the flue gases. Depending on the sulphur content of the fuel burnt and the conditions of combustion (e.g. % of excess air used), the concentration of SO_2 in flue gases varies from 0.05 to 0.4%. However, in metallurgical operations such as smelting of sulphide ores, the SO2 concentration in stack gases may be 5 to 10%.

SO_2 is oxidized to SO_3 in atmospheric air by photolytic and catalytic processes involving ozone, NOx and hydrocarbons, giving rise to the formation of *photochemical smog*. Oxidation of SO_2 can take place in presence of catalysts such as NOx, metal oxides, soot and dust. Under normal humid conditions of the atmosphere, SO_3 reacts with water vapors to produce droplets of H_2SO_4 aerosol which gives rise to the so called "*acid rain*" (already discussed in previous chapter).

$$SO_2 + O_3 \longrightarrow SO_3 + O_2$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \longrightarrow (H_2SO_4)_n$$

$$SO_2 + \tfrac{1}{2} O_2 + H_2O \xrightarrow[\text{soot etc.}]{\text{metal oxides}} H_2SO_4 \xrightarrow{\text{aerosol}} (H_2SO_4)_n$$

The sulphuric acid and sulphate aerosols can easily reach the pulmonary region of lungs, causing serious respiratory problems particularly in old people. The H_2SO_4 formed lowers pH, impairs enzymatic functions and destroys various functional molecules. It is n important constituent of acid rain and causes serious damage to building and structural materials.

Control of SO_2 emission

Control of SO_2 emissions from man-made sources is contemplated on the following lines:

1. Removing SOx from flue gases before letting them out into the atmosphere. Chemical scrubbers such as lime stone or citric acid are suggested.

$$CaCO_3 \quad CaO + CO_2$$

$$CaO + SO_2 \longrightarrow CaSO_3$$

$$SO_2 + H_2O \longrightarrow HSO_3 + H^+$$

$$HSO_3 + H_2cit^- \longrightarrow (HSO_3.H_2cit)^{2-}$$

2. Removing sulphur from the fuels used for combustion. Pyritic sulphur in coal can be removed by grinding and washing in coal washries. However, organically bound sulphur cannot be easily removed from coals. Research is in progress to synthesize special type of micro-organisms using bio-technology, which are capable of converting organically bound sulphur into soluble form.
3. Utilizing low-sulphur fuels.

8.6 OXYACIDS OF SULPHUR

The following are the min oxyacids of sulphur:

1. **Sulphurous acid series**
   - (a) Sulphurous acid, H_2SO_3
   - (b) Thiosulphurous acid, $H_2S_2O_2$
   - (c) Hyposulphurous acid, $H_2S_2O_4$
   - (d) Pyrosulphurous acid, $H_2S_2O_5$
2. **Sulphuric acid series**
   - (a) Sulphuric acid, H_2SO_4
   - (b) Thiosulphuric acid, $H_2S_2O_3$
   - (c) Pyrosulphuric acid, $H_2S_2O_7$
3. **Thionic acid series**
   - (a) Dithionic acid, $H_2S_2O_6$
   - (b) Polythionic acid, H_2SnO_6 (N2, 3, 4, 5, 6)
4. **Peroxy acid series**
   - (a) Permonosulphuric acid, H_2SO_5
   - (b) Perdisulphuric acid, $H_2S_2O_8$

1. Sulphurous acid, H_2SO_3

Preparation

This acid is known only in solution and is formed by dissolving SO_2 in water.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

A saturated solution obtained at 3^0C gives out the crystals of sulphurous acid with varying number of water molecules of crystallization but mostly $H_2SO_3.6H_2O$.

Properties

(i) It is a dibasic acid and ionizes as:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$$

(ii) On heating, it gives sulphuric acid and sulphur; hyposulphurous acid is also formed as an intermediate product.

$$3H_2SO_3 \longrightarrow H_2SO_4 + H_2S_2O_4 + H_2O$$

$$H_2S_2O_4 \longrightarrow H_2SO_4 + S$$

(iii) It is slowly oxidized by oxygen of the air to sulphuric acid.

$$2H_2SO_3 + O_2 \longrightarrow 2H_2SO_4$$

(iv) It reacts with halogens to form sulphuric acid.

$$H_2SO_3 + H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

$$H_2SO_3 + H_2O + I_2 \longrightarrow H_2SO_4 + 2HI$$

(v) It acts as an oxidizing agent towards strong reducing gents. Thus H_2S is oxidized to S and HI to I_2 etc.

$$H_2SO_3 + 2H_2S \longrightarrow 3S + 3H_2O$$

(vi) It also acts as reducing agent. Thus it reduces iodate to iodine, ferric salts to ferrous salts and decolorizes the dilute neutral solution of potassium permanganate.

$$5H_2SO_3 + 2KIO_3 \longrightarrow 2KHSO_4 + 3H_2SO_4 + H_2O + I_2$$

$$2FeCl_3 + H_2SO_3 + H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

$$5KMnO_4 + 5H_2SO_3 \longrightarrow 2KHSO_4 + 2MnSO_4 + H_2SO_4 + 3H_2O$$

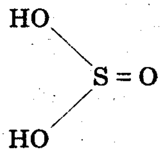
(vii) Its salts are known as *sulphites* and *bisulphites*. They are obtained by saturating alkali solution with sulphur dioxide.

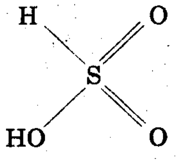
$$2NaOH + SO_2 + H_2O \longrightarrow Na_2SO_3 + 2H_2O$$

$$K_2CO_3 + 2SO_2 + H_2O \longrightarrow 2KHSO_3 + CO_2 + H_2O$$

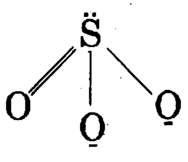
Structure

Sulphurous acid may be represented by either of the two formulae:





Now it is believed that the two forms of to acid shown above exist in equilibrium with each other. X-ray analysis of the crystals of Na_2SO_3 has show that SO_3^{2-} ion has a *pyramidal* structure with three O-atoms in the triangle.



2. Sulphuric acid, H_2SO_4

Sulphuric acid is a substance of very great commercial importance, for it finds use in the manufacture of fertilizers, acids and heavy chemicals, dyes and coal-tar products, leaquers and plastics, explosives, textiles, paints and pigments and numerous other products. It is also used in refining of oil, in leather tanning and in metallurgy. It has been said that the civilization and development of a country can be judged by the amount of sulphuric acid it consumes.

Preparation

Essentially the manufacture of sulphuric acid involves the conversion of sulphur dioxide into sulphur trioxide which is then dissolved in water to give sulphuric acid. Sulphur dioxide for the purpose is obtained from different sources such as burning sulphur, roasting of sulphide ores, burning of hydrogen sulphide etc. Conversion of sulphur dioxide to sulphuric acid is done by the following two processes:

1. The lead chamber process.
2. The contact process.

1. The Lead Chamber Process

In this process sulphuric acid is obtained by the oxidation of SO_2 by nitrogen peroxide, NO_2. SO_2 is the first oxidized by nitrogen peroxide (*also called nitrogen dioxide*) to sulphur trioxide, SO_3 which reacts with steam forming sulphuric acid. Nitrogen peroxide itself is reduced to nitric oxide, no which is subsequently oxidized back to nitrogen peroxide by atmospheric oxygen. The various reactions are represented as:

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

$$SO_3 + H_2O \text{ (steam)} \longrightarrow H_2SO_4$$

$$2NO + O_2 \text{ (air)} \longrightarrow 2NO_2$$

It is, however, observed that if the chambers are insufficiently supplied with steam, lead chamber crystals are formed which consist of nitroso-sulphuric acid, $HSO_4.NO$. It is formed as a reaction intermediate during the formation of H_2SO_4.

$$NO + NO_2 \longrightarrow N_2O_3$$

$$2SO_2 + N_2O_3 + O_2 + H_2O \longrightarrow 2HSO_4.NO$$

$$H_2O + 2HSO_4.NO \longrightarrow 2H_2SO_4 + NO + NO_2$$

The various parts of the plant along with their functions are described below.

(i) **Pyrites burners:** These are brick furnaces in which sulphur or iron pyrites in lumps is burnt, the supply of air being regulated by sliding doors below and above the pyrites.

$$S + O_2 \longrightarrow SO_2$$

$$4FeSO_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(ii) **Nitre Pots:** Here $NaNO_3$ or KNO_3 is heated with conc. H_2SO_4 to produce nitric acid vapors. These vapors mix with

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

the hot gases coming from the sulphur burners and going to glover tower and are reduced by SO_2 to give a mixture of NO and NO_2.

$$2HNO_3 + 2SO_2 \longrightarrow 2SO_3 + H_2O + (NO+NO_2)$$

(iii) **Glover tower:** The gases now enter the glover tower. The tower is of lead, lined inside with acid resisting material and packed with flint. There are two tanks at the top. One contains the dilute chamber acid and the second the nitrated acid ($HSO_4.NO$) from the base of Gay.Lassac tower. Both these acids flow down slowly over flint pieces and meet an ascending stream of hot gases. The major functions of this tower are:

(a) Cooling of the burner gases.

(b) Concentration of the chamber acid to about 80%.

(c) Conversion of some SO_2 to H_2SO_4.

(d) Recovery of NO and NO_2 from niroso-sulphuric acid.

(e) Cleaning of the burner gases.

(iv) **Lead Chambers:** After passing through the Glover tower, the gases (SO_2, O_2, NO, NO_2 and moisture) are led to a series of lead chambers which are made of lead but supported in wooden frames. Steam from a low-pressure boiler or more usually a very fine spray of water is admitted into these chambers from the top. H_2SO_4 is formed by the interaction of SO_2, oxides of nitrogen and H_2O. It is called *Chamber acid* and contains 60-70% H_2SO_4. It is pumped to the Glover tower for its further concentration.

(v) **Gay-Lassac tower:** The residual gases coming from the last lead chamber (N_2, NO, NO_2, SO_2, O_2) are led to the Gay-Lassac tower. This tower is lined with lead and is packed with coke soaked with 78% H_2SO_4 (Glover acid). This acid absorbs oxides of nitrogen in the exit gases forming nitroso-sulphuric acid, $HSO_4.NO$.

$$2H_2SO_4 + NO + NO_2 \longrightarrow 2HSO_4.NO + H_2O$$

The nitroso-sulphuric acid so produced collects at the base of Gay-Lassac tower and is pumped to the top of the Glover tower for the recovery of oxides.

(vi) **Coolers:** The coolers consist of a number of tanks made of lead. Coils of lead pipes carrying cold water are present in them. The acid from the Glover tower enters the first cooler at 130-150^{0}C and leaves the last at 30-35^{0}C.

Purification of Chamber acid

The Chief impurities present in the chamber acid are arsenic oxide, lead sulphate and oxides of nitrogen. These are removed as follows:

Lead Sulphate is removed by diluting the acid when the insoluble lead sulphate is separated.

Arsenic oxide is removed by passing H_2S through the dilute acid, when it is precipitated in the form of sulphide.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

Nitrogen oxides are expelled by distilling the dilute acid with ammonium sulphate. These oxides are reduced to elementary nitrogen which escapes.

$$(NH_4)_2SO_4 + NO + NO_2 \longrightarrow 2N_2 + H_2SO_4 + 3H_2O$$

It is not always necessary to purify the chamber acid. For most purposes it is used as such. Whenever pure acid is needed it is prepared by the *contact process* rather than by the purification of chamber acid.

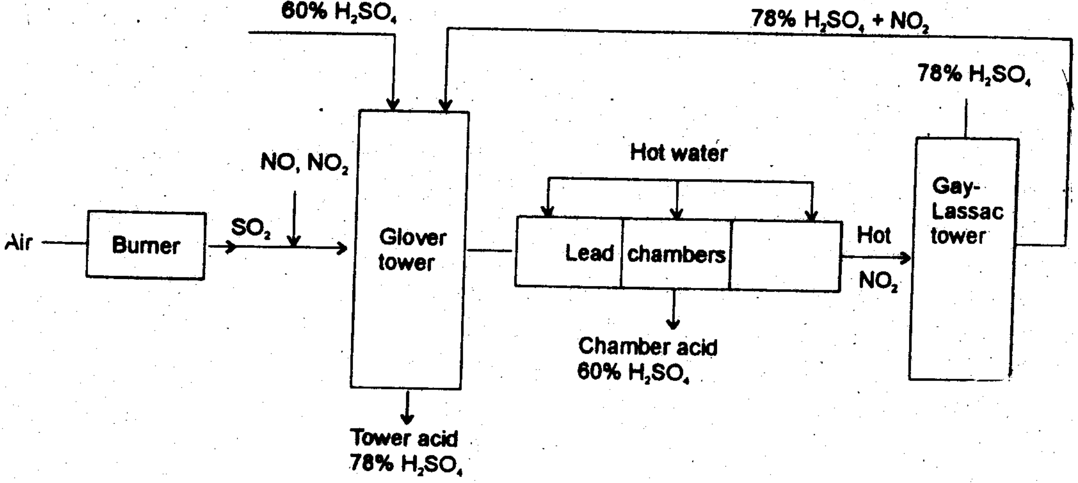


Fig. 8.1 Flow sheet diagram for Lead Chamber Process.

2. The Contact Process

Sulphur dioxide obtained by the burning of sulphur or pyrites is made to combine with oxygen under suitable conditions in order to get sulphur trioxide.

$$S + O_2 \longrightarrow SO_2$$

$$4FeSO_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{,}000 \text{ cals.}$$

The SO_3 so formed is dissolved in sulphuric acid and the *oleum* or *pyrosulphuric acid* which results is diluted with water to get sulphuric acid of required concentration.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

We have seen that the production of SO_3 is reversible and exothermic reaction. Moreover it proceeds with a decrease in volume (i.e., 3 volumes change to 2 volume). According to Le-Chatelier's principle the formation of SO_3 is favored by:

(i) **Low temperature:** This reaction is exothermic; naturally the formation of SO_3 does not require high temperature. At low temperature no reaction takes place between SO_2 and O_2. Thus a temperature between 400-500^{0}C is maintained and the reaction occurs with adequate speed.

(ii) **High pressure:** Since the reaction proceeds in the forward direction with decrease in volume, a high pressure will favour the formation of SO_3. Therefore, the gases are given a pressure of 1.5 to 2 atmospheres.

(iii) **Excess of oxygen:** A slight excess of air in the reaction mixture helps to carry the reaction in the direction of formation of SO_3. Best results are obtained when O_2 and SO_2 are present in molecular proportion of 3:2.

(iv) **Use of Catalyst:** Even at 400-500^{0}C the rate of reaction is very slow. Therefore, to increase the reaction velocity, a suitable catalyst is used. The commonly used catalysts are:

(a) Fe_2O_3 with a little CuO

(b) V_2O_5

(c) Platinized asbestos, platinized magnesium sulphate.

The best results are obtained when platinum is used. But it is very costly and rapidly loses its activity due to poisoning by A_2O_3, sulphuric acid fog, dust etc. Now-a-days most of the sulphuric acid plants use V_2O_5 as a catalyst in place of platinum because it is cheaper and is not easily poisoned.

The various parts of the plant along with their functions are described below.

(i) **Sulphur burners:** In these sulphur or pyrites (FeS_2) is burnt to get sulphur dioxide. Traces of SO_3 are also produced which give

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + H_2O \longrightarrow 2Fe_2O_3 + 8SO_2$$

Sulphuric acid fog with water vapors present in air.

(ii) **Purification unit:** The gases from the sulphur burners containing about 8% SO_2, 1% O2 and the rest N_2 are not pure. They contain impurities of A_2O_3, sulphur dust and H_2SO_4 fog which act as poisons on the catalyst surface. These impurities can, however, be removed by suitable treatment.

The gases are first passed through *dust remover* where the heavy dust particles settle down under the influence of gravity or are made to settle down with the help of a Cottrell electrical precipitator. The gases are then led through a *cooling pipe* into the *scrubber* where these are washed by a down-coming spray of water. This treatment serves to remove "acid fog". The gases are now dried by passing through the *drying tower* containing coke moistened with conc. H_2SO_4 and then freed from arsenic in the *arsenic purifier* which contains precipitated $Fe(OH)_3$ placed on horizontal shelves. In order to be sure that the gases are free from dust and As_2O_3 particles, the gases are now led in the *testing box*. Here a strong beam of light is thrown against the gases and if any particles in suspension or in colloidal state are present, they are illuminated due to *Tyndal Effect.*

(iii) **Preheater and contact converter:** The purified gases are then led into the preheater where the gases are preheated to 400-450^{0}C (optimum temperature) by the hot gases (mainly SO_2 and N_2) from the converter which are themselves thereby cooled. The hot gases now enter into an iron cylinder which is called a *contact converter* or *tower* and is fitted inside with vertical iron tubes which are packed with suitable catalyst. The incoming gases circulate round the hot tubes and then pass down them when SO_2 is oxidized to SO_3. Since the reaction is

exothermic, the heat produced raises the temperature to about 580^{0}C. The rate of flow of gases is so adjusted that the temperature is kept 400-450^{0}C in the converter.

(iv) **Absorption tower:** The SO_3 formed in the converter is passed up an absorption tower where it meets a descending stream of conc. sulphuric acid. The acid absorbs the SO_3 to form *fuming sulphuric acid* or *oleum* which is then diluted with the calculated quantity of water to get sulphuric acid of required concentration.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7 \text{ (oleum)}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Water cannot be used for absorbing SO_3 because in doing so a large amount of heat is evolved resulting in the formation of a dense log of minute particles of H_2SO_4 which does not easily condense down.

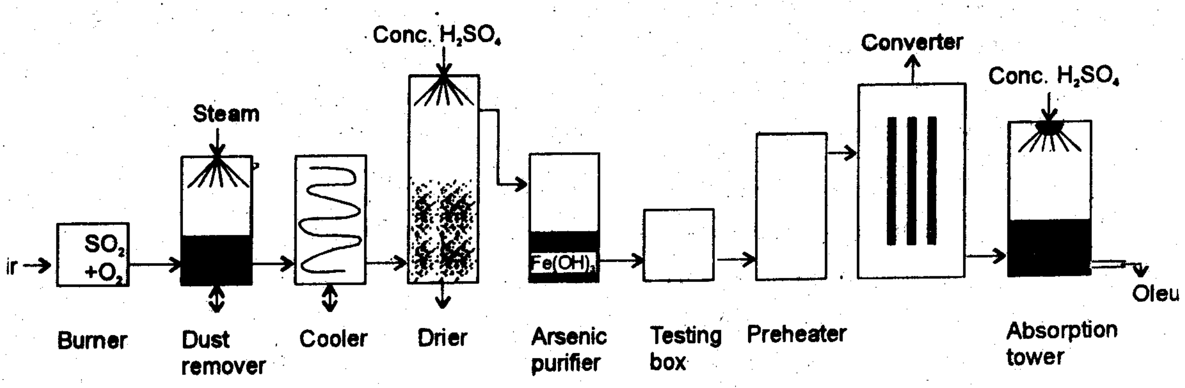


Fig. 8.2 Flow sheet diagram for contact process.

Comparison of the Contact and Lead Chamber Processes.

(i) Sulphuric acid obtained by the Contact process is of higher purity than that obtained by lead chamber process.

(ii) Sulphuric acid obtained by the contact process needs no further concentration. It is highly concentrated. The acid obtained by the Chamber process is maximum 78% and needs further concentration.

(iii) The cost of production of sulphuric acid by Chamber process is considered to be lower than that of the Contact process because of the high cost of platinum metal. But the use of V_2O_5 in place of platinum has reduced the cost of production in the contact process as well.

(iv) The Contact process is mainly used especially when acid is required for the manufacture of explosives, fine chemicals, lead accumulators etc. while the Chamber process is used for commercial acid.

Properties

Ordinary concentrated sulphuric acid (18*M*) contains about 97% H_2SO_4. Pure (100%) H_2SO_4 is a thick colourless oily liquid with a melting point of 10.5°C. It has specific gravity 1.84 at 15°C. It is highly soluble in water. When heated to its boiling point 290°C, it partially decomposes to SO_3 and H_2O. Great care should be taken when the acid is to be diluted. It is a strong *dibasic acid* and gives two types of salts which are called *bisulphates* (HSO_4^-) and *sulphates* (SO_4^{-2}).

1. **Acidic Property:** Dilute aqueous solution of sulphuric acid is a typical strong acid. It ionizes in two steps:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$
$$HSO_4 + H_2O \rightleftharpoons H_3O^+ + SO_4^{-2}$$

The two steps of ionization differ widely, the first ionization is almost complete but the second ionization which involves the break up of the hydrogen sulphate, HSO_4^- takes place to a much smaller extent.

In the pure acid, the *hydrogen sulphate* has proton affinity resulting in the following reaction:

$$H_2SO_4 + H_2SO_4 \longrightarrow H_3SO_4^+ + HSO_4^-$$

(i) It neutralizes alkalis to form sulphates and bisulphates.

$$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$$
$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

(ii) It reacts with carbonates and bicarbonates to evolve CO_2.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$$
$$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2CO_2 + 2H_2O$$

(iii) Dilute sulphuric acid reacts with all metals except antimony, bismuth, mercury, copper, lead and noble metals.

$$H_2SO_4 + Zn \longrightarrow ZnSO_4 + H_2$$

(iv) It reacts with ammonia and forms ammonium sulphate.

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$$

(v) The ability of mixture of concentrated HNO_3 and sulphuric acid to nitrate organic compounds, e.g., benzene to nitrobenzene, is believed to be due to the formation of the nitronium ion, NO^{2+} in acid solution.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

(vi) The solutions of Ba^{2+} and Pb^{+2} react with sulphate ions to produce insoluble sulphates.

$$H_2SO_4 + Ba^{2+}(aq.) \longrightarrow BaSO_4\downarrow + 2H^+$$

$$H_2SO_4 + Pb^{2+}(aq.) \longrightarrow PbSO_4\downarrow + 2H^+$$

2. **Dehydrating property:** Because of its great affinity for water concentrated sulphuric acid can be used to remove water from those gases with which it does not react such as oxygen, chlorine, sulphur dioxide, etc., and is used in desiccators. It also removes combined water, e.g., from sugars and organic compounds, thus:

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + 11H_2SO_4 \longrightarrow 12C + 11(H_2SO_4.H_2O)$$

$$\underset{\text{(oxalic acid)}}{(COOH)_2} \xrightarrow{H_2SO_4} H_2O + CO + CO_2$$

$$\underset{\text{(ethanol)}}{C_2H_5OH} \xrightarrow{H_2SO_4} C_2H_4 + H_2O$$

The charring of wood starch, cotton and wool fibres by concentrated sulphuric acid results from the same dehydrating effect.

3. Oxidizing property: Dilute sulphuric acid has no oxidizing action but concentrated sulphuric acid especially when hot tends to oxidize substances according to the general equation.

$$H_2SO_4 + X \longrightarrow H_2O + SO_2 + XO$$

The following reactions illustrate the oxidizing action of sulphuric acid:

(i) Hot concentrated H_2SO_4 reacts with both metals and non-metals liberating SO_2.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

(ii) The oxidizing effect of sulphuric acid is noticeable in its reaction with bromide and iodides. It oxidizes a part of hydrogen bromide formed by the first reaction to bromide.

$$KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + Br_2 + SO_2$$

Iodides actually reduce the acid to sulphur and hydrogen sulphide.

$$KF + H_2SO_4 \longrightarrow KHSO_4 + HI$$

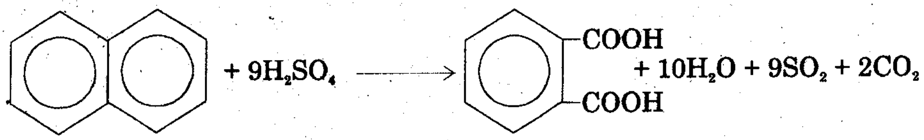
$$6HI + H_2SO_4 \longrightarrow 4H_2O + S + 3I_2$$

$$8HF + H_2SO_4 \longrightarrow 4H_2O + H_2S + 4I_2$$

It is unble to oxidize the chloride ion and fumes of HCl are evolved.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

(iii) The oxidizing property of sulphuric acid is used commercially in the preparation of phthalic acid, $C_8H_6O_4$, from naphthalene, $C_{10}H_8$. Mercuric sulphate is used as catalyst.



(Naphthalene) **(Phthalic acid)**

4. Sulphonating Property: Benzene reacts with conc. H_2SO_4 to form benzene sulphoric acid. It is an important chemical reaction.

$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_2OH + H_2O$$

5. Reaction with PCl_5: Sulphuric acid is supposed to possess the formula $SO_2(OH)_2$. Thus PCl_5 can replace two OH groups by Cl.

$$SO_2(OH)_2 + PCl_5 \longrightarrow SO_2(OH)Cl + POCl_3 + 2HCl$$

$$SO_2(OH)_2 + PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

Uses

Sulphuric acid is used:

(i) in the manufacture of chemical manures like ammonium sulphate and calcium superphosphate.

(ii) in the manufacture of other acids like nitric acid, hydrochloric acid, phosphoric acid etc.

(iii) in petroleum refining.

(iv) in the manufacture of coal-tar, dyes and a number of pharmaceuticals.

(v) in the manufacture of explosives.

(vi) in the textile, paper and dyeing industries.

(vii) for cleansing metals before enameling, electroplating, galvanizing etc.

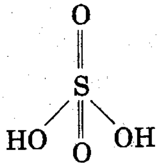
(viii) in storage batteries.

(ix) in the manufacture of sulphates, bisulphates and sodium carbonate.

(x) in the laboratory as an important reagent and as a drying and dehydrating agent.

Structure

Sulphuric acid molecule possesses a tetrahedral geometry as shown below. Sulphur atom is surrounded by four oxygen atoms and is sp^3 hybridized.



8.7 THIONIC ACIDS

The term thionic acids is used for the compounds in which two sulphonic groups, $-SO_2OH$ or $-SO_3H$ are linked together either directly or through one or more sulphur atoms. All the members of this class of acids can be represented by a general formula H_2SnO_6, where n=2,3,4,5,6. The thionic acids are named on the basis of number of sulphur atoms as given below:

1. Dithionic acid, $H_2S_2O_6$ (2S atoms)
2. Trithionic acid, $H_2S_3O_6$ (3S atoms)
3. Tetrathionic cid, $H_2S_4O_6$(4S atoms)
4. Pentathionic acid, $H_2S_5O_6$ (5S atoms)
5. Hexathionic acid, $H_2S_6O_6$ (6S atoms)

The free thionic acids are unstable, they are known only in solution and as salts.

1. Dithionic acid, $H_2S_2O_6$

Preparation

Dithionic acid is obtained from its salts by treatment with dilute H_2SO_4. The salts are obtained by the oxidation of sulphurous acid by ferric hydroxide or by manganese dioxide.

$$2Fe(OH)_3 + 3H_2SO_4 \longrightarrow Fe_2(SO_3)_3 + 6H_2O$$

$$2MnO_2 + 3H_2SO_3 \longrightarrow MnSO_4 + MnS_2O_6 + 3H_2O$$

The solution when treated with barium hydroxide, forms a precipitate of barium sulphate and ferrous hydroxide or manganese hydroxide and leaves barium dithionate in solution. The latter when treated with exact quantity of sulphuric acid yields a solution of dithionic acid.

$$BaS_2O_6 + H_2SO_4 \longrightarrow BaSO_4 + H_2S_2O_6$$

The aqueous solution of the acid can be concentrated by evaporation in vacuo until its specific gravity is about 1.35.

Properties

(*i*) Dithionic acid exists in solution only. It decomposes on concentration above a specific gravity of 1.35.

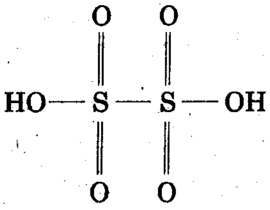
$$H_2S_2O_6 \longrightarrow H_2SO_4 + SO_2$$

(ii) On hydrolysis, it gives sulphuric and sulphurous acid.

$$H_2S_2O_6 + H_2O \longrightarrow H_2SO_4 + H_2SO_3$$

Structure

In $H_2S_2O_6$ two sulphonic acid groups, $-SO_2OH$ are directly linked with each other. Since the acid is dibasic, it has two -OH groups linked directly with S-atom. Thus the dithionic acid and dithionic ion have the following structures.



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

The structure of $S_2O_6^{-2}$ ion has approximately tetrahedral bond angles about each sulphur atom. Thus S-O bond distance is 1.43Å as compared to 1.44Å in SO_4^{-2} ion. The short bond distance suggests considerable double bond character.

2. Trithionic acid, $H_2S_3O_6$

Preparation

(i) Trithionic acid is not very stable. Its **potassium salt** is prepared by passing sulphur dioxide through a concentrated solution of potassium thiosulphate or by digesting potassium hydrogen sulphite solution with sulphur for many hours.

$$2K_2S_2O_3 + 3SO_2 \longrightarrow 2K_2S_3O_6 + 3S$$

$$6KHSO_3 + 2S \longrightarrow 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O$$

(ii) Trithionates are also obtained by treating ice-cold saturated solution of sodium thiosulphate with hydrogen peroxide.

$$2Na_2S_2O_3 + 4H_2O_2 \longrightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$$

The acid is obtained from its salts by treatment with dilute H_2SO_4.

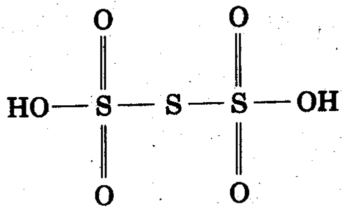
Properties

(i) The aqueous solution of the trithionic acid readily decomposes on heating or concentration.

$$H_2S_3O_6 \longrightarrow H_2SO_4 + SO_2 + S$$

(ii) The trithionates are mild reducing agents. They are oxidized by air to sulphates, sulphur dioxide and sulphur.

Structure



$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-S-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

3. Tetrathionic acid, $H_2S_4O_6$

Preparation

(i) It is a strong acid and is known only in solution. The tetrathionates are prepared by the action of iodine on thiosulphates.

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$2PbS_2O_3 + I_2 \longrightarrow PbS_4O_6 + PbI_2$$

Lead iodide is filtered off and the solution of lead tetrathionate is treated with sulphuric acid.

(ii) Tetrathionate can also be obtained by the anodic oxidation of $NaHS_2O_3$.

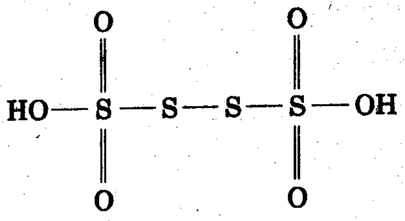
$$2NaHS_2O_3 \xrightarrow[\text{oxidation}]{\text{anodic}} Na_2S_4O_6$$

Properties

The tetrathionic acid is a colourless liquid and is fairly stable in dilute solutions. When concentrated beyond a point, it decomposes as:

$$H_2S_4O_6 \longrightarrow H_2SO_4 + SO_2 + 2S$$

Structure



$$\mathrm{HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-S-S-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH}$$

4. Pentathionic acid, $H_2S_5O_6$

Preparation

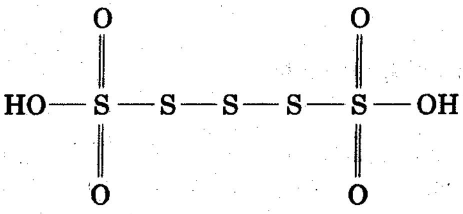
When H_2S is passed into a concentrated solution of sulphurous acid at 0^0C a solution called *Wackenroder's solution* is formed. Besides pentathionic acid, this solution also contains much sulphur and other thionic acids. Wackenroder's solution has been the subject of much investigation but the nature of reactions involved is still in doubt. The best method of obtaining pentathionic acid is by spontaneous decomposition of thiosulphuric acid solution below 0^0C in the presence of little As_2O_3. The acid itself cannot be isolated.

Properties

The acid and its salts decompose on heating into sulphuric acid or sulphates, sulphur dioxide and sulphur.

$$H_2S_5O_6 \longrightarrow H_2SO_4 + SO_2 + 3S$$

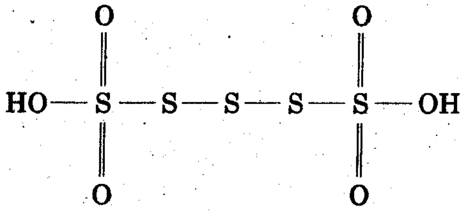
Structure



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

5. Hexathionic acid, $H_2S_6O_6$

Hexathionic acid is said to have been prepared in solutions described above as obtained from H_2S and sulphur dioxide. The aqueous solution is very unstable. It possesses the following structure:



$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

8.8 PERACIDS OF SULPHUR

Two important acids containing peroxide, -O-O- link are known. These are

1. Permonosulphuric acid (Caro's acid), H_2SO_5
2. Perdisulphuric acid (Marshall's acid), $H_2S_2O_8$

- **Permonosulphuric acid, H_2SO_5**

Preparation

(i) Pure acid can be prepared by the action of chlorosulphuric acid on nhydrous H_2O_2.

$$HOSO_2Cl + H_2O_2 \longrightarrow H_2SO_5 + HCl$$

(ii) By the action of SO_3 on H_2O_2.

$$SO_3 + H_2O_2 \longrightarrow H_2SO_5$$

(iii) When concentrated sulphuric acid is subjected to electrolysis in a diaphragm cell at low temperature, using a small smooth platinum electrode (anode), a solution of H_2SO_5 is obtained.

$$H_2SO_4 + [O] \longrightarrow H_2SO_5$$

Properties

(i) Caro's acid in the anhydrous state is a white crystalline solid having melting point 45°C and hygroscopic. It is stable for some days but gradually loses oxygen.

(ii) When diluted with water, it gives H_2O_2

$$H_2SO_4 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

(iii) It carbonizes wool and cellulose.

(iv) It is a powerful oxidizing agent. Thus it oxidizes Mn(II), Ag(I), Co(II), Ni(II) etc. salts to peroxides and liberates Cl_2, Br_2 and I_2 from respective halides.

$$2AgNO_3 + H_2SO_5 \longrightarrow 2H_2SO_4 + 2NHO_3 + Ag_2O_2 \downarrow$$
$$2KI + H_2SO_5 \longrightarrow K_2SO_4 + H_2O + I_2$$

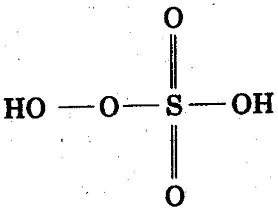
It also oxidizes SO_2 to SO_3, HCl to Cl_2 etc.

(v) No solid salts of H_2SO_5 of M_2SO_5 type are known. However, a solution of $KHSO_5$ is said to be formed by the action of H_2O_2 on $KClSO_3$.

$$KClSO_3 + H_2O_2 \longrightarrow KHSO_5 + HCl$$

Thus H_2SO_5 is a *monobasic acid.*

Structure



$$HO-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

2. Perdisulphuric acid, $H_2S_2O_8$

Preparation

(i) Anhydrous peroxy-disulphuric acid can be prepared by the action of H_2O_2 (1 mole) on chlorosulphuric acid (2moles).

$$2ClSO_2OH + H_2O_2 \longrightarrow H_2S_2O_8 + 2HCl$$

(ii) It may be obtained by the electrolysis of fairly concentrated (50-60%) sulphuric acid at low temperature. The bisulphate ions liberated at the anode are oxidized by nascent oxygen.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$2HSO_4^- + H_2O + O \longrightarrow H_2S_2O_8 + 2OH^-$$

(iii) By the action of concentrated H_2SO_4 on concentrated H_2O_2.

$$H_2SO_4 + 2H_2O_2 \longrightarrow H_2S_2O_8 + 2H_2O$$

Properties

(i) It is a colourless, hygroscopic, crystalline compound (m.p=65°C) which is fairly stable at ordinary temperature.

(ii) On heating, $H_2S_2O_8$ decomposes into SO_3 and O_2. It is also decomposed by light.

$$2H_2S_2O_8 \xrightarrow{\Delta} 2H_2SO_4 + 2SO_3 + O_2$$

(iii) In aqueous solution, it is slowly hydrolysed into H_2SO_4 and H_2SO_5.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2$$

(iv) The anhydrous acid vigorously reacts with organic compounds.

(v) The acid and its salts (which are called *perdisulphates*) are strong oxidizing agents. Following examples show the oxidizing property of perdisulphates.

$$Mn^2+ 2H_2O + S_2O_8^{-2} \longrightarrow MnO_2 + 4H^+ + 2SO_4^{-2}$$

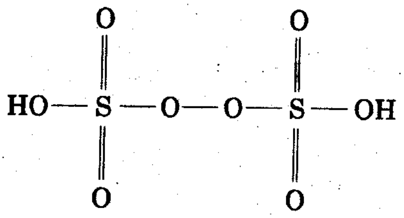
$$2Fe^{2+} + S_2O_8^{2} \longrightarrow 2Fe^{3+} + 2SO_4$$

$$2Ag^+ + 2H_2O + S_2O_{8_2} \longrightarrow Ag_2O_2 + 2H^+_2 + 2HSO_4^-$$

$$2Cl + S_2O_8^{2} \longrightarrow Cl_2 + 2SO_4^{2}$$

$$2I + S_2O_8 \longrightarrow I_2 + 2SO_4$$

Structure



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-OH$$

8.9 USE OF HYPO IN PHOTOGRAPHY

Sodium thiosulphate, $Na_2S_2O_3.5H_2O$ is commercially known as *hypo* and is used as a "fixer" in photography which has made possible to preserve beautiful scenes and figures. The process of film developing involves a redox reaction.

Black and white photographic film contains small grains of silver bromide, evenly spread over a thin gelatin coating on paper. Exposure of film to light activates the silver bromide as follows:

$$AgBr + light \longrightarrow AgBr^*$$

Where the asterisk denotes AgBr excited by light. The number of silver bromide grains activated depends upon the intensity of light falling/striking the photographic film/plate. Next the exposed film is treated with a ***developer***, a solution containing a mild reducing agent such as hydroquinone.

$$2AgBr^*(s) + C_6H_6O_2(aq.) \longrightarrow 2Ag(s) + 2HBr(aq.) + C_6H_4O_2(aq.)$$

In this redox process, the Ag^+ ions in the excited silver bromide, $AgBr^*$ are preferentially reduced to metallic silver, and hydroquinone is oxidized to quinone. The oxidation step, which at first is not obvious, can be clarified by writing the above reaction as two half-reactions:

Oxidation

$$C_6H_6O_2(aq) \longrightarrow C_6H_4O_2(aq.) + 2H^+ + 2e^-$$

Reduction

$$2Ag^+(aq.) + 2e^- \longrightarrow 2Ag(s)$$

The sum of these half-reactions is

$$2Ag^+(aq.) + C_6H_6O_2(aq.) \longrightarrow 2Ag(s) + C_6H_4O_2(aq.) + 2H^+(aq.)$$

which is the net ionic equation for the redox process. The amount of black metallic silver particles formed on the film is directly proportional to the amount or intensity of light that originally fell on the film. The unreacted (i.e., the unexcited) AgBr must be removed from the film at this stage; otherwise, it also would slowly be reduced by hydroquine and the *entire* film would eventually turn black. To prevent this undesired reaction, the film is quickly treated with a "*fixer*", a sodium thiosulphate solution, to remove the silver ions:

$$AgBr\,(s) + 2S_2O_3^{-2}(aq.) \longrightarrow [Ag(S_2O_3)_2]^{3-}(aq.) + Br^-(aq.)$$

What has been described is the preparation of a black and white *negative*. A positive print can be obtained by shining light through the negative onto another piece of photographic paper and repeating the developing procedure. Because white regions of the subject appear black in a negative, they are opaque and leave unexcited (white) areas in the positive print. This process therefore inverts the light and dark areas of the negative to produce the desired picture.

Questions

Q.1 Write the names of elements present in group VIA (16) of the periodic table. Discuss the general group trends of these elements.

Q.2 Discuss the gradation in properties of group VIA (16) elements in respect of oxidation states, metallic character, formation of oxides, formation of hydrides and polymorphism.

Q.3 Compare the properties of oxygen with sulphur.

Q.4 *(a)* Write the names of various oxides of sulphur. How is SO_2 prepared?

(b) Complete and balance the following equations:

(i) $SO_2 + H_2O \longrightarrow$

(ii) $SO_2 + NaOH \longrightarrow$

(iii) $SO_2 + H_2S \longrightarrow$

(iv) $SO_2 + PbO_2 \longrightarrow$

(v) $SO_2 + Cl_2 \longrightarrow$

Q.5 Discuss the role of SO_2 in environmental pollution. How can its emission be controlled?

Q.6 *(a)* Give the chemistry of contact process for the manufacture of H_2SO_4. Draw a neat labeled diagram of the process.

(b) Discuss the advantages of contact process over the lead chamber process.

Q.7 *(a)* Discuss the process and reactions involved in the production of H_2SO_4 by lead chamber process.

(b) The civilization and development of a country is judged by the amount of consumption of sulphuric acid. Comment on this statement.

Q.8 *(a)* Name the basic raw materials required for H_2SO_4 manufacture.

(b) Compare the Contact and Chamber processes for the manufacture of H_2SO_4.

(c) What is oleum? How is it obtained?

Q.9 *(a)* Write some uses of sulphuric acid.

(b) What happens when?

(i) H_2SO_4 reacts with Zn.

(ii) H_2SO_4 reacts with PCl_5

(iii) H_2SO_4 is treated with alcohol

(iv) H_2SO_4 reacts with KBr

(v) H_2SO_4 reacts with Cu

(c) H_2SO_4 acts as dehydrating agent. Comment.

Q.10 What are thionic acids? How they are usually prepared? Discuss the properties and structures of these acids.

Q.11 What are persulphuric acids? How they are usually prepared? Discuss the properties and structures of these acids.

Q.12 What is "Hypo"? Discuss its use in photography.

Q.13 Justify/comment on the following statements.

(a) Sulphur is a member of VIA (16) group.

(b) H_2O is a liquid but H_2S is a gas.

(c) SO_2 is acidic in nature.

(d) SO_2 causes air pollution.

(e) Hypo is used in photography.

(f) Oxygen resembles with sulphur.

(g) H_2SO_4 obtained by Contact process is of higher purity.

(h) Sugar gets charred when heated with conc. H_2SO_4.

(i) H_2O has higher melting point than H_2S.

(j) Oxygen forms only difluoride, while sulphur forms a hexafluoride.

(k) AgBr is used in photography.

(l) H_2SO_4 is a stronger acid than H_2SO_3.

Chapter Nine

HALOGENS

9.1 INTRODUCTION

Group VIIA (17) of the periodic table consists of fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). These are collectively known as halogens (Greek *halos*, salt, genes, *born*) or "salt producer" because they all have high electronegativity and form negative ions such as are found in ionic salts. Most of these elements exist in sea water, notably in the form of their sodium compounds. Astatine is an unstable element of radioactive origin. All the elements have seven electrons in their outer most shells with two electrons in s–orbital and five electrons in the p-orbital as shown in Table 9.1.

Table 9.1 Electronic Configuration of Group VIIA(17) Elements

Element	At. No.	Electronic Configuration
F	9	$1s^2, 2s^2\ 2p^5$
Cl	17	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^5$
Br	35	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^5$
I	53	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 5s^2\ 5p^5$
At	85	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6\ 4d^{10}, 4f^{14}5s^2 5p^6\ 5d^{10}, 6s^2 6p^5$

It is obvious from the above configurations that all the elements have ns^2p^5 configuration in their valence shell. Two electrons are in ns–orbital and the remaining five electrons are in *np*–orbitals and are distributed in accordance with the *Hund's rule*. The shell previous to the outer most shell contains in fluorine the group 's^2' (saturated), in chlorine 's^2p^6' (saturated), in bromine '$s^2p^6d^{10}$' (saturated) while in iodine and astatine '$s^2p^6d^{10}$' (unsaturated). This shows why fluorine differs from chlorine and these two from the remaining elements. All the halogens are capable of completing their octet either by accepting an electron to form halide ion X^-, or by sharing one electron to form single covalent bond.

Some of the important physical properties of group VIIA (17) elements are summarized in Table 9.2

Table 9.2 Some Physical Properties of Group VIIA (17) Elements

Property	F	Cl	Br	I
Atomic number	9	17	35	53
Atomic weight	19.0	35.5	79.9	126.9
Density (g/cm^3)	1.11 (b.p)	1.56 (b.p)	3.12	4.94 (solid)
Ionization potential I (kJmol^{-1})	1680	1255	1140	1010
Melting point (°C)	−220	−110	−7	113
Boiling point (°C)	−118	−34	59	183
Atomic radius (nm)	0.064	0.099	0.114	0.133
Electronegativity	4	3.2	3	2.7
Electrode potential(V)	+3.06	+1.36	+1.06	+0.538
Electron affinity	338	355	331	302

9.2 GRADATION OF CHARACTERISTIC PROPERTIES WITHIN THE GROUP.

The gradation in the physical and chemical properties of the elements with the rise of atomic number is as follows:

(i) **Diatomic nature:** All the halogens exist as covalent diatomic molecules (X_2 molecules). These discrete molecules are held together by weak van der Waals forces which explain the volatile nature of these elements. Halogens range in physical properties from an almost colourless gas (F_2) through a dark red volatile liquid (Br_2) to an almost black crystalline solid (I_2) molecules. The fall in volatility is due to an increase in van der Waals forces of attraction between the molecules.

(ii) **Melting and boiling points:** These increase from fluorine to iodine because of the greater interactions between the molecules of large size.

(iii) **Electronegativity:** Halogens have large values of electronegativity. The electronegativity of halogens decreases down the group. F has the highest value and would be able to form hydrogen bonding in HF.

(iv) **Electron affinity:** Electron affinity values decrease from Cl to I. The electron affinity value of F is less than that of Cl. This small value is due to electron-electron repulsion of the 2nd shell.

(v) **Dissociation energy:** This does not show a regular trend. The dissociation energy of fluorine molecule is very low, about 158 kJmol^{-1}. This is due to the repulsion between non-bonding electrons. The possibility of multiple bonding

involving d-orbitals in Cl_2, Br_2, and I_2 accounts for the increased dissociation energy of these molecules. Thus

$$Cl_2 > Br_2 > I_2$$

(vi) **Oxidizing power:** By virtue of their tendency to gain electrons these elements behave as good oxidizing agents. The oxidizing power of the halogens decreases on descending the group. The high oxidizing power of halogens is favored by *(a)* low heat of dissociation of X_2, *(b)* a high electron affinity of the atom, and *(c)* a higher hydration energy of the ion. Fluorine is so strong oxidizing agent that it oxidizes water to oxygen. Iodine is a much weaker oxidizing agent. This is illustrated by the decreasing redox potential as we go down the group from fluorine to iodine.

(vii) **Colour:** All the halogens are coloured. Their colour is due to the fact that their molecules absorb light in the visible region by means of which the outer electrons are excited to the higher energy levels. The amount of energy required for the excitation decreases progressively from fluorine to iodine as the size of atom increases. Thus there is a progressive deepening of colour of the halogens from fluorine to iodine. Fluorine absorbs violet light (higher energy) and hence appears pale yellow while iodine vapours absorb yellow light (lower energy) and appears deep violet.

(viii) **Oxidation states:** Halogens exhibit the oxidation state of −1 in their ionic compounds. Fluorine is always univalent and has always the oxidation number of −1. Among other halogens, the oxidation states of +1, +3, +5 and +7 are possible (when they combine with elements of higher electronegativity). The oxidation states of +4 and +6 are met in their oxides ClO_2, BrO_3 and oxyacids.

(ix) **Ionization potential:** Ionization energies are very high and decrease from F to I. Since this value of F is very high, fluorine has no tendency to lose an electron to form F^+ ion. Iodine which has the least value loses an electron to form I^+ ion which is found in many compounds like ICl, ICN etc.

(x) **Reactivity:** All the halogens are the most reactive elements as a family. Fluorine is the most reactive due to its high electronegativity, small size, extremely high oxidizing power and low dissociation energy of F–F bond. The reactivity decreases with atomic number, e.g., in the displacement reactions we find that fluorine displaces all the remaining three halogens from their salts. Chlorine displaces only bromine and iodine, bromine displaces only iodine while iodine displaces none.

(xi) **Formation of interhalogens:** Two different halogen atoms, due to the difference in their electronegativity values, combine with one another to form a number of covalent compounds which are called interhalogen compounds e.g., ICl, IF_5, IF_7 etc.

(xii) **Formation of oxy-acids:** Excepting F, all other halogens form oxy-acids. These are mainly of four types viz. HXO (hypohalous acids), HXO_2 (halous acids), HXO_3 (halic acids), and HXO_4 (perhalic acids).

(xiii) **Formation of hydrides:** All the halogens react with hydrogen to form the volatile covalent hydrides of HX formula.

9.3 ANOMALOUS BEHAVIOUR OF FLUORINE

Like other elements such as C, N and O which are the first members of their respective groups, fluorine also differs from the other members of its own group due to *(a)* its small size *(b)* its higher electronegativity *(c)* non-availability of d-orbitals in its valence shell, and *(d)* low bond energy. The following are the major points of difference:

(i) Fluorine is always univalent, the oxidation number being −1, other halogens do show higher covalencies, e.g., +1, +3, +5 etc.

(ii) No oxyacid of fluorine is known. Other halogens form a number of oxyacids.

(iii) Fluorine is the most reactive element among halogens. This is due to the minimum value of F-F bond dissociation energy.

(iv) On account of the high electronegativity of F atom, hydrogen bonding occurs in HF while it is absent in HCl, HBr and HI.

(v) Fluorides are ionic while other halides have frequently molecular lattices.

(vi) Fluorides of Ag, Ca, Mg, Ba, Sr, lanthanides and actinides are insoluble in water but other halides of these metals are soluble.

(vii) HF ionizes only slightly in aqueous solution and is, therefore, a weak acid. HCl, HBr and HI, on the other hand, ionize almost completely and are thus strong acids.

(viii) F^- ion has a greater tendency to give complex ions like $[AlF_6]^{-3}$, $[FeF_6]^{-3}$ etc. The remaining halide ions show this tendency to a lesser extent.

(ix) Many of the reactions of elementary fluorine are exothermic. The fluorination of organic compounds with fluorine takes place with explosive violence.

(x) Because of the non-availability of d-orbitals in its valence shell, fluorine does not combine with F^- ions to give polyhalide ion, F_3^- while other members of the group give such ions (e.g., Cl_3^-, Br_3^-, I_3^-, I_5^- etc.)

9.4 CHEMISTRY OF FLUORINE

Occurrence

Fluorine is very reactive and hence does not occur free in nature but is widely found in combined state as fluorides. Its chief minerals are:

(i) Fluorspar, CaF_2

(ii) Cryolite, Na_3AlF_6

(iii) Flurapatite, $CaF_2.3Ca_3(PO_4)_2$

Preparation

It is prepared commercially by the electrolysis of fused KHF_2 or by the electrolysis of anhydrous HF to which KHF_2 is added to conduct electricity. Many different types of electrolytic cells have been used.

Fluorine is more easily prepared by *Dennis's method.* This method involves the electrolysis of fused $NaHF_2$ or KHF_2 in a copper vessel which apparently becomes coated with a protecting film of fluoride, with graphite electrodes. The electrolyte is fused electrically in a copper V-shaped tube (Fig. 9.1) and current of 5 ampere at 12 volts is employed. The ends of the copper V-shaped tube are covered with copper caps into which the graphite electrodes are fixed with bakelite cement. The V-shaped copper tube is thickly covered with an insulating layer of asbestos cement to prevent the loss of heat.

When a current of required strength is passed through perfectly anhydrous KHF_2, H_2 is liberated at the cathode and F_2 at the anode. F_2 liberated at the anode is passed through U-tube containing NaF which removes HF vapours coming with F_2. The reactions taking place are:

$$KHF_2 \longrightarrow KF + HF$$

$$HF \longrightarrow H^+ + F^-$$

$$2H^+ + 2e^- \longrightarrow H_2 \text{ (at cathode)}$$

$$2F^- - 2e^- \longrightarrow F_2 \text{ (at anode).}$$

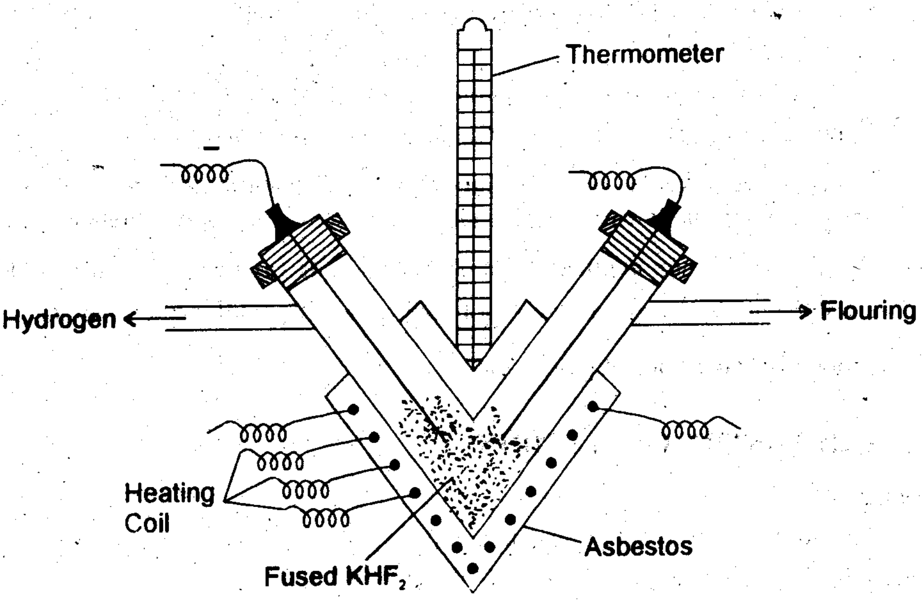


Fig. 9.1. Electrolytic cell for the preparation of fluorine gas.

Properties

(*i*) Fluorine is a pale yellow gas with pungent smell. The liquid fluorine has a density 1.14. It is a poisonous gas and hence should be handled carefully.

(ii) It is the most reactive element as is evident from the fact that it ignites in contact with most of the oxidizing substances.

(iii) It combines with most metals (e.g., Na, Ca, Mg, Al, Ni, Pt, Au etc.) non-metals (e.g., H, C, S, P, Cl, Br, I etc.) and metalloids (e.g., As, Sb) to form the fluorides.

$$2Na + F_2 \longrightarrow 2NaF$$

$$2Au + 3F_2 \longrightarrow 2AuF_3$$

$$Cl_2 + F_2 \longrightarrow 2ClF$$

$$S + 3F_2 \longrightarrow SF_6$$

(iv) It combines with xenon to form the definite fluorides, XeF_2, XeF_4 and XeF_6 depending upon temperature, pressure and mixing ratio of the constituents.

(v) It reacts vigorously with water giving O_2 and O_3.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

$$F_2 + H_2O \longrightarrow OF_2 + H_2$$

(vi) It displaces chlorine and iodine from chlorides and iodides.

$$2NaCl + F_2 \longrightarrow 2NaF + Cl_2$$

$$2KI + F_2 \longrightarrow 2KF + I_2$$

(vii) It is a powerful oxidizing agent; it oxidizes potassium chlorate to perchlorate.

$$KClO_3 + F_2 + H_2O \longrightarrow KClO_4 + 2HF$$

(viii) It reacts with NH_3 to form N_2 and some NF_3.H_2S burns in the atmosphere of F_2 forming SF_6 and HF.

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF$$

$$NH_3 + 3F_2 \longrightarrow NF_3 + 3HF$$

$$H_2S + 4F_2 \longrightarrow SF_6 + 2HF$$

(ix) It also reacts with hydrocarbons explosively and gives rise fluorinated hydrocarbons like CHF_3, CH_2F_2, CF_4 etc. which are called *fluorocarbons*.

Uses

(i) It is of considerable use in the preparation of fluorocarbons which are non-inflammable and chemically inert and are used as solvents, lubricants and insulators.

(ii) It is used as a refrigerant in many of the cooling processes.

(iii) A new series of organic compounds of considerable practical use have also been isolated under the name of *Freons* used in refrigeration and air-conditioning.

(iv) It finds considerable use as DDFT, which similar to DDT, is extremely efficient as a fungicide and fumigant.

(v) In nuclear physics and high voltage electricity, fluoride as SF_6 finds very great use e.g., in the separation of isotopes of uranium.

9.5 CHEMISTRY OF CHLORINE

Occurrence

Being one of the most reactive elements, chlorine does not occur in the free state. In the combined state it occurs in large quantities as *chlorides*. Common salt (NaCl) is the most important chloride present in sea water and occurs as rock salt at **Khewra Salt Mines** in Pakistan. The other important chloride minerals are:

(i) Sylvine, KCl

(ii) Carnallite, $KCl.MgCl_2.6H_2O$

(iii) Chlorapatite, $3Ca(PO_4)_2.CaCl_2$

Preparation

Chlorine is manufactured on industrial scale by the electrolysis of brine or the aqueous solution of sodium chloride, chlorine evolving at the anode. Sodium hydroxide is also obtained at the same time.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

On electrolysis Na^+ and H^+ ions move towards the cathode where H^+ ions are discharged in preference to Na^+ ions. Similarly OH^- and Cl^- ions move towards the anode but Cl^- ions give up their electrons in preference to OH^- ions. Thus we get hydrogen at the cathode and chlorine at the anode. Accumulation of Na^+ and OH^- ions occurs in the cell and the overall ionic equation is:

$$2Na^+ + 2Cl^- + 2H_2O \longrightarrow H_2 + Cl_2 + 2Na + OH^-$$

Various types of electrolytic cells are used for this purpose but Nelson Cell (Fig. 9.2) is more common. In the Nelson cell, the anode consists of a carbon rod which is suspended in a perforated steel U-tube which also acts as the cathode and is separated from the anode by a layer of asbestos deposited on the inner wall of the tube. The brine on electrolysis evolves chlorine which is drawn from the anode. Chlorine is sold in the market in steel cylinders. The electrolytic method surpasses all the other methods in the purity and the cheapness of the process.

Chlorine may also be prepared on industrial scale by *Deacon's process*. In this process the oxidation of HCl is carried out by atmospheric oxygen in the presence of cupric chloride as catalyst. The acid is generated by the action of sulphuric acid on common salt at high temperature.

$$4HCl + O_2 \xrightleftharpoons{CuCl_2} 2Cl_2 + 2H_2O$$

The reaction is reversible and should be done at low temperature (400-450^{0}C). The catalytic action of cupric chloride is explained by the reactions given below:

$$2CuCl_2 \longrightarrow Cu_2Cl_2 + Cl_2$$

$$2Cu_2Cl_2 + O_2 \longrightarrow 2CuO.CuCl_2$$

$$CuO.CuCl_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

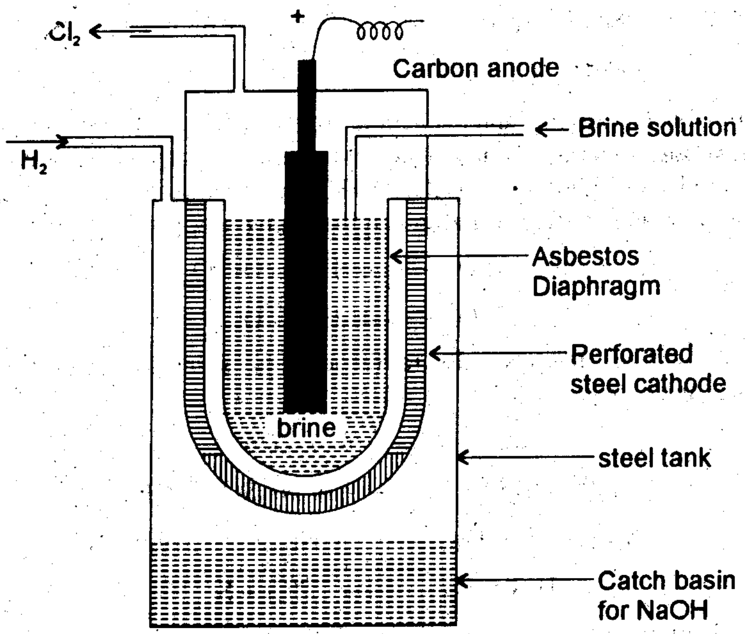


Fig. 9.2. Nelson cell for the manufacture of Cl_2 and NaOH.

Properties

(i) Chlorine is greenish yellow gas with a pungent irritating odor. It produces headache if inhaled even in small quantities. It liquefies under pressure at –3°C and liquid chlorine possesses a yellow colour.

(ii) It is highly reactive and directly combines with metals (e.g., Na, Fe, Al, Cu etc.) and non-metals (e.g., P, S, B, As, Sb etc.) to form chlorides.

$$Cu + Cl_2 \longrightarrow CuCl_2$$

$$2Al + Cl_2 \longrightarrow 2AlCl_3$$

$$2P + 3Cl_2 \longrightarrow 2PCl_3$$

$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$

(iii) It has great affinity for hydrogen with which it gives HCl. This affinity is evident from the following reactions:

$$Cl_2 + H_2 \longrightarrow 2HCl$$

$$2H_2O + 2Cl_2 \longrightarrow 4HCl + O_2$$

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

(iv) It reacts with ammonia and gives NH_4Cl.

$$8NH_3\,(\text{excess}) + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

$$4NH_3 + 3Cl_2(\text{excess}) \longrightarrow NCl_3 + 3NH_4Cl$$

(v) It is a strong oxidizing and bleaching agent because of the nascent oxygen it produces with reactin of water. It reacts with water to produce hydrochloric acid (HCl) and hypochlorous acid (HClO). HClO so produced evolves nascent oxygen which is responsible for oxidizing and bleaching properties of chlorine.

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

$$HClO \longrightarrow HCl + O$$

Thus, it oxidizes ferrous salts to ferric salts, sulphites and thiosulphates to sulphate, and so on.

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$

$$Na_2SO_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl$$

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl + S$$

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

It also liberates iodine from an iodide solution and bromine from a bromide.

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

$$(Cl_2 + 2e^- \longrightarrow 2Cl^-)$$

In the presence of moisture, Cl_2 bleaches organic and vegetable coloring matter like indigo, litmus, linen, silk, wood, pulp etc. The bleaching action is due to the following reaction.

$$Cl_2 + 2H_2O \longrightarrow 2HCl + O$$

$$\text{Coloured matter} + O \longrightarrow \underset{\text{(oxidation matter)}}{\text{Colourless matter}}$$

Bleaching effect of Cl_2 is permanent because there is no reducing agent in the atmosphere and as such the colourless matter is not converted back to the coloring matter.

(vi) Chlorine also kills disease germs and is, therefore, extensively used for sterilization of drinking water.

(vii) Chlorine forms addition compounds with SO_2, CO and hydrocarbons.

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2 \text{ (Sulphuryl chloride)}$$

$$CO + Cl_2 \longrightarrow COCl_2 \text{ (Carbonyl chloride)}$$

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2 \text{ (Ethylene dichloride)}$$

(viii) When passed in cold dilute solution of alkalies, it forms chlorides and hypochlorites

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$$

With hot concentrated alkali solutions, chlorates are produced.

$$Cl_2 + 2NaOH \longrightarrow NaClO_3 + 5NaCl + 3H_2O$$

Uses

Chlorine is used:

(i) in the sterilization of water for drinking purposes.

(ii) in the manufacture of bleaching powder, chlorates, hypochlorites, perchlorates, ethylene chloride, carbon tetrachloride, hydrochloric acid and a number of synthetic organic compounds.

(iii) in the extraction of gold by *Plattner's process.*

(iv) in the bleaching of cotton textiles, paper and rayon.

(v) in the manufacture of poisonous gases like phosgene and mustard gas etc.

9.6 CHEMISTRY OF BROMINE

Occurrence

It is never found free in nature. It occurs mostly in the form of bromides of sodium, potassium, magnesium and calcium. Sea water also contains these salts. Carnallite, $MgCl_2.Kcl.6H_2O$ also contains 0.2% bromine as bromide.

Preparation

Bromine is obtained on commercial scale from *Carnallite*. When KCl has been crystallized from the saturated solution of Carnallite, the mother liquor thus obtained contains these bromides. Bromine is recovered from this mother liquor by treatment with chlorine.

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

The plant used for the recovery of bromine is shown in Fig. 9.3. The mother liquor obtained as above is allowed to flow down a tower packed with earthenware balls up which a current of chlorine is passing. The liberated bromine vapors along with unreacted Cl_2 pass out of the top of the tower. These vapours are passed through condenser where most of bromine liquefies. The bromine vapors escaping the condenser are caught in the tower filled with iron fillings which react with bromine forming iron bromide, Fe_3Br_8 which is also treated for the recovery of bromine.

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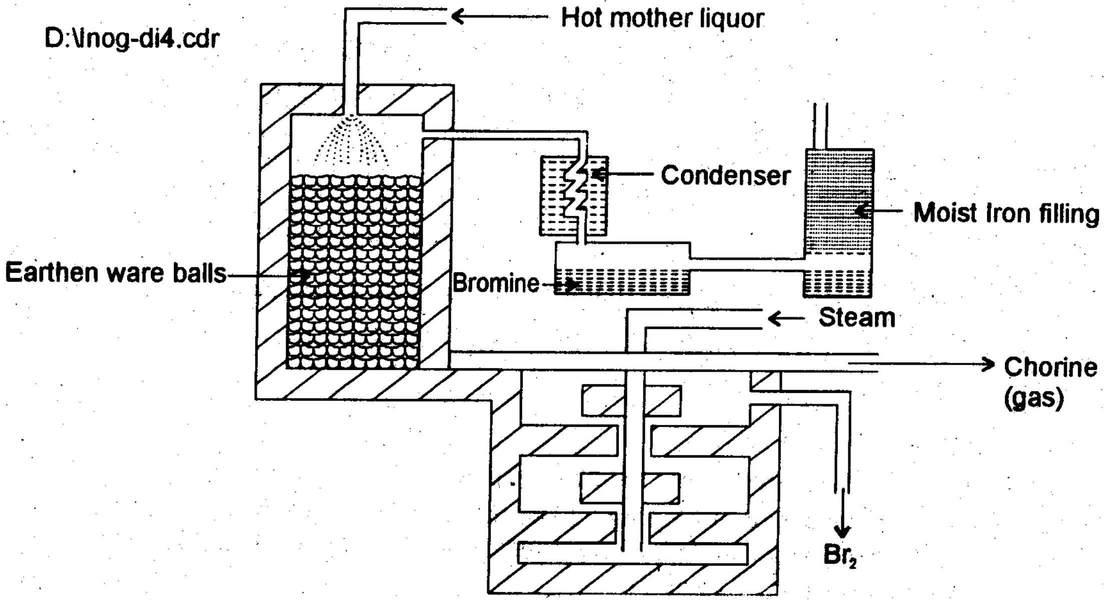


Fig. 9.3. Manufacture of bromine

The spent mother liquor is passed from the bottom of the tower to a container having shelf-like partitions. A current of steam is blown in this container which expels any bromine that might have come down with the spent liquor in the dissolved state:

The bromine so obtained may contain the impurities of water, chloride and iodine. This impure bromine is distilled with KBr to remove Cl_2.

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

Iodine is removed by adding copper sulphate solution which precipitates iodine as Cu_2I_2. The moisture is expelled by distilling it with conc. H_2SO_4, when pure bromine is obtained.

Properties

(i) Bromine is a reddish brown liquid with density of 3.11 at 20°C. It boils at 58.5°C and freezes at -7.2°C. It has an irritating disagreeable odor. The vapors attack the eyes and mucous membrane of the nose and throat. It is poisonous and attacks the skin forming painful blisters.

(ii) It is soluble in water, chloroform, carbon disulphide, alcohol and ether.

(iii) It is highly reactive, very much similar to chlorine. Its reaction with hydrogen is comparatively less vigorous.

$$H_2 + Br_2 \longrightarrow 2HBr$$

(iv) It reacts with many metals and non-metals forming bromides like MBr (M=Na, K); MBr_3 (M=P, As, Sb, Bi).

(v) It gives interhalogens with other halogens like BrX (X=F, Cl, I) and BrF_3 etc.

(vi) It reacts with water forming HBr and O_2

$$2H_2O + 2Br_2 \longrightarrow 4HBr + O_2$$

(vii) It displaces iodine from a solution of iodine.

$$2KI + Br_2 \longrightarrow 2KBr + I_2$$

(viii) It is a good oxidizing agent and oxidizes sulphite to sulphate, nitrite to nitrate, H_2S to S, SO_2 to H_2SO_4 etc.

$$Br_2 + SO_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4$$

$$Na_2SO_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + 2HBr$$

$$Na_2S_2O_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + 2HBr + S$$

$$Na_3ASO_3 + Br_2 + H_2O \longrightarrow Na_3ASO_4 + 2HBr$$

(ix) With caustic soda solution, it gives a hypobromite, NaBrO in cold and a bromate, $NaBrO_3$, when heated

$$2NaOH + Br_2 \longrightarrow NaBr + NaBrO + H_2O$$

$$6NaOH + 3Br_2 \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$$

(x) It is also used as bleaching agent, but its action is weaker than Cl_2 due to slow decomposition of H_2O by it even in presence of sun light.

Uses

Bromine is used:

(i) as a germicide

(ii) in the manufacture of bromides which are used in medicines, photography etc.

(iii) as an oxidizing gent

(iv) in the manufacture of ethylene bromide which is used to increase the efficiency of tetraethyl lead, an anti-knocking compound.

(v) as a laboratory reagent.

(vi) in the manufacture of dyes, tear gas etc.

9.7 CHEMISTRY OF IODINE

Occurrence

Iodine is not found free in nature. In the combined state it occurs as iodides in sea water (0.001%), sea weeds (1.5%) and sponges. It is also found in crude Chile saltpetre as $NaIO_3$ (0.2%).

Preparation

Iodine is manufactured from sea weeds on commercial basis. Sea weeds are the plants growing in deep sea water. These contain KI and NaI. The sea weeds of *Laminaria* variety are dried and burnt in shallow pits to ash known as *kelp*. The kelp so obtained is digested with water. The water extract is obtained by filtration. It contains sulphates and chlorides (e.g., KCl, NaCl) which are less soluble and crystallize out first, the mother liquor left behind is a dark coloured solution and contains about 12% iodine as NaI and

KI. It is treated with conc. H_2SO_4 and MnO_2 in cast iron retorts. The vapours of iodine so evolved are condensed in stone wave receivers called *aludels*. (Fig. 9.4). The mother liquor which contains mainly sodium iodide is oxidized to I_2.

$$2NaI + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + 2H_2O + I_2$$

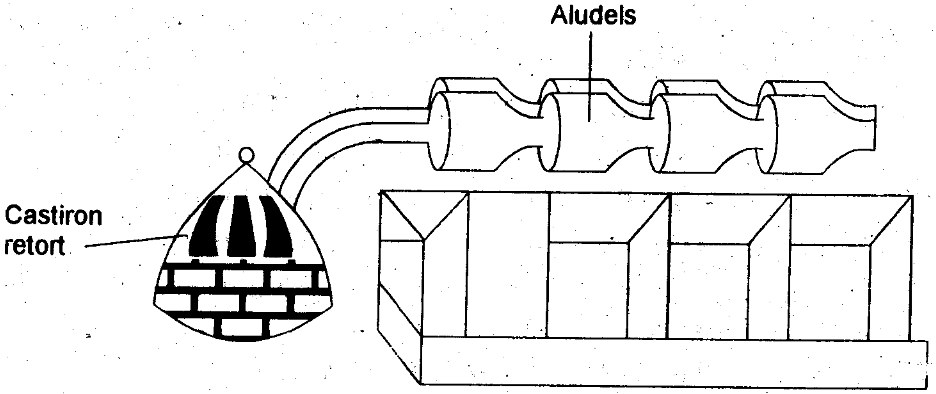


Fig. 9.4 Manufacture of iodine from sea weeds.

Iodine can also be prepared from Chile saltpetre. The mineral is treated with water and then crystallized, so that the bulk of $NaNO_3$ separates out and $NaIO_3$ being more soluble remains in mother liquor. Calculated amount of sodium hydrogen sulphite is added to the mother liquor which reduces the iodate, and iodine separates out.

$$2NaIO_3 + 5NaHSO_3 \longrightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$$

Properties

(i) Iodine is a grey black solid and its crystals possess a metallic lustre. However, its vapours are violet in colour. It melts at 113°C and boils at 184°C.

(ii) It is only slightly soluble in water giving a light brown solution. It is soluble in CCl_4 and CS_2 forming a violet solution.

(iii) It dissolves in KI to form KI_3.

$$KI + I_2 \longrightarrow KI_3$$

(iv) Iodine solution is decolourized by alkali solutions when heated forming iodide and iodate.

$$6NaOH + 3I_2 \longrightarrow 5NaI + NaIO_3 + 3H_2O$$

But if cold dilute solution of NaOH is taken, then hypoiodide is formed.

$$2NaOH + 3I_2 \longrightarrow NaI + NaIO + H_2O$$

(v) It reacts with many metals and non-metals to give iodides like Fe_3I_8, HgI_2, PbI_2, AsI_3, SbI_3, HI etc.

(vi) It oxidizes H_2S to S, $Na_2S_2O_3$ to $Na_2S_4O_6$, SO_2 to H_2SO_4 etc.

$$H_2S + I_2 \longrightarrow 2HI + S$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

$$SO_2 + H_2O + I_2 \longrightarrow 2HI + H_2SO_4$$

$$SnCl_2 + I_2 + 2HCl \longrightarrow SnCl_4 + 2HI$$

(vii) When warmed with alcohol and alkali, iodine gives iodoform.

$$C_2H_5OH + 6KOH + 4I_2 \longrightarrow CHI_3 + HCOOK + 5KI + 5H_2O$$

(viii) It is absorbed by unsaturated oils, thus iodine value of oil is determined. It is added to the double bond.

$$RCH = CHR + I_2 \longrightarrow RCHI.CHIR.$$

(ix) It turns freshly prepared solution of starch blue.

(x) Iodine, with water and red phosphorus gives HI.

$$2P + 5I_2 + 8H_2O \longrightarrow 10HI + 2H_3PO_4$$

Uses

(i) It is largely used in medicine, e.g., tincture of iodine, iodex as antiseptic and analgesic.

(ii) Solutions of iodine in KI are used in the treatment of goiter.

(iii) It is used in the manufacture of dyes.

(iv) It is used in analytical chemistry as an important reagent.

(v) AgI is used in photography.

(vi) NaI is added to table salt for supplying the body needs of iodine.

9.8 OXYACIDS OF HALOGENS

Fluorine forms no oxyacids. This is presumably due to the fact that fluorine has higher electronegativity than oxygen. Oxyacids given by Cl, Br and I are classified into four series:

1. Hypohalous acids, HXO
2. Halous acids, HXO_2
3. Halic acids, HXO_3
4. Perhalic acids, HXO_4

This classification depends on the oxidation state shown by the halogen atoms in these acids. Thus in these acids the halogen atoms show +1, +3, +5 and +7 oxidation states respectively. Some of these acids are quite unstable and are known only in solution or as salts. Different members of each series are given in Table 9.3.

Table 9.3 Oxyacids of Halogens

Oxidation States	Chlorine	Bromine	Iodine
+1	$HClO$	$HBrO$	HIO
+3	$HClO_2$	$HBrO_2$	--
+5	$HClO_3$	$HBrO_3$	HIO_3
+7	$HClO_4$	--	HIO_4
			H_5IO_6

General Properties

(i) In various molecules each hydrogen is a part of an –OH group and not directly attached to the halogen atom.

(ii) In the series of oxyacids of the same halogen in different oxidation states, the *acidic character* and *thermal stability* of these acids increase while the *oxidizing power* decreases with the increase of oxidation states of the halogen atoms. For example, the acidic character and thermal stability of the four oxyacids of the chlorine are in the order:

$$HClO\ (+1) > HClO_2\ (+3) > HClO_3\ (+5) > HClO_4\ (+7)$$

(iii) In the series of oxyacids of different halogens in the same oxidation state, the *thermal stability* and *acidic character* of these acids decrease, in general, with the increase of atom number of the halogen atom (i.e., with the decrease of electronegativity of halogen atom). For example, thermal stability and acidic character of HXO acids (X=Cl, Br, I) are in the order:

$$HClO\ (Cl=3.0) > HBrO\ (Br=2.8) > HI\ (I=1.2)$$

Note that that in the series of HXO_3, HIO_3 is the most stable. Iodine displaces bromine from $HBrO_3$ and bromates. Both iodine and bromine displace chlorine from $HClO_3$ and chlorates.

The clear cut generalization about oxyacids can be made as follows. Increasing oxygen content leads to:

(a) an increase in thermal stability.

(b) an increase in acid strength.

(c) a decrease in oxidizing power.

Here we shall discuss the oxyacids of chlorine.

1. Hypochlorous acid, $HClO$

Preparation

This acid is known only in solution. It is best prepared by shaking chlorine water with freshly precipitated mercuric oxide, HgO.

$$2Cl_2 + 2HgO + H_2O \longrightarrow HgCl_2 + 2HClO$$

Commercially it is prepared by passing CO_2 into a suspension of bleaching powder in water and then distilling.

$$2CaOCl_2 + CO_2 + H_2O \longrightarrow CaCl_2 + CaCO_3 + 2HClO$$

It may also be obtained by passing chlorine through water.

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

Properties

(i) The concentrated solution of the acid is yellow in colour while the dilute solution is colourless. It is a weak acid, even weaker than H_2CO_3.

(ii) The dilute solution of the acid is fairly stable in the dark while concentrated solution is unstable and hence decomposes into HCl and O_2. By heating or exposure to light.

$$2HClO \xrightarrow{\Delta} 2HCl + O_2$$

(iii) It dissolves Mg with the evolution of H_2, Fe and Al with the evolution of H_2 and Cl_2, while with Co, Ni and Cu it evolves Cl_2 and O_2.

$$Mg + 2HClO \longrightarrow Mg(OCl)_2 + H_2$$

(iv) It acts as a powerful oxidizing and bleaching agent. This behaviour of the acid is due to the fact that the acid can liberate the nascent oxygen quite easily.

$$HClO \longrightarrow HCl + O$$

Thus it liberates I_2 from the acidified KI solution and oxidizes $Cr(OH)_3$ to chromate in alkaline medium.

$$2KI + HCl + HClO \longrightarrow 2KCl + H_2O + I_2$$

$$2Cr(OH)_3 + 2NaOCl + 4NaOH \longrightarrow 2Na_2CrO_4 + 5H_2O + 3NaCl$$

(v) With alkalies, it forms salts called hypochlorites. Sodium hypochlorite ($NaClO$) and calcium chloro-hypochlorite, $Ca(OCl)Cl$, bleaching powder are two important salts.

Uses

It is used for bleaching paper pulp etc.

Structure

$$H—O—Cl \text{ (linear)}$$

2. Chlorous acid, $HClO_2$

Preparation

It is obtained by treating a suspension of barium chlorite with dilute sulphuric acid and filtering off the precipitate of $BaSO_4$.

$$Ba(ClO_2)_2 + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4\downarrow$$

Its salt is obtained by the action of alkali on chlorine peroxide, ClO_2. A mixture of chlorate and chlorite is formed.

$$2KOH + 2ClO_2 \longrightarrow KClO_2 + KClO_3 + H_2O$$

Properties

(i) The freshly prepared solution of the acid is colourless but it soon decomposes to ClO_2 which colours the solution yellow.

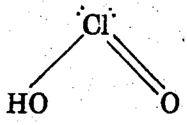
(ii) It undergoes auto-oxidation at ordinary temperature and changes into a mixture of HClO and $HClO_3$.

$$2HClO_2 \longrightarrow HClO + HClO_3.$$

(iii) The acid and its salts liberate I_2 from an iodide.

$$4KI + HClO_2 + H_2O \longrightarrow 4KOH + HCl + 2I_2$$

Structure



(angular shape)

3. Chloric acid, $HClO_3$

Preparation

The acid is known only in solution. It is conveniently prepared by the action of dilute H_2SO_4 on barium chlorate, $Ba(ClO_3)_2$.

$$Ba(ClO_3)_2 + H_2SO_4 \longrightarrow 2HClO_3 + BaSO_4\downarrow$$

Insoluble $BaSO_4$ is filtered off and the acid can be concentrated by evaporating in vacuum over sulphuric acid.

It can also be obtained by the action of potassium chlorate on hydrofluorosilicic acid.

$$2KClO_3 + H_2SiF_6 \longrightarrow K_2SiF_6 + 2HClO_3$$

Properties

(i) Concentrated acid is a colourless and pungent smelling liquid. It is fairly stable in the dark.

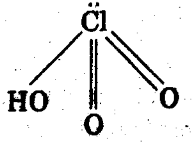
(*ii*) It decomposes on heating into perchloric acid, chlorine dioxide and water.

$$3HClO_3 \xrightarrow{\Delta} HClO_4 + 2ClO_2 + H_2O$$

(*iii*) It is a powerful oxidizing agent converting iodide into iodine.

$$6KI + HClO_3 + 5HCl \longrightarrow 6KCl + 3I_2 + 3H_2O$$

Structure



(trigonal pyramidal)

4. Perchloric acid, $HClO_4$

Preparation

It is the most stable oxyacid of chlorine. Anhydrous perchloric acid is prepared by distilling potassium perchlorate, $KClO_4$ with 96% H_2SO_4 under 10–20 mm pressure at 90–160°C.

$$KClO_4 + H_2SO_4 \longrightarrow KHSO_4 + HClO_4$$

It is purified by distilling at 40-60°C under 60mm pressure.

Properties

(*i*) The pure acid is a colourless fuming liquid (b.p = 90°C). It decomposes explosively when heated, and sometimes, merely after standing for some days.

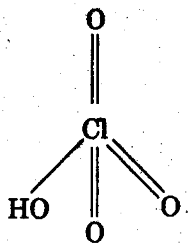
(*ii*) Combustible matterials, e.g., wood, paper and charcoal inflame spontaneously in contact with the acid.

(*iii*) It forms hydrates with 1, 2, 3, molecules of water of crystallization.

(*iv*) Aqueous solution of the acid is quite stable and does not decompose and hence can be kept indefinitely.

(*v*) It is highly dangerous acid and produces severe wounds on the skin.

Structure



(Tetrahedral)

9.9 INTERHALOGEN COMPOUNDS

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity, the halogen atoms combine with each other and give rise to the formation of binary covalent compounds which are called *interhalogen compounds*. These compounds are of four types:

1. AB type, (ClF, BrF, IF, BrCl, ICl, IBr)
2. AB_3 type, (ClF_3, BrF_3, IF_3, ICl_3)
3. AB_5 type, (ClF_5, BrF_5, IF_5)
4. AB_7 type, (IF_7).

'A' halogen atom is larger than 'B' atom. Interhalogen compounds are named as the halides of less electronegative halogen atom. Thus ClF is called *chlorine monofluoride* and not *fluorine monochloride*, since the electronegativity of Cl-atom is less than that of F-atom.

Some generalization can be made about these compounds as given below.

(a) Fluorine is never found as the central atom in the structure of these compounds. Firstly, fluorine seldom achieves a positive oxidation state and secondly, it cannot expand its coordination numbner beyond 4.

(b) The halogen with the largest atomic number is the central atom in any interhalogen combinations.

(c) The greater the difference of electronegativity between the halogens, the greater will be the number of bonds formed to the central atom of the structure.

Here we shall discuss the chemistry of each type by taking one example.

1. AB Type Interhalogens

Iodine monochloride, ICl

- **Preparation**

It is prepared by adding iodine to liquid chlorine and keeping the mixture at 30-35°C for 24 hours.

$$I_2 + Cl_2 \longrightarrow 2ICl$$

From this product, two forms of ICl can be separated by fractional melting.

It can also be obtained by reacting aqueous solution of potassium iodide and iodate with HCl.

$$KIO_3 + 5KI + 6HCl \longrightarrow 3I_2 + 2H_2O + 6KCl$$

$$KIO_3 + 2I_2 + 6HCl \longrightarrow KCl + 5ICl + 3H_2O$$

Properties

(*i*) It solidifies on standing even at room temperature (15-25°C). From this solid two forms of the compound may be obtained:

α-form having ruby red crystals (m.p=27.2°C) and β-form having brown red crystals (m.p=13.9°C). These two forms are identical in the gaseous state.

(*ii*) ICl is soluble in water and gets hydrolysed by it.

$$5ICl + 3H_2O \longrightarrow 2I_2 + 3HIO_3 + 5HCl$$

(*iii*) It also dissolves in alkalies to form iodine, iodate and chloride.

$$5ICl + 6NaOH \longrightarrow 2I_2 + NaIO_3 + 5NaCl + 3H_2O$$

(*iv*) It is an electrical conductor and in the molten state ionizes as:

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

(*v*) It reacts with PCl_5, $SbCl_5$, $AlCl_3$ etc. to form ionizing acidic solution.

$$ICl + PCl_5 \longrightarrow I^+[PCl_6]^-$$

Structure

$$I —— Cl \quad \text{(linear)}$$

2. AB_3 Type Interhalogens

Iodine trichloride ICl_3

Preparation

It is obtained by the action of excess of chlorine on iodine or on ICl at 100°C.

$$I_2 + 3Cl_2(\text{excess}) \longrightarrow ICl_3$$

$$ICl + Cl_2(\text{excess}) \longrightarrow ICl_3$$

It is also formed when dry HCl gas reacts with heated I_2O_5.

$$I_2O_5 + 10HCl \longrightarrow 2ICl_3 + 5H_2O + 2Cl_2$$

Properties

(*i*) It is a lemon yellow crystalline solid which fumes readily.

(*ii*) It is soluble in organic solvents, liq. NH_3 and liq. SO_2.

(*iii*) It forms crystalline additive compounds with metallic chlorides.

$$MCl + ICl_3 \rightleftharpoons MICl_4$$

(*iv*) It is completely hydrolysed by water.

$$2ICl_3 + 3H_2O \longrightarrow 5HCl + HIO_3 + ICl$$

(*v*) It dissociates on heating at 68°C giving ICl and Cl_2.

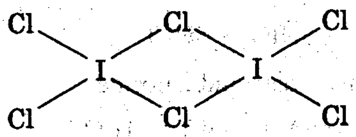
$$ICl_3 \xrightarrow{\Delta} ICl + Cl_2$$

(*vi*) It reacts with CS_2 as:

$$4ICl_3 + 3CS_2 \longrightarrow CCl_4 + 2CSCl_2 + 2S_2Cl_2 + 2I_2$$

Structure

Most of this type of compounds have T-shaped structure. However, X-rays analysis of the crystals of ICl_3 shows that it has dimeric structure.



(Dimeric structure)

3. AB_5 Type Interhalogens

Iodine pentafluoride, IF_5

Preparation

It is formed by the direct combination of the elements or by the action of F_2 on heated I_2O_5.

$$2I_2O_5 + 10F_2 \longrightarrow 4IF_5 + 5O_2$$

It may also be prepared by heating together AgF and I_2.

$$3I_2 + 5AgF \longrightarrow IF_5 + 5AgI$$

Properties

(*i*) It is a colourless liquid (b.p=98°C). Its vapors attack the respiratory organs.

(*ii*) It decomposes on heating to I_2 and IF_7.

$$7IF_5 \xrightarrow{\Delta} I_2 + 5IF_7$$

(*iii*) It is readily hydrolysed by water.

$$2IF_5 + 5H_2O \longrightarrow I_2O_5 + 10HF$$

(*iv*) It reacts with I_2O_5 and gives white crystals of $1OF_3$.

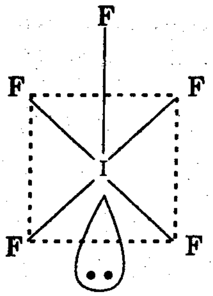
$$3IF_5 + I_2O_5 \longrightarrow 5IOF_3$$

(*v*) The oxides of P_2O_5, V_2O_5, Sb_2O_5, Cr_2O_3 and WO_3 dissolve in hot IF_5 to form POF_3, VOF_3, $SbF_5.IO_2$, CrO_2F_2 and $WO_3.2IF_5$ respectively.

(*vi*) It gives addition product with certain potassium salt.

$$IF_5 + KF \longrightarrow KIF_6$$

Structure



(Square pyramidal structure)

4. AB_7 Type Interhalogens

Iodine heptafluoride, IF_7

Preparation

It may be prepared by refluxing IF_5 in a current of excess of F_2 through a tube of Pt heated at 270⁰C.

$$IF_5 + F_2 \xrightarrow{270°C} IF_7$$

When iodine reacts with excess of F_2 at 300°C, IF_7 is formed.

Properties

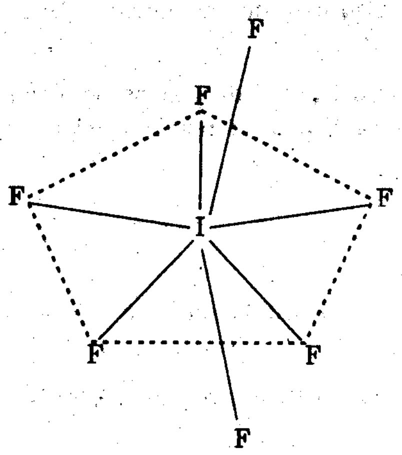
(i) It is a colourless gas and can be condensed to a colourless liquid or to a crystalline solid.

(ii) It reacts with most metals (except the platinum group), non-metals and water to give periodate and fluoride ions.

$$IF_7 + 6H_2O \longrightarrow 7HF + H_5IO_6$$

(iii) It explodes when heated with H_2.

Structure



(Pentagonl bipyramidal shape)

9.10 PSEUDOHALOGENS AND PSEUDOHALIDES

There are certain uninegative groups which show a similarity to halide ions in both their ionic and covalent compounds. These groups are known as *pseudohalogens*. They would form covalent dimers just like halogen molecules. The covalent dimer of four of these has been isolated. These are:

Cyanogen, $(CN)_2$

Thiocyanogen, $(SCN)_2$

Selenocyanogen, $(SeCN)_2$

Azidocarbondisulphide, $(SCSN_3)_2$

Preparation

Cyanogen $(CN)_2$ is made by heating AgCN alone or $Hg(CN)_2$ with $HgCl_2$.

$$2AgCN \longrightarrow 2Ag + (CN)_2$$

$$Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2$$

Thiocyanogen is released by the action of bromine on AgSCN suspended in ether.

$$2AgSCN + Br_2 \longrightarrow 2AgBr + (SCN)_2$$

Selenocyanogen is displaced by iodine from AgSeCN.

$$2AgSeCN + I_2 \longrightarrow 2AgI + (SeCN)_2$$

Azidocarbondisulphide is formed as white crystals when $KSCSN_3$ is oxidized with H_2O_2.

$$CS_2 + KN_3 \longrightarrow KSCSN_3 + H_2O_2 \longrightarrow (SCSN_3)_2$$

Similarities between Halogen and Pseudohalogens

The following points show the similarities between the halogens and pseudohalogens.

(i) Like halogens, pseudohalogens are also dimeric and fairly volatile in the free state.

(ii) With hydrogen the uninegative groups form hydrogen pseudohalides just like hydrogen halides. However, they are weak acids compred with halogen acids.

HCl PKa = −7.0
HCN PKa = 8.9
HN_3 PKa = 4.4

(iii) The silver, lead and mercurous salts of pseudohalides are sparingly soluble in water just like corresponding halides.

(iv) Like halogens, pseudohalogens also react with alkalies. For example,

$$Cl_2 + 2KOH \longrightarrow KCl + KOCl + H_2O$$
$$(CN)_2 + 2KOH \longrightarrow KCN + KOCN + H_2O$$

(v) Like halogens, they also form addition compounds with olefins and other unsturated molecules.

$$C_2H_4 + Br_2 \longrightarrow BrC_2H_4Br$$
$$C_2H_4 + (SCN)_2 \longrightarrow NCSC_2H_4SCN$$

(vi) Inter-pseudohalogen compounds and pseudohalogen – halogen compounds are known. Cyanogen chloride and bromode, CNCl and CNBr result from the action of Cl_2 and Br_2 on HCN. Some compounds CN(SCN) and CN(SeCN) have been obtained in crystalline form.

(vii) Pseudohalides form ions analogous to polyhalide ions. $NH_4(SCN)_3$ and $K(SeCN)_3$ resemble KI_3.

(viii) Like halide ions, pseudohalide ions also form complex ions with transition metal ions. For example

$[FeF_6]^{-3}$, $[CoCl_4]^{-2}$
$[Fe(CN)_6]^{-3}$, $[Hg(CN)_4]^{-2}$

(ix) Like halide ions, a pseudohalide ion is oxidized to the parent pseudohalogen by suitable oxidizing agents.

$$2Fe^{3+} + 2SCN^- \longrightarrow 2Fe^{2+} + (SCN)_2$$

or simply by heating the lead (IV) salts.

$$Pb(SCN)_4 \xrightarrow{\Delta} Pb(SCN)_2 + (SCN)_2$$
$$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2$$

(x) Like halide ions, pseudohalide ions also form ionic as well as covalent compounds. Ionic compounds are given by these ions with metals while covalent compounds are given by these ions with non-metals. For example,

AgCl(AgCN),	$PbCl_2$ [$Pb(SCN)_2$]	ionic
ICl (ICN),	$SiCl_4$[$Si(NCS)_4$]	Covalent

(xi) Pseudohalogens are also isomorphous to halogen. For example, Cl_2 is isomorphous to (CN_2) and similarly Br_2 is isomorphous with $(SCN)_2$.

(xii) Like halide ions, pseudohalide ions also have more than one pair of electrons and hence can coordinate with two metal ions simultaneously. Consequently like halide ions, pseudohalide ions can also act as bridging ligands.

Questions

Q.1 (a) What are halogens? Write the electronic configuration of all the members of group VIIA (17).

(b) Explain gradation in properties and general group trends of group VIIA (17)of the periodic table.

Q.2 (a) In what important respects does fluorine resemble and differ the members of its family.

(b) Give the reasons for the abnormal behaviour of fluorine.

Q.3 (a) How is fluorine commercially prepared. Discuss its characteristic properties and anomalous behaviour with respect to other halogens.

(b) Complete and balance the following equations:

(i) $S + F_2 \longrightarrow$

(ii) $H_2O + F_2 \longrightarrow$

(iii) $KI + F_2 \longrightarrow$

(iv) $NH_3 + F_2 \longrightarrow$

(v) $H_2S + F_2 \longrightarrow$

Q.4 (a) Give various methods for the manufacture of chlorine gas. Also write some uses of chlorine.

(b) What happens when?

(i) Cl_2 reacts with SO_2

(ii) Cl_2 reacts with CO

(iii) Cl_2 reacts with NaOH

(iv) Cl_2 reacts with H_2O

(v) Cl_2 treated with H_2S

Q.5 (a) What are the important sources of Br_2? How is it obtained on a large scale?

(b) Starting from Br_2, how will you prepare KBr, $HBrO_3$, HBr gas, $NaBrO_3$ and NaBrO.

(c) What are the uses of Br_2?

Q.6 (a) How is iodine manufactured?

(b) Complete and balance the following equations:

(i) $KI + I_2 \longrightarrow$

(ii) $NaOH + I_2 \longrightarrow$

(iii) $H_2S + I_2 \longrightarrow$

(iv) $P + I_2 + H_2O \longrightarrow$

(v) $Na_2S_2O_3 + I_2 \longrightarrow$

Q.7 *(a)* Name the various oxyacids of chlorine. Discuss their preparation, properties and structures.

(b) Which is the strongest acid of the following?

$HClO_2$, $HClO_3$, $HClO$ and $HClO_4$

Q.8 What are interhalogens? Discuss the chemistry of AB, AB_3, AB_5 and AB_7 type interhalogens.

Q.9 *(a)* What are pseudohalogens? How are they prepared?

(b) How do halogens resemble with pseudo halogens?

Q.10 Justify/comment on the following statements:

(a) Chlorine is a stronger oxidizing agent than iodine.

(b) Fluorine cannot be prepared by the electrolysis of aqueous NaF solution.

(c) Bond energy of F_2 molecule is very small.

(d) F_2 has greater reactivity.

(e) F_2 is the most reactive of all the elements.

(f) Fluorine does not form oxy–acids.

(g) HI is the stronger acid than HF.

(h) HF molecule is polymeric in the gaseous state while other halogen acids do not show this property.

(i) Electronegativity of halogens decreases in the order

$$I > Br > Cl > F$$

(j) Fluorine differs from other halogens.

(k) Fluorine is a non–metal while iodine shows metallic character.

(l) Iodine is more soluble in KI solution than in H_2O.

(m) The strength of oxy–acids of chlorine decreases in the following order:

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

(n) The strength of halogen–acids decreases in the following order

$$HF > HI > HCl > HBr$$

(o) Fluorine is pale yellow in colour while iodine appears deep violet.

(p) Halogens exhibit variable oxidation states.

(q) The electron affinity of fluorine is smaller than chlorine.

(r) ClF_3 is known as interhalogen.

(s) IF_5 has square pyramidal structure.

(t) Cyanogen resembles with halogens.

Chapter Ten

ZERO GROUP ELEMENTS

10.1 INTRODUCTION

Group VIIIA (18) of the periodic table consists of helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). All these gaseous elements are generally called *inert gases* because they are chemically inert substances and exist only in the free state. These gases are also called *noble gases* because of the chemical inertness. Sometimes they are also called *rare gases* because they exist only in minute quantities in the atmosphere.

The noble gases are found in the atmosphere to the extent of about 1 percent by volume. Argon is the principal constituent there of. The noble gas content of the atmosphere is given below:

He: 0.0005 per cent by volume

Ne: 0.0015 per cent by volume

Ar: 0.94 per cent by volume

Kr: 0.0001 per cent by volume

Xe: 0.00001 per cent by volume

Many gases issuing from mineral springs are found to contain appreciable quantities of helium (0.7 to 2.0 per cent). Helium and also sometimes, neon are found in certain minerals of radioactive origin, e.g., *pitchblende, cleveite, monazite* sand and *thorianite* in the absorbed state. Radon is obtained only in the radioactive decay of radium, thorium or actinium. It does not gather in quantities since its half-life period is very short (3.82 days).

Except helium, all other elements have eight electrons in their outer most shell with two electrons in the s–orbital and six electrons in the p–orbital as shown in Table 10.1

Table 10.1 Electronic configuration of Group VIIIA(18) Elements

Element	At. No.	Electronic Configuration
He	2	$1s^2$,
Ne	10	$1s^2, 2s^2\,2p^6$
Ar	18	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6$
Kr	36	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6$
Xe	54	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6\,4d^{10}, 5s^2\,5p^6$
Rn	86	$1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6\,4d^{10},$ $5s^2 5p^6 5d^{10}, 6s^2 p^6$

It is obvious from the above configurations that all the elements have ns^2p^6 configuration (except helium) in their valence shell. In other words all the elements have saturated shells.

Chemical Inertness of Rare Gases

The chemical inertness of these elements is due to the following reasons:

1. We have already seen that the atoms of rare gases have saturated shells. They all have eight electrons in their outer most shells, except helium which has two. They have, therefore, no tendency either to lose, gain or share electrons with atoms of other elements. These elements thus do not enter into chemical combinations.
2. The atoms of these elements have all the electrons paired. Thus, the electrons are not available for sharing with the electrons of other atoms. Hence they cannot form covalent compounds.
3. The electronegativity and electron affinity of these elements are zero. Thus, these elements have no tendency to accept electrons and hence, are unable to form compounds.
4. The ionization potentials of these gases are very high. Hence, the removal of electron from the outer most shell is very difficult.

Some of the important physical properties of group VIIIA (18) elements are summarized in Table 10.2.

Table 10.2 Physical properties of Group VIIIA(18) Elements

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic weight	4.00	20.18	39.94	83.80	131.30	222.00
Boiling Point (°C)	−268.9	−246.1	−185.9	−153.2	−108.0	−61.8
Melting Point (°C)	−272.2	−248.6	−189.4	−156.6	−111.5	−71.0
Atomic radius (nm)	0.05	0.07	0.094	0.109	0.130	–
Ionization energy I(kJmol^{-1})	2372	2080	1521	1351	1170	1037
Density (g/cm^3)	0.126	1.204	1.65(s)	2.6	3.06	4.4

10.2 POSITION IN THE PERIODIC TABLE

The noble gases namely, helium, neon, argon, krypton, xenon and radon occupy a peculiar position in chemistry. They formed practically no chemical compounds, and yet for that very reason they provided the key to the whole problem of valency and interpretation of the periodic classification.

The inert gases were not known at the time of Mendeleev when he gave his original classification of elements. He did not leave gaps for these gases although he left gaps for several other unknown elements. After their discovery a new group was introduced into the periodic tale. In the modern periodic table, these may be placed in the *zero group* as well as in *VIII group* because of the following reasons.

1. These elements are chemically inert. The existence of such a group is expected from the fact that there must be a separating group between strongly electronegative halogens of VIIA group and strongly electropositive alkali metals of 1A group. Therefore, these elements should be placed in between VIIA group and 1A group, i.e., in the zero group. This is also in agreement with the law of periodic system, since only zero valency might be expected in group VIIIA from the way in which negative valency decreases with increase of group number from group IVA onward (e.g., C, -4; N, -3;, O, -2; F, –1 and Ne,0).
2. Valency is defined as the combining capacity of the element. The electronic configurations of these elements given as: He→($1s^2$), Ne→2, ($2s^2p^6$), Ar→2, 8($3s^2p^6$), Kr→2, 8, 18($4s^2p^6$), Xe→2, 8, 18, 18($5s^2p^6$), Rn→2, 8, 18, 32, 18($6s^2p^6$) indicate that the atoms of these elements have saturated shells. They have, therefore, no tendency either to lose, gain or share electrons with the atoms of other elements. In other words, their combining capacity or valency is zero. Therefore, these elements should be placed in the zero group.
3. Electronic configurations of inert gases as given above indicate that, except helium which has $1s^2$ configuration, all the other elements have eight electrons in the outer most shell. Therefore, on this basis they should be placed in the VIII group.

10.3 ISOLATION OF NOBLE GASES

Helium is commercially obtained from natural gases and certain minerals. Radon is produced as a product of radioactive change; for the remaining gases atmosphere is the only available source. The chief method for the isolation of these gases is the *fractional distillation* of liquid air. Some chemical methods are also known but they are of little importance. Fractionation of liquid air is being described below:

Isolation of the Noble Gases from Liquid air

Industrially, the noble gases are obtained by the fractionation of liquid air. The method is based on the differences in the boiling points of different constituents of liquid air at atmospheric pressure. The boiling points of these gases are:

Helium	-268.9^0C	(4.1K)
Neon	-246.1^0C	(26.9K)
Nitrogen	-195.8^0C	(77.9K)
Argon	-185.9^0C	(87.1K)
Oxygen	-183^0C	(90K)
Krypton	-153.2^0C	(119.8K)
Xenon	-108^0C	(165K)

Because of the differences in boiling points, the noble gases from liquid air come in three different fractions:

(i) First fraction —— mixture of nitrogen, neon and helium

(ii) Second fraction —— mixture of argon and oxygen

(iii) Third fraction —— mixture of oxygen, krypton and xenon.

The separation of the gases from these fractions is described below.

First fraction: The first fraction containing He, Ne and N_2 is passed through a spiral tube cooled by liquid nitrogen. Here most of the nitrogen is condensed and a mixture of He, Ne and some N_2 passes out. The remaining nitrogen is removed by passing the mixture over heated calcium carbide.

$$CaC_2 + N_2 \xrightarrow{800°C} CaCN_2 + C$$

The gaseous mixture containing He and Ne is then passed through a spiral tube cooled by liquid H_2 at -253^0C when Ne solidifies (b.p=-246^0C) and is collected at the bottom, while He in the gaseous state escapes from the top.

Second fraction: The second fraction containing argon and oxygen is passed through a column which is provided with a coil in which liquid N_2 is being circulated. Here most of the oxygen condensed while more of argon escapes at the top. The argon so obtained, still contains some oxygen which is removed by passing over heated copper.

$$2Cu + O_2 \longrightarrow 2CuO$$

Third fraction: From the third fraction containing liquid O_2, Kr and Xe, oxygen is removed by evaporation. The remaining liquid becomes richer in Kr and Xe. These two may be separated easily by fractional evaporation as there is a wide difference in their boiling points. (Kr = −153.2°C, Xe=108°C).

10.4 GENERAL CHARACTERISTICS AND TRENDS

General characteristics and group trends of noble gases are as follows:

(i) **Electronic structures:** All the inert gases with the exception of helium have an octet of electrons (s^2p^6) in their outer most shells. The two electrons of helium form the complete shell, $1s^2$. Many of the properties of the noble gases including their inertness are ascribed to these closed shell structures.

(ii) **Ionization energies:** The noble gases have higher ionization energies than any other elements. The atoms are hence polarizable only with difficulty.

(iii) **Melting and boiling points**: All the noble gases are low boiling gases whose physical properties vary fairly systematically with atomic number. The melting and boiling points of the helium are the lowest of any known substance. The boiling points increase with increasing atomic number.

(iv) **Atomic radii**: There is a systematic increase in their atomic radii with rise of atomic numbers.

(v) **Forces of attraction between atoms of noble gases**: The noble gases are monoatomic and the fact that these gases can be liquefied shows the existence of some forces of attraction between the atoms. Since there are no ordinary electron pair interactions between noble gas atoms, these weak forces must be of vander Waals type. The magnitude of these forces seldom exceeds a few kJ/mol and such forces are proprotional to the polarizability and inversely proportional to the ionization potentials of the atoms. The polarizability of the noble gas atoms increases with increasing atomic radius, thus leading to increased van der Waals forces between the atoms. This is in accord with the rise of melting and boiling points on passing from helium to radon.

(vi) **Chemical reactivity**: All these elements are almost chemically inert. Their ability to enter into chemical combinations with other atoms is very limited. This ability would be expected to increase with decreasing ionization energy down the group. According to the present knowledge, the threshold of actual chemical activity is reached only at Kr. The chemical activity of Xe is markedly greater. That of radon is presumably still greater but it is difficult to assess in detail because of the experimental limitations. Recent researches have shown that under certain specified conditions, they enter into chemical combinations and form some rare chemical compounds which are described below:

Helides: These are compounds of helium which are formed by sparking helium at low pressure in presence of mercury, tungsten etc; e.g., $HgHe_2$, WHe_2, FeHe. In these compounds, it is supposed that helium is adsorbed on the surface of metal and therefore, these compounds are not considered as true chemical compounds.

Hydrates: The inert gases Ar, Kr and Xe form compounds with water at low temperature and high pressure. These compounds are known as hydrates. The compounds like $Ar.6H_2O$, $Kr.6H_2O$ and $Xe.6H_2O$ have been obtained and studied.

Clathrates: The inert gases Ar, Kr and Xe form solid compounds with certain organic molecules such as phenol, hydroquinone under pressure. In these compounds the inert gases are enclosed into the crystal lattices of the organic molecules. These compounds are known as clathrates. These are also referred to as *cage compounds*.

Compounds with BF_3: Booth and Wilson in 1935 reported that argon forms a number of unstable compounds with varying numbers of BF_3 molecules, e.g., $Ar.BF_3$, $Ar.2BF_3$, $Ar.3BF_3$, $Ar.6BF_3$, $Ar.8BF_3$ and $Ar.16BF_3$. In these compounds, argon atom donates a pair of electrons to boron atom.

Compounds with fluorine: Xenon has been found to combine with the most electronegative, fluorine to form XeF_2, XeF_4 and XeF_6.

10.5 CHEMISTRY OF XENON COMPOUNDS

1. Xenon difluoride, XeF_2

Preparation

(i) It is obtained by irradiating a mixture of xenon and fluorine with light from a high pressure mercury arc.

$$Xe + F_2 \longrightarrow XeF_2$$

(ii) It may also be made by heating xenon and fluorine in the ratio of 1:3 in a nickel tube at 400°C. On cooling the vapors it is obtained as colourless solid.

$$Xe + F_2 \xrightarrow[400^0C]{Ni} XeF_2$$

Properties

(i) Xenon difluoride is a white crystalline solid at room temperature and can be sublimed. Its melting point is 140°C.

(ii) It acts as a fluorinating agent, since it can fluorinate ethylene, propylene, benzene, nitric oxide, nitrogen peroxide and sulphur trioxide.

$$2H_2C{=}CH_2 + 2XeF_2 \longrightarrow FH_2C{-}CH_2F + F_2HC{-}CH_3 + 2Xe$$

$$C_6H_6 + XeF_2 \longrightarrow C_6H_5F + Xe + HF$$

$$2NO + XeF_2 \longrightarrow 2NOF + Xe$$

(iii) It is hydrolysed in water especially in alkaline solution.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

(iv) It can oxidize a number of compounds and is itself reduced to Xe.

$$H_2 + XeF_2 \longrightarrow 2HF + Xe$$

$$I_2 + XeF_2 \longrightarrow 2IF + Xe$$

$$2HCl + XeF_2 \longrightarrow Cl_2 + 2HF + Xe$$

$$2Cl^- + XeF_2 \longrightarrow Cl_2 + 2F^- + Xe$$

(v) It undergoes substitution reactions when treated with strong protonic acids like HSO_3F, $HClO_4$, CF_3COOH etc.

$$XeF_2 + 2HX \longrightarrow XeX_2 + 2HF$$

$$(X = SO_3F^-, ClO_4^-, CF_3COO^- \text{ etc.})$$

(vi) It can react with covalent pentafluorides like PF_5, SbF_5 etc. and form addition products called *adducts*.

$$XeF_2\ SbF_5 \longrightarrow XeF_2.SbF_5$$

$$XeF_2 + IF_5 \longrightarrow XeF_2.IF_5$$

2. Xenon tetrafluoride, XeF_4

Preparation

This is the easiest of xenon fluorides to prepare and it is obtained when a mixture of xenon and fluorine in the ratio of 5:1 is heated in a nickel vessel at 400°C and 6 atmospheric pressure for few hours.

$$Xe + 2F_2 \xrightarrow[6\text{ atm.}]{400^0C} XeF_4$$

Properties

(i) Xenon tetrafluoride is a white crystalline solid at room temperature and can be sublimed readily. Its melting point is 117°C.

(ii) It is a strong fluorinating agent, since it can fluorinate a number of compounds. For example,

$$2SF_4 + XeF_4 \longrightarrow 2SF_6 + Xe$$

$$Pt + XeF_4 \longrightarrow PtF_4 + Xe$$

$$2C_6H_6 + XeF_4 \longrightarrow 2C_6H_5F + 2HF + Xe$$

$$4NO + XeF_4 \longrightarrow 4NOF + Xe$$

(iii) It is very susceptible to hydrolysis and gives XeO_3 (an explosive).

$$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 3O_2 + 24HF$$

(iv) It can oxidize a number of compounds and itself is reduced to Xe. For example,

$$XeF_4 + 2H_2 \xrightarrow{130^0C} 4HF + Xe$$

$$XeF_4 + 2Hg \longrightarrow 2HgF_2 + Xe$$

$$XeF_4 + 4I^- \longrightarrow 2I_2 + 4F^- + Xe$$

(v) When it is warmed with excess of xenon, XeF_2 is obtained.

$$XeF_4 + Xe\ (Excess) \longrightarrow 2XeF_2$$

(vi) It can react with covalent pentafluorides like PF_5, AsF_5, SbF_5 etc. and forms addition products called *adducts*.

$$XeF_4 + SbF_5 \longrightarrow XeF_4.SbF_5$$

$$XeF_4 + PF_5 \longrightarrow XeF_4.PF_5$$

3. Xenon hexafluoride, XeF_6

Preparation

(i) It is very difficult to prepare. However, it is prepared by heating a mixture of Xe and F_2 in the ratio of 1:20 in a nickel vessel at 200-250°C and 50 atmospheric pressure.

$$Xe + 3F_2 \longrightarrow XeF_6$$

(ii) It is also formed by the reduction of XeF_4 with O_2F_2 at −130°C.

$$XeF_4 + O_2F_2 \longrightarrow O_2 + XeF_6$$

Properties

(*i*) Xenon hexafluoride is a colourless solid at 43°C; it becomes yellow above 43°C and melts to a yellow liquid at 47.7°C. Its vapour is also yellow.

(*ii*) It is stable at room temperature and can be stored indefinitely in a nickel container. With quartz and glass it reacts rapidly to give $XeOF_4$.

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

(*iii*) It is extremely readily hydrolysed.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

(*iv*) Out of the three xenon fluorides, XeF_6 is the best fluorinating agent.

(*v*) It can oxidize a number of compounds and is itself reduced to Xe.

$$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$$

$$XeF_6 + 6HCl \longrightarrow 3Cl_2 + 6HF + Xe$$

(*vi*) On strong heating it decomposes to give XeF_4 and XeF_2.

$$2XeF_6 \xrightarrow{\Delta} XeF_4 + XeF_2$$

(*vii*) It also reacts with covalent fluorides and forms adducts.

$$XeF_6 + BF_3 \longrightarrow XeF_6.BF_3$$

$$XeF_6 + SbF_5 \longrightarrow XeF_6.SbF_5$$

4. Xenon trioxide, XeO_3

Preparation

(*i*) It can be obtained in small quantities by the hydrolysis of XeF_4 or XeF_6.

$$2XeF_4 + 3H_2O \longrightarrow XeO_3 + Xe + 6HF + F_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

(*ii*) It can also be prepared by hydrolysing $XeOF_4$.

$$XeOF_4 + 2H_2O \longrightarrow XeO_3 + 4HF$$

Properties

(*i*) XeO_3 is a white non-volatile deliquescent solid and soluble in water. It explodes violently, when dry, on gentle heating, rubbing or pressing. It produces the same effect as T.N.T.

(*ii*) Its aqueous solution is weakly acidic due to the formation of xenic acid.

$$XeO_3 + 2H_2O \longrightarrow H_2XeO_4 \longrightarrow H^+ + \underset{\text{(xenate ion)}}{HXeO_4^-}$$

(*iii*) It is a strong oxidizing agent and oxidizes Pu^{3+} to Pu^{4+} in the presence of H^+ ions.

$$6Pu^{3+} + XeO_3 + 6H^+ \longrightarrow 6Pu^{4+} + Xe + 3H_2O$$

(iv) It reacts with $XeOF_4$ to form XeO_2F_2.

$$XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$$

5. Xenon oxytetrafluoride, $XeOF_4$

Preparation

(i) It is prepared by the controlled hydrolysis of XeF_6 with equimolar quantity of water.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

(ii) It is also formed when XeF_6 is kept in glass or silica.

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

Properties

(i) It is a colourless mobile liquid which can be stored unchanged in nickel containers for long period.

(ii) It reacts with hydrogen to form xenon gas at 300°C.

$$XeOF_4 + 3H_2 \longrightarrow Xe + H_2O + 4HF$$

(iii) With silica, it results in the formation of explosive trioxide, XeO_3.

$$XeOF_4 + SiO_2 \longrightarrow XeO_3 + SiF_4$$

(iv) It reacts with water to form explosive trioxide, XeO_3.

$$XeOF_4 + 2H_2O \longrightarrow XeO_3 + 4HF$$

(v) It reacts with XeO_3 to give XeO_2F_2.

$$XeOF_4 + XeO_3 \longrightarrow 2XeO_2F_2$$

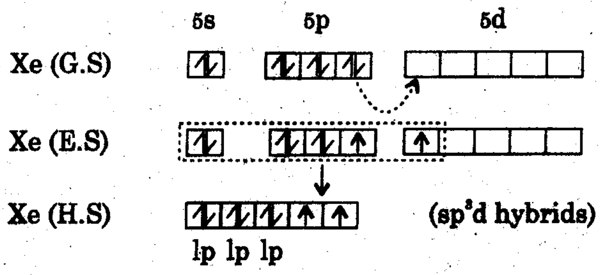
(vi) It also forms a few complexes with fluoride ion accepters e.g., $XeOF_4.2SbF_5$.

10.6 NATURE OF BONDING AND STRUCTURE OF XENON COMPOUNDS

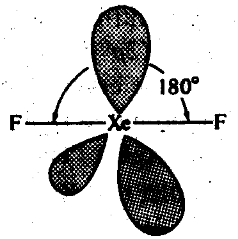
Bonding in noble gas compounds has so far been considered only in relation to fluorides, and special emphasis has been placed on whether a particular theoretical treatment can predict the geometry of fluoride correctly. There are currently two approaches to the problem of bonding in noble gas compounds. Neither is completely satisfactory but between the two they account adequately for the properties of these compounds.

1. Valence Bond Approach

The valence bond approach would treat the xenon fluorides by means of expanded valence shells through promotion of electrons to the 5d orbitals. Let us discuss the geometries of various fluorides. In XeF_2 molecule, Xe atom undergoes sp^3d hybridization having two partially filled orbitals for fluorine atoms.



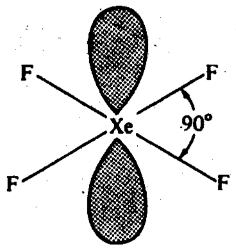
The *sp³d* hybridization results in trigonal bipyramidal structure. The three equatorial hybrid orbitals have lone pairs and the remaining axial hybrid orbitals have one electron each. These orbitals overlap with $2p_x$ orbitals of two F-atoms and form two Xe-F sigma bonds. Due to the presence of lone pairs, XeF_2 molecule assumes a linear shape with Xe-F bond lengths equal to 2.0Å. (Fig. 10.1)



Linear molecule with three nonbonding electron pairs at the points of an equilateral triangle

Fig. 10.1 Geometry of XeF_2 molecule.

In XeF_4 molecule, Xe atom undergoes sp^3d^2 hybridization having four partially filled orbitals for four fluorine atoms. The sp^3d^2 hybridization results in square bipyramidal structure in which Xe is the central atom. The two lone pair of electrons occupy axial position in order to have minimum lone pair repulsion. Other four equatorial hybrid orbitals overlap with $2p_x$ orbitals of four F-atoms resulting in a square planar geometry. (Fig. 10.2)



Square planar molecule with two nonbonding electron pairs, one above and one below the plane of the molecule

Fig. 10.2. Geometry of XeF_4 molecule.

Geometries of XeF_6, XeO_3 and $XeOF_4$ are shown in Fig. 10.3.

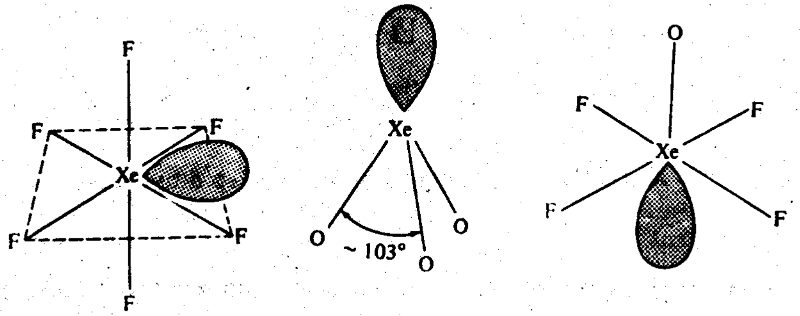


Fig. 10.3. Geometries of XeF_6, $XeOF_4$ and Xe_2O_3 molecules.

2. Molecular Orbital Theory:

The molecular orbital theory involves three centres, four electron bonds. Consider the linear F-Xe-F molecule. A 5*p* orbital on the xenon can overlap with a fluorine bonding orbital (either a pure p orbital or hybrid) to form the usual trio of three-central orbitals: bonding, non-bonding and anti-bonding (Fig. 10.4). Filling in the four electrons [Xe($(5p^2)$ + $F(2p^1)$ + $F(2p^1)$] results in a filled bonding orbital and a filled non-bonding orbital. A single bond (or bonding MO) is thus spread over the F-Xe-F system. A second p–orbital at right angles to the first can form a second three-centre F-Xe-F bond (XeF_4). The nature of the *p*–orbitals involved in the bonding allows one to predict that XeF_2 will be linear and XeF_4 square planar.

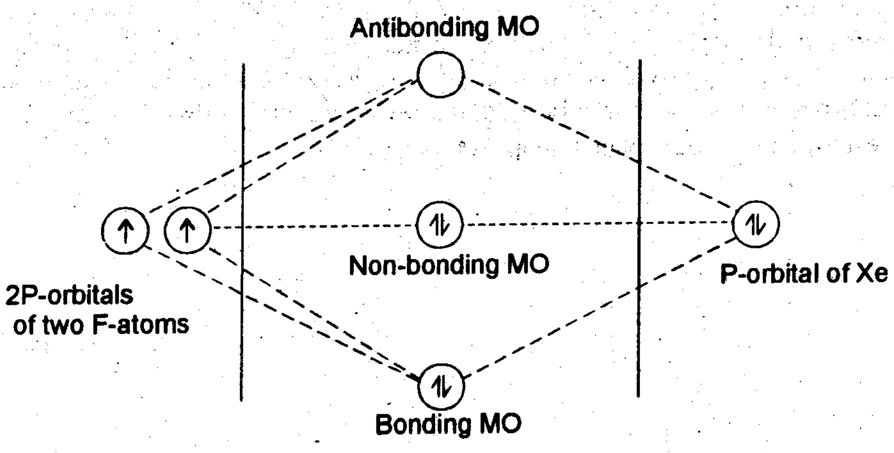


Fig. 10.4. Molecular orbital diagram for XeF_2 molecule.

10.7 LABORATORY AND COMMERCIAL USES OF NOBLE GASES

Of all the noble gases, only helium and argon which are available easily and in plenty have got many uses. The uses are due to their chemical inertness and low boiling points. Important uses of noble gases are given below:

Helium

(i) It is used in gas cooled atomic reactors as a heat transfer gas, i.e., as a cooling medium.

(ii) It is used in the treatment of asthma with oxygen.

(iii) It is used for filling in balloons and airships as it is a light and non-combustible gas.

(iv) The mixture of helium and oxygen is used for respiration by sea divers.

(v) Liquid helium is used for producing low temperatures required for research work.

(vi) It is used for producing inert atmosphere in the welding and metallurgy of certain metals which are easily oxidizable, e.g., Al, Mg, Ti etc.

(vii) It is used in the preservation of food.

(viii) It is used for filling electrical transformers.

(ix) It is used as a pressuring agent in rockets to expel liquid O_2 and H_2.

(x) It is used in signal lights.

(xi) It is used in gas thermometers for low temperature measurements.

(xii) Helium nucleus (alpha particles) is used in artificial radioactivity.

Neon

(i) It is used in neon discharge lamps and signs which are used for advertising purposes, since the neon lights are visible from long distances and even visible through fog and mist.

(ii) It is used in protective electrical devices like voltage stabilizers, current rectifiers etc.

(iii) It is also used in television sets, sound movies etc. to give ready response to electrical potentials.

Argon

(i) A mixture of argon and nitrogen (15%) is filled in electric bulbs to increase the life of filament and to low the heat conductivity.

(ii) It is used for producing inert atmosphere in welding and metallurgy of certain metals which are easily oxidized.

(iii) It is used in filling fluorescent tubes and radio-valves.

(iv) It is mixed with neon in neon signs to obtain the lights of different colours.

(v) It is also used in Geiger counters to detect radioactivity.

Krypton

(i) It is used in high efficiency miner's cap lamps.

(ii) It is used in filling luminous tubes.

(iii) It is used in ionization chambers to detect cosmic rays.

(iv) It is also used to produce intense light in cinematography.

Xenon

(i) It is used in discharge tubes for producing high speed flash of bluish light used in quick photography.

(ii) Liquid xenon is used in bubble chambers for the detection of gamma photon and neutral mesons.

Radon

(i) It is used in the preparation of ointment for the treatment of cancer and other diseases.

(ii) It is used for photographing the interior of opaque materials for locating the defects in steel castings.

Questions

Q.1 What are noble gases? Write their atomic number and electronic configuration.

Q.2 Discuss the position of inert gases in the periodic table. On the basis of electronic configuration of noble gases account for their inertness.

Q.3 *(a)* Name the inert gases. Discuss their position in the periodic table. Why do they show chemical inertness?

(b) Discuss the important compounds of xenon.

Q.4 *(a)* What are noble gases? Discuss the structure of following compounds.

- *(i)* XeF_2
- (ii) XeF_4
- (iii) XeF_6
- (iv) XeO_3

(b) Write some applications of noble gases.

Q.5 *(a)* What noble gases? Discuss general characteristics of noble gases.

(b) Write some commercial uses of noble gases.

Q.6 Discuss the chemistry of the following compounds:

- *(i)* XeF_2
- *(ii)* XeF_4
- *(iii)* XeF_6
- *(iv)* $XeOF_4$

Q.7 Justify/comment on the following statements:

- *(a)* Noble gases are monoatomic.
- *(b)* Noble gases are also known as inert gases.
- *(c)* Noble gases are also known as rare gases.
- *(d)* The electronegativity and electron affinity of noble gases is zero.
- *(e)* Although xenon has a stable configuration, yet it forms fluorides.
- *(f)* XeF_2 has linear geometry.
- *(g)* Xenon forms compounds with fluorine but helium and neon fail to do so.
- *(h)* It is difficult to liquefy helium.
- *(i)* Xenon and bromine do not form compounds like xenon fluorides.
- *(j)* Zero group has been placed at the extreme right of the periodic table and not before first group.
- *(k)* The chemical reactivity increases from helium to xenon in the zero group.

Chapter Eleven

TRANSITION ELEMENTS

11.1 INTRODUCTION

The elements lying between *s* and *p*–block elements of the periodic table are collectively known as *transition elements*. These elements either in their atomic state or in any of their common oxidation state have partially filled (n–1) *d* orbitals. Since in these elements the differentiating electron enters the (n–1) th d-orbitals of the (n–1) th main shell, these are also called *d-block elements*. Thus, strictly according to this definition Zn, Cd, Hg and their divalent cations should be excluded from *d*-block elements, since they do not have partially filled (n–1) *d*-orbitals. Similarly Cu, Ag, Au and their monovalent cations are also not considered to be transition metals or ions. In order to maintain a rational classification of elements these elements are generally studied with *d*-block elements.

The transition elements occupy the large middle section flanked by *s* and *p*–blocks in the periodic table. In fact the very name 'transition' is given to these elements because of their position between the s and *p*–block elements. The penultimate shell of electrons in their atoms is being expanded from eight to eighteen by the addition of *d*-electrons. The elements make up the three complete rows corresponding to the filling of 3*d*, 4*d* and 5*d* sub shells. The three series of the elements, thus, consists of the following elements (Table 11.1).

Table 11.1 Transition Elements (*d*-block)

1st Series Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic No. 30	21	22	23	24	25	26	27	28	29
2nd series Cd	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag
Atomic No. 48	39	40	41	42	43	44	45	46	47
3rd series La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic No. 80	57	72	73	74	75	76	77	78	79

* Lanthanum is followed by a group of fourteen elements (58-71) which form the lanthanide series.

11.2 ELECTRONIC CONFIGURATIONS OF *d*-BLOCK ELEMENTS

d–block elements are located in between *s* and *p*–block elements in the long form of the periodic table. They occur in fourth and subsequent periods of the periodic table. In the building up of the electronic configurations of atoms, in general, electrons are filled in levels in the order 1*s*, 2*s*, 2*p*, 3*s*, 3*p*...... When we come to 3*d* and 4*s* levels, certain complications arise in energy levels. Up to calcium (Z=20) 4s-level is filled before 3*d*-level. After calcium the energy of 3*d*-level begins to rise somewhat higher than that of 4*s*-level (*i.e.*, 3*d* > 4s). Consequently the ten elements: Sc (Z=21) to Zn (Z=30) fill their 4*s* orbitals first and then 3*d* orbitals. Thus these ten elements which constitute the *first transition series* have the electronic configuration as shown in Table 11.2. These ten elements are also called *3d series elements*, since in these 3*d*-orbitals are being progressively filled. On similar basis the elements: Y (Z=39) to Cd (Z=48) constitute the *second series* (also called 4*d* series) and the elements: La (Z=57) and Hf (Z=72) to Hg (Z=80) form the *third series* (5*d* series). The electronic configurations of the second and third series elements are also given in the same table which clearly shows that the general valence shell configuration of the atoms of *d*-block elements may be written as: $(n\text{-}1)\, d^{1.....10}\, ns^{0,\,1,\,2}$

Table 11.2 Valence Shell Configurations of *d*-block Elements

					1st Series					
	21	22	23	24	25	26	27	28	29	30
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10
					2nd Series					
	30	40	41	42	43	44	45	46	47	48
	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd
5*s*	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10
					3rd Series					
	57	72	73	74	75	76	77	78	79	80
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6*s*	2	2	2	2	2	2	2	1	1	2
5*d*	1	2	3	4	5	6	7	9	10	10

It may be noted from the table that the elements Cr and Mo prefer to have $3d^5 4s^1$ and $4d^5 5s^1$ outer configuration rather than the expected configurations, $3d^4 4s^2$ and $4d^4 5s^2$ respectively. Similarly Cu, Ag and Au prefer d^{10} configurations to d^9 and Pd prefers d^{10} to d^8. The reason of these abnormal configurations is that the half-filled (i.e., d^5) and completely filled (i.e., d^{10}) levels have greater stability and consequently the configurations having such levels are more stable.

11.3 GENERAL CHARACTERISTICS OF *d*-BLOCK ELEMENTS

Some important characteristics of 3d-series elements are described as follows:

1. **Metallic character:** All the transition elements are metals, since the number of electrons in the outermost shell is very small, being equal to 2. They are hard, malleable and ductile. These metals are good conductor of heat and electricity.

2. **Melting and boiling points:** The transition metals have very high melting and boiling points as compared to those of *s*–block elements.

3. **Ionization potentials:** The ionization potential values of most of the d-block elements lie in between those of *s* and *p*–block elements. This indicates that the *d*-block elements are less electropositive than *s*–block elements and more than *p*–block elements. Thus d-block elements do not form ionic compounds so readily as the alkali and alkaline earth metals do. Unlike *s*–block elements, *d*-block elements form covalent compounds as well.

4. **Variable oxidation states:** Most of transition metals show several oxidation states in their compounds. These states are exhibited only in few complexes and further more these are unstable. The cause of showing different oxidation states is that in addition to using electrons in the outer-most sub-shell namely '*ns*' in compound formation, a variable number of inner $(n-1)$ *d* electrons can also be used for this purpose. The energy difference between $(n-1)$ *d* orbitals and ns orbitals of transition metals is very small. As a result the electrons may easily shift from $(n-1)$ *d* to *ns* or from *ns* to $(n-1)$ *d* orbitals.

5. **Atomic volumes and densities:** The atomic volumes of the metals are much lower than those of alkali and alkaline earth metals. As the inner orbitals get filled, the increased nuclear charge pulls the electronic cloud inward. The atomic volume, therefore, decreases. The decrease in atomic volume increases the density. Accordingly the densities of transition elements are very high as compared to those of alkali and alkaline earth metals.

6. **Atomic and ionic radii:** The atomic and ionic radii values generally decrease on moving from left to right in the series. This is due to the fact that as the nuclear charge increases with increasing atomic number across any series, the attraction of the electrons towards the nucleus increases and this increase in attraction leads to a decrease in the radii values across the period.

7. **Paramagnetic behaviour:** Many transition metals, atoms and cations with partially filled d-sub-shell exhibit paramagnetic behaviour i.e., they are attracted into a magnetic field. The paramagnetism is caused by the presence of unpaired electrons. An electron has two types of motion: *spin motion* (i.e., spinning of the electron on its axis) and *orbital motion* (i.e., moving of the electron in an orbital). It is also known from elementary Physics that the movement of an electric charge produces a magnetic field. Consequently an electron spinning on its axis also creates a magnetic moment which is called the *spin moment* of the electron. The orbital motion produces a magnetic moment just like an electric current traveling in a loop of wire. The magnetic moment produced in this way is called *orbital*

moment of the electron. The observed magnetic moments are combination of these two moments. Both these two moments arise due to the presence of unpaired electrons.

8. **Complex formation:** The cations of transition metals have a tendency to form complexes with several ligands. This tendency is due to the following reasons:

(i) The cations are relatively very small in size and hence have high positive charge density which makes it easy for the cations to accept the lone pairs of electrons from the ligands.

(ii) The cations have vacant $(n-1)$ d-orbitals, which are of appropriate energy to accept lone pair of electrons from the ligands for bonding with them.

9. **Interstitial compounds:** Small non-metallic atoms (e.g., H, B, C, N etc.) are able to fit into the interstitial sites of transition metal lattices to form the compounds which are called *interstitial compounds*. These have variable composition and cannot, therefore, be expressed by simple formulae, i.e., these are non-stoichiometric.

10. **Catalytic properties:** Most of the transition metals and their compounds are used as catalysts. Some common examples are: Pt, Ni, Fe, Cr, V_2O_5 etc. Catalytic power of these metals is due to either the use of d-orbitals or the formation of interstitial compounds which adsorb and activate the reacting substances.

11. **Colour:** Most of the compounds of transition metals are coloured in the solid or in solution states. The colour of the transition metal ions is due to the presence of unpaired electron or incomplete d-orbitals. When white light is allowed to fall on a coloured substance, it absorbs from it the light of a particular colour whose wavelength is in the visible region and reflects the remaining light which has the colour complementary to that of the absorbed light. This complementary colour which is actually the colour of the reflected light is the colour of the substance. The colour of the ions is related to the number of unpaired electrons:

Number of unpaired electrons	**Colour of the ions.**
0	Sc^{3+}, Zn^{2+} (colourless)
1	Cu^{2+} (blue)
2	Ni^{2+} (green)
3	Cr^{3+} (deep green)
4	Fe^{2+} (green)

12. **Alloy formation:** They form alloys with one another and with other metals, e.g., brass (Cu-Zn), bronze (Cu-Zn-Sn), German silver (Cu-Zn-Ni) etc.

Some selected properties of the elements of first transition series are summarized in Table 11.3

Table 11.3 Some Properties of the Elements of First Transition Series.

Element Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic vol.(c.c)	15	6.6	8.3	7.2	7.3	7.1	6.7	6.6	7.1	9.2
Density (g/cc)	3	4.5	6.1	7.2	7.4	7.8	8.9	8.9	8.9	7.1
Atomic radii (Å)	1.44	1.32	1.22	1.18	1.17	1.17	1.16	1.15	1.17	1.25
Ionic radii (Å)	–	0.90	0.88	0.84	0.80	0.76	0.74	0.72	0.69	0.74
Melting point(°C)	1539	1668	1900	1875	1245	1536	1495	1453	1083	419.5
Boiling point(°C)	2730	3260	3450	2665	2150	3000	2900	2730	2595	906
I.P (eV)	6.5	6.8	6.7	6.7	7.4	7.9	7.8	7.6	7.7	9.4
Standard oxidation potential (Volts)	–	1.60	1.20	–	1.18	0.41	0.28	0.25	0.34	0.76

11.4 IMPORTANT TERMS IN COORDINATION CHEMISTRY

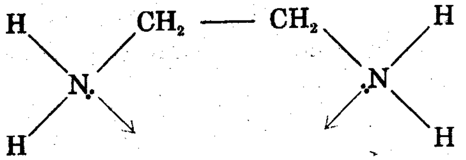
Before we go further, let us define and illustrate a few terms that will make our discussion of coordination chemistry easier.

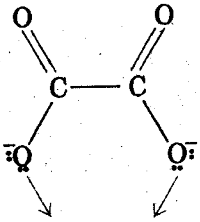
1. **Complex ion:** It is a charged molecular species containing of a metallic atom or ion to which is attached one or more charged or uncharged molecules. For example, $[Fe(CN)_6]^{3-}$, $[Ag(NH_3)_2)]^+$ etc.

2. **Coordination compound:** A compound formed between a metal ion and ligands, each capable of independent existence, through electron pair sharing using electrons from the ligand. Further, the association will produce observable changes in the chemistry of both, the metal ion and the ligand. For example, $K_3[Fe(CN)_6]$, $[Ag(NH_3)_2]Cl$ etc.

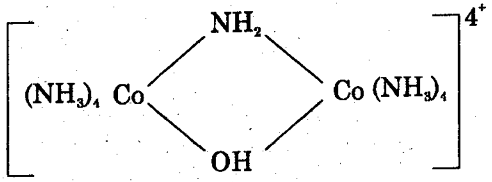
3. **Ligand:** The ligand may be an atom alone or a group containing an atom which is coordinated to the central atom. A ligand with more than one potential coordinating atom is multidentate. For example, Cl^-, NH_3, H_2O etc.

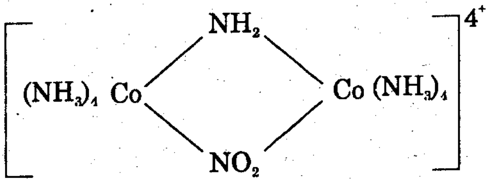
4. **Chelate ligand:** A chelate ligand is one using more than one of its coordinating atoms. For example, ethylenediamine (en) oxalate ion, glycinate ion etc.





5. **Bridging group:** A bridging group is a group attached to two nuclear atoms in a polynuclear complex (i.e., containing more than one nuclear atom). For example,





6. **Double salt and complex salt:** When solutions containing two or more salts in stoichiometric proportions are allowed to evaporate, we get crystals of compounds known as *molecular* or *addition compounds*. These are of two types depending on their behaviour in aqueous solution.

   The addition compounds which are stable in the solid state only but dissociate into their individual components when dissolved in water or any other ionic solvent are called *double salts*. The physical and chemical properties of a double salt are the same as those of the individual compounds. For example, Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$ etc.

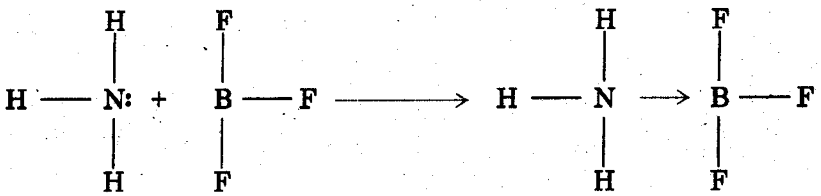
   On the other hand, those addition compounds which retain their identities in the solid as well as in water or any other ionic solvent are known as *complex salts* or *coordination compounds*. Their properties are entirely different from those of their individual constituents. Hexamminechromium (III) chloride, $[Cr\ (NH_3)_6]\ Cl_3$ and potassium hexachloroplatinate (IV) are the examples of complex salts.

7. **Coordination sphere:** The central metal atom or ion and the ligands that are directly attached to it are enclosed in a square bracket which Werner has called the coordination sphere. It is represented by [ ].

8. **Coordination number:** It is the total number of atoms of the ligands that can coordinate to the central metal ion. Numerically coordination number represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands. Thus in $[Fe\ (CN)_6]^{3-}$, the C.N. of Fe^{3+} is three while in $[Ni(NH_2–CH_2–CH_2–NH_2)_3]^{2+}$, the C.N of Ni^{2+} is six, since each ethylene diamine molecule, NH_2-CH_2-CH_2-NH_2 has two donor atoms.

11.5 COORDINATE BOND FORMATION

According to Lewis concept, an *acid* is a species which can accept a pair of electrons and a *base* is a species which can donate a pair of electrons. According to this view a base makes available a share in an electron pair and an acid accepts a share in an electron pair, to form a *coordinate covalent bond.* Such bonds are frequently represented by arrows, as shown below.



$$H-\underset{H}{\overset{H}{N}}: + \underset{F}{\overset{F}{B}}-F \longrightarrow H-\underset{H}{\overset{H}{N}} \longrightarrow \underset{F}{\overset{F}{B}}-F$$

Most d-transition metal ions have vacant d-orbitals that can accommodate shares in electron pairs, and they show a marked tendency to act as Lewis acids in forming coordinate covalent bonds in *coordination compounds* or *coordination complexes* or *complex ions*. Examples of transition metal ions or molecules showing coordinate covalence are $[Cr(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$, $[Fe(CO)_5]$ and $[Ag(NH_3)_2]^{2+}$.

The bonding in transition metal complexes was not well understood until the pioneering research of Alfred Werner, a Swiss Chemist of 1890s who won the Nobel Prize in Chemistry in 1913. Although tremendous advances have been made in the field of coordination chemistry, Werner's classic work still remains the most important contribution. He studied in detail the compounds of Co(III), Pt(IV) and Pt(II). Much of the early work was done with ammonia and the complexes formed were known as metal amines.

Table 11.4 Interpretation of Experimental Data by Werner

Formula	Moles of AgCl precipitated per formula unit	True Formula
$PtCl_4.6NH_3$	4	$[Pt(NH_3)_6]Cl_4$
$PtCl_4.5NH_3$	3	$[Pt(NH_3)_5Cl]Cl_3$
$PtCl_4.4NH_3$	2	$[Pt(NH_3)_4Cl_2]Cl_2$
$PtCl_4.3NH_3$	1	$[Pt(NH_3)_3Cl_3]Cl$
$PtCl_4.2NH_3$	0	$[Pt(NH_3)_2Cl_4]$

Prior to Werner's work the formulas of transition metal complexes were written with dots, $CrCl_3.6H_2O$, $AgCl.2NH_3$ just like double salt. Werner was able to isolate platinum (IV) compounds with the formulas given in the first column of Table 11.4. He added excess silver nitrate to solutions of carefully weighed amounts of each of the five salts. The precipitated silver chloride was collected by filtration, dried, and weighed to determine the number of moles of silver chloride produced, and therefore the number of chloride ions precipitated per formula unit. The results appear in the second column. Werner reasoned that the precipitated chloride ions must be free, while the unprecipitated chloride ions directly bound to platinum so they could not be removed by silver ions. He concluded that the correct formulations are the ones listed in the last column.

11.6 NOMENCLATURE OF COORDINATION COMPOUNDS

Werner was the first scientist to give more comprehensive system of nomenclature. Certain modifications are introduced by the International Union of Pure and Applied Chemistry (IUPAC) in Werner's method of nomenclature. A coordination compound is either an ionic salt or a neutral molecule; the salts are designated in the usual fashion of using a two-word name and non ionic compounds are given in one-word name. The general rules of naming the compounds are:

1. **Order of listing ions:** The cation is named first and then anion. This is usual practice while naming a salt.

NaCl	Sodium chloride
$[Cr(NH_3)_6]Cl_3$	Hexamminechromium (III) chloride
$K_2[PtCl_6]$	Potassium hexachloroplatinate (IV)

2. **Writing formulae of complexes:** In formulae the usual practice is to place the central atom first (except in formulae which are structural) with the ionic and neutral ligands following and the formula for the whole complex enclosed in square brackets.

$$[PtCl_2(NH_3)_2], [Co(NO_2)_3(NH_3)]$$

3. **Naming of coordination spheres:** In naming the coordination sphere, ligands are named in alphabetical order. The prefixes di=2, tri=3, tetra=4, penta=5, hex=6 etc., are used to specify the number of particular kind of coordinated ligand. For complicated ligands (usually chelating gents), other prefixes such as bis=2, tris=3, tetrakis=4, pentakis=5, and hexakis=6 indicate the number of ligands.

$[Cr(H_2O)Cl(en)_2]SO_4$	Aquachlorobis (ethylenediamine) chromium (III) sulphate

4. **Name of ligands:** The names of anionic ligands, end in the suffix-o. Examples are:

	Ion	Ligand
F^-	(fluoride)	Fluoro
Cl^-	(chloride)	Chloro
Br^-	(bromide)	Bromo
I^-	(iodide)	Iodo
O^{2-}	(oxide)	Oxo

OH^-	(hydroxide)	Hydroxo
CN^-	(cyanide)	Cyano
CO_3^{2-}	(carbonate)	Carbonato
H^-	(hydride)	Hydride (Hydro)
SO_4^{2-}	(sulphate)	Sulphato
NO_3^-	(nitrate)	Nitrato
$S_2O_3^{2-}$	(thiosulphate)	Thiosulphato
NO_2^-	(nitrite)	Nitro (ONO Nitrito)
S^{2-}	(sulphide)	Sulphido

5. **Neutral ligands:** The names of neutral ligands, are usually unchanged. Some important examples are NH_3, ammine, H_2O aqua, CO, carbonyl, NO, nitrosyl.

6. **Order of ligands:** The ligands are listed in alphabetical order regardless of the number of each. The name of the ligand is treated as one unit thus, "diammine" is listed under "a" and dimethylamine under "d".

$K_2[OSCl_5N]$	Potassium pentachloronitridoosmate (IV)
$[Co(NH_2)_2(NH_3)_4]OC_2H_5$	Diamidotetramminecobalt (III) ethoxide
$[Pt(NH_3)_4Cl(NO_2)]SO_4$	Tetraamminechloronitroplatinum (IV) sulphate.

7. **Termination of names:** The suffix "ate" at the end of the name of the complex signifies that it is an anion. If the complex is neutral or cationic, no suffix is used. The English stem is usually used for the metal, but where the naming of an anion is awkward, the Latin stem is substituted.

$Ca_2[Fe(CN)_6]$	Calcium hexacyanoferrate (II)
$K_3[Fe(CN)_5CO]$	Potassium carbonylpentacyanoferrate (II)
$[Ni(DMG)_2]$	Bis (dimethylglyoximato) nickel (II)

8. **Oxidation states:** The oxidation state of the central atom is indicated by Roman numeral in parentheses following the name of the complex. For a negative state a minus sign is used before the Roman numeral and 0 is used for zero.

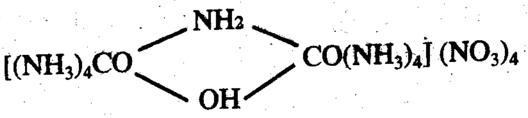
$K_4[Ni(CN)_4]$	Potassium tetracyanonickelate (0)
$Na[Co(CO)_4]$	Sodium tetracarbonylcobltate (–I)

9. **Modes of attachment:** In some cases different names are already in use for alternative modes of attachment. For example, thiocyanato (-SCN) and isothiocyanate (–NCS), nitro ($-NO_2$) and nitrito (–ONO).

$Na_3[Co(NO_2)_6]$	Sodium hexanitrocobaltate (III)

$[Co(ONO)(NH_3)_5]SO_4$	Pentaamminenitritocobalt (III) sulphate
$[Co(NCS)(NH_3)_5]Cl_2$	Pentaammineisothiocyantocobalt (III) chloride.

10. **Bridging groups:** A bridging group is indicated by adding the Greek letter "μ" immediately before its name and separating the name from the rest of the complex by hyphens. Two or more bridging groups of the same kind are indicated by di-μ-etc. If two or more kinds of bridging groups are present, they are listed in alphabetical order.

$[NH_3)_5Cr{-}OH{-}Cr(NH_3)_5]Cl_5$	μU-hydroxobis [pentaamminechromium (III)] chloride
$[(CO)_3Fe(CO)_3Fe(CO)_3]$	Tri-μ-carbonylbis (tricarbonyliron)
 $\left[(NH_3)_4CO\begin{smallmatrix}NH_2\\ OH\end{smallmatrix}CO(NH_3)_4\right](NO_3)_4$	μ-amido-μ-hydroxobis [tetraamminecobalt(III)] nitrate
$[Br_2Pt(SMe_2)_2PtBr_2]$	Bis (-μ-dimethylsulphido) bis[dibromoplatinum(II)]

11. **Symbols for some ligands:** While writing the formula of a complex compound symbols are used to designate certain ligands. For example,

ethylenediamine	en
Pyridine	Py
Ethylenediaminetetraacetato	EDTA
Dimethyl glyoximato	DMG etc.

12. **Optical and geometrical isomers:** When a complex is optically active, '*d*' and '*l*' refers to the direction of rotation right and left, respectively. Geometrical isomers are named using the prefix cis- or trans-.

Several examples are given to illustrate the rules.

$K_2[Cu(CN)_4]$	Potassium tetracyanocuprate (II)
$[Ag(NH_3)_2]Cl$	Diamminesilver chloride
$Na[Al(OH)_4]$	Sodium tetrahydroxoaluminate (III)
$Na_2[CrOF_4]$	Sodium tetrafluorooxochromate (IV)
$[Cr(H_2O)_6](NO_3)_3$	Hexaaquachromium (III) nitrate
$[Co(en)_2Br_2]Cl$	Dibromobis (ethylenediamine) cobalt (III) chloride
$[Ni(CO)_4]$	Tetracarbonylnickel (0)
$[Pt(NH_3)_4][PtCl_6]$	Tetraamineplatinum (II) hexachloroplatinate (IV)
$[Fe(H_2O)_5(NCS)]SO_4$	Pentaaquathiocyanatoiron (III) sulphate

$[Co(NH_3)_4(H_2O)Cl]Cl_2$	Tetraammineaquachlorocobalt (III) chloride
$[RuCl_3\{[P(C_6H_5)_3\}_2]$	Trichlorobis (triphenyl phosphine) ruthenium (III)
$Na_2[Sn(OH)_6]$	Sodium hexahydroxostannate (IV)
$K_4[Ni(CN)_2(OX)_2]$	Potassium dicyanobis (oxalato) nickelate (II)
$[Cu(NH_3)(H_2O)Br_2]$	Ammineaquadibromocopper (II)

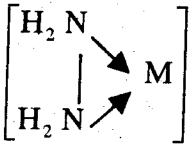
11.7 CHELATING LEGANDS AND CHELATES

A chelating ligand is a bidendate or polydentate ligand which is attached to the same central metal atom by two or more of its donor atoms resulting in the formation of a complex having a strain-free ring structure. The complex having the ring structure is called chelate or chelated complex. The chelate is also called by various other names like *cyclic complex, ring-type complex* etc. The formation of a chelate is called *chelation or cyclisation.*

Examples of the formation of chelates

(i) When two molecules of ethylenediamine, $NH_2 — CH_2 — CH_2 — NH_2$ (en) which is a bidentate ligand, get attached with one Cu^{2+} ion through its two N-donor atoms of each molecule, complex ion viz. $[Cu\ (NH_2 — CH_2—CH_2—NH_2)_2]^{2+}$ or $[Cu(en)_2)]^{2+}$ which contains two 5-membered rings is obtained. In the formation of this complex ion, ethylenediamine molecule (bidentate ligand) acts as a chelating ligand and the complex ion thus formed is called a chelate [see Fig. 11.1 (a)].

(ii) When three oxalate ions, $C_2O_4^{2-}$ or ox^{2-} get attached with one Fe^{3+} ion, $[Fe\ (C_2O_4)_3]^3$- or $[Fe(ox)_3]^{3-}$ ion is obtained. This complex ion is a chelate. This chelate has three 5-membered rings. In the formation of this chelate $C_2O_4^{2-}$ ion which is a bidentate ligand acts as a chelating ligand [see Fig. 11.1 (b)].

It is may be noted that OH^-, Cl^- and NH_2^- ions cannot serve as chelating ligands, because the angle between the lone pairs do not allow them to span adjacent coordination positions of one and the same metal atom. Hydrazine ($H_2\ddot{N} — \ddot{N}H_2$) cannot function as a chelating ligand, since a 3-membered ring-type complex formed  is very strained and hence is unstable.

Thus every polydentate ligand is not necessarily a chelating ligand.

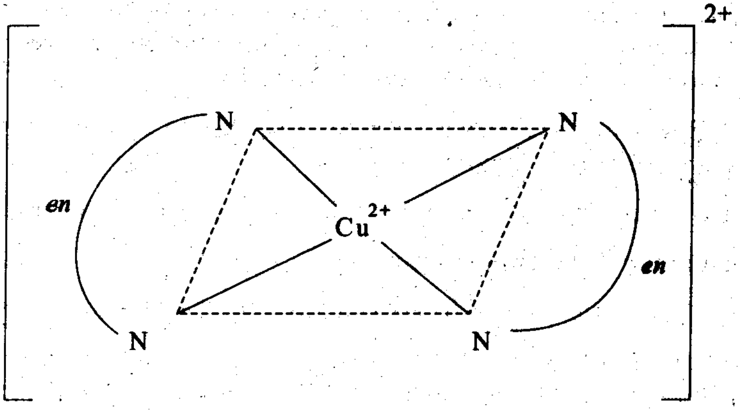
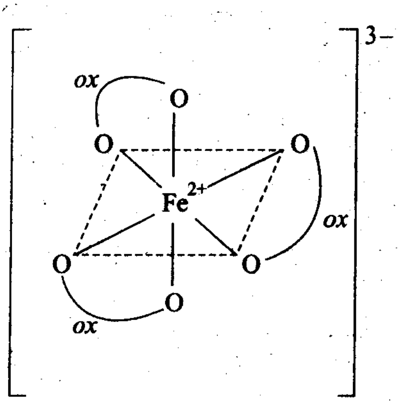


Fig.11.1. Structure of (a) $[Cu(NH_2—CH_2—CH_2—NH_2)]^{2+}$ and of (b) $[Fe(C_2O_4)_3]^{3-}$ or $[Fe(ox)_3]^{3-}$ chelated complex ions.

Classification of chelates

Chelates which do not carry any charge are called ***inner metallic complexes of the first order***. These chelates are neutral (non-electrolyte) in nature. Example of such chelates are $[Cr^{3+}(gly)_3]^0$, $[Co^{3+}(acac)_3]^0$, $[Cu^{2+}(big)_2]^0$ etc.



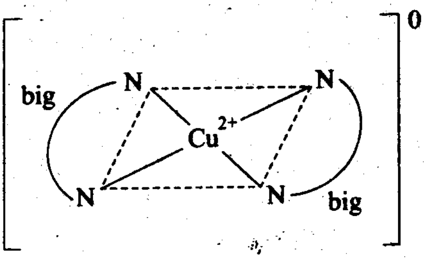


Fig.11.2. Structure of $[Cu^{2+}(big)_2]^0$. Here big is the abbreviation for biguanide ion which is a bidentate ligand.

The chelates which carry some charge are called *inner-metallic complexes of the second order.* These chelates are ionic in nature. Examples of such chelates are $[Co^{3+}(en)_3]^{3+}$, $[Co^{2+}(acac)_3]^-$ etc. the structure of $[Cu^{2+}(big)_2]^0$ is shown in Fig. 11.

Properties of inner metallic complexes

(i) Neutral inner metallic complexes are usually insoluble in water but dissolve in organic solvents immiscible with water. This property has been used for the separation of metals by solvents extraction method.

(ii) The formation of a chelated complex may lead to the change in color. This property permits colorimetric estimation.

(iii) Most of the chelated complexes have low melting points and are volatile.

Factors affecting the stability of chelates

Following are important factors which influence the stability of chelates.

1. *Size of the chelate ring.* Chelates having 6-membered rings including the metal atom are more stable than those having 5-membered rings which in turn, are more stable than the chelates with 4-membered rings and so on.
2. *Number of chelate rings.* Greater in the number of chelate rings, greater is the stability of the chelate.
3. *Resonance effects.* Resonance enhances the stability of the chelate.
4. *Chelate effect.* The chelated complexes are known to be more stable than the non-chelated complexes. This effect is known as chelate effect.

11.8 APPLICATIONS OF COORDINATION COMPOUNDS

Coordination (complex) compounds are of great importance. These compounds constitute the minerals, plants and are also present in animals. These play important functions. Besides these, the coordination compounds are also used in the field of metallurgy, biochemistry, ion-exchange, textile dyeing, analytical chemistry etc. Complex compounds of various metals have been used for various purposes. For example;

(i) Many complex compounds are used as electrolytes for electroplating. These complexes deliver the metal ions for reduction. For example, $K[Ag(CN)_2]$ and $K[Au(CN)_2]$ are used as electrolytes for silver and gold plating.

(ii) Several complex compounds are used as catalysts for different reactions *e.g.*, $Co_2(CO)_8$ acts as a catalyst in the conversion of olefins into alcohol.

(iii) Complex compounds like sodium metapolyphosphate are used to remove Ca^{2+} and Mg^{2+} ions from hard water forming complexes with these ions. The formation of complex compounds prevents the scale formation in boilers.

(iv) Ca-EDTA chelate, $Ca[EDTANa_2]$ is used in the treatment of lead poisoning, *i.e.*, for the removal of lead from the body.

(v) Within the animal cell, Fe(II)-Fe(III) protein based coordination compound of hemoglobin family, called *cytochrome-c* acts as catalyst for the utilization of oxygen in the basic cell metabolism of the fundamental life process.

(vi) Chlorophyll, an important constituent of plants, is a chelate compounds containing Mg^{2+} in the centre linked with pyrrole nuclei.

(vii) Hemoglobin, the red coloring pigment of blood, is an iron chelate responsible for oxygen transport in the living systems.

(viii) In quantitative analysis, chelating agents are becoming increasingly important. For example, Ni^{2+} ion is estimated with dimethylglyoxime through the formation of Ni-DMG complex. Thus the formation of this chelate can be used for the identification, estimation of Ni^{2+} and also for its separation from Co^{2+} ion.

(ix) Disodium salt of ethylenediamine tetraacetic acid has been used for the estimation of metal ions like Mg^{2+}, Ca^{2+} etc. by complexometric titrations.

(x) Ethylenediamine tetraacetic acid has been used for softening water which does a lot of harm in industrial boilers and other equipments by forming a scale in them.

(xi) The accumulation of excess of Cu^{2+} in the liver leads to malfunctioning of the CNS. In order to remove the excess Cu^{2+} ions, penicillamine (chelating agent) is given to the patient. This Cu^{2+}- chelate goes out of the body through urine.

(xii) Certain chelating ligands such as dimethylglyoxime, acetylacetone, dithioxone etc. form chelates with many metallic ions which carry no charge. These complexes are usually insoluble in water but dissolve in organic solvents. Thus various metal ions can be separated from each other through solvent extraction.

(xiii) Coordination compounds are used as invisible inks. For example, $Co[(H_2O)_6]Cl_2$ is used as invisible ink.

(xiv) Coordination compounds are also used as detergents and antioxidants.

(xv) Complex compounds are also widely used as catalysts in synthetic reactions, particularly organometallic reactions and polymerization reactions.

(xvi) Moreover, coordination compounds are also used as indicator in the determination of certain metal ions and in the photography for fixing of images.

11.9 WERNER'S COORDINATION THEORY

In 1893 Werner put forward a theory, called Werner's coordination theory, to explain the formation of complex compounds like the ammines of Pt(IV) and Co(III). More important postulates of this theory are:

1. Each metal possesses two types of valencies: *(a)* primary valency and *(b)* secondary valency.

   In modern terminology, *(a)* corresponds to oxidation state and *(b)* to coordination number.

2. Every element tends to satisfy both of its primary and secondary valences. In order to meet this requirement a negative ion my often show a dual behaviour, i.e., it may satisfy both primary and secondary valences.
3. Every metal has a fixed number of secondary valences.
4. The ligands which satisfy the secondary valences are always directed towards fixed position in space.
5. The geometry of a complex is determined by the number and arrangement of ligands in space.
6. The primary valences are non-directional.

Applications of Werner's Theory to Coordination Compounds

Werner's theory has successfully been applied to elucidate the structures, isomerism and nature of coordination compounds. Let us apply this theory to explain the structures and nature of ammines given by Co(III). On the basis of this theory, these ammines can be designated as shown in Fig. 11.2

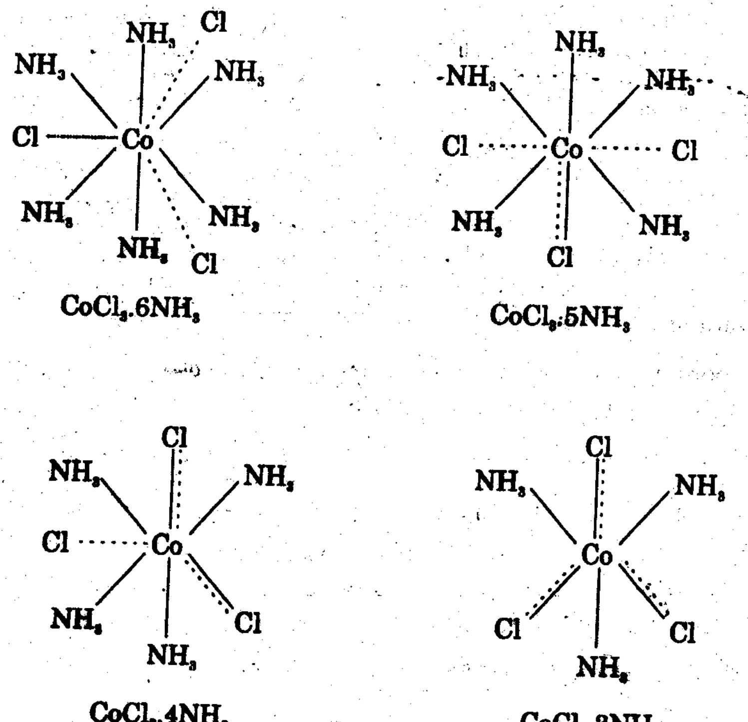


Fig. 11.3. Designations of Co(III) ammines on the basis of Werner's theory.

1. **$CoCl_3.6NH_3$:** This ammine has six NH_3 molecules that satisfy the secondary valency of the metal ion, viz; Co^{3+} ion and their attachment with the central metal ion is shown by thick lines. The primary valency is satisfied by three chloride ions whose attachment to Co^{3+} ion is shown by dotted lines. As all the three Cl^- ions are loosely bound, they are immediately precipitated as AgCl on the addition of $AgNO_3$ solution. Thus the solution of this compound should conduct current to

give four ions in all viz. $[Co(NH_3)_6]^{3+}$ and $3Cl^-$ which have been confirmed by conductivity measurements. Thus this ammine is formulated as $[Co(NH_3)_6]Cl_3$.

2. **$CoCl_3.5NH_3$:** This ammine has five NH_3 molecules. On the basis of Werner's theory one Cl^- ion does the dual function, since it satisfies both the primary and secondary valency. Werner therefore, showed its attachment with the central metal ion by a combined dashed – solid line ------------. This Cl^- ion, being non-ionic, is not precipitated as AgCl by $AgNO_3$ solution and hence it is different from the other two Cl^- ions, which being ionic, are precipitated as AgCl. Thus the total number of ions obtained is three: one complex ion, $[Co(NH_3)_5Cl]^{2+}$ and two Cl^- ions. Hence this ammine is formulated as $[Co(NH_3)_5Cl]Cl_2$.
3. **$CoCl_3.4NH_3$:** This ammine has four NH_3 molecules. One ionizable chlorine (primary valency) is shown to be attached by dotted lines. Two non-ionizable chlorine ligands perform dual function of satisfying both types of valences. Thus this ammine has only one ionic chloride ion which get precipitated as AgCl by $AgNO_3$ solution. Consequently this ammine is formulated as $[Co(NH_3)_4Cl_2]Cl$.
4. **$CoCl_3.3NH_3$:** All the chlorine ligands are non-ionizable and perform dual function of satisfying both the primary and secondary valences. Thus this ammine has no ionic Cl^- ion and hence behaves as a non-electrolyte (neutral molecule). Consequently it is formulated as $[Co(NH_3)_3Cl_3]$.

The formulation of all these ammines has been shown as follows:

Werner's formula	Modern formula	Cation	Anion	Total no. of ions	
$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}$		$3Cl^-$	4
$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_6Cl]^{2+}$		$2Cl^-$	3
$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^+$		Cl^-	2
$CoCl_3.3NH_3$	$[Co(NH_3)_3Cl_3]$		--	--	--

11.10 SIDGWICK'S ELECTRONIC CONCEPT OF COORDINATION

In 1916 Lewis introduced a concept of two electron covalent bond between two atoms in a molecule. According to this concept a covalent bond is formed between two atoms of a molecule by the sharing of an electron pair. Sidgwick (1927) extended this Lewis concept of covalent bond and introduced a new concept of coordinate bond which is also sometimes called *dative* or *polar bond*.

According to Sidgwick's concept the ligands donate the electron pair to the central metal ion and thus form a coordinate bond, M←L which indicates that the ligand, L has donated an electron air to the metal ion, M. This concept is based on the fact that all the ligands contain at least one lone pair of electrons. Thus on the basis of Sidgwick's concept, the structure of complex ions such as $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5Cl]^{2+}$ etc. can be represented as shown in figure 11.4.

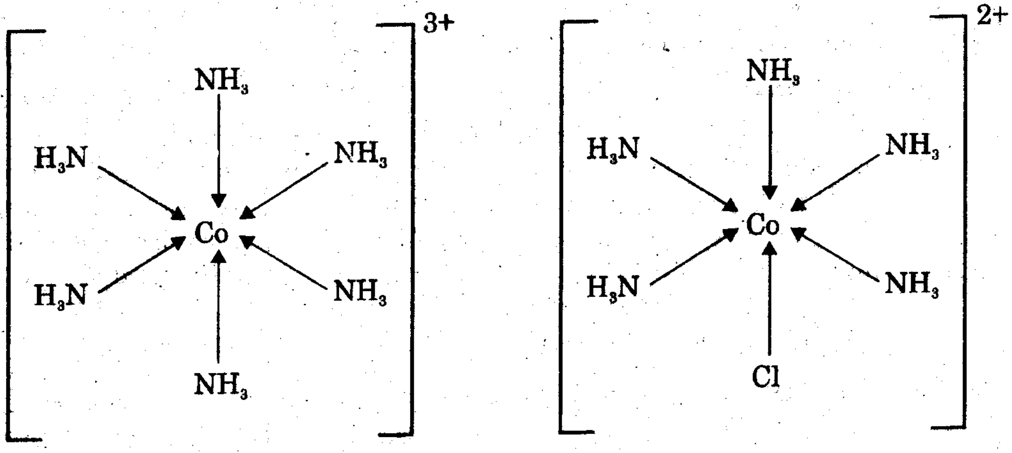


Fig. 11.4 Structures of [$Co(NH_3)_6]^{3+}$ and [$Co(NH_3)_5Cl]^{2+}$ ions.

It is obvious that the net charge on the complex ion is algebraic sum of the oxidation number of the central metal and the charge on the ligands. For example, the net charge, on the complex ion, $[Co(NH_3)_5Cl]^{2+}$ is +2 because Co^{3+} possesses +3 oxidation state and Cl^- has -1 charge and the algebraic sum is $+3-1 = +2$.

Sidgwick's Effective Atomic Number Rule (EAN Rule)

On the basis of his concept of coordinate bond, Sidgwick postulated that the central metal atom would surround itself with sufficient ligands that the total number of electrons around the metal would be the same as that in a rare gas. The number of electrons surrounding the coordinated metal is called its *effective atomic number*, which is symbolized as EAN. This is called *effective atomic number rule*.

The EAN can be calculated as follows:

EAN = Z–n +2 x C.N.

where Z = atomic number of the metal

n = oxidation state of the metal

C.N. = coordination number of the metal ion

Calculation of EAN can be illustrated by taking example of $[Co(NH_3)_6]^{3+}$ complex ion.

Atomic number of cobalt = 27

n = 3

C.N. = 6

EAN = 27–3 + 2 x 6

= 24 + 12

= 36

The validity and exception of EAN concept are given in Table 11.5.

Table 11.5 Validity and Exception of EAN Concept

Complex ion	Oxidation state	Coordination number	EAN
$[Fe(CN)_6]^{4-}$	+2	6	26–2+12 = 36 (Kr)
$[Co(NH_3)_6]^{3+}$	+3	6	27–3+12 = 36 (Kr)
$[PdCl_6]^{2-}$	+4.	6	46–4+12 = 54 (Xe)
$[Fe(CN_6)]^{3-}$	+3	6	26–3+12 = 35
$[Cr(NH_3)_6]^{3+}$	+3	6	24–3+12 = 33

octahedral/Tetr

11.11 VALENCE BOND THEORY

This theory was first developed by Pauling. It deals with the electronic structure of central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes. Pauling's theory was latter on slightly modified by Huggins to overcome certain limitations. The modified version of the theory is based on the following assumptions:

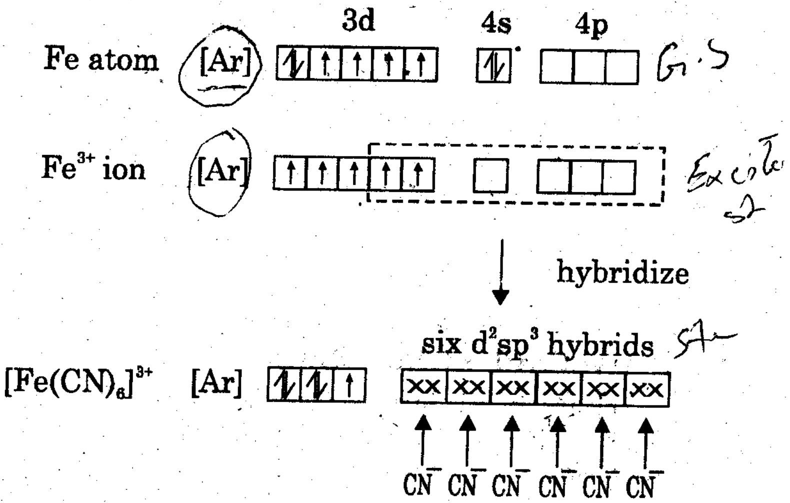
1. The central metal atom or ion makes available a number of empty s, p and d-orbitals equal to its coordination number.
2. The vacant orbitals hybridize together to form hybrid orbitals which are equivalent in energy and have definite geometry.
3. The ligands have at least one d-orbital containing a lone pair of electrons.
4. Vacant hybrid orbitals of the metal atom or ion overlap with the filled σ-orbitals of the ligands to form ligand → metal σ–bond. This bond which is generally known as coordinate bond is a special type of covalent bond and shows the characteristics of both the overlapping orbitals.
5. The non-bonding electrons of the metal atom or ion are then rearranged in the metal orbitals which do not participate in forming the hybrid orbitals. This arrangement of non-bonding electrons takes place according to Hund's rule.

VBT As Applied to Octahedral Complexes

On the basis of VBT, octahedral complexes are of two types: (1) Inner-orbital octahedral complexes which result from d^2sp^3 hybridization of the central metal atom or ion (2) Outer-orbital octahedral complexes which result from sp^3d^2 hybridization.

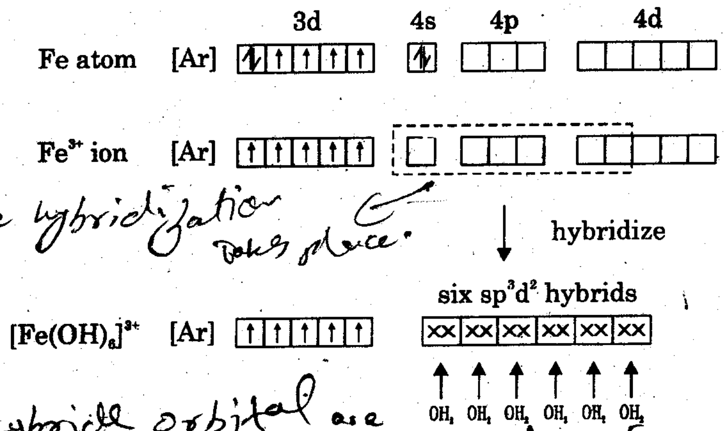
1. **Inner-Orbital Complexes:** The formation of these complexes can be explained on the basis of VBT by considering the complex ion viz. $[Fe\ (CN)_6]^{3-}$. This hexacyano ferrate (III) ion (also known commonly as the ferricyanide ion) involves Fe^{3+} (a d^5 ion), but its magnetic moment indicates only one unpaired electron per iron atom. The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are involved in d^2sp^3 hybridization. Since CN^- ion is a strong ligand, (can donate electrons more

effectively); this forces pairing of all but one of the non bonding 3*d* electrons of Fe^{3+}.



Since only inner *d*–orbitals are used in hybridization, $[Fe\ (CN)_6]^{3-}$ is called an *inner-orbital complex.* It is obvious from the above configuration that none of the original 3*d* electrons of Fe^{3+} ion is involved in bonding. Such type of complexes is also called *spin paired* or *low spins* complexes. $[Fe(CN)_6]^{3-}$ ion, is known to be paramagnetic (attracted by external magnetic field), with magnetic moment corresponding to one unpaired electron per iron atom. Other examples of inner-orbital octahedral complexes are: $[Co\ (NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Mn(CN)_6]^{3-}$ etc.

2. **Outer-Orbital Complexes:** The formation of these complexes can be explained on the basis of VBT by taking the example of hexaaquairon (III) perchlorate, $[Fe(OH_2)_6](ClO_4)_3$. The $[Fe(OH_2)_6]^{3+}$ ion is known to be paramagnetic, with a magnetic moment corresponding to five unpaired electrons per iron atom. To account for the experimentally observed fact that this ion has five unpaired electrons, each 3*d*-orbital is assumed to have one unpaired electron in the complex. The vacant $4d_{x2-y2}$ and $4d_{z2}$ orbitals are hybridized with the vacant 4*s* and 4*p* orbitals. The valence bond description of the bonding in $[Fe(OH_2)_6]^{3+}$ ion is as follows.



Here hybridization takes place.

B.H

Hybride orbital are called degenerate orbital due to equal energy.

Each of the six water ligands now donates two electrons into one of the six sp^3d^2 hybrids, forming the six coordinate covalent bonds. As in the previous case, none of the original 3*d* electrons of Fe^{3+} ion is involved in bonding. Since a set of outer *d*-orbitals is involved in the hybridization, $[Fe(OH_2)_6]^{3+}$ is called an *outer-orbital complex*. The coordination compounds of this type are also called *spin free* or *high spin complexes*. Other examples of outer-orbital complexes are $[CoF_6]^{3-}$, $[Cr(OH_2)_6]^{3+}$, $\{Mn(OH_2)_6]^{2+}$ etc.

The structures of $[Fe(CN)_6]^{3-}$ and $[Fe(OH_2)_6]^{3+}$ are shown in Fig. 11.5 (a) and (b).

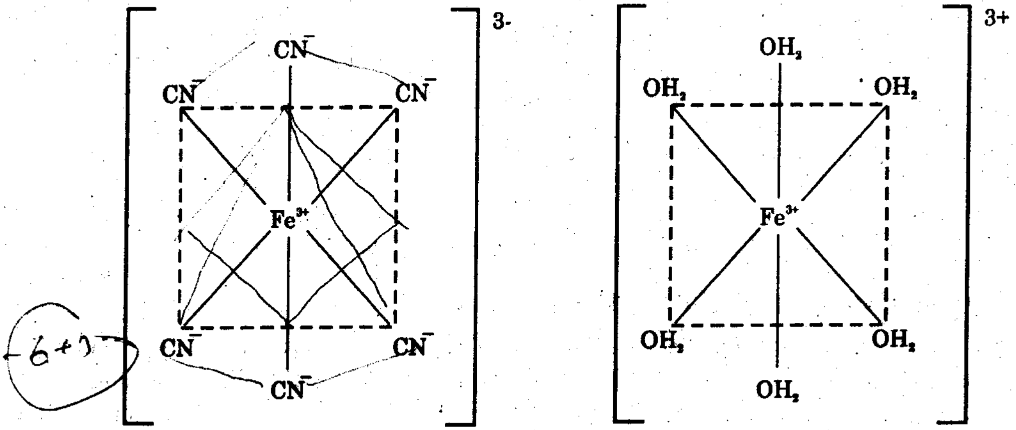
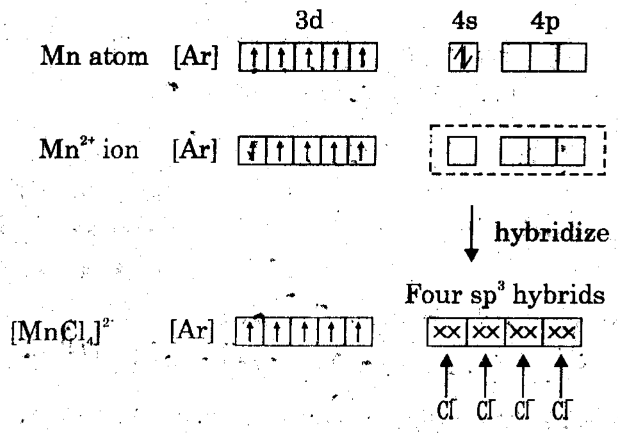


Fig. 11.5 (a) Structure of $[Fe(CN)_6]^{3-}$ (b) Structure of $[Fe(OH_2)_6]^{3+}$

VBT As Applied to Tetrahedral Complexes

Tetrahedral complexes result from sp^3 hybridization. In sp^3 hybridization one s and three p-orbitals should belong to the same shell. The formation of tetrahedral complexes on the basis of VBT can be explained by taking the example of complex ion $[MnCl_4]^{2-}$. This complex ion is paramagnetic corresponding to the presence of five unpaired electrons and hence the configuration of Mn^{2+} ion in the free state and in the complex ion remains the same.



means mixing

Example of some tetrahedral complexes are: $[NiCl_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{3-}$, $Ni(CO)_4$ etc.

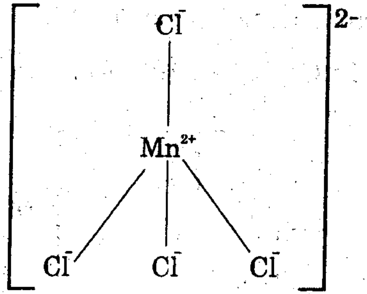


Fig. 11.6(a). Tetrahedral structure of $[MnCl_4]^{2-}$ ion.

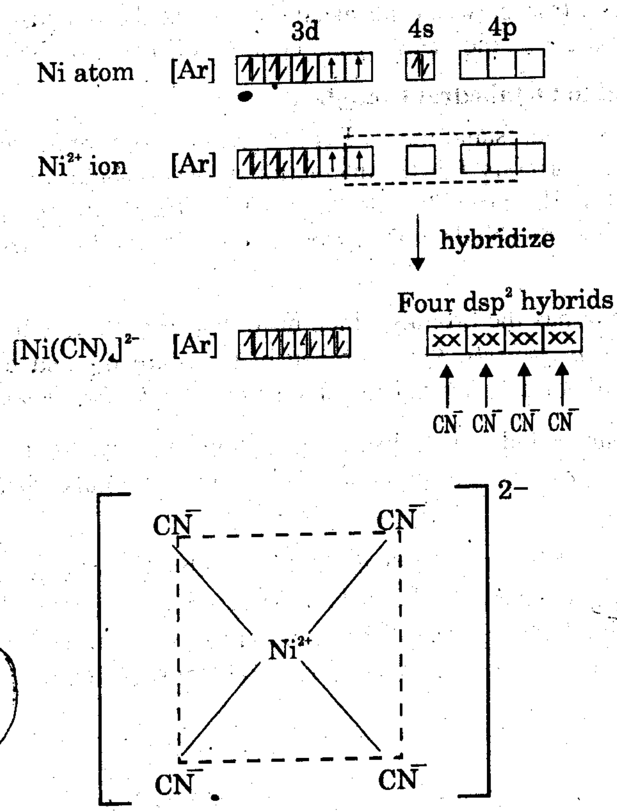
VBT As Applied to Square Planar Complexes

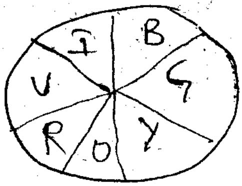
Square planar complexes result from dsp^2 hybridization (utilizing $d_{x^2-y^2}$ orbital) at the central metal ion. The metals most commonly forming square planar complexes are Cu (II), Au(III), Co(II), Ni(II), Pt(II) and Pd(II). For example, the tetracyanonickelate (II) ion, $[Ni(CN_4)]^{2-}$ is square planar and diamagnetic.

Limitations of VBT

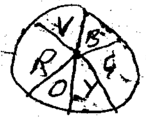
1. The valence bond theory cannot account for the relative stabilities for different shapes and different coordination numbers in metal complexes.
2. The VBT cannot explain the magnetic moment data of some complexes.
3. This theory does not explain the absorption spectra, colour of transition metal ions and heats of formation etc.

4. This theory is unable to explain the nature of some of the complexes of copper.
5. This theory cannot account for the relative rates of reactions of analogous metal complexes.
6. Too much stress has been laid on the metal ion while the importance of ligand is not properly stressed.





Spectrum of light



R = 760 nm
V = 436 nm

Fig. 11.6(b). Square planar structure of [Ni(CN)$_4$]$^{2-}$ ion.

11.12 CRYSTAL FIELD THEORY (CFT)

applied on ionic crystal to indicate color.

This theory advanced by Bethe and Van Vleck was originally applied mainly to ionic crystals and is, therefore called *Crystal Field Theory* (CFT). It was not until 1952 Orgel popularised its use for Inorganic Chemists. On the basis of this theory the bonding between the metal and the ligand is totally ionic. This is a basic difference between VB theory and CF theory. The former assumes the bond to be essentially covalent. The CFT determines the effect of different electrostatic fields caused by the different geometries of the complexes and different basic strengths of the ligands on the energies of the d-orbital of the central metal atom or ion. This theory can explain very well (a) colour (b) magnetic properties and (c) spectra of transition metals. Salient features of CFT are:

1. The central metal cation is surrounded by ligands which contain one or more lone pairs of electrons.
2. The ionic ligands (Cl^-, F^-, CN^- etc.) are regarded as negative point charges and the neutral ligands (H_2O, NH_3 etc.) are regarded as point dipoles or simply dipoles.
3. If the ligand is neutral, the negative end of this ligand dipole is orientated towards metal cation.
4. The interaction between the metal cation and the ligands is regarded as purely electrostatic, i.e., the metal-ligand bond is considered to be 100% ionic.

CFT As Applied to Octahedral Complexes

In order to understand the CFT it is necessary to have a firm grasp of the spatial orientation of the d-orbitals. It is the interaction of the d-orbitals of a transition metal with ligands surrounding the metal that produces CFT effects. On the basis of orientation of the lobes of the five d-orbitals with respect to coordinates, these have been divided into two groups:

(i) This group has the orbitals which have their lobes along the axes and hence are called *axial orbitals*. Quite obviously these are d_{z2} and d_{x2-y2} orbitals. Group theory calls these e_g orbitals in which e refer to *doubly degenerate set.*

(ii) This group includes the orbitals whose lobes lie between the axes and are called *non-axial orbitals*. Group theory calls these t_{2g} orbitals wherein t refers to *triply degenerate set.*

In the case of free metal ion all the five *d*-orbitals are degenerate, i.e., these have the same energy. Let us take the example of an octahedral complex, $[ML_6]^{n+}$ in which the central metal cation M^{n+} is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown in figure 11.7

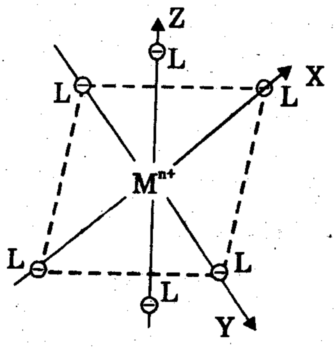


Fig. 11.7 Octahedral symmetry of $[ML_6]^{n+}$ ion.

Since the ligand donor atoms approach the metal ion along the axes during the formation of octahedral complexes, there are greater repulsions among ligand electrons and metal electrons in the e_g orbitals than among ligand electrons and those in t_{2g} orbitals. Crystal Field theory proposes that the approach of the six donor atoms (point charges) along the axes sets up an electric field (the crystal field) that removes the degeneracy of the set of *d*-orbitals and splits them into two sets, the t_{2g} set at lower energy and e_g set at higher energy. This separation of five *d*-orbitals of the metal ion into two sets having different energies is called *crystal field splitting* or *energy level splitting*. This concept of crystal field splitting makes the basis of CFT.

The energy gap between t_{2g} and e_g sets is denoted by $\Delta_0$or 10Dq. This energy difference arises because of the difference in electrostatic field exerted by the ligands on t_{2g} and e_g sets of orbitals of the central metal ion. Δ_0 or 10Dq is called the ***crystal field splitting energy.*** Δ_0 is proportional to the crystal field strength of the ligands, that is, how strongly the ligand electrons repel the metal electrons. With the help of simple geometry it can be shown that the energy of t_{2g} orbitals is $0.4\Delta_0$*less* than that of hypothetical degenerate d-orbitals and hence, that of e_g orbitals is $0.6\Delta_0$ *above* that of the hypothetical degenerate d-orbitals. Thus, we find that t_{2g} set loses an energy equal to $0.4\Delta_0$ while e_g set gains an energy equal to $0.6\Delta_0$ The $0.4\Delta_0$ is said to be the *crystal field stabilization energy* (CFSE) for the complex. The CFSE for metal ions in octahedral complexes have been calculated by assigning a value of $0.4\Delta_0$for each electron present in t_{2g} orbitals and $-0.6\Delta_0$for each electron present in an e_g orbital.

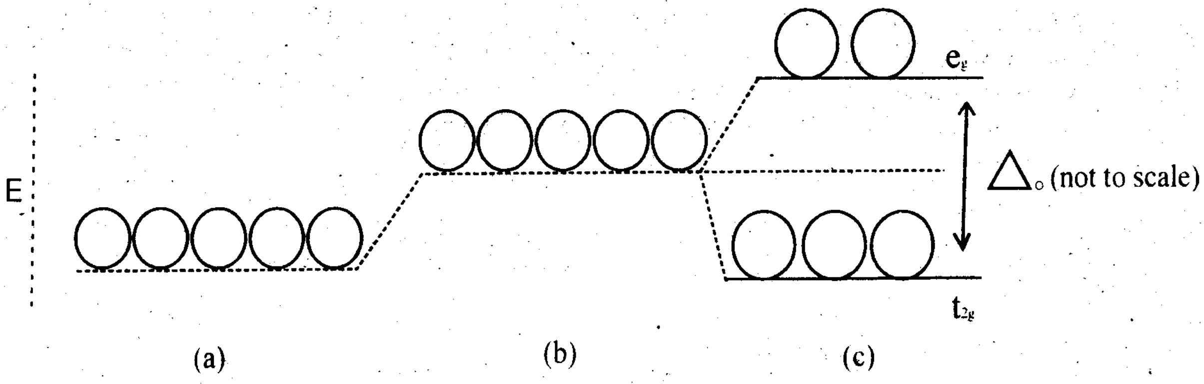


Fig. 11.8 The energies of d-orbitals (a) in a free metal ion (b) in a spherical crystal field and (c) in octahedral crystal field.

The d-electrons on the metal ion occupy the t_{2g} set in preference to high energy e_g set. In fact, the t_{2g} orbitals are called *nonbonding orbitals* in octahedral complexes, but the e_g orbitals are called *antibonding orbitals*, because electrons that are forced to occupy these orbitals are quite strongly repelled by the close approach of the ligand electrons, and tend to destabilize the octahedral complex.

Factors Affecting the Magnitude of Δ_0: The extent of crystal field splitting depends upon the nature of central cation and the nature of ligand. The complex compound having the central cation with higher oxidation state has higher value of Δ_0 than that having the central cation with lower oxidation state. For example,

$$\Delta_0 \text{ for } [Fe(OH_2)_6]^{3+} > \Delta_0 \text{for } [Fe(OH_2)_6]^{2+}$$

The magnitude of $\Delta_0$also varies from strong (er) to weak (er) ligand. Strong (er) ligands are those which exert a high splitting power while the weak (er) ligands are those which have a weak (er) field on the central metal cation and consequently relatively lower splitting power. The common ligands can be arranged in order of their increasing splitting power to cause *d*-orbitals splitting. This series is called *spectrochemical series* and is given below.

$$I^- < Br^- < Cl^- \sim SCN^- < F^- < OH^- < H_2O < NH_3 < en < NO_2^- < CN^- < CO$$

Let us now consider the cases of the hexafluorocobaltate (III) ion $[CoF_6]^{3-}$, and the hexaamminecobalt (III) ion, $[Co(NH_3)_6]^{3+}$, both contain a d^6 ion. The former is a paramagnetic outer orbital complex and the latter is a diamagnetic inner-orbital complex. Since it, magnetic moment indicates that $[CoF_6]^{3-}$ also has four unpaired electrons per ion, the electrons must be arranged with four in t_{2g} orbitals and two in e_g orbitals. On the other hand, $[Co(NH_3)_6]^{3+}$ is diamagnetic, and all six *d*-electrons must be paired in the t_{2g} orbitals.

The difference in configuration is a consequence of the relative magnitudes of the crystal field splitting, Δ_0, due to the different crystal field strengths of fluoride and ammonia ligands. The ammonia molecule more readily donates electrons into vacant metal orbitals than does the very electronegative fluoride ion, which holds its electron very strongly. As a result of the crystal field splitting generated by the close approach of six ammonia molecules to the metal ion Δ_0 is greater than that produced by the approach of six fluoride ions. This situation is shown in figure 11.10.

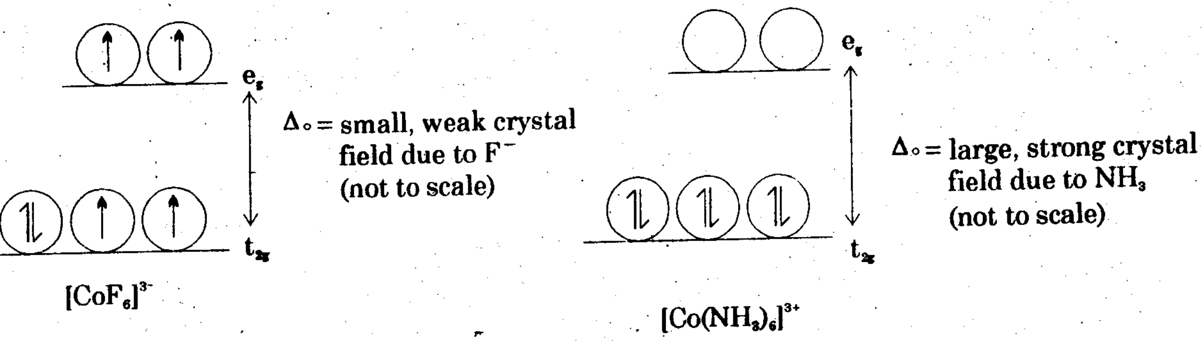


Fig. 11.10 Relative crystal field splittings (Δ_0) of d-orbitals in Co(III) complexes.

The crystal field splitting for $[CoF_6]^{3-}$ ion is so small that an energetically more favourable situation results if two electrons remain unpaired in the antibonding e_g orbitals. This is an example of *high spin complex*. For high spin complex electron pairing energy, $P > \Delta_0$. A high spin complex in the crystal field treatment corresponds to an outer orbital complex by valence bond treatment.

In contrast, the $[Co(NH_3)_6]^{3+}$ ion is *low spin complex*. The Δ_0 generated by the strong field ligand, ammonia, is greater than electron pairing energy, so electrons become paired in t_{2g} orbitals. A low spin complex corresponds to an inner-orbital complex by the valence bond treatment. Low spin configurations exist only for octahedral complexes having metal ions with d^4, d^5, d^6 and d^7 configurations. For d^1–d^3 and d^8–d^{10} ions only one possibility exists. In each case the configuration is designated as high spin. All d^n possibilities are shown in Table 11.6.

Table 11.6 High and Low Spin Octahedral Configurations

d^n	Examples	High Spin	Low spin
d^1	Ti^{3+}	_ _ e_g ↑ _ _ t_{2g}	– same as high spin
d^2	V^{3+}, Zr^{2+}	_ _ e_g ↑ ↑ _ t_{2g}	– same as high spin
d^3	V^{2+}, Cr^{3+}	_ _ e_g ↑ ↑ ↑ t_{2g}	– same as high spin
d^5	Mn^{2+}, Fe^{3+}	↑ ↑ e_g ↑ ↑ ↑ t_{2g}	_ _ e_g ↑↓ ↑↓ ↑ t_{2g}
d^7	Co^{2+}, Rh^{2+}	↑ ↑ e_g ↑↓ ↑↓ ↑ t_{2g}	↑ e_g ↑↓ ↑↓ ↑↓ t_{2g}

CFT As Applied to Tetrahedral Complexes

The CF splitting of the *d*-orbitals for a tetrahedral structure is more difficult to visualize. We must first try to picture a tetrahedron placed inside a cube. Note that the four corners of the tetrahedron are located at the four corners of the cube as shown in figure 11.9. The four ligands are lying between the three axes viz. x, y and z-axes which pass through the centre of the six faces of the cube. By an analogous line of reasoning it can be shown that the electrostatic field of four charges surrounding an ion causes the *d*-shell to split up. In this case the d_{xy}, d_{yz} and d_{xz} orbitals are lying directly in the path of ligands, these orbitals will experience greater force of repulsion from the ligands than those of d_{x2-y2} and d_{z^2} orbitals which are lying in space between the ligands. Thus the energy of d_{xy}, d_{yz} and d_{xz} (t_2) set orbitals will be increased while that of d_{x2-y2} and d_{z2} (e) set orbitals will be decreased.

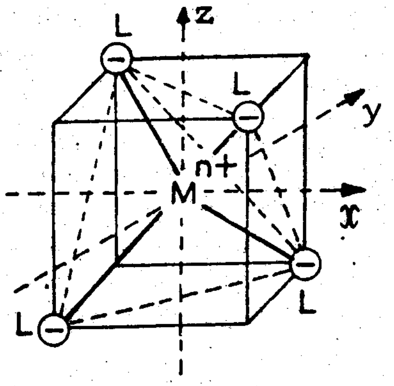


Fig. 11.11. A sketch showing the tetrahedral arrangement of four negative charges around a cation M^{n+}

The energy difference between t_2 and e sets for tetrahedral complex is represented by Δ_t. Because a octahedral splitting is caused by six ligands, while a tetrahedral splitting is caused by only four ligands, the tetrahedral splitting caused by a given set of four ligands is smaller than the octahedral splitting caused by six of the same ligands. An approximate relationship is that $\Delta_t \approx 0.45\Delta_0$.

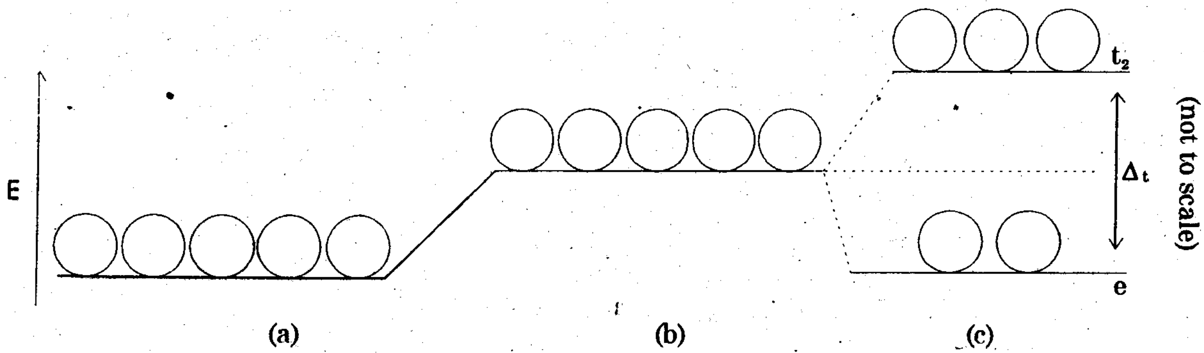


Fig. 11.12 The energy of d-orbitals (a) in a free metal ion (b) in a spherical crystal-field and (c) in tetrahedral crystal field.

Example 11.1

Calculate the crystal field stabilization energy (CFSE) for d^1, d^5 and d^7 ions configuration for low and high spin octahedral complexes.

Solution

The crystal field stabilization energies for metal ions in octahedral complexes is calculated by assigning a value of $0.4\Delta_0$ for each electron present in t_{2g} orbitals and $-0.6\Delta_0$ for each electron present in e_g orbitals.

1. *d*^{1} ion

_ _ e_g	_ _ e_g
↑ _ _ t_{2g}	↑ _ _ t_{2g}
high spin	low spin

CFSE = 0.4 x 1 = 0.4

(high & low spin)

2. *d*^{5} ion

↑ ↑ e_g	_ _ e_g
↑ ↑ ↑ t_{2g}	↑↓ ↑↓ ↑ t_{2g}
high spin	low spin

CFSE (high spin) = 0.4 x 3 – 0.6 x 2 = 0.0

CFSE (low spin) = 0.4 x 5 – 0.0 = 2.0

3. *d*^{7} ion

↑ ↑ e_g	↑ _ e_g
↑↓ ↑↓ ↑ t_{2g}	↑↓ ↑↓ ↑↓ t_{2g}
high spin	low spin

CFSE (high spin) = 0.4 x 5 – 0.6 x 2 = 0.8

CFSE (low spin) = 0.4 x 6 – 0.6 x 1 = 1.8

Example 11.2

Which complex of the following pairs has the larger value of Δ_0?

(i) $[Co(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$

(ii) $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$

(iii) $[Co(OH_2)_6]^{2+}$ and $[Co(OH_2)_6]^{3+}$

Solution

(i) Since CN^- is stronger ligand than NH_3 (i.e., CN^- ion has greater field stronger than NH_3), $\Delta_0$for $[Co(CN)_6]^{3-}$ is greater than Δ_0 for $[Co(NH_3)_6]^{3+}$

(ii) $[Co(NH_3)_6]^{3+}$ ion has greater value of Δ_0 than that of $[CoF_6]^{3-}$.

(iii) The charge on Co in $[Co(OH_2)_6]^{3+}$ is higher than that on Co in $[Co(OH_2)_6]^{2+}$. Thus Δ_0 for $[Co(OH_2)_6]^{3+}$ is higher.

11.13 LIGAND FIELD THEORY (LFT) OR (MOLECULAR ORBITAL THEORY (MOT))

The crystal field theory (CFT) takes no account of possible covalent bonding in complexes - and regards the bonding as purely electrostatic. But the physical measurements such as electron spin resonance (ESR), nuclear magnetic resonance

(NMR) etc. suggest that there is some measure of covalent bonding also in complexes. It is because of this reason that a kind of modified form of CFT has been suggested in which some parameters are empirically adjustable to allow for covalence in complexes. This modified form of CFT is often called *Ligand Field Theory*, LFT. However, LFT is sometimes also used as a general name for the whole gradation of theories from CFT to the molecular orbital theory, MOT. Cotten and Wilkinson have called LFT, *Adjusted Crystal Field Theory*, ACFT.

MOT As Applied to Octahedral Complexes

The covalent bonding in octahedral complexes may be considered in terms of MOT. According to MOT covalent bonds are formed by the maximum overlap of atomic orbitals of the central metal atom or ion and those of ligand producing molecular orbitals. These molecular orbitals specify the region (in space) in which the electronic charge is most likely to be found. Instead of being localized upon a single nucleus, these MO's extend over all the molecule. The calculations for obtaining the MO's from first principles are very different. This can be done very elegantly and systematically using some principles of Group Theory. Here we shall simply deal with the results. The MO's we shall be using here will be of LCAO type and we shall consider the formation of MO's specifically in octahedral complexes.

The ligand field representation of metal complexes is quite complicated but it resembles with the molecular orbital representation of simple molecules. A ligand field diagram for a coordination compound may be built on the same principles as that for simple molecules. The atomic orbitals of the metal ion and ligands are placed on the two extreme ends of the diagram while the MO's are introduced in the middle of the diagram. Usually metal ions have (n−1) *d*, *ns* and *np* orbitals available for bonding. The other higher or lower orbitals being of very different energies do not take part in bond formation. The metal orbitals are placed on the L.H.S and the ligand orbitals (represented by a single energy level) are placed on the R.H.S of the diagram. The overlapping of atomic orbitals of the metal ion with the ligand orbital results in the formation of bonding, non-bonding and antibonding molecular orbitals. The MO diagram for $[Co\ F_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ ions are shown in figures 11.13 and 11.14 respectively.

N.B. When metal orbitals are rotated in octahedral field, the following symmetry representations are obtained.

d-orbitals = $t_{2g} + e_g$

s-orbitals = a_{1g}

p-orbitals = t_{1u}

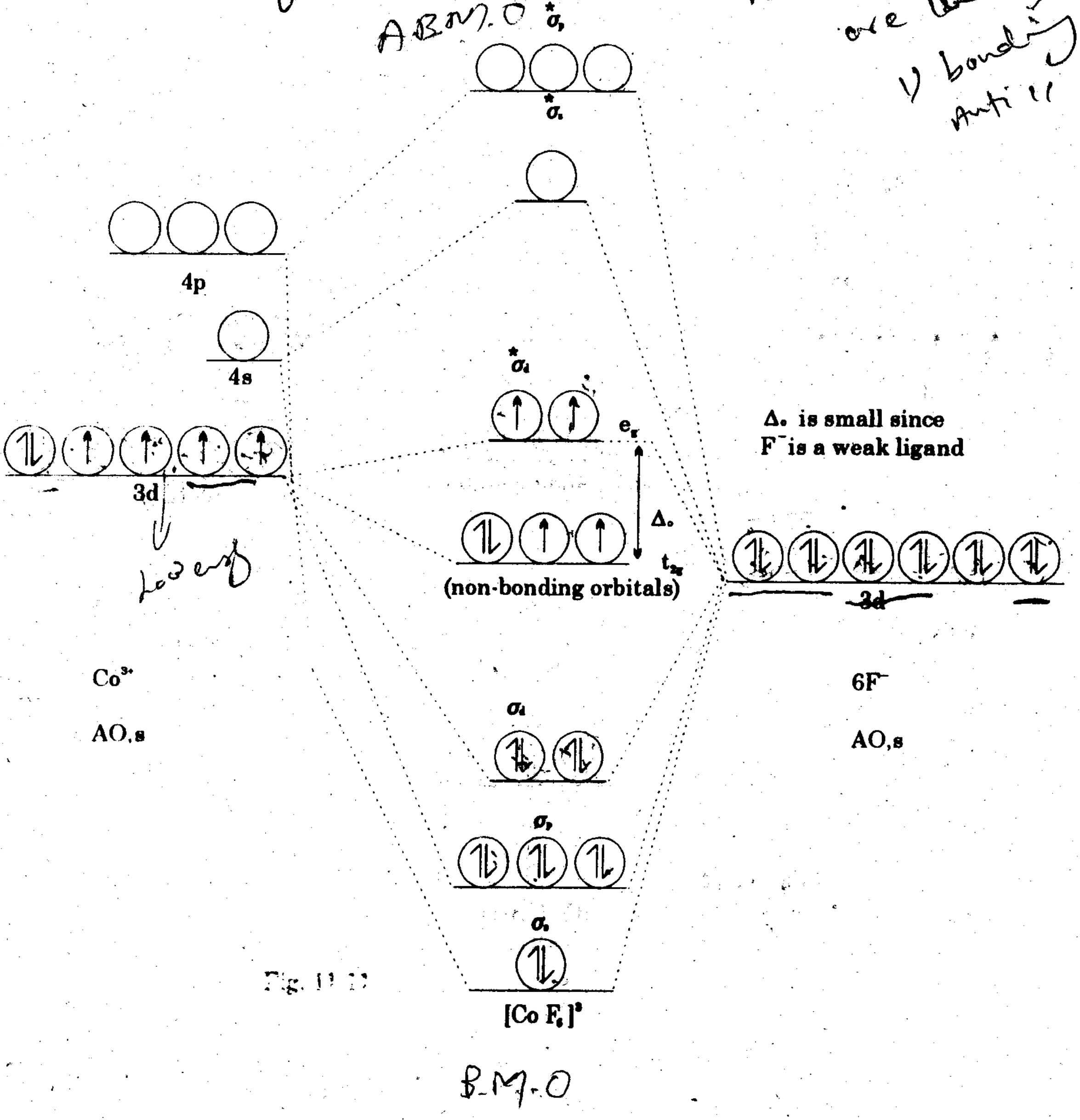
Where a = non-degenerate

e = doubly degenerate

t = triply degenerate

To ~~atto~~ Two or more atomic orbitals ~~mix~~ together to form molecular orbital.

molecular orbital are ~~two~~ types
1) bonding
Anti ''



Paramagnetic due to unpair electron in antibonding MO

Fig. 11.13. MOT energy level diagram of $[Co F_6]^{3-}$ ion (not to scale)

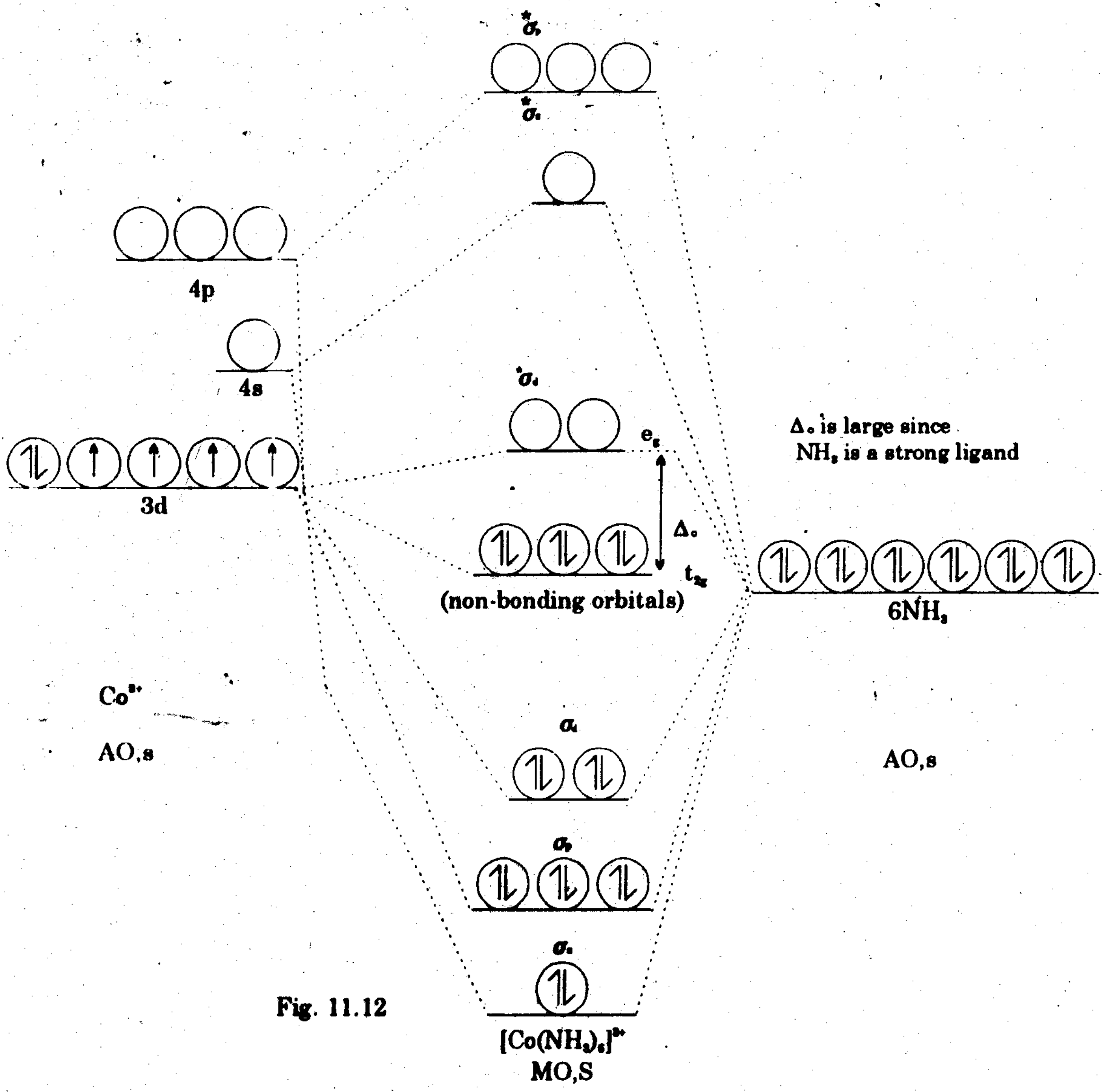


Fig. 11.12

Diamagnetic behaviour
due to no unpaired electron in A.B.M.O.

Fig. 11.14. MOT energy level diagram of $[Co(NH_3)_6]^{3+}$ ion (not to scale)

It is obvious from the diagrams that the magnitude of Δ_0 is larger for $[Co(NH_3)_6]^{3+}$ ion than for $[Co\ F_6]^{3-}$ ion because NH_3 is a stronger ligand but F^- ion is a weaker ligand. The energy of pairing of electrons is less than Δ_0 in $[Co\ (NH_3)_6]^{3+}$, and the electrons, therefore, remain paired. Thus $[Co(NH_3)_6]^{3+}$ is diamagnetic in nature. On the other hand, the energy of pairing of electrons is greater than Δ_0 and, therefore, electrons remain unpaired. The presence of unpaired electrons in σ^*_d orbitals is responsible for paramagnetic behaviour of $[Co\ F_6]^{3-}$.

11.14. COLOUR AND MAGNETIC BEHAVIOUR OF COORDINATION COMPOUNDS

It has been seen that the solution of the transition metal complexes formed by the metal cations having no unpaired electrons in d-orbitals are colourless while the solution of the transition metal complexes given by transition metal cations having one or more unpaired electrons in the *d*-orbitals are coloured. The colour of the transition metal complexes can well be explained by considering the example of $[Ti(OH_2)_6]^{3+}$ ion which is an octahedral complex and has purple colour. Now when white light is allowed to fall on this complex ion, the ion absorbs radiation from the white light (i.e., visible spectrum). The maximum absorption takes place at a wavelength of 5000Å. The absorbed light of this wavelength is green and the transmitted light corresponding to this absorbed light is purple which is the colour of the $[Ti(OH_2)_6]^{3+}$ ion (fig. 11.15)

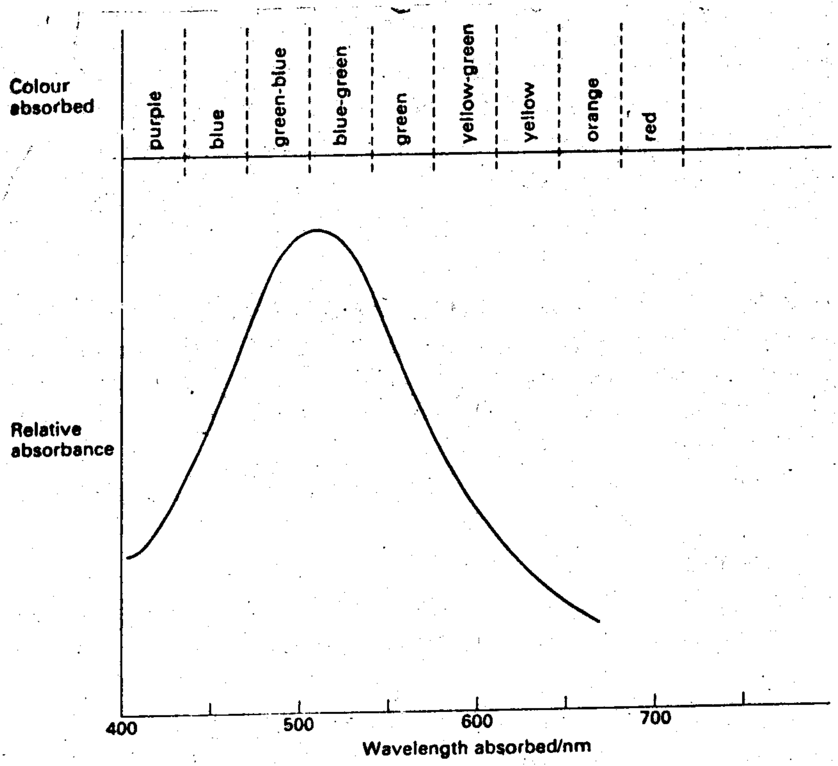


Fig. 11.15. Absorption spectrum of the $[Ti(H_2O)_6]^{3+}$ *ion.*

The cause of colour can also be explained on the basis of CFT. We know that Ti^{3+} ion has the configuration $t_{2g}^1 e_g^\circ$. Now when white light is allowed to fall on $[Ti(OH_2)_6]^{3+}$ ion, the unpaired electron present in t_{2g} set of orbitals moves from lower energy t_{2g} set to higher energy e_g set, since the energy of radiation absorbed by unpaired t_2g electron is the same as the energy difference between t_{2g} and e_g sets. (Fig. 11.16). This type of electronic transition from t_{2g} to e_g level is called *d–d* transition which is the cause of the colour of $[Ti(OH_2)]^{3+}$ ion.

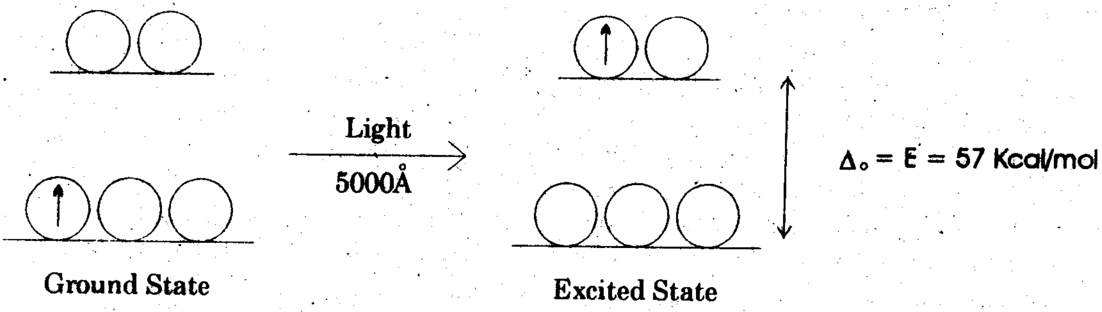


Fig. 11.16. The d-d electronic transition in $[Ti(OH_2)_6]^{3+}$

Crystal field theory can be used to find out the number of unpaired electrons (n) in a given octahedral complex. The substitution of n value in the spin only formula, $\mu = \sqrt{n(n+2)}$ gives the value of magnetic moment, μ of the given complex compound. From the knowledge of μ value the valence state of the central metal cation and the nature of the bonding in the complex (i.e., whether the complex is high spin or low spin). can be known.

11.15 ISOMERISM IN COORDINATION COMPOUNDS

The coordination compounds which have the same molecular formula but have their ligands attached to the central metal atom in different ways are called **isomers**. These isomers have different properties. The phenomenon that gives rise to different isomers is called *isomerism.*

Isomerism may be of two types viz., structural isomerism and stereo (space) isomerism.

1. Structural Isomerism

This isomerism arises due to the difference in the structures of complex (coordination) compound. This isomerism is of the following types:

1. *Conformation isomerism*

In this isomerism two isomers have different geometries but are otherwise identical. For example $[N^{2+}(P.Et.Ph_2)_2Br_2]$ complex (four coordination complex) gives two conformation isomers. One of these is green and paramagnetic while the other is brown and diamagnetic. The green form is tetrahedral while the brown form is square planar. Thus these have different geometries but the coordination number of Ni^{2+} ion in both the isomers is the same (=4).

2. *Ionisation isomerism*

The complex compound showing ionization isomerism are called ionization isomers. These isomers have the same molecular formulae and are produced when the ligands given in the coordination sphere and the anions present out side the coordination sphere are exchanged with each other. Thus both the complex compounds of each of the following pairs are ionization isomers to each other.

(i) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5(SO_4)Br$

(ii) $[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4Cl(NO_2)Cl$

(iii) $[Pt(NH_2)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

3. *Hydrate isomerism*

This type of isomerism is similar to ionization. Hydrate isomers are obtained when the H_2O molecules acting as ligands are replaced by the anions present outside the coordination sphere. $CrCl_3.6H_2O$ exists in three hydrate isomers which are $[Cr(H_2O)_6]Cl_3$ (I), $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (II) and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (III) These have different physical and chemical properties, e.g.,

(i) (I) is violet, does not lose water over conc. H_2SO_4 and all the three Cl^- ions as precipitated as AgCl with $AgNO_3$ solution.

$$\underset{\text{(I) (violet)}}{[Cr(H_2O)_6]Cl_3} + \underset{\text{(solution)}}{3AgNO_3} \longrightarrow \underset{\text{white ppt.}}{3AgCl\downarrow} + [Cr(H_2O)_6](NO_3)_3$$

or $$3Cl^- + 3Ag^+ \longrightarrow 3AgCl\downarrow$$

(ii) (II) is blue-green, loses only one H_2O molecule over conc. H_2SO_4 and only two Cl^- ions are precipitated as AgCl with $AgNO_3$ solution.

$$\underset{\text{(II) (green)}}{[Cr(H_2O)_5Cl]Cl_2.H_2O} + \underset{\text{(solution)}}{2AgNO_3} \longrightarrow \underset{\text{white ppt.}}{2AgCl} + [Cr(H_2O)_5Cl](NO_3)_2.H_2O$$

or $$2Cl^- + 2Ag \longrightarrow 2\,AgCl\downarrow$$

(iii) (III) is blue-green, loses two H_2O molecules over conc. H_2SO_4 and only and Cl^- ion is precipitated by $AgNO_3$ solution.

$$\underset{\text{(II) (green)}}{[Cr(H_2O)_4Cl_2].2H_2O} + \underset{\text{(solution)}}{AgNO_3} \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + [Cr(H_2O)_4Cl_2]NO_3.2H_2O$$

or $$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$$

The behavior of these isomers over conc. H_2SO_4 as mentioned above indicates that the number of H_2O molecules outside the coordination sphere in (I), (II), (III) is equal to zero, one and two respectively.

The action of $AgNO_3$ solution on these isomers indicates that (I), (II) and (III) have three, two and one Cl- ions outside the coordination sphere.

Other examples of hydrate isomers are given below:

(i) $[Co(en)_2(H_2O)Cl]Cl_2$ and $[Co(en)_2Cl_2]Cl.H_2O$

(ii) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H2O$

(iii) $[Cr(py)_2(H_2O)Cl_2]Cl$ and $[Cr(py)_2(H_2O)Cl_3].H_2O$

4. *Coordination isomerism*

This type of isomerism is shown by those complex compounds which are composed of complex cation and complex anion. Coordination isomers are obtained when some or all ligands of both the coordination spheres are interchanged with each other. Thus both the complex compound of each of following pairs are coordination isomers to each other. In these pairs the central metallic atom in the two coordination spheres may be the same or different.

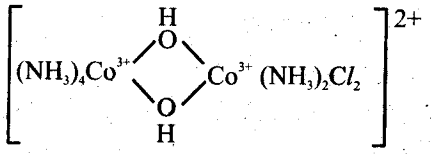
(i) $[Cr^{3+}(NH_3)_6]^{3+}[Cr^{3+}(CN)_6]^{3-}$ and $[Cr^{3+}(NH_3)_4(CN)_2]^{+}[Cr^{3+}(CN)_4(NH_3)_2]^{-}$

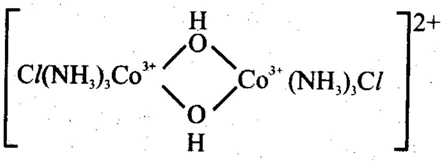
(ii) $[Pt^{2+}(NH_3)_4]^{2+}[Pt^{2+}Cl_4]^{2-}$ and $[Pt^{2+}(NH_3)_3Cl]^{+}[Pt^{2+}Cl_3(NH_3)]^{-}$

(iii) $[Co^{3+}(NH_3)_6]^{3+}[Cr^{3+}(CN)_6]^{3-}$ and $[Co^{3+}(CN)_6]^{3-}[Cr(NH_3)_6]^{3+}$

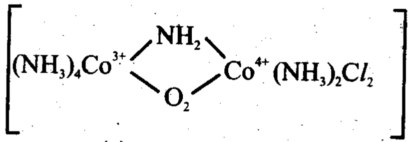
5. *Coordination position isomerism*

This type of isomerism is shown by those complex compounds which contain bridging ligands and arises when the non-bridging ligands are differently placed round the central metal atom. Thus (I) and (II) are coordination position isomers to each other, since, NH_3 molecules and Cl^- ions (non-bridging ligands) are differently placed round two Co^{3+} ions.

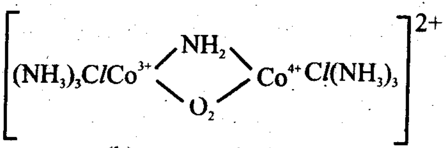




The following binuclear complexes of cobalt also show coordination position isomerism, since the terminal ligands viz. six NH_3 molecules and two Cl^- ions can be placed in an unsymmetrical and symmetrical manner round the central cobalt atom.



(a) unsymmetrical

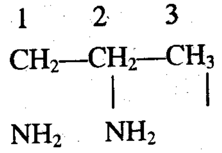


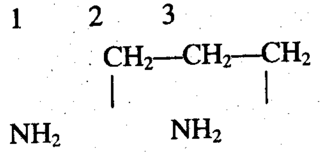
(b) symmetrical

6. *Ligand isomerism*

There are certain ligands which exist as isomers, e.g., diamine derivatives of propane exist in two isomeric forms which are called 1, 2-diamino propane or propylene diamine (*pn*) and 1, 3-diamino propane or trimethylene diamine (*tn*). The structure of propane, *pn* and *tn* are given below:

$$\overset{1}{C}H_3—\overset{2}{C}H_2—\overset{3}{C}H_3$$


$$\underset{NH_2}{\overset{1}{CH_2}}—\underset{NH_2}{\overset{2}{CH_2}}—\overset{3}{CH_3}$$


$$\underset{NH_2}{\overset{1}{CH_2}}—\overset{2}{CH_2}—\underset{NH_2}{\overset{3}{CH_2}}$$

pn and *tn* both are bidenate (neutral) ligands. When these ligands get coordinated to the metal atom, two isomers are obtained. These are called ligand isomers and the isomerism is called ligand isomerism. Thus $[Co^{3+}(pn)_2Cl_2]$+ and $[Co^{3+}(tn)_2Cl_2]^+$ are ligand isomers whose structures are given below in Fig. 11.17. Both these isomers have octahedral geometry.

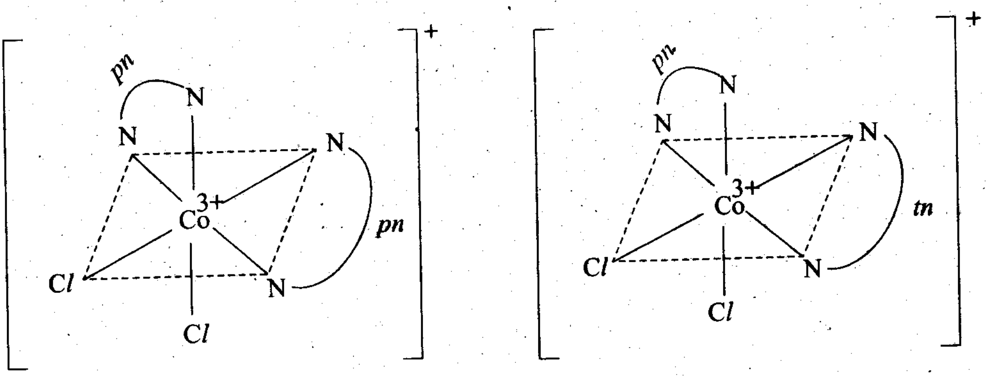


Fig .11.17 (a) Structure of $[Co^{3+}(pn)_2Cl_2]^+$ ion. *(b) Structure of $[Co^{3+}(tn)_2 Cl_2]^+$ ions.*

7. *Polymerisation isomerism*

This type of isomerism is found in those complex compounds whose formula appear to be polymers of some simple complex compound. These entire complex compounds have the same ratio of different metal atoms and ligands in them. For example the following complex compounds are polymerization isomers to each other, since (ii) and (iii) complexes appear to be dimmer of (i) complex and (iv) complex appears to be the pentamer of (i) complex. The ration Co^{3+} : NH3 : NO_2^- in all the complexes is 1 : 3 : 3.

Complex compound		Number of		
		Co^{3+}	NH_3	NO_2^-
(i)	$[Co(NH_3)_3(NO_2)_3]$	1	3	3
(ii)	$[Co(NH_3)_6][Co(NO_2)_6]$	2	6	6
(iii)	$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	2	6	6
(iv)	$[Co(NH_3)_5(NO_2)]_3\,[Co(NO_2)_6]_2$	5	15	15

2. Stereo Isomerism

Stereo isomerism is exhibited by those compounds which have the same position of atoms or groups but these atoms or groups have different arrangement round the central atom. The compounds showing stereo isomerism are called **stereo isomers**. Stereo isomerism may be of two types viz. geometrical (or cis-trans) isomerism and optical (or d-l or mirror-image) isomerism.

1. Geometrical (or cis-trans) Isomerism

The complex compounds which have the same ligands in the coordination sphere but the relative position of the ligands round the central metal atom is different are called geometrical isomers and the phenomenon is called *geometrical isomerism.*

In a given complex compounds the two ligands may occupy positions either adjacent to to each other or opposite to each other. The complex compound having two ligands occupying the adjacent positions to each other is called *cis-isomer* while that in which the two ligands occupy opposite positions is called *trans-isomer*. Thus geometrical isomerism is also called *cis-trans isomerism.*

Geometrical isomerism is not found in complex compounds with coordination number 2 and 3, since in these cases all the positions occupied by the ligands round the central metal are adjacent to one an other. Geometrical isomerism is most common with complex compounds having coordination number 4 and 6.

Geometrical isomerism in 4-coordinated complex compounds

Complexes having central atom with 4-coordination number may have either tetrahedral or square planar geometry.

Geometrical isomerism in tetrahedral complxes

Geometrical isomerism cannot be shown by tetrahedral complexes, since all the four ligands in this geometry have adjacent position (i.e., cis position) to one another and all the four bond angles are the same (= 109.5°)

Geometrical isomerism in square planar complexes

Before discussing the geometrical isomerism exhibited by various types of square planar complexes, we should know how cis and trans isomers of a square planar complex are named. A square planar complex having similar ligands at opposite positions (180° apart) is called trans-isomer. Thus a square planar complex having two similar ligands at 1-3 and 2-4 positions is called trans-isomer. Cis and trans-isomers are also named by numbering system. Thus in $[Pd^{2+}Cl_2BrI]^{2+}$, if two Cl^- ions are placed cis to each other or at 1-2 positions, it is named as *cis-dichloro bromoiodo palladium (II)* ion or 1,2-dichloro *bormoiodo palladium (II) ion.* On the other, if two Cl^- ions are placed trans to each other or at 1-3 positions, it is named as *trans-dichlorobromoiodo palladium (II) ion* or *1, 3-dichlorobromoiodo palladium (II) ion* (See Fig. 11.18)

Important examples of square planar complexes are $[Pt(NH_3)_2Cl_2]^0$, $[Pt(py)_2Cl_2]^0$, $[Pd(NH_3)_2(NO_2)_2]^0$ etc. These complexes exist in cis- and trans-isomers. These isomers of $[Pt^{2+}(NH_3)_2Cl_2]^0$ are shown in Fig. 11.18. In (*a*) since both NH_3 molecules and both Cl^- ions are cis to each it is called cis-isomer. On the other hand, in (*b*) since both NH_3 molecules and both Cl^- ions are trans with respect to each other, it is called trans-isomer.

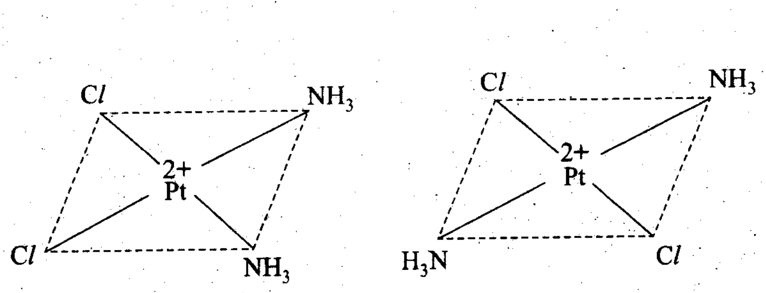


Fig. 11.18. cis-and trans-isomers of $[Pt^{2+}(NH_3)_2Cl_2]^0$

Geometrical isomerism in 6-coordinated complexes: Octahedral complexes

We know that a complex compounds having central atom with coordination number equal to 6 is octahedral in shape. Before discussing the geometrical isomerism exhibited by various types of octahedral complexes, we should know how *cis*- and *trans*-isomers of an octahederal complex are named. In an octahedral complex, if two similar ligands are placed on any of the twelve edges of the octahedron, they are said to be in *cis* position. On the other hand, if two similar ligand are lying on a straight line which passes through the centre (where the metal ion is placed), they are said to be in *trans* position. Thus in an octahedral complex, the two ligands at positions 1-6, 2-4 and 3-5 are *trans* to each other and the two ligands occupying positions 1-2, 1-3, 2-3, 3-6, 6-4 etc. are *cis* to each other. (See Fig. 11.19)

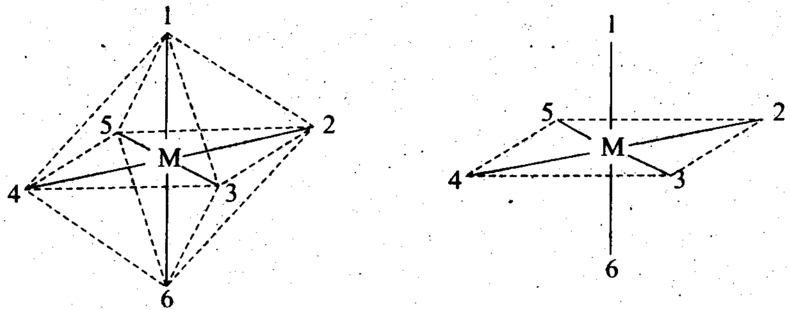
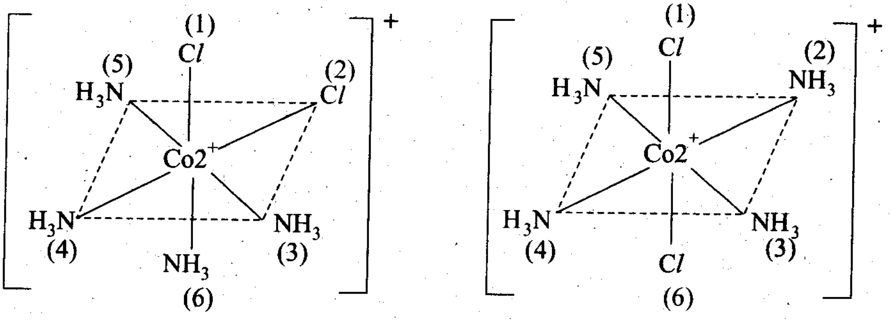


Fig. 11.19. Numbering of six ligands in a regular octahedral complex round the central ion, M.

The above numbering system of ligands can be exemplified by considering the nomenclature of *cis*- and *trans*- isomers of $[Co^{3+}(NH_3)_4Cl_2]^+$ ion which is an octahedral complex ion. *Cis*-isomer of this ion in which two Cl^- ions are *cis* to each other is also called 1,2-dichlorotetrammine cobalt (III) ion]. Similarly, *trans*- isomer of this ion in which two Cl^- ions are trans to each other is also called 1, 6-dichlorotetrammine cobalt (III) ion. [See Fig. 11.18 (*a*) & (*b*)].Important examples of octahedral complexes of this type are $[Co^{3+}(NH_3)_4Cl_2]^+$, $[Co^{3+}(NH_3)_4(NO_2)_2]^+$ etc. These complexes exist in *cis* and *trans*- isomers.



(a) cis-isomer (1,2-dichlorotetrammine cobalt (III) ion). (yellow-brown)

(b) trans-isomer (1, 6-dichlorotetrammine cobalt (III) ion). (yellow)

Fig 11.20. cis-and trans-isomers of $[Co^{3+}(NH_3)_4Cl_2]^+$

3. Optical (or *d-l* or mirror-image) Isomerism

When the solutions of certain complex compounds are placed in the path of a plane polarized light (the waves of the plane-polarized light vibrate only in one direction; vibrations in other directions are cut off), they rotate its plane through a certain angle which may be either to the left or to the right. This property of a complex of rotating the plane of polarized light is called its *optical activity* and the complex possessing this property is said to be *optically active*. Optically active complexes are said to exist in the following forms:

(*a*) One which rotates the plane of polarized light towards right (i.e., in clockwise direction) is said to be dextro-rotatory or *d*-form., *d*-form is also represented by placing (+) sign before its name or formula.

(*b*) One which rotates the plane of polarized light towards left (i.e., in anti-clockwise direction) is called levo rotatory or *l*-form is also represented by putting (—) sign before its name or formula. (+), dextro, and (-), levo, refer to the sign of rotation of the optical isomer at the sodium D line wavelength. The *d*- and *l*-form have the following characteristics: (i) Since *d*-and *l*-forms are capable of rotating the plane of polarized light, these are said to be optically active forms or optical isomers and this phenomenon is called optical activity or optical isomerism. These two forms have exactly identical physical and chemical properties, although they differ in their action on polarized light. (ii) *d*-and *l*-forms can be superimposed on each other and hence *d*-and *l*-forms are also called mirror-image isomers. These optical isomers are also called optical antipods or enantimorphs (Latin: enantio = opposite; morphs = forms) or enantimorphs. Form this description it follows that optical isomerism can also be called mirror-image isomerism or enantimorphism or enantimoerism.

(*c*) The isomer which is not capable of rotating the plane of polarized light is called optically inactive. Such an isomer is called meso, racemic, *dl*or (± form). A racemic substance is composed of 50% *d*- and 50% *l*-form. The solution of a racemic (*dl* mixture) from in a solvent which contains equimolecular amount of *d*-and *l* form is symmetrical and hence optically inactive, because the rotation (of the plane of polarized light) produced by one isomer, say *dl*-isomer is balanced or compensated by equal but opposite rotation produced by the (i.e., *l*-isomer.

Optical inactivity produced in *dl*-mixture is said to be due to external compensation.

Conditions for a molecule to show optical isomerism

A molecule in which the grouping of the atoms is a symmetric is called an asymmetric or dissymmetric molecule. An asymmetric molecule has the following features:

(i) An asymmetric molecule never has a plane of symmetry (also called mirror-image plane) which is defined as an imaginary plane dividing the molecule in such a way that the part of it on one side of the plane is the mirror image of that on the other side of the plane. The molecules possessing such a plane of symmetry are always inactive while those having no plane of symmetry are optically active and hence show optical isomerism.

(ii) An asymmetric molecule cannot be superimposed on its mirror image.

Thus the most necessary and sufficient condition for a molecule to show optical isomerism (i.e., to exist in *d*-and *l*-forms) is that the molecule should be asymmetric, (i.e., it should have no plane of symmetry) and should not be super imposable on its mirror image.

Optical isomerism in 4-coordinated complexes: Tetrahedral complexes

Here we shall discuss optical isomerism in the following types of tetrahedral complexes.

1. *[Ma$_4$] and [Ma$_3$b] type complexes.* Tetrahedral complexes of [Ma$_4$] and [Ma$_3$b] type are not able to show optical isomerism because all the possible arrangements of the ligands round the central ion, M are exactly equivalent.
2. *[Mabcd] type complexes.* Since the central atom (M) in tetrahedral complexes of [Mabcd] type is surrounded by four different ligands, the tetrahedral complex of this type is expected to produce a pair of enantiomarphs. For example [As^{3+} (CH$_3$) (C$_2$H$_5$) (S)(C$_6$H$_4$COO)]$^{2+}$ ion (tetrahedral) exists in two optical isomers as shown in Fig. 11.21.

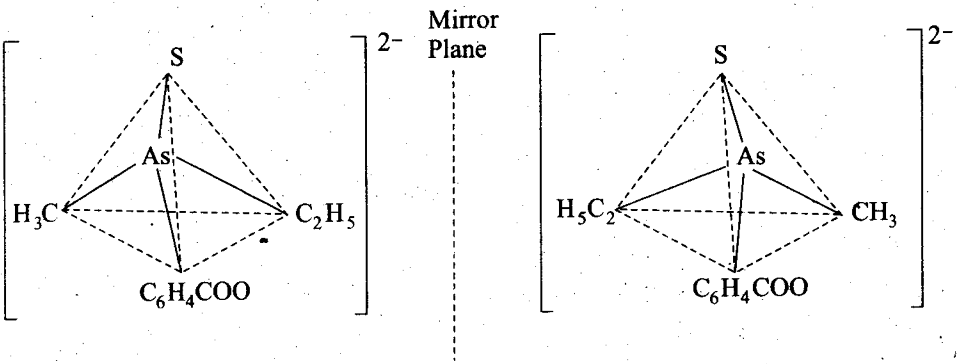


Fig. 11.21. Optical isomers of tetrahedral complex ion, [As(CH$_3$)(C$_2$H$_5$)(S)(C$_6$H$_4$COO)]$^{2-}$

Here it may be noted that 4 different groups round the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetrical (i.e., unsymmetrical), i.e., it should have no plane of symmetry so that it can exist in two mirror-image forms.

Optical isomerism in 6-coordinated complexes: Octahedral complexes

Here we shall discuss the optical isomerism in octahedral complexes of the following type:

3. [$Ma_2b_2c_2$] type complexes. $[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion is an important example of octahedral complex of [$Ma_2b_2c_2$] type. We have already stated that $[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion can exist theoretically in five geometrical isomers, but only three have been isolated. In cis-isomer two identical ligands occupy the adjacent positions of the octahedron. This *cis*-isomer exists in two optical (mirror-image) isomers which are mirror-image to each other as shown in Fig. 11.22. *Trans*-form of this complex ion is symmetrical and hence is optically inactive form. Thus it is a trans-meso form.

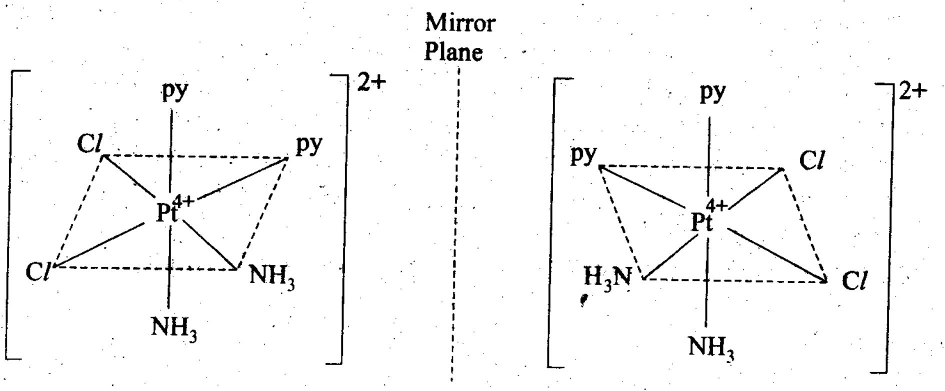


Fig. 11.22. Mirror-image isomers of $[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion.

3. [Mabcdef] type complexes. $[Pt^{4+}(py)(NH_3)(NO_2)ClBrI]^0$ is the only example of octahedral complex of this type. We have already stated that, theoretically, this complex can exist in 15 geometrical isomers. Each of these 15 geometrical isomers exists in optically active *d*-and *l*-forms, giving a total of 30 optically active isomers. *d*- and *l*-isomers for one of the 15 geometrical isomers are given in Fig. 11.23.

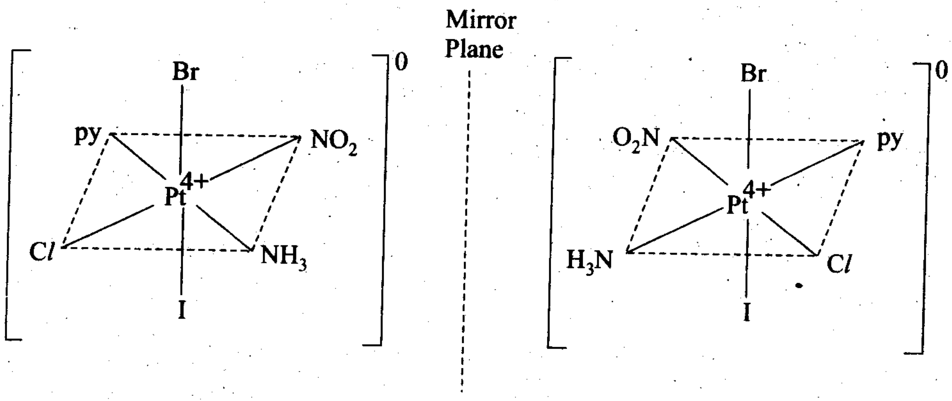


Fig. 11.23. Optical (d-and l-) forms of $[Pt^{4+}(py)(NH_3)(NO_2)ClBrI]^0$

Questions

Q.1. What are transition metals? Why are they called so? Discuss their position in the periodic table.

Q.2.*(a)* What are d-block elements? Discuss the general characteristics of *d*-block elements.

(b) Distinguish among the terms ligands, donor atoms and chelates.

Q.3.*(a)* What property of transition metals allows them to form the coordination compounds easily?

(b) Why is it that zinc is not considered as a transition element?

(c) Explain the difference between a double salt and a complex compound with suitable examples.

Q.4.*(a)* Transition elements are characterized by variable oxidation states, coloured ions, catalytic activity and formation of complexes. Illustrate this statement by detailed reference to three transition elements selected from titanium to copper exclusively.

(b) What properties of the transition elements are consistent with their being metals.

Q.5. Name the following complexes according to IUPAC system of nomenclature.

(i) $[Co(NH_3)_4(H_2O)Br](NO_3)_2$

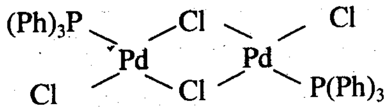
(ii) $Na[Au(CN)_2]$

(iii) $Na_3[Fe(C_2O_4)_3]$

(iv) $[Co(en)_3]Cl_3$

(v) $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]Cl_5$

(vi)



(vii) $[Ni(CO)_2(Ph_3P)_2]$

(viii) $Na[Mn(CO)_5]$

(ix) $Na_4[NiF_6]$

(x) $K_2[Cu(CN)_4]$

Q.6. Write the formulas of the following compounds:

(i) Sodiumtetracyanocadmate

(ii) Hexaamminecobalt (III) chloride

(iii) Diaquadicyanocopper (II)

(iv) Rubidiumtetracyanozincate

(*v*) Pentacarbonyl iron (0)

(*vi*) Sodium pentacyanocobaltate (II)

(*vii*) Hexaammineruthenium (III) tetrachloronickelate (II)

(*viii*) Potassium dicyanobis (oxalato) nickelate (II)

(*ix*) Tetracarbonyl nickel (0)

(*x*) Tris (ethylenediamine) cobalt (III) nitrate.

Q.7.(*a*) What is Werner's theory of coordination compounds? Discuss its salient features.

(*b*) Discuss Werner's theory with reference to cobalt ammines and platinum ammines.

Q.8.(*a*) Explain the term "primary and secondary valences of Werner", giving examples.

(*b*) Indicate the primary and secondary valances of the central metal cation in the following complex compounds:

$$[Co(NH_3)_6]Cl_3, [Pt(NH_3)_2]Cl_2, K_4[Fe(CN)_6], K_2[PtCl_4].$$

Q.9.(*a*) Discuss the term "Effective atomic number" (EAN) used in relation to coordination chemistry.

(*b*) Calculate the effective atomic number of the central atom in the following complex species:

$$[PdCl_4]^{2-}, K_4[Fe(CN)_6], [Cu(NH_3)_4]^{2+}, Ni(CO)_4$$

Q.10. What are the fundamental postulates of Werner's theory of coordination compounds? Explain with suitable examples.

Q.11.(*a*) Discuss Valence bond theory as applied to coordination compounds.

(*b*) Give the hybridization and sketch the structures of each of the following complexes on VBT:

$$[Cr(NH_3)_6]^{3+}, [Co(CN)_6]^{3-}, [NiCl_4]^{2-}, [Cd(CN)_4]^{2-}$$

12.(*a*) How are the structures of coordination compounds explained on the basis of VBT.

(*b*) Why are the dz^2 and $d_{x^2-y^2}$ orbitals utilized in d^2sp^3 and sp^3d^2 hybridization rather than two of the d_{xy}, d_{yz} and d_{xz} orbitals.

Q.13.(*a*) Explain the terms outer-orbital and inner-orbital complexes with suitable examples.

(*b*) On the basis of spectrochemical series, determine whether the following complexes are inner-orbital or outer-orbital and diamagnetic or paramagnetic:

(*i*) $[Cu(OH_2)_6]^{2+}$

(ii) $[Mn\,F_6]^{3-}$

(iii) $[Cr(NH_3)_6]^{3+}$

(iv) $[Cr\,Cl_4\,Br_2]^{3-}$

(c) Discuss the major defects of VBT when applied to metallic complexes.

Q.14. Discuss the usefulness of VBT when applied to coordination compounds. Draw the geometries of the following complex species on the basis of VBT:

$[Mn\,(CN)_6]^{4-}$, $[Co\,F_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Cu(NH_3)_4]^{2+}$

Q.15.*(a)* Discuss the essentials of crystal field theory.

(b) What are strong and weak field ligands? Explain with suitable examples.

Q.16.*(a)* Give an account of crystal field theory as applied to coordination compounds.

(b) Distinguish between low spin and high spin complexes with suitable examples.

Q.17. Write out the electron distribution in t_{2g} and e_g orbitals for the following in an octahedral field.

Metal ion	Ligand field strength
Mn^{2+}	Weak
Mn^{2+}	Strong
Fe^{3+}	Strong
Cu^{2+}	Weak
Ni^{2+}	Weak

Q.18.*(a)* What is crystal field splitting? Give an account of the important factors which influence the magnitude of crystal field splitting.

(b) Which of the following ion pairs has large crystal field splitting value (♦). Give the reason for your answer.

(i) $[NiCl_4]^{2-}$ or $[Ni(CO)_4]^\circ$

(ii) $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$

(iii) $[Co\,F_6]^{3-}$ or $[Co(NH_3)_6]^{3+}$

(iv) $[Co\,Cl_4]^{2-}$ or $[Co(NH_3)_6]^{2+}$

Q.19.*(a)* What is crystal field stabilization energy? Calculate the crystal field stabilization energy for each of the following system:

(i) d^4 (high spin octahedral)

(ii) d^6 (low spin octahedral), and

(iii) d^5 (tetrahedral)

(b) Which of the complex ion namely $[Fe(CN)_6]^{3-}$ and $[Fe(OH_2)_6]^{2+}$ is an outer-orbital complex and why?

(c) How does the CFT explain the absorption spectrum and magnetic properties of the complexes.

Q.20.*(a)* Write a note on spin free and spin paired complexes.

(b) Calculate the CFSE of spin free and spin paired d^6 octahedral complexes.

(c) Describe clearly what Δ is. Why is Δ for a tetrahedral ligand field always less than Δ for an octahedral complex? How is it related to the spectrochemical series?

Q.21.*(a)* Give an account of the ligand field theory (LFT) as applied to coordination compounds.

(b) Draw molecular orbital diagrams of the following complexes:

(i) $[Co(NH_3)_6]^{3+}$

(ii) $[Fe(CN)_6]^{3-}$

(iii) $[Co\,F_6]^{3-}$, and

(iv) $[Fe(OH_2)_6]^{3+}$

Q.22. What are coordination compounds? Discuss their applications in various fields.

Q.23. What are chelates? Discuss various factors affecting the stability of chelates. Give applications of chelates.

Q.24. What is isomerism? Discuss various types of isomerism encountered in coordination compounds.

Q.25. What do you mean by stereoisomerism of complex compounds? Discuss the geometrical and optical isomerism of the following complex compounds

(i) $[Co\,(en)_2\,Cl_2]^+$ (ii) $[Co\,(en)_2\,(NH_3)Cl]^{2+}$

(iii) $[Co\,(en)_2\,(NH_3)_2Cl_2]^+$

Q.26. Name different kinds of isomerism possible in coordination compounds, quoting one suitable example in each case.

Q.27. Draw the various isomers of $[Co\,(NH_3)_4Cl_2\,]^+$.

Q.28. Write note on optical isomerism of octahedral complexes.

Q.29. Justify/comment on the following statements:

(a) Transition elements are also known as *d*-block elements.

(b) Zn is not considered as a member of the *d*-block elements.

(c) Most of the transition elements and their compounds are used as catalyst.

(d) Most of the transition metal ions are coloured.

(e) The IUPAC name of $K_2[PtCl_4]$ is potassium hexachloroplatinate (V).

(f) The oxidation state of Ni in $Ni(CO)_4$ is zero.

(g) The secondary valency of Co in $CoCl_3.6NH_3$ is four.

(h) The complex $[Cr(NH_3)_6]^{3+}$ does not obey EAN rule.

(i) $[Fe(CN)_6]^{3-}$ is an example of outer-orbital complex.

(j) $[Fe(OH_2)_6]^{3+}$ is an example of inner-orbital complex.

(k) $[Ni(CN)_4]^{2-}$ ion has tetrahedral geometry.

(l) $[Zn(NH_3)_4]^{2+}$ ion has square planar geometry.

(m) $[Co(NH_3)_6]^{3+}$ ion has sp^3d^2 hybridization.

(n) The magnitude of Φ_0 for $[Co(NH_3)_6]^{3+}$ ion is greater than for $[Co F_6]^{3-}$ ion.

(o) $[Fe(CN)_6]^{3-}$ has only one unpaired electron while $[Fe(OH_2)_6]^{3+}$ has five.

(p) $[Ni(CN)_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic.

(q) $[Ni(NH_3)_6]^{2+}$ is octahedral while $Ni(CO)_4$ is tetrahedral.

(r) $[Co F_6]^{3-}$ is paramagnetic while $[Co(NH_3)_6]^{3+}$ is not.

(s) Geometrical isomerism is not found in complex compounds with coordination number 2 and 3.

(t) Geometric isomerism is most common with complex compounds having coordination number 4 and 6.

(u) Geometrical isomerism cannot be shown by tetrahedral complexes.

(v) Tetrahedral complexes of $[Ma_4]$ and $[Ma_3b]$ type are not able to show optical isomerism

Chapter Twelve

METALLURGY

12.1 COPPER

Copper is the second anciently known metal, the first being gold. It was named as *cuprun* by the Romans because the Island of Cyprus was the main source of the metal at that time. It is placed in group 1B (11) of the periodic table.

Occurrence

Copper is found in both the native and combined forms. The native copper is remarkably pure (99.5%) and is only a minor source of copper. Native copper is found in U.S.A., China, Russia and Mexico. In the combined form it is found as:

Sulphide Ores

(i) Copper Pyrites, $CuFeS_2$ or $Cu_2S.Fe_2S_3$

(ii) Copper glance, Cu_2S

Oxide Ores

(i) Cuperite, Cu_2O

(ii) Melaconite, CuO

Carbonate Ores

(i) Malachite, $CuCO_3.Cu(OH)_2$

(ii) Azurite, $2CuCO_3.Cu(OH)_2$.

In Pakistan copper ores are found in North Waziristan Agency, Chitral State, Dir State, Gilgit Agency, Hazara District and in Chaghi District (Balochistan). Saindak Metals (Pvt.) Limited has implemented Saindak Copper Gold Project in Chaghi but the project stands closed since January, 1996 due to lack of working capital. The ambitious project was first of its kind in large scale metal mining in Pakistan and was implemented to produce 15,810 tonnes blister copper per annum with contained gold (1.47 tonnes) and silver (2.76 tonnes)

Extraction

Copper is extracted mostly from copper pyrites by the dry process. The important principles involved in the process are given below:

(i) **Concentration:** The finely-powdered ore is concentrated by froth-flotation process. This process is especially suitable for sulphide ores. The finely divided ore, mixed with water and a small amount of pine oil (a foaming agent), is taken in a flotation tank. The whole mass is then agitated by passing compressed air

through it. The oil forms a foam (or froth) with air. The ores particles which are preferentially wetted by oil) rise to the surface along with froth. On the other hand, the gangue particles wetted by water become and settle down slowly to the bottom.

(ii) **Roasting:** The concentrated ore is heated strongly in the presence of excess of air in a reverberatory furnace. During roasting copper pyrites decompose to cuprous and ferrous sulphides, a part of which may be oxidized to corresponding oxides.

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

Simultaneously, moisture is eliminated and impurities like sulphur, arsenic and antimony are removed in the form of their volatile oxides.

$$S + O_2 \longrightarrow SO_2\uparrow$$

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

$$4Sb + 3O_2 \longrightarrow 2Sb_2O_3$$

(iii) **Smelting:** The roasted ore is mixed with coke and sand and heated in the presence of excess of air in a water jacketed blast furnace (Fig. 12.1). The oxidation of ferrous sulphide which started during roasting proceeds further and the so formed ferrous oxide combines with sand to form a fusible slag.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

Further the cuprous oxide reacts with ferrous sulphide to form ferrous oxide (iron has greater affinity for oxygen than copper).

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

Thus most of the iron is converted into oxide which is removed as slag. Slag is removed from the slag hole while the molten mass containing mostly cuprous sulphide with a little ferrous sulphide (FeS) called *matte* is taken out from the exit at the bottom.

(iv) **Bessemerization:** The molten matte is now transferred to a Bessemer converter which is a pear-shaped furnace made of steel plates and provided with a basic lining of lime or magnesia. It can be tilted in any position. It is fitted with pipes known as twyers through which sand and hot air is blown. Following reactions take place in Bessemer Converter:

(a) Conversion of FeS to $FeSiO_3$ (slag)

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

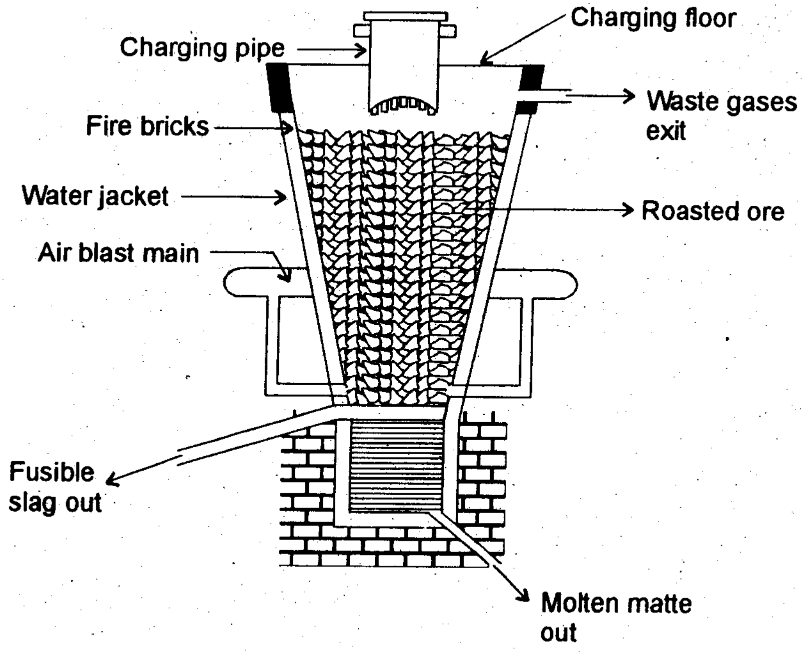


Fig. 12.1 Blast furnace for copper smelting

(b) Partial Oxidation of Cu_2S to Cu_2O

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

(c) Reduction of Cu_2O by Cu_2S to metallic copper

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2\uparrow$$

The molten metal is poured off into sand moulds by tilting the converter and allowed to stand. On cooling, dissolved sulphur dioxide escapes out causing blisters on the surface of copper. Thus the copper so produced is known as *blister copper.* It is about 98% pure.

(v) **Refining:** Purest possible form of copper is obtained by the electrolytic refining of blister copper. The impure copper is cast into blocks which are made anodes. The cathodes consist of thin sheet of pure copper. The electrolyte consists of a solution of copper sulphate and dilute sulphuric acid. On passing an electric current, copper from the crude anodes go into solution and pure copper is deposited on cathodes. Impurities like nickel, zinc and iron pass into solution as sulphates, while impurities like silver and gold (which are not affected by sulphate ions) settle down undissolved as the *anoae mud.* The copper obtained in this way is almost 100 percent pure.

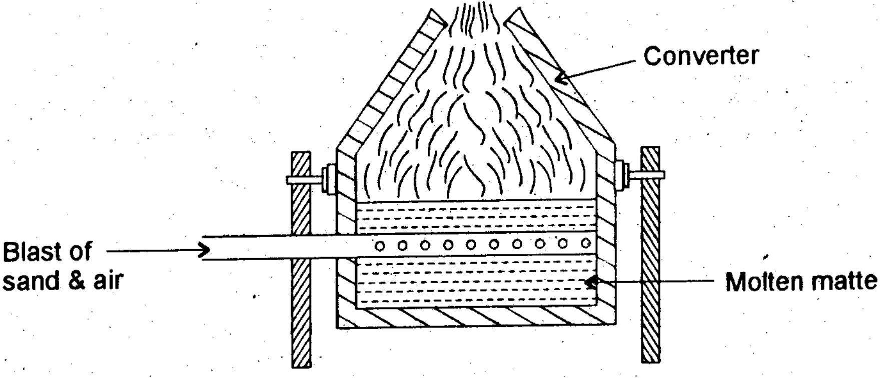


Fig. 12.2 Bessemer converter for copper

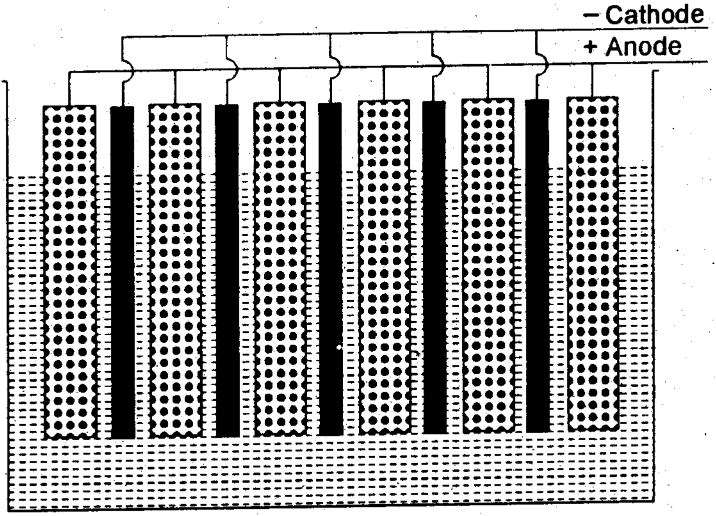


Fig. 12.3 Electrolytic refining of copper

Hydrometallurgy of Copper

As the name indicates this process is used for extracting copper from low grade ores. The essential features of the process are summarized below.

A large heap containing about 100,000 tonnes of the finely powdered ore is exposed to air and water in big tanks. The moist air gradually oxidizes copper and iron sulphides to their sulphates. The process is completed in about a year.

$$2Cu_2S + 5O_2 \longrightarrow 2CuSO_4 + 2CuO$$

$$CuS + 2O_2 \longrightarrow CuSO_4$$

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$2Fe_2S_3 + 11O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

The pale green liquid draining from the bottom of the heaps contains mainly copper sulphate. Copper is precipitated from pale green solution by means of iron.

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu\downarrow$$

The precipitated copper is dried, melted and then refined.

Uses of Copper

Copper is most useful metal because of its characteristic properties like excellent electrical conductivity and stability in air and water. Its important uses are summarized below:

1. It is used for making electrical wires, cables and conducting apparatus.
2. It is used as a coinage metal and in ornaments and jewellery for making them hard.
3. It is used for making water stills, kettles, vacuum pans, steam pipes etc.
4. It is used in electroplating and electrotyping.
5. It is used for making scientific apparatus such as calorimeters.
6. Copper salts are largely used as insecticides and colouring materials.
7. Large quantities of copper are used for making its various alloys like brass, bronze, gun-metal, etc.

12.2 ALUMINIUM

((For metallurgy of aluminium see Chapter No.5)

12.3 IRON AND STEEL

Iron is a metal of great utility in our day to day life. It is placed in group VIII of the periodic table.

Occurrence

Iron is the second most abundant (the first being aluminium) metal occurring in the earth crust (4.5%). It rarely occurs in the free state because of its high reactivity. In the combined form it is largely found as oxides, carbonates and sulphides. The important ores of iron are mentioned below.

(i) ***Haematite***, Fe_2O_3. It is chief ore of iron having about 70% of iron.

(ii) ***Magnetite*** Fe_3O_4. It contains about 72.4% of iron

(iii) ***Siderite***, $FeCO_3$.

(iv) ***Limonite***, $2Fe_2O_3.H_2O$

(v) ***Iron Pyrites***, FeS_2. Iron pyrites, although, occurs, abundantly is not used as a source of iron. It is used in the manufacture of sulphuric acid.

In Pakistan, deposits of iron ores are found at Mazari Tang (Kohat), Langrial (Hazara), Chaghi (Quetta) and Kalabagh - Makarwal areas. The reserves of iron ores are estimated about 300.000,000 tonnes in Pakistan.

Commercial Forms of Iron

Four varieties of commercial iron are known. These differ from each other mainly in their carbon contents.

(i) **Pig Iron:** It is the most impure form of iron. It contains the highest proportion of carbon (1.5-4.5%) along with traces of other impurities like S, P, Si, Mn etc. It is brittle and usually converted to other forms of iron.

(ii) **Cast iron:** When pig iron is remelted and cooled, cast iron is obtained. It contains usually 2-4% carbon. Rapid cooling produces white cast iron while slow cooling produces grey cast iron.

(iii) **Wrought iron:** It is the purest form of iron and contains the lowest percentage of carbon (0.12 - 0.25%). Other impurities present in wrought iron are S, P, Mn etc.

(iv) **Steel:** Iron which contains 0.25 to 1.5% carbon and hardened by quenching is called steel. It usually contains some manganese also. It is the most important form of iron and finds extensive applications.

Manufacture of Iron (Pig and Cast Iron)

Pig and cost iron is usually obtained from haematite according to the following steps:

(i) **Concentration:** The ore is crushed to small pieces of 3.5cm size and then concentrated by gravity separation process to remove earthy impurities like clay and sand. The washed ore is then subjected to electromagnetic separation in which non-magnetic impurities are separated from magnetic ore particles.

(ii) **Calcination:** The concentrated ore is heated strongly in the presence of excess of air in shallow kilns. Following changes occur during this treatment.

Most of the moisture is removed.

Sulphur and arsenic are oxidized to their oxides.

$$S + O_2 \longrightarrow SO_2\uparrow$$

$$4As + 3O_2 \longrightarrow 2As_2O_3$$

Carbonates are decomposed into oxides evolving CO_2

$$FeCO_3 \longrightarrow FeO + CO_2\uparrow$$

Ferrous oxide is oxidized to ferric oxide and thus the loss of iron is avoided because ferrous oxide forms a slag with sand.

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

The entire mass becomes porous which is more suitable for reduction to metallic iron in the blast furnace.

(iii) **Smelting:** The calcined ore is smelted, i.e., reduced with carbon in the presence of a flux to remove silicious impurities. This operation is carried out in a *blast furnace*. It is made of steel and lined with fire bricks with cylindrical shape. The furnace is about 100 feet high and 25 feet in diameter (Fig. 12.4). The charge consisting of calcined ore, coke and lime in the ratio of 8:4:1 is introduced into the furnace by means of double cup and cone arrangement. A hot blast of air is admitted through the twyers. The down coming charge meets the upward moving hot air blast and the following reactions take place in the different zones of furnace.

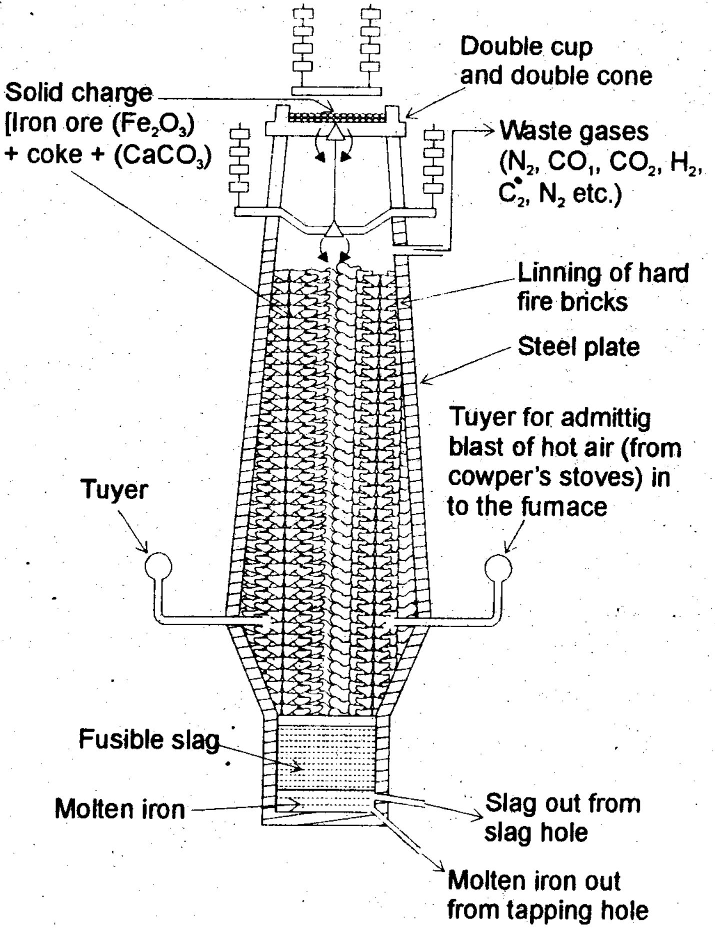


Fig. 12.4 Blast furnace of iron

The Upper Zone: This zone is near the mouth of the furnace. The temperature range in this zone is 300-700°C. Carbon of the coke burns in oxygen of the hot air to form carbon dioxide which is reduced to CO by carbon.

$$C + O_2 \longrightarrow CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

Carbon monoxide reduces iron oxide to *spongy iron through the following stages.

$$3Fe_2O_3 + CO \xrightarrow{300^0C} 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \xrightarrow{500^0C} 3FeO + CO_2$$

$$FeO + CO \xrightarrow{600^0C} Fe + CO_2$$

(* Since the temperature in this zone is too low to melt iron, the metal so produced is also called spongy iron).

Simultaneously a part of lime-stone decomposes at about 700^{0}C to lime.

$$CaCO_3 \xrightarrow{700^0C} CaO + CO_2$$

$$CaCO_3 + C \longrightarrow CaO + 2CO$$

The middle zone: The temperature range in the middle zone is 900-1200^{0}C. Following reactions take place in this zone.

CO_2 is reduced to CO accompanied by heat absorption.

$$CO_2 + C \longrightarrow 2CO$$

At about 1000^{0}C, calcium carbonate is almost completely decomposed to give CaO which acts as a flux and combines with SiO_2 present as impurity (gangue) in the ore to form calcium silicate (slag).

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Silicates, phosphates and manganates are reduced to Si, P and Mn respectively which are partly absorbed by iron and partly by slag.

The lower zone: This is the lowest and hottest part of the furnace, the temperature range is 1200-1500^{0}C. Following reactions occur in this zone.

The coke burns by the blast of hot air to produce CO_2 and a lot of heat.

$$C + O_2 \longrightarrow CO_2 + 97{,}000 \text{ cals.}$$

The spongy iron which has absorbed C, S, Si and P in the middle zone melts in this zone at about 1300^{0}C and collects at the bottom of the hearth.

At the bottom of the furnace the molten iron sinks down while the fusible slag, being lighter, floats over the molten iron in a separate layer. The slag and the molten iron are periodically removed from their respective holes. The mixture of waste gases containing N_2(58%), CO(25%), CO_2(10.5%), hydrogen etc. known as *blast furnace gas*, is cleaned by passing through a dust catcher. It is burnt with air to produce heat which is utilized for preheating the air blast admitted through tuyeres. The iron obtained from blast furnace is an impure variety and is known as *pig iron*. It is weak and brittle and is not suitable for structural purposes. Generally the composition of pig iron is:

Fe = 92–94%   Mn = 0.5 – 1.5%
C = 2.5 – 4.5%   P = 0.1 – 2%
Si = 0.5 – 3%   S = 0.05 – 0.5%

Pig iron is further purified by remelting in a vertical furnace (called *cupola*) resembling a blast furnace with coke and lime. About 1 part of coke is added for every 10 parts of pig iron together with a small amount of limestone to remove some of the impurities. The molten metal is poured into moulds of desired shape. The iron thus obtained is known as *cast iron*. It has good casting properties, wear resistance and great compressive strength. An average composition of the cast iron is given below.

Fe = 92%   P = 1.5%
C = 4.5%   S = 0.27%
Sn = 1%

Manufacture of Wrought Iron

Wrought iron is the purest form of iron containing 0.12 – 0.25% carbon along with traces of S, P, Mn etc. It is obtained by purifying cast iron in a special type of furnace called *Puddling furnace*, the process being known as *puddling* (stirring). The furnace has a low roof to deflect the hot gases and flames downwards to melt the cast iron. The hearth of the furnace is lined inside with haematite (Fe_2O_3).

The cast iron is placed on the hearth and melted by hot gases. The molten mass is stirred (puddled) thoroughly with iron rods called rabbles through the door to ensure intimate contact with the lining of the hearth.

Oxygen of the haematite (Fe_2O_3) oxidizes carbon, sulphur, silicon, manganese, and phosphorous to their corresponding oxides. Oxides of C and S escape directly as gases while the oxides of Mn, Si and P form slags.

$$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO\uparrow$$
$$3S + 2Fe_2O_3 \longrightarrow 4Fe + 3SO_2\uparrow$$
$$3Si + 2Fe_2O_3 \longrightarrow 4Fe + 3SiO_2\uparrow$$
$$4P + 5O_2 \longrightarrow 2P_2O_5 \text{ (slag)}$$

With the removal of impurities, melting point of iron rises and iron starts solidifying. When the oxidation of impurities is complete, the material (iron + slag) is taken out in the form of balls or *blooms*. The slag is then removed by hammering. The Wrought iron may be easily hammered and drown into wires. It is soft, grey, tough, ductile, malleable and can be welded. The presence of slag gives strength and toughness to the metal and makes it resistant towards rusting and corrosion.

Manufacture of Steel

Steel is an alloy of iron with carbon (0.25 – 1.5%), manganese (upto 1.0%), sulphur (upto 0.5%), silicon (upto 0.03%) and phosphorus (upto 0.05%). Sometimes other elements like chromium, nickel, tungsten, vanadium and molybdenum are also added to make special steels or alloy steels.

Since the amount of carbon in steel lies in between the cast iron and wrought iron, steel can be obtained either by removing a part of carbon from cast iron or by adding carbon to wrought iron. Although there are several methods for making steel, only the important ones are discussed below.

1. **Bessemer process.** This method involves the oxidation of impurities of pig iron by oxygen of air into volatile gases or slag followed by the addition of required amounts of carbon and manganese. This process is carried out in a *Bessemer Converter.*

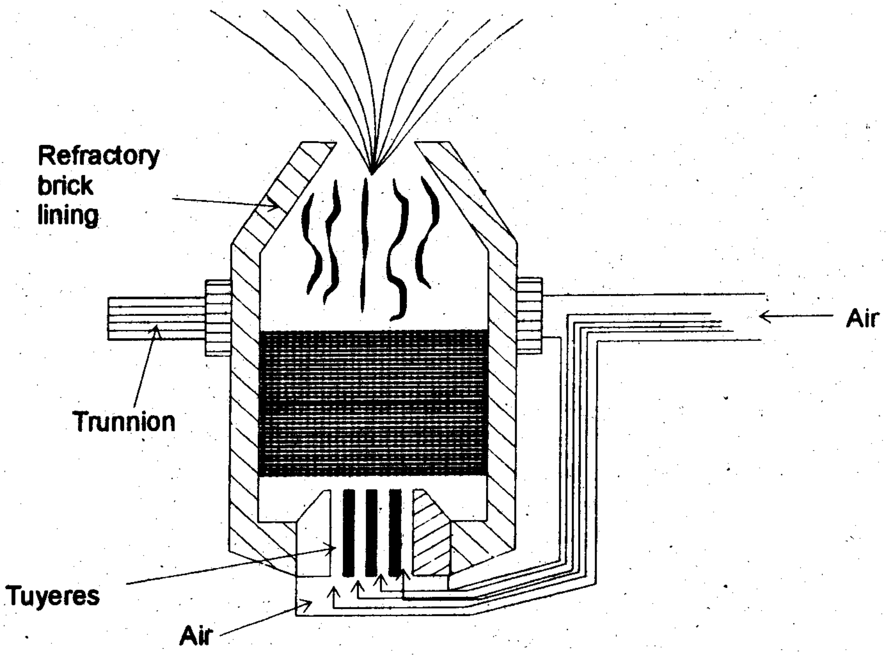


Fig. 12.5 Bessemer's converter used for the manufacture of steel

Bessemer converter is a pear–shaped furnace made of steel plates and is lined inside with silica (SiO_2) or magnesia (MgO) depending upon the nature of impurities present in Cast iron. If the impurities are Si, P and/or S, a basic lining of lime (CaO) or magnesia (MgO) is used (*basic process*). On the other hand, if the impurity is Mn and Si, a lining of silica (SiO_2) bricks is used (*acid process*). At the base, the converter is provided with a number of holes to admit a hot blast of air. (Fig. 12.5)

To start with, the converter is turned into the horizontal position and molten pig iron directly from the blast furnace is introduced into it. It is now brought almost to vertical position and a blast of hot air is passed. As the air passes upwards through the molten metal it oxidizes the impurities like Si and Mn (in acid process) and P (in basic process) to corresponding oxides which are removed as slag.

$$Si + O_2 \longrightarrow SiO_2$$

$$2Mn + O_2 \longrightarrow 2MnO$$

$$MnO + SiO_2 \longrightarrow MnSiO_3$$

Similarly,

$$4P + 5O_2 \longrightarrow 2P_2O_5$$

$$S + O_2 \longrightarrow SO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2.$$

After 5–10 minutes of blowing, oxidation of carbon starts to form carbon monoxide which burns with a blue flame at the mouth of the converter. When whole of the carbon is oxidized, the blue flame disappears. At this stage, a calculated amount of *spiegeleisen* (an alloy of iron, carbon and manganese) is added and the blast of air is continued just for a moment to ensure complete mixing. At the end of operation, the converter is tilted to pour out the molten iron.

2. **Operation hearth process.** This is the most modern process used for the manufacture of steel. A schematic diagram of an open hearth furnace which is used for the manufacture of steel from cast iron by this process is shown in figure 12.6. An open hearth furnace is like a reverberatory furnace with the dish in the shape of a large oval dish. The hearth of the furnace is lined either with basic lining like dolomite or acidic lining like silica, depending upon the nature of impurities. An open hearth furnace utilizes the heat from waste gases obtained from blast furnace. Hot waste gases obtained from the blast furnace are passed through a brick-work chamber which gets heated and the gases going out of this chamber are at a much lower temperature. After some-time fuel gases are passed into the hot chamber and the fuel gases are made to heat another brick work chamber. The fuel gas preheated in the hot chamber burns and thus supplies more heat. After sometime the direction of the gases is reversed so that the incoming gases are always preheated. Thus we see that an open hearth furnace works on the regenerative principle of heat economy and hence this furnace is also called *regenerative furnace*.

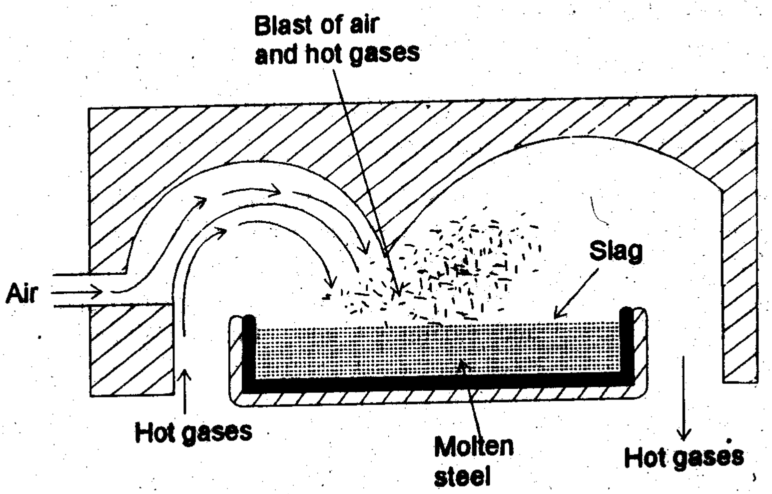


Fig. 12.6 An open hearth furnace for steel

In order to manufacture steel, the charge consisting of a mixture of pig iron or cast iron, scrap iron and haematite ore (Fe_2O_3) is melted on the hearth of the furnace by forcing preheated air and burning gaseous fuels. The following reactions take place in the furnace.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO\uparrow$$

$$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2\uparrow$$

$$2Fe_2O_3 + 3Si \longrightarrow 4Fe + 3SiO_2\uparrow$$

$$5Fe_2O_3 + 6P \longrightarrow 10Fe + 3P_2O_5$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2$$

Samples are withdrawn from the hearth from time to time and analysed for carbon contents. The carbon content of the steel is adjusted by adding the appropriate amount of spiegeleisen as in the Bessemer process.

Advantages Of the Open Hearth Process

Open hearth process has the following advantages over the Bessemer process.

(i) Scrap iron, low grade cast iron and even the iron ore (haematite) can be directly converted into steel.

(ii) The temperature can be controlled more effectively since external source of heat is employed.

(iii) Since the product is analysed from time to time, the composition and quality of the product can be well controlled.

(iv) No iron is lost as slag since no blast of hot air is passed through the molten metal.

(v) The steel obtained is of uniform and of high quality.

(vi) The process is economical and simple.

Now-a-days *Duplex process* is being used for the manufacture of large quantities of steel. This process is a combination of Bessemer's process and open hearth process. In this process the molten pig iron is first treated in an acid Bessemer's converter to remove Si, Mn and a part of C. The molten pig iron is then transferred to open-hearth furnace with a basic lining to remove P and remaining C and is finished off as usual.

Alloy Steels

Many useful alloys of steel are manufactured by adding metals in small amounts. Some important alloys of such type are:

1. **Nickel Steel:** (Fe = 96.5%, Ni = 3.5%)

   It is used for making cables, automobiles and aeroplanes parts etc.

2. **Stainless Steel** (Fe = 84.5%, Cr=11.5%, Ni=2%)

   It is used for making cutlery, utensils, surgical instruments, automobile parts etc.

3. **Invar:** (Fe = 64%, Ni = 3.5%)

   It is used for making measuring instruments and clock pendulums.

4. **Silicon Steel:** (Fe = 85%, Si = 15%)

   It is used for making pumps and pipes for carrying acids. For making cores of transformers and electromagnets.

12.4 NICKEL

History and Occurrence The world 'nickel' is derived from the name of the mineral kupfer nickel (a german word-meaning false copper) having the appearance of copper but without any copper content from which the metal was isolated for the first time in 1751 by Cornstedt.

In nature nickel is found in the form of sulphide, arsenide or silicate and is usually associated with copper, iron and magnesium. Chief ores of nickel are:

(i) *Pentlandite,* (Ni, Cu, Fe)S. It contains about 22% of nickel.

(ii) *Garnierite,* $(Ni, Mg)H_2SiO_4$. It contains about 8% of nickel.

(iii) *Kupfer nickel or nicollite,* (NiAs).

(iv) *Nickel glance,* NiAsS.

Pentlandite is the principal source of nickel.

Extraction Nickel is mostly extracted from its sulphide ore (pentlandite). The complete process involves the following steps:

(i) **Crushing and concentration of the ore** The ore is first crushed in big jaw crushers and then in ball mills. The finely powdered ore is concentrated by the usual froth floatation process using water and pine oil when the rock particles are removed and a concentrated mass consisting of NiS, CuS and FeS is obtained.

(ii) **Roasting** The concentrated ore is then heated on the hearth of a reverberatory furnace in presence of excess of air. During roasting most of the free sulphur is oxidised to sulphur dioxide and iron sulphide is partially oxidised to iron oxide, while copper and nickel sulphides, present in the ore, usually remain unaffected.

$$S + O_2 \longrightarrow SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

(iii) **Smelting** The roasted ore is mixed with silica (SiO_2), coke and some limestone (CaO) and smelted in a blast furnace. Following changes occur during smelting.

(a) Most of the ferrous sulphide which escaped during roasting is now oxidised to ferrous oxide.

(b) Any ferric oxide; if formed, during roasting is reduced by coke to ferrous oxide.

(c) Whole of the ferrous oxide combines with silica to form ferrous silicate (slag).

$$FeO + SiO_2 \longrightarrow \underset{\text{slag}}{FeSiO_3}$$

The slag, being lighter, floats above the unaffected sulphides of nickel and copper together with some amount of iron. The lower layer of matte consisting of Ni and Cu sulphides is separated from the upper layer of slag.

(iv) **Bessemerisation** The molten matte, containing sulphides of copper and nickel together with a small quantity of ferrous sulphide, is mixed with requisite amount of silica and transferred to a Bessmer converter having a basic lining. A hot blast of air is blown in when most of sulphur is oxidised to sulphur dioxide and ferrous sulphide is converted to ferrous silicate (slag) through ferrous oxide. The slag is continuously skimmed off and the resulting bessemerized matte, thus obtained, contains about 56% nickel, 25 — 30% copper, 14 — 17% sulphur and traces of iron.

The bessemerised matte is either converted into monel metal (an alloy containing 60 percent nickel) or pure nickel.

A. Conversion of Bessemerised Matte Into Monel Metal The bessemerised matte is roasted again when nickel and copper sulphides are converted into their oxides. The roasted material is then heated with carbon in an open hearth or electric furnace when the nickel and copper oxides are reduced to the metals. The resulting product contains about 60% nickel and 39% copper (the rest being sulphur, manganese, etc.) and is known as monel metal. It resembles nickel in appearance and properties and is thus sometimes may be used as substitute for nickel.

B. Conversion of Bessemerised Matte Into Pure Nickel The removal of copper and subsequently conversion of the matte to nickel may be carried out by the three processes, namely (i) Mond's process, (ii) Electrolytic process, (iii) Orford process.

Out of these, Mond's process is the most important and discussed below.

Mond's process The process is based on the following two facts.

(i) Only nickel (not copper, iron and cobalt) forms a volatile nickel carbonyl with carbon monoxide below 80°C.

(ii) The nickel carbonyl decomposes at 180°C to give back nickel and carbon monoxide.

$$Ni + 4CO \underset{180^\circ}{\overset{50-80^\circ}{\rightleftharpoons}} Ni(CO)_4$$

The complete process involves the following steps.

(a) *Roasting* The mate obtained from the bessemer converter is roasted in a special type of furnace in order to oxidise sulphur and sulphides to the corresponding oxides.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS + 7O_2 \longrightarrow 2Fe2O_3 + 4SO_2$$

$$2CuS + 3O_2 \longrightarrow 2CuO + 2SO_2$$

$$2NiS + 3O_2 \longrightarrow 2NiO + 2SO_2$$

(b) *Leaching* (removal of copper). The above oxide mixture is treated with 15% sulpuric acid at 80°C when most of the copper oxide and ferrous oxide are dissolved as their sulphates, leaving nickel oxide as insoluble.

(i) $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

(ii) $FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$

(c) *Reduction of nickel oxide* The residue consisting mainly of nickelous oxide (NiO) is heated to 300 — 360°C in a current of water gas (a mixture of CO and H_2) in a tower, called reducer. Under these conditions, iron oxide is not affected, while nickel oxide is reduced to the metallic state by the hydrogen of the water gas.

(i) $NiO + H_2 \longrightarrow Ni + H_2O$

(ii) $NiO + CO \longrightarrow Ni + CO_2$

Thus the product obtained from reducer is mainly nickel with small amounts of copper, cobalt and ferric oxide.

(d) *Volatilization* The reduced product is then placed on shelves in a tower, called volatilizer, kept at a 50 — 60°C and a current of carbon monoxide is passed through it. Only nickel forms volatile carbonyl under these conditions.

$$Ni + 4CO \xrightarrow{50-80^\circ} Ni(CO)_4$$

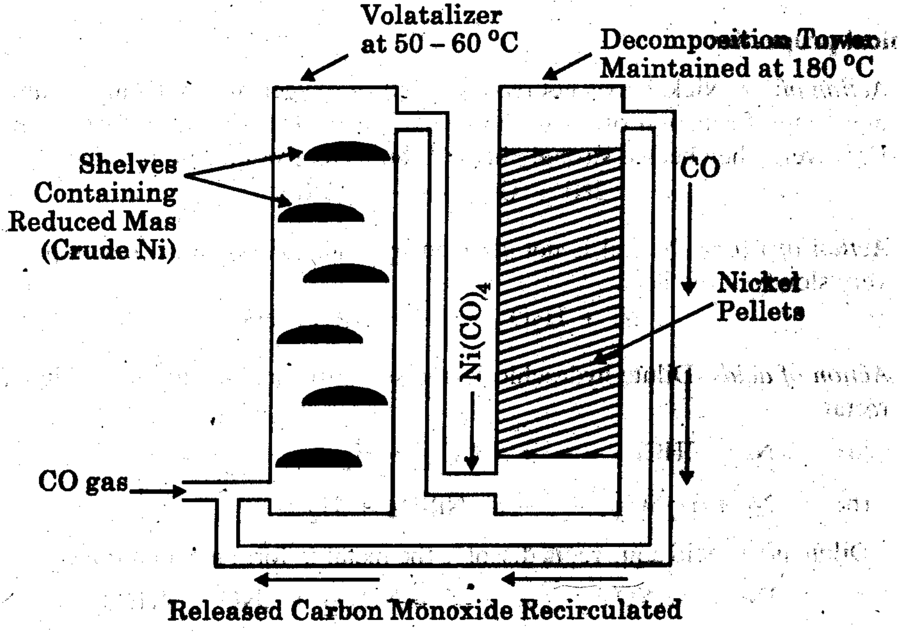


Fig. 12.7 Mond's process of extracting nickel.

(e) *Decomposition of nickel carbonyl* The nickel carbonyl vapours are led to tower (decomposer) maintained at 180°C and containing fine granules of nickel. Here nickel carbonyl decomposes and nickel formed starts depositing over the nickel granules which grow in size.

$$Ni(CO)_4 \xrightarrow{180^\circ} Ni + 4CO\uparrow$$

The carbon monoxide thus generatedis used again in volatilize for the further formation of nickel carbonyl.

The nickel granules having nickel coating are removed and more fine particles are reintroduced in the decomposer.

(f) *Refining* Nickel obtained as above is 99.8% pure and can be further purified by electrolysis. During electrolysis, nickel ammonium sulphate solution is electrolysed at 25°C in a cell consisting of impure nickel block as anode and a thin strip of pure nickel as cathode. On passing electronic current, pure nickel is deposited on the cathode while impurities like silver, gold, lead, platinum, etc. form the anode mud.

Physical properties

(i) Nickel is a soft silvery-white metal capable of taking high polish. It is quite malleable and ductile.

(ii) It is heavy metal (sq. gravity 8.8) with 1450°C as its m.p. and 2900°C as b.p.

(iii) It is slightly magnetic.

(iv) It has high electrical and thermal conductivities.

(v) Finely divided nickel can absorb large quantities of hydrogen (one volume of the metal can absorb 17 volumes of the gas).

Chemical properties

(i) *Action of air* Nickel does not react wit hair or oxygen at room temperature. This is due to the formation of a thin protective layer of oxide on surface of the metal. However, when heated strongly in air, it burns to give nickelous oxide.

$$2Ni + O_2 \longrightarrow 2NiO$$

(ii) *Action of water* Nickel is not affected by water. However, it decomposes steam very slowly at red heat.

$$Ni + H_2O \longrightarrow NiO + H_2$$

(iii) *Action of acids* Dilute hydrochloric and sulphuric acid solutions slowly attack the metal.

(a) $Ni + 2HCl \longrightarrow NiCl_2 + H_2$

(b) $Ni + H_2SO_4 \longrightarrow NiSO_4 + H_2$

Dilute nitric acid aqua regia dissolve the metal to form nickel nitrate.

$$3Ni + 8HNO_3 \longrightarrow 3Ni(NO_3)_2 + 2NO + 4H_2O$$

Concentrated and fuming nitric acid makes the metal passive.

(iv) *Action of alkalis* Nickel remains unaffected by caustic alkalis even when these are fused.

(v) *Action of chlorine* Nickel, when heated in a current of dry chlorine, forms chloride.

$$Ni + Cl_2 \longrightarrow NiCl_2$$

(vi) *Action with carbon monoxide* Nickel combines with carbon monoxide at about 60°C to form volatile nickel carbonyl which plays an important part in the extraction of nickel.

Uses The principal uses of nickel are summarised below.

(i) *In nickel plating* Due to its silvery-white lustre, hardness and great resistance to atmospheric corrosion, nickel is largely used for electroplating iron and other metals. The article to be plated is cleaned and made cathode in the electrolytic cell having nickel ammonium sulphate nickel sulphate as electrolyte, the anode being bars of nickel of high purity.

(ii) *As catalyst* Finely divided nickel is used as a hydrogenating catalyst in organic chemistry, the most familiar example is the hydrogenation of oils in the manufacture of vegetable ghee.

(iii) Since nickel is not attacked by alkalies, it is also used in making laboratory wares such as spatulas, crucibles and tongs for alkali fusion purpose.

(iv) *In alloy formation* Alloys containing 3 — 5% nickel with other metals are well known for their toughness and elasticity and thus find extensive use in industry. A few important alloys of nickel are given below.

(a) *Invar* It is an alloy steel containing 35% Ni with a little manganese and carbon. Because of its low coefficient of expansion it is used in pendulums of clocks and other precision instruments.

(b) *Monel metal* (Ni 60%, Cu39%, Mn and Fe etc.) It is acid-proof and hence used in boilers, turbine blades, propellers, etc. Moreover, it has a shining and hence used in making decoration pieces.

(c) *Nichrome* (Ni 60%, Cr 15%, Fe 15%). It has very high melting point and shows a marked resistance to heat, electricity and chemical reagents. It is used for making resistance coils, heating elements in electric iron, toasters, and other electrical appliances.

(d) *German silver or nickel silver* (Cu 60%, Ni 20%, Zn 20%). It is used in making cheap ornaments and domestic utensils.

(e) *Platinoid* (Cu 60%, Ni 14%, W 2%). (It is used for making rheostats, wheatstone bridges and potentiometers.

(f) *Platinate* It contains 46% nickel and has the same coefficient of expansion as glass or platinum. Wires drawn out of it can be sealed in glass apparatus and electric bulbs.

12.5. CHROMIUM

History and occurrence The metal chromium was discovered by Vanquelin in 1797. It was named chromium because it formed a large number of coloured salts (Greek word, chroma-colour). Chromium does not occur free in nature. It is found n the form of oxides; the chief ores of chromium are (i) *Chromite* or *chrome iron* ($FeO \cdot Cr_2O_3$), (ii) *Chrome ochere* (Cr_2O_3), (iii) *Crocoisite* ($PbCrO_4$).

Extraction Chromite, when reduced with carbon, lime and fluorspar in electric furnace, gives an alloy of chromium and iron (ferrochrome). Ferrochrome contains 60–70 per cent chromium and 1 — 8% carbon and is used in the manufacture of chrome-steel.

$$FeO \cdot Cr_2O_3 + 4C \longrightarrow \underbrace{2Fe + 2Cr}_{\text{ferrochrome}} + 4CO \uparrow$$

In case pure chromium is to be obtained, pure chromic oxide free from iron must be reduced. Thus the complete process for obtaining pure chromium form chromite involves the following step.

(i) **Concentration** The ore is finely powdered and concentrated by the gravity process, i.e., by washing it with a rapidly flowing current of water which washes away the gangue particles leaving behind the heavier particles of the ore.

(ii) **Roasting** The concentrated ore is mixed with excess of sodium carbonate and a little lime and roasted on the hearth of a reverbertory furnace in presence of excess of air.

$$4FeO \cdot Cr_2O_3 + 8NaCO_3 + 7O_2 \longrightarrow \underset{\substack{\text{sod. chromate}\\ \text{(soluble)}}}{8Na_2CrO_4} + 2Fe_2O_3 \downarrow + 8CO_2 \downarrow$$

The roasted ore is extracted with water and filtered to remove the insoluble ferric oxide. The filtrate containing sodium chromate is treated with a calculated quantity of sulphuric acid when sodium dichromate and sodium sulphate are formed.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$$

The solution is concentrated when the less soluble sodium sulphate crystallises out first leaving behind the more soluble sodium dichromate in solution. The solution (filtrate) is further concentrated to get crystals of $Na_2Cr_2O_7$.

(iii) **Reduction of dichromate to oxide** This may be performed in the following ways.

(a) *Reduction with carbon* The dichromate is reduced with carbon to give sodium chromite.

$$\underset{\text{sod.chromate}}{Na_2Cr_2O_7} + 3C \xrightarrow{\text{heat}} \underset{\text{sod.chromite}}{Na_2Cr_2O_4} + 3CO\uparrow$$

Sodium chromite so obtained is treated with water to form chromic oxide which is separated by filtration.

$$Na_2Cr_2O_4 + H_2O \longrightarrow Cr_2O_3 + 2NaOH$$

(b) *By forming ammonium dichromate* Sodium dichromate is heated with ammonium chloride when the ammonium dichromate first formed decomposes to give chromic oxide with the evolution of nitrogen.

$$Na_2Cr_2O_7 + 2NH_4Cl \longrightarrow (NH_4)_2Cr_2O_7 + 2NaCl$$

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4H_2O + N_2\uparrow$$

Green chromic oxide residue is washed with water and dried.

(iv) *Reduction of oxide to chromium* Reduction of oxide may be carried out by either of the following two processes.

(a) *Goldschmidt's aluminothermic process* (alumino thermic process). A mixture of well dried chromium trioxide and aluminium powder in the ratio of 3: 1 is placed in a large size fire clay crucible surrounded by sand*. The charge covered with an ignition mixture of magnesium powder plus barium oxide. The mixture is burnt by means of magnesium ribbon inserted into an ignition mixture. The large amount of heat evolved in the highly exothermic reaction melts the alumina as well as the liberated chromium which collects in the lower layer under the alumina. The addition of some potassium dichromate improves the yield by raising the reaction temperature.

---

* The function of lime is to keep the mass porous.

** The functions of sand is to prevent the loss of heat by radiation.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr\ (\Delta H = -112\ \text{kcal})$$

(b) *Carbon reduction process* (Deville's process). Chromic oxide is heated with carbon in the presence of lime or fluorspair in an electric furnace.

$$Cr_2O_3 + 3C \longrightarrow 2Cr + 2CO$$

As described in the beginning of extraction that, chromite ore, $FeO \cdot Cr_2O_3$ is directly converted to ferrochrome by this process.

Physical Properties. Chromium is a brilliant silvery metal (m.p. 1840°C, b.p. 2200°C). It is malleable and can take very high polish producing a brilliant surface which is not tarnished even after long exposure to atmosphere. It is hard and brittle.

Chemical Properties

(i) *Action of air* Chromium is not affected by air at ordinary temperature and therefore, does not tarnish in air. But on heating in air or oxygen, it is superficially oxidised to green chromic oxide, Cr_2O_3. It burns in oxy-hydrogen flame to form Cr_2O_3.

$$4Cr + 3O_2 \longrightarrow 2Cr_2O_3$$

(ii) *Action of water* Chromium is not attacked at all by water under ordinary conditions. However, when red hot it decomposes steam to give chromic oxide and hydrogen.

$$2Cr + 3H_2 \longrightarrow Cr_2O_3 + 3H_2$$

(iii) *Action of acids* Chromium dissolves in dilute hydrochloric acid forming chromous and chromic chlorides.

$$Cr + 2HCl \longrightarrow CrCl_2 + H_2$$

$$2Cr + 6HCl \longrightarrow 2CrCl_3 + 3H_2$$

Similarly, dilute sulphuric acid react with chromium to form chromous sulphate.

$$Cr + H_2SO_4 \longrightarrow CrSO_4 + H_2$$

The blue chromous salts change into green chromic salts due to oxidation in air.

$$4CrCl_2 + 4HCl + O_2 \longrightarrow 4CrCl_3 + 2H_2O$$

Hot concentrated sulphuric acid dissolves chromium to form chromic sulphate and sulphur dioxide.

$$2Cr + 6H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 6H_2O + 3SO_2$$

Dilute nitric acid does not attack the pure metal whereas the concentrated nitric acid makes it passive due to the formation of an insoluble surface layer of chromic oxide.

(iv) *Action of alkalies* The metal is not attacked by alkalies under ordinary conditions.

(v) *Action of halogens* Heated chromium combines directly with fluorine or dry chlorine to form chromichalides.

$$2Cr + 3F_2 \longrightarrow 2CrF_3$$

$$2Cr + 3Cl_2 \longrightarrow 2CrCl_3$$

Uses Chromium is used mostly for chrome plating and in making alloys.

1. **Chrome plating** On account of its brightness and resistance to corrosion by air, water and CO_2, chromium is now-a-days extensively used for plating metals (chrome plating). Thus the chrome plating not only protects the article from rusting but also improves its appearance.

In practice, the article (generally steel) to be chrome-plated is first plated with nickel or copper or both because chromium does not deposit in good form directly on steel. The object to be chrome plated is made the cathode, while the anode is made of lead. The electrolytic bath consists of a solution of chromic acid and sulphuric acid. During electrolysis, the chromate ions (CrO_4^{2-}) are reduced to chromic ions (Cr^{3+}) which lose their charge at the cathode and yield a deposit of chromium in the form of a coherent hard layer with a bright bluish-white appearance.

2. **Chromium alloys** On account of its resistance to corrosion, greater, strength and hardness, chromium is extensively used in making alloys of great utility. Important chromium alloys/steels are mentioned below.

(a) *Nichrome* (Ni = 58 – 62%, Cr = 8 – 14%, Fe = 23 – 26%, C = 0.2 – 1%) On account of its high m.p. high resistance and high resistance of oxidation, it is used in making resistance wire used in electrical goods.

(b) *Stellite* (Cr, CO and W). It is used in making surgical instruments, high speed tools and automobile parts.

(c) *Chrome steels* These are alloys of Cr, C and Fe. In these, chromium is added in the form of ferrochrome. Important chromium steels are:

(i) Stainless steel. It has 12% Cr and 0.3% carbon, the rest being iron. It is used in making cutlery, surgical instruments, etc.

(ii) Nickel steel. It is used for locomotive wheels.

(iii) Nickel steel. It is used in motor industry.

(iv) Chromium-tungsten steel. It is used in high speed tools.

3. Salts of chromium are used (i) in tanning of leather, (ii) as mordant in dyeing, (iii) as an oxidising agent, (iv) in fire works, (v) as refractory material, and as (vi) catalyst.

Questions

Q.1 (a) Write down the important ores of copper. Discuss the extraction of copper from sulphide ores. How is it purified.

(b) Write down some uses of copper.

Q.2 How is copper found in nature? Give details of the extraction of copper from its ores. How is it refined?

Q.3 What are important ores of aluminium? Discuss the extraction and refining of aluminium from its ore.

Q.4 What are the sources of aluminium? Describe its extraction and purification?

Q.5 (a) Write down the names of iron ores alongwith formulae.

(b) Discuss the reactions which take place in various zones of blast furnace and also write down the three principal constituents of slag obtained from the blast furnace.

Q.6 (a) Distinguish between cast iron, wrought iron and steel.

(b) Describe the blast furnace for the manufacture of pig iron with reactions.

Q.7 (a) What is steel? How is it manufactured. Discuss the reactions taking place during its manufacture.

(b) Discuss some advantages of open hearth process over Bessemer's process.

Q.8 Describe a process for converting pig iron into steel together with the nature of chemical changes involved.

Q. 9. Write down important ores of Nickel. Discuss the extraction of Nickel from its principal ore pentladite.

Q. 10. Discuss the different of chemical reactions involved in the metallurgy of Nickel.

Q. 11. Discuss various types of alloys of Nickel giving the important uses.

Q. 12. Write down important ores of Chromium. Discuss the extraction of Chromium from its principal ore Chromite.

Q. 13. Discuss the different of chemical reactions involved in the metallurgy of Copper.

Q. 14. What is chrome plating? Discuss its important in industry.

Q. 15. Discuss various types of alloys of Chromium giving the important uses.

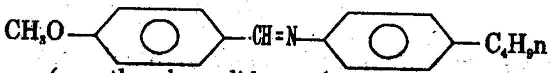
Chapter Thirteen

MODERN MATERIALS

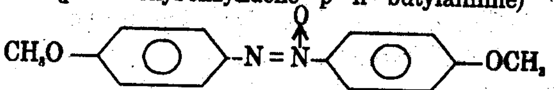
13.1 LIQUID CRYSTALS

An organic compound is normally characterized by a well-defined melting point at which it passes from the three-dimensional, ordered arrangement of the crystal to the disordered *isotropic* liquid. Certain compounds do not behave in this simple manner, and on heating, the crystals pass through one or more intermediate states before the isotropic liquid is produced. These opaque intermediates states are fluids in varying degree and exhibit many optical properties of crystals. Since their properties are intermediate between those of the crystal and the isotropic liquid, they are termed *liquid crystals* or *mesomorphic states*. Hence liquid crystals may be defined as the molecules that are large, rigid and linear and have some of the structure of solids and some of the freedom of motion associated with liquids.

The liquid crystals have a structure between that of a liquid and that of a crystalline solid. In a liquid state the molecules have random arrangement and they are able to move past each other. On the other hand, the molecules in the solid state have an ordered arrangement and are in fixed positions. In a liquid crystal, however, the molecules are arranged parallel to each other and flow like a liquid. Thus the liquid crystals have the fluidity of a liquid and optical properties of a crystal.



(p-methoxybenzylidene - p' - n - butylaniline)



(p-azoxyanisol)

(p-quinquephenyl)

(p-n-octyloxybenzoic acid)

For liquid crystalline properties to occur, a compound must undergo the overall process of melting in steps. The three-dimensional order of the crystal must break down in steps and this is most likely to occur if the molecules are geometrically anisotropic and give rise to anisotropic intermolecular attractions. Many thousand organic substances and some polymers exhibit liquid crystallinity. Some liquid crystalline compounds are given below.

Types of Liquid Crystals

Liquid crystals are divided into following three categories:

1. **Smectic Liquid Crystals:** They have a structure that resembles a handful of cigars as shown in figure 13.1a. Not only do the molecules all point in the same direction, they are so well ordered that they form planes perpendicular to the axes of the molecules. The layers can slide past each other.
2. **Nematic Liquid Crystals:** Nematic liquid crystals are slightly less well ordered. The molecules still point in the same direction, but they start and stop at different positions within the liquid, as shown in figure 13.1b.
3. **Cholesteric Liquid Crystals:** They have a structure similar to nematic liquid crystals, but each plane of molecules is twisted slightly in relation to the plane above or below. These liquid crystals received their names from the fact that many derivatives of cholesterol form this structure. The slight twist in the planes of these structures tends to make these crystals coloured. The fact that changes in the amount of twisting lead to changes in colour make these crystals sensitive indicators of changes in temperature or pressure.

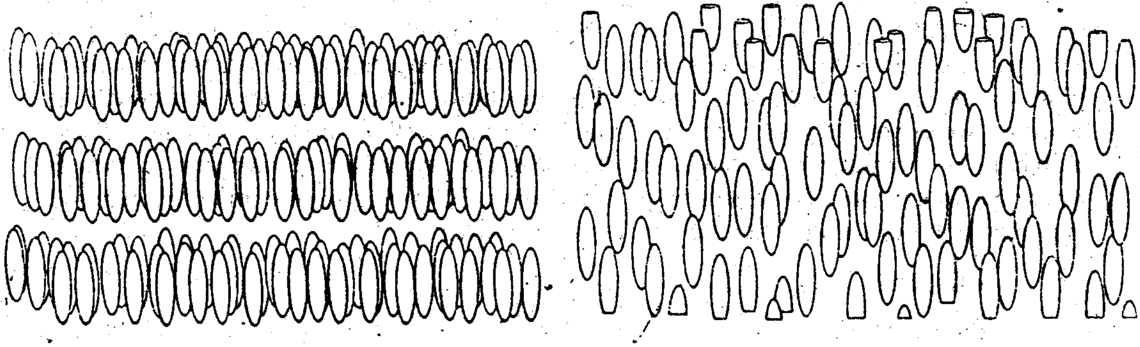


Fig. 13.1 The structures of (a), smectic and (b) nematic liquid crystals.

Applications of Liquid Crystals

A number of organic compounds and biological tissues behave as liquid crystals. Important uses are given below:

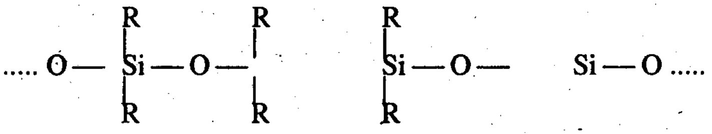
1. Liquid crystals are used routinely in the display of electrical devices such as digital watches, calculators, and computers. These LCD devices take advantage of the fact that the weak bonds that hold molecules together in a liquid crystal are easily affected by changes in pressure, temperature, or electromagnetic fields.
2. The temperature-dependent variation in the colour of cholesteric liquid crystals had led to the use of these substances in the measurement of temperature and temperature gradients.
3. Cholesteric liquid-crystal substances, when applied to the surface of the skin, have been used to locate the veins, arteries, infections, tumours, and the fetal placenta, which are warmer than the surrounding tissues.
4. Nematic liquid crystals are useful research tools in the application of magnetic resonance. Molecules that are dissolved in nematic liquid crystal solvents give a highly resolved nmr spectrum.
5. Some liquid crystals have been used in chromatographic separations, as solvents to direct the course of chemical reactions and to study molecular rearrangement and kinetics.
6. Oscillographic and TV displays using liquid crystals screens are also being developed. Other applications include radiation and pressure sensors, optical switches and shutters, etc. Polymers that form the intermediate phase are important in the fabrication of light weight, ultra-high-strength and temperature resistant fibres.

13.2 INORGANIC POLYMERS

Polymers are the substances formed by combining together a large number of small molecules. The small molecules which are used to form polymer are called *monomers*. Polystyrene, polyproplyene, polyvinyl chloride etc. are typical examples of polymers. All these polymers have backbone of carbon atoms and are organic in nature. Most of the organic polymers tend to become brittle when cold and deteriorate on heating. Moreover they tend to be flammable and swell in organic solvents. These problems are minimized with the development and synthesis of inorganic polymers whose backbone consist of atoms other than carbon. Following are the important types of inorganic polymers along with their properties and uses.

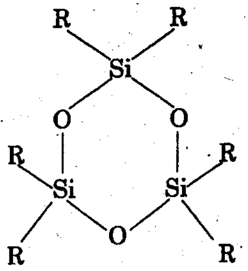
1. Silicones

Silicones are synthetic polymerized organo-silicon polymers containing –Si–O–Si–O–Si– linkages along with –C–C–C– linkages present as the side chains. The silicones may be linear, cyclic or cross-linked as shown below.

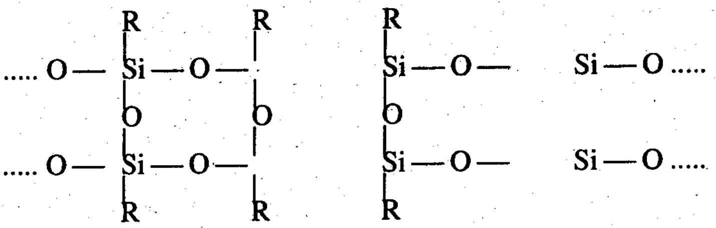


$$\ldots\ldots O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{|}}\qquad\underset{R}{\overset{R}{Si}}-O-\qquad Si-O\ldots\ldots$$

Linear silicon



Cyclic silicone



Cross-lined silicone

Here R stands for CH_3, C_2H_5 or C_6H_5 groups

Silicones are obtained by the hydrolysis and subsequent condensation of dialkyl or diaryl substituted silicon chloride, R_2SiCl_2. The Si–OH bonds subsequently expel water and form Si–O–Si linkages. The lower silicones are oily liquids, but the higher members containing long chains or ring structures are waxy and rubbery solids. They are remarkably stable towards heat and chemical reagents. They are not wetted by water and are non-toxic and chemically inert.

Silicones are present in the form of oils, greases or rubbers. They are highly stable and non-volatile even on heating. They are, therefore, used in high temperature oil baths, high vacuum pumps, paints, vaseline greases, polishes, water proofing treatments for fabrics and leather. They are also used as insulating materials for electric motors and other electric appliances, since they can withstand high temperature without charring.

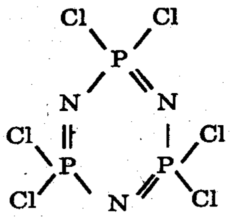
2. Phosphazenes

The phosphazene polymers are a group of cyclic or linear compounds in which the polymer backbone consists of alternating phosphorous and nitrogen atoms. The repeat unit in these polymers is $-N{=}PCl_2-$. These polymers are prepared by polymerizing the ring shaped trimmer $(PNCl_2)_3$ and then substituting chlorines with various groups. The trimer $(PNCl_2)_3$ is obtained by treating PCl_5 with NH_4Cl at 146^{0}C.

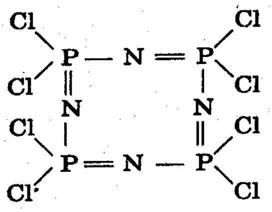
$$NH_4Cl + PCl_5 \xrightarrow[\text{refluxing } Cl_2HCCHCl_2]{146^0C} (NPCl_2)_n$$

The major product and the easiest to separate is the trimer, n=3. Smaller amounts of tetramer and other oligomers up to n=8 have been characterized and higher polymers exist.

$$[PNCl_2]_3 \xrightarrow{\Delta} [PNCl_2]_x$$

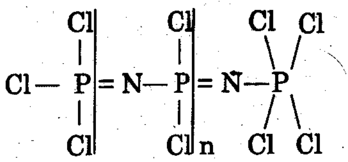


Trimer



Tetramer

Higher cyclic polymers have been characterized but none studied so extensively as the trimer and tetramer. Linear polymers are also known. If excess PCl_5 is used in the preparation, it is possible to isolate the linear polymers of the type:



Analogous bromo compounds may be prepared in the same manner except that bromine should be added to suppress the decomposition of PBr_5.

$$PBr_5 \longrightarrow PBr_3 + Br_2$$

$$PBr_5 + NH_4Br \xrightarrow[Br_2]{excess} [NPBr_2]_n$$

The phosphazene polymers are generally non-flammable. Some of them are glasses and others are elastomers. Their elasticity is more than natural rubber. They retain their elasticity even at low temperatures. They are used to replace blood vessels because they do not react with living tissues. They are also used as crystals, in silicone manufacture and in flame-proofing fabrics.

3. Polymeric Sulphur Nitride

Polymeric sulphur nitride (also called polythiazyl) is an important inorganic polymer which is composed of atoms of two non-metals, i.e., sulphur and nitrogen. This polymer is prepared from tetrasulphur tetranitride.

$$S_4N_4 \xrightarrow{Ag} S_2N_2 \longrightarrow (SN)n$$

Tetrasulphur tetranitride (S_4N_4) is bright orange solid insoluble in water but soluble in organic solvents. Although the crystals are reasonably stable to attack by air, they are explosively sensitive to shock or friction. The ammonolysis of sulphur monochloride (S_2Cl_2) either in solution in an inert solvent or heated over solid ammonium chloride, yields tetrasulphur tetranitride:

$$6S_2Cl_2 \xrightarrow[CCl_4]{NH_3} S_4N_4 + S_8 + 12NH_4Cl$$

The S_4N_4 is pumped in a vacuum line over silver wool at 220°C, and S_2N_2 is collected on a cold finger at −195°C. It is then sublimed to a trap at 0°C, where it polymerizes slowly to a lustrous golden material. The resulting product is analytically pure, and this purity is necessary for it to show metallic properties to a high degree: a conductivity of 2.5×10^3 ohm^{-1} cm^{-1} at room temperature and becomes a superconductor at low temperature.

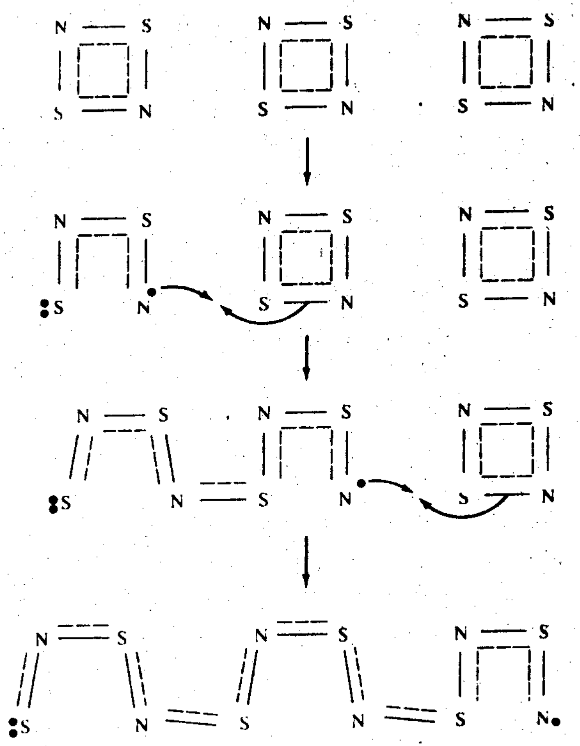


Fig. 13.2. Polymerization of S_2N_2 to form (SN)n chains

13.3 ENGINEERING CERAMICS

Ceramics comprises all engineering materials or products that are inorganic except metals and alloys and are usually rendered serviceable through high temperature processing. Ceramics has also been defined as the field of high temperature technology. because usually either in the manufacture or in the application and use of ceramic materials high temperatures are involved. The important products of ceramic industries are building bricks and tiles, sewer pipes, drain tiles, refractory bricks of all kinds, electrical and chemical porcelain and stoneware, whiteware, china, floor and wall tiles. enamels and abrasives and insulators in spark plugs.

The ceramic materials which might be used in place of other engineering materials such as metals, woods or plastics, are termed as *engineering ceramics*. These materials withstand high temperatures, resist greater pressures, have superior mechanical properties and can protect against corrosive chemicals.

Basic Raw Materials

The three main raw materials used for ceramic industry are clay, feldspar and sand.

1. **Clay:** Clays are more or less impure hydrated silicates that have resulted from the weathering of igneous rocks. Clays include kaolinite ($Al_2O_3.2SiO_2.2H_2O$), montmorillonite (Mg, (Ca) $O.Al_2O_3.5SiO_2.nH_2O$), and illite (K_2O, MgO, Al_2O_3, SiO_2, H_2O all in variable amounts).
2. **Feldspar:** There are three common types of feldspar, potash ($K_2O.Al_2O_3.6SiO_2$), soda ($Na_2O.Al_2O_3.6SiO_2$), and lime ($CaO.Al_2O_3.6SiO_2$), all are used in ceramic products to some extent.
3. **Sand:** Sand or flint is the third main constituent of ceramic industry. For light coloured ceramic products, sand with a low iron content is used.

In addition to the principal raw materials, a wide variety of other minerals, salts and oxides is used as fluxing agents and special refractory ingredients. Some common fluxing agents which lower temperatures are borax, boric acid, soda ash, sodium nitrate, pearl ash, apatite, cryolite, iron , lead oxide etc.

Manufacture

All ceramic products are made by combining various amounts of the raw materials, shaping, and heating to firing temperatures. These temperatures may be as low as 700^0C or as high as 2000^0C. Such temperatures cause a number of reactions, which are the main bases for the chemical conversions.

1. Dehydration at 150 to 650^0C.
2. Calcination at 600 to 900^0C.
3. Oxidation of ferrous iron and organic matter at 350 to 900^0C.
4. Silicate formation at 900^0C and higher.

Some of the initial chemical changes are relatively simple such as calcination of $CaCO_3$ and the dehydrations and decompositions of kaolinite. Other reactions, such as silicate formations are quite complex and change with the temperature. The common ingredient of all ceramic products is clay, and therefore the chemical reactions which occur on heating clay are quite important. The first effect of the heat is to drive off the water of hydration, this occurs at about 600 to 650^0C and absorbs much heat, leaving an amorphous mixture of alumina and silica.

$$Al_2O_3.2SiO_2.2H_2O \longrightarrow Al_2O_3 + 2SiO_2 + 2H_2O$$

In fact, a large proportion of the alumina can be extracted with HCl at this stage. As heating is continued, the amorphous alumina changes at 940^0C to a crystalline form of alumina with the evolution of considerable heat. At a slightly higher temperature, beginning at about 1000^{0}C, the silica and alumina combine to form mullite ($3Al_2O_3.2SiO_2$). At a still higher temperature, the remaining silica is converted into crystalline cristobalite.

$$\underset{\text{kaolinite}}{3(Al_2O_3.2SiO_2.2H_2O)} \longrightarrow \underset{\text{mullite}}{3Al_2O_3.2SiO_2} + \underset{\text{cristobalite}}{4SiO_2} + 6H_2O$$

An actual ceramic body contains many more ingredients than clay itself. Hence the chemical reactions are more involved, and there will be other chemical species besides mullite and cristobalite present in the final product. All ceramic bodies undergo a certain amount of vitrification, or glass formation, during heating, and the degree of vitrification depends upon the relative amounts of refractory and fluxing oxides in the composition, the temperature, and the time of heating.

Applications

1. When ceramic objects are mixed with other materials, the resulting material show greater toughness. Such a mixture of ceramic and other materials is called *ceramic_Composite*. The temperature limits of such bonded materials are exceedingly high; they are employed for aerospace hardware such as heat shields and rocket nozzles.
2. *Cermets* consisting of an intimate mixture of ceramic and metallic components are used to obtain certain physical properties not found solely in either of the components. They are used in lining for brakes and clutches because of the greater weights and high speeds involved and also non lubricating bearings in the temperature range from 370 to 815^{0}C.
3. Ceramic fibres are used for thermal insulation, for zone curtains in annealing furnaces, and for high temperature – low voltage wiring circuits of space and aircraft equipment.
4. Ceramic–fibres–reinforced metals, metal impregnated ceramics, ceramic–reinforced plastics, and metal–ceramic laminates have been developed and used to withstand high temperatures.
5. Ferromagnetic ceramic materials are used in electrical devices such as television sets, computers, magnetic switches, transformers, recroders and memory devices.
6. Thermistors are ceramic materials with limited electrical conductivity that increases with temperature. They are used as heating elements and electrical switches.
7. Ceramic composites are widely used in cutting-tool equipment. For example, cast iron and nickel alloys can be cut with composite of alumina and silicon carbide.
8. Ceramic oxides containing copper, lanthanum and barium show superconducting behaviour. They find applications in electrical generators and electric motors.

13.4 FIBRE GLASS

Among the man-made inorganic fibres, by far glass is produced by the largest volume. Fibre glass, although not a new product, owes its enhanced usefulness to its extreme fineness (about 10μm, but it may be down to 5μm or less). It can be drawn into thread or blown into a mat for insulation, tape and air filters. The drawn fibres are used to reinforce various plastics and the composite product is fabricated into pipes, tanks and supporting goods.

Raw Materials

A special glass, low in silica, is used for the production of fibres. The average composition of the glass used is as follows:

SiO_2 (55%)	B_2O_3 (10%)	Al_2O_3 (14%)
CaO (13%)	MgO (5%)	Na_2O (0.5%)
BaO (1%)		

Manufacture

Fibre glass is made in two basic forms, continuous filament (4-15 μm dia) and fibres (6–9 μm dia and 20–40 cm long). Single filaments can be combined into a strand that is easily unwound from a spool. The product is twisted textile yarn. Staple fibres that meet diameter and minimum length requirements are twisted together into a tow that can also be easily unwound from a spool. The end product is staple yarn. Glass fibres that do not meet these requirements are not suited for textile applications, but may be used for thermal and sound insulation in the form of *glass wool.*

In the continuous–filament operation, the glass marbles, are remelted in small electric furnaces fitted with perforated platinum bushings on the lower face through which the glass flows by gravity. The normal bushing contains 102 or 204 orifices arranged in rows. On starting, operators bunch and draw the coarse filaments downward through an opening in the floor to a high–speed winding device below. This device operating at a speed of nearly two miles a minute draws the filaments and winds them as a strand upon a tube. The result of this operation is to cause the molten glass to draw down to a fibre very much smaller than the diameter of the aperture through which it originally flowed. By controlling the temperature (and hence the viscosity), the orifice size, and the rate of pull, it is possible to control the fibre diameter precisely.

The staple–fibre process also begins by remelting glass marbles in a small electric furnace with a similar perforated platinum bushing at the bottom through which fine streams of molten glass flow by gravity. The streams are seized by high pressure jets of steam or air rapidly into long but discontinuous fibres. While in flight, a fibre lubricant is sprayed on the fibres, which then pass through a drying flame to remove water. They collect upon a revolving drum as a web. The resulting web of fibres on the drum is drawn off through guides and wound on tubes, and, after drafting and twisting to form yarns, sent to weaving and textile fabrication. The resulting yarns may also be dyed or given a variety of different finishes according to their ultimate use.

Applications

1. Fibrous glass continuous–filament strands and fine yarns are used for magnet wire covering, and both continuous filament and staple-fibre yarns and tapes are used for the insulation of various types of wires and cables.
2. Fibrous glass sleevings and tubing, either plain, varnished or saturated are used for the supplementary insulation of lead wires in electrical equipment.
3. Glass fabrics are used in commercial and industrial applications as pipe wrapping where an incombustible material is required.
4. Glass yarns and strands are used in the formation of reinforced plastics. Similar strands are also used for the reinforcement of certain rubbers, for the manufacture of high strength gypsum plastboards, and in parallel or random layer for the reinforcement of high strength water proofing and vapour–barrier laminated papers.
5. Fibre glass is used to make panels in cars and is useful materials for aircraft components.
6. Optical fibres made from silica glass have excellent optical properties and are used to transmit television programmes, telephone conversations, computer outputs etc.
7. Recent developments include the manufacture of all glass papers using exceedingly fine fibres in the range of 0.5μm to 3μm in diameter.

13.5 THIN FILMS

Thin films refer to films having thickness in the range of 0.1μm to 300μm. They have been used for decorative purposes for well over a thousand years. One of the earliest thin films was "gold leaf" formed by controlled beating of gold to a thickness of 0.1μm. As early as the seventh century, glass and ceramics were decorated by painting a pattern with a silver salt, then heating the painted object to cause reduction of the salt to a thin film of metallic silver. Now-a-days several types of thin films are used for different purposes such as decorative, protective, conductive, resistive, magnetic, insulating etc. In addition to metallic and inorganic films, organic polymeric materials can also be applied as thin films.

Desirable Properties of Thin Films

Thin film must possess the following desirable properties.

1. It should adhere well to the object.
2. It should have a uniform thickness.
3. It should be impermeable to other materials.
4. It should be thermally stable.
5. It should be chemically stable.
6. It should possess low density.
7. It may possess some special properties such as optical or magnetic behaviour.

Film Deposition Techniques

Several techniques for depositing thin films are being used. Some of these techniques are described below.

1. **Electrolytic Deposition:** This is one of the oldest known methods used for the preparation of metal coatings on the cathode and anode of a cell. The method involves the movement of metallic ions in solution to the electrodes under the influence of the applied electric field. At the cathode, the ions accept electrons, are neutralized, and incorporated into the metallic lattice. The supply of cations to the cathode is affected by current density, temperature and agitation of the electrolyte, convection in the immediate vicinity of the cathode, diffusion and migration velocity of the ions, specific weight of the ions and geometric form of the cathode. All these factors influence the conditions of film formation and final film structure and properties.

   Metals on which anodic films can be formed are known as valve metals because of the rectifying characteristic of their anodic oxides. The electrolytic cell used for the production of anodic oxide films contains an electrolyte in which a valve metal anode and an inert cathode are immersed while constant current and voltage are maintained. When the positive terminal is connected to the anode and negative to the cathode, electrolysis and simultaneous growth of the oxide film on the anode result.

2. **Sputtering:** Sputtering is a process in which the material is removed from a source, carried by a plasma and deposited on the substrate. It is the main competition to the vacuum evaporative process and yields more consistent sheet resistivity values and improved temperature coefficient of resistance. For the deposition of complex metal oxides and alloys, sputtering is generally preferred. Sputtering involves the use of high voltage to remove material from the source. Atoms are removed from the source material and carried through the ionized gas within the chamber and deposited on the substrate. The largest surface is the cathode and the substrate is made the anode. The chamber contains an inert gas such as argon. Some of the sputtered atoms develop sufficient energy to penetrate several atomic layers of substrate surface, resulting in adhesion anchoring and films of excellent adhesion. It is suitable for depositing multilayers films and films of complex alloys. Sputtering is widely used to form thin films of silicon, titanium, aluminium, gold. It is also employed for the applications of carbides, nitrides, borides etc. to metal tool surfaces and formation of soft lubricating films such as molybdenum disulphide. The disadvantages of this techniques are the higher cost of equipment and operation and slower deposition rates.

3. **Photopolymerization:** This technique is used for depositing polymer films. The equipment required for gas-phase photopolymerization includes a vacuum system, provisions for introducing gaseous monomer or vaporizing the liquid monomer and a UV source. The polymerization mechanism involves a two step process: the gaseous monomers are first attached to the vessel surface by chemisorption or physical adsorption, and then activated with ultraviolet light. The UV polymerization process utilizes low energies of about 5eV causing free

radical formation. The resultant free radicals couple to form polymers at a rate that generally increases with increasing light intensity. A variety of monomers, including tetrafluoroethylene and hexachlorobutadiene, have been polymerized to yield pin hole free films.

Uses of Thin Films

1. They are used for decorative and protective purposes.
2. They are used to form conductors, resistors and even microelectronic circuits.
3. They are used to form photovoltaic cells that convert solar energy into electrical energy.
4. They are used as optical coatings on lenses to minimize the amount of reflected light.
5. They are used to coat metal surfaces to increase their hardness. For example, diamond thin films are used to get hardness and wear resistance on cutting tools.
6. Today, reflecting films prepared by vacuum evaporation are used to regulate the temperature of the satellites by controlling solar absorbancy.
7. They are also used for the metallization of glass and ceramics.

13.6 SEMI–CONDUCTORS

Semi–conductors are solids which exhibit a feeble electrical conductivity that increases with increase in temperature. Semiconductivity appears in insulators that are slightly contaminated with foreign substances, and in compounds, such as ZnO and Cu_2O, which do not contain exactly stoichiometric amounts of metal and nonmetal. Typical metals are good conductors of electricity. They become better conductors when they are cooled to lower temperatures. Some metals are such good conductors at very low temperatures that they no longer have a measurable resistance and therefore become superconductors. Semiconductors show the opposite behaviour, – they become much better conductors as the temperature increases. The difference between the temperature dependence of metals and semi conductors is so significant; it is often the best criterion for distinguishing between these materials.

Semi–conductors are very sensitive to impurities: Pure silicon or germanium is an insulator, similar to diamond in both crystal structure and electronic structure. The conductivity of silicon or germanium can be increased by a factor of up to 10^6 by adding as little as 0.01% of an impurity. Metals, on the other hand, are fairly insensitive to impurities. It takes a lot of impurity to change the conductivity of a metal by as much as a factor of 10; and unlike semi conductors, metals become poor conductors when impure.

The differences in the way metals, semi–conductors, and insulators conduct electricity can be explained with the diagram in Fig. 13.3. Metals have partially filled bands of orbitals that allow electrons to move from one end of the crystal to the other. They therefore conduct an electric current. All the bands in an insulator are either filled or empty. Furthermore, the gap between the highest energy filled band and the lowest energy empty band in an insulator is so large that it is difficult to excite electrons from one of these bands to the other. As a result, it is difficult to move electrons through an insulator.

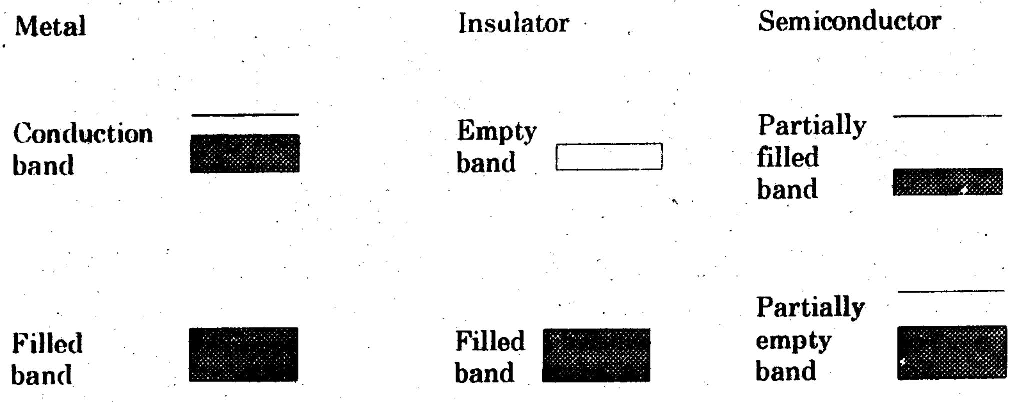


Fig. 13.3 Band theory diagrams for a metal, an insulator and a semi conductor

Semi–conductors also have a band structure that consists of filled and empty bands. The gap between the highest energy filled band and the lowest energy empty band is small enough, however, that electrons can be excited into the empty band by the thermal energy these electrons carry at room temperature. Semi–conductors therefore fall between the extremes of metals and insulators in their ability to conduct an electric current. Semi–conductors become better conductors at high temperatures. As the temperature increases, the number of electrons with enough thermal energy to be excited from the filled band to the empty band increases and the semiconductor becomes a better conductor.

The conductivity of a semi–conductor can be improved by adding impurities to them, as boron, aluminium and arsenic to germanium or silicon. These impurities reduce the energy gap and allow more electrons to flow into the empty conduction bands. This phenomenon is called *doping* and the treated substances are called *doped semi conductors*. Let us look at what happens when we add a small amount of arsenic to germanium or silicon. Arsenic atoms have one more valence electron than germanium or silicon atoms. Arsenic atoms can therefore lose an electron to form As^+ ions, which can occupy some of the lattice points in the crystal where silicon or germanium atoms are normally found. As a result, the extra electrons from the arsenic atoms occupy orbitals in a very narrow band of energies that lie between the filled and empty bands of semiconductor, as shown in Fig. 13.4. This structure decreases the amount of energy required to excite an electron into the lowest energy empty band in the semiconductor and therefore increases the number of electrons that have enough energy to cross this gap. As a result, this "doped" semiconductor becomes a very much better conductor of electricity. Because the electric charge is carried by a flow of particles, these semiconductors are called *n-type*.

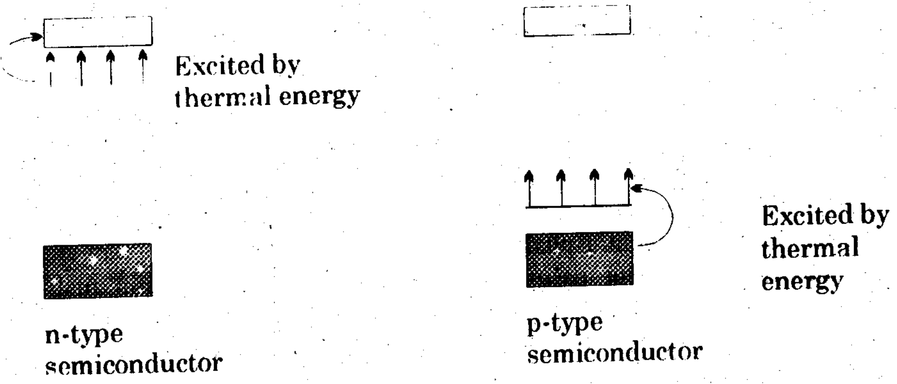


Fig. 13.4 Band theory diagrams for n-type and p-type doped semiconductors

It is also possible to dope silicon or germanium with one of the elements in Group IIIA, such as indium. Indium atoms have one less electron than silicon and germanium atoms, and they can capture electrons from the highest energy filled band of orbitals to form holes in this band. The presence of holes in a filled band has the same effect as the presence of electrons in the empty band. It allows the solid to carry the electric current. The electric charge is now carried by a flow of *positive* particles, or holes, so these semiconductors are called *p-type*.

Because semiconductors tend to carry a much smaller electric current than metals, it is easier to control the current's flow. Furthermore, bringing n-type and p-type semiconductors together produces a device, the *transistor*, that has a natural one-directional flow of electrons, which can be stopped by applying a small voltage in the opposite direction. This junction between n-type and p-type semiconductors was the basis of revolution in industrial technology that followed the discovery of the transistor. The modern electronic industry is based on integrated circuits in which silicon or germanium doped materials are used to get the desired electronic characteristics.

Optoelectronics is a main segment of the semiconductor industry. Optoelectronic devices include the light emitting diode (LED), semiconductor laser, and various photodetectors, including the photovoltaic cells. Photodetectors rely on light induced carrier generation. The simplest such device is a photodetector, which is merely a semiconductor device.

13.7 COMPOSITE MATERIALS

When two or more materials with very different properties are combined together they form a composite material. The different materials work together to produce a new material, which combines all of the properties of the previously separate materials Within the composite it is still possible to easily tell the different materials apart. They do not tend to blend or dissolve each other. Composite Materials can be either man-made but they may also exist in nature. e.g. Mud Bricks, Car Tyres, Concrete and Fibreglass.

A composite material consists of two or more physically and/or chemically distinct, suitably arranged or distributed phases, with an interface separating them. It has characteristics that are not depicted by any of the components in isolation. Most commonly, composite materials have a bulk phase, which is continuous, called the *matrix*, and one dispersed, non-continuous, phase called the *reinforcement*, which is usually harder and stronger.

The concept of composite material is ancient: to combine different materials to produce a new material with performance unattainable by the individual constituent. An example is adding straw to mud for building stronger mud walls. Some more recent examples, but before engineered materials became prominent, are carbon black in rubber, steel rods in concrete, cement/asphalt mixed with sand, fiberglass in resin etc. In nature, examples abound: a coconut palm leaf, cellulose fibers in a lignin matrix (wood), collagen fibers in an apatite matrix (bone) etc. The essence of the concept of composites is this: the bulk phase accepts the load over a large surface area, and transfers it to the reinforcement, which being stiffer, increases the strength of the composite. The significance here lies in the there are numerous matrix materials and as many fiber types, which can be combined in countless ways to produce just the desired properties.

Most research in engineered composite materials has been done since 1965. Today, given the most efficient design, of say an aerospace structure, a boat or a motor, we can make a composite material that meets or exceeds the performance requirements. Most of the savings are in weight, strength/weight, etc.

Components of Composite Materials

*** Bulk phase: matrix materials**

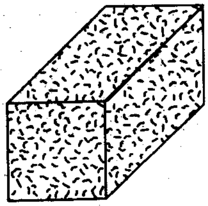
Polymers
Metals
Ceramics

*** Reinforcement: fibers and particulate**

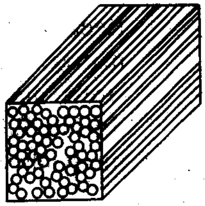
Glass
Carbon
Organic
Boron
Ceramic
Metallic

*** Interface**

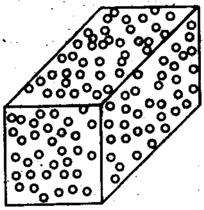
1. Fibers as the reinforcement (Fibrous Composites):
a. Random fiber (short fiber) reinforced composites



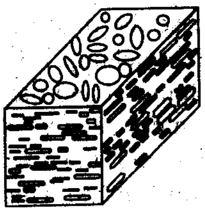
b. Continuous fiber (long fiber) reinforced composites)



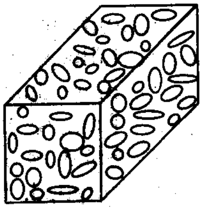
2. Particles as the reinforcement (Particulate composites):



3. Flat flakes as the reinforcement (Flake composites):



4. Fillers as the reinforcement (Filler composites):



Classification of Composite Materials

The reinforcement system in a composite material strongly determines the strengthening mechanism in a composite. It is thus convenient to classify composites according to the characteristics of the reinforcement, such as length orientation etc. (Fig. 13.5)

Properties of Composites

We will consider the results of incorporating fibers in a matrix. The matrix, besides holding the fibers together, has the important function of transferring the applied load to the fibers. It is of great importance to be able to predict the properties of a composite, given the component properties and their geometric arrangement.

a) Fiber reinforced composite materials typically exhibit anistrophy. That is, some properties vary depending upon which geometric axis or plane they are measured along.

b) For a composite to be isotropic in a specific, such as Young's modulus, all reinforcing elements, whether fibers or particles have to be randomly oriented. This is easily achieved for discontinuous fibers, since most processing methods tend to impart a certain orientation to the fibers.

c) Continuous fibers in the form of sheets are usually used to deliberately make the composite anisotropic in a particular direction that is known to be principally loaded axis or plane.

d) Because of a difference in the thermal expansion properties of fibers and matrix, the composite is not allowed to deform uniformly under thermal stress. and this can lead to microcracking of the matrix and debonding at the interface. This is a particularly important concern in dental composite materials where thermal stresses are significant.

e) In a ductile matrix, like most polymers and metals, a strong interfacial bond is important, since the fibers carry most of the load in such matrices. Fibers tend to fail first, usually by cohesive failure through the fiber cross-section. This is because the fibers cannot strain as much as the matrix (e.g. carbon in eposy). Cracks are few, and tend to propogate slowly. When the cracks hit the interface, strong interfacial bonds stop them.

f) In a brittle matrix, like ceramics, the matrix carries most of the load, which is usually compressive (like in teeth or bone), and fibers are added only to increase toughness. That is, to increase the time to catastrophic failure by holding the matrix together after cracking. Fibers here are more ductile than the matrix (e.g. glass in alumina) and the matrix fails first. As the cracks propagate and reach the interface, a weak interfacial bond is desired. This enhances debonding, and the cracks are not stopped, but deflected along the length of the fibers. This effectively delays the time it takes the cracks to propagate through the entire matrix, and thus increases toughness.

Application of Composite Materials

Composite materials have fully established themselves as workable engineering materials and are now relatively common place around the world, particularly for structural purposes. Early military applications of polymer matrix composites during World War II led to large-scale commercial exploitation, especially in the marine industry, during the late 1940s and early 1950s. Today, the aircraft, automobile, leisure, electronic and medical industries are quite dependent on fiber-reinforced plastics, and these composites are routinely designed, manufactured and used. Less exotic composites, namely particulate or mineral filled plastics are also widely used in industry because of the associated cost reduction. Some typical applications of polymer matrix composites are listed in Table 13.1.

Table 13.1. Some applications of polymer matrix composites. (Adapted from Hull, 1981)

Industrial sector	Examples
Aerospace	Wings, fuselage, radomes, antennae, tail-planes, helicopter blades, landing gears, seats, floors, interior panels, fuel tanks, rocket motor cases, nose cones, launch tubes.
Automobile	Body panels, cabs, spoilers, consoles, instrument panels, lamp-housings, bumpers, leaf springs, drive shafts, gears, bearings.
Boats	Hulls, decks masts, engine shrouds, interior panels
Chemical	Pipes, tanks, pressure vessels, hoppers, valves, pumps, impellers
Domestic	Interior and exterior panels, chairs, tables, baths, shower units, ladders.
Elecrical	Panels, housings, switchgear, insulators, connectors
Leisure	Motor homes, caravans, trailers, golf clubs, racquets, protective helmets, skis, archery bows, surfboards, fishing rods, canoes, pools, diving boards, playground equipment.

In a similar manner to polymers and ceramics, metals may be reinforced by continuous fibers, discontinuous fibers or particulates. Silicon carbide and alumina are the most frequently employed reinforcements and a wide range of composites have been produced. However, most metal matrix composites are still under development and there are only a few examples of commercial components currently in service (Table 13.2)

Recent interest has concentrated on transport applications and consequently the light metals, particularly aluminum and its alloys, have received the most attention. The Young's modulus of aluminum and its alloys is relatively low for metals and hence there is considerable potential for improvement by reinforcement. However the reader will recall that the forte of metals is their good ductility and toughness and obviously it is desirable that these properties are not degraded in metal matrix composites.

Table 13.2. Some applications of ceramic and metal matrix composites.

Industrial sector	Application	
	Ceramic matrix	Metal matrix
Aerospace	Afterburners, brakes, heat shields, rocket nozzles	Struts, antennae
Automobile	Brakes	Piston, crowns
Manufacturing	Thermal insulation, cutting tools, wire drawing dies.	
Electrical		Superconductors, contacts, filaments, electrodes
Medical	Prostheses, fixation plates	

Questions

Q.1 (a) What are liquid crystals? Discuss different types of liquid crystals?

(b) Write some uses of liquid crystals in modern technology.

Q.2 What are inorganic polymers? Discuss the chemistry and uses of some inorganic polymers used in modern industry.

Q.3 (a) What do you mean by engineering ceramics? What raw materials are used for ceramic products.

(b) Briefly discuss the manufacture of ceramic products.

(c) What are the uses of engineering ceramics in modern industry.

Q.4 What is fiber glass? How is it manufactured? What are its applications in modern industry.

Q.5 (a) What are thin films? Write the characteristic features of thin films.

(b) Briefly discuss important techniques for depositing thin films.

(c) Write some uses of thin films.

Q.6 (a) What are semiconductors? How do they differ from metals and insulators.

(b) Briefly discuss the Band theory of semiconductors.

Q.7 (a) Differentiate between metals and semi conductors.

(b) How does the conductivity of semiconductors be increased?

(c) What is doping? Discuss n-type and p-type semiconductors.

Q. 8 What are composite materials? How would you classify them? Write some uses of composite materials.

Q. 9 Write short notes on the following.

(a) Thin films

(b) Liquid crystals

(c) Semiconductors

(d) Fibre glass

Chapter Fourteen

NUCLEAR CHEMISTRY

14.1. INTRODUCTION

Nuclear Chemistry is that branch of chemistry which is concerned with the structure of the nucleus and how this structure influences the nuclear stability. It also deals with phenomena by means of which one nucleus is changed into another, such as the process of radioactivity and of nuclear transformation. In ordinary chemical reactions, there is a rearrangement of the atomic electrons but the atomic nuclei remain unaffected. On the other hand, in a nuclear reaction, there is a change in the number of protons or neutrons (or both), thus resulting in the formation of new nuclei. The energy released in ordinary chemical reactions is usually less and therefore, does not affect the stability of the nucleus. However, the energy released during nuclear changes, is sufficiently high to break the chemical bonds and is used to induce chemical reactions.

Nuclear chemistry is subdivided into two branches (a) radiochemistry, and (b) radiation chemistry.

(*a*) **Radiochemistry.** It deals with the study of radioactive atomic species and their applications in various fields.

(*b*) **Radiation Chemistry.** It is now limited to chemical effects produced by radiation while interacting with a system.

Nuclear chemistry has become a very important and fascinating branch of science due to the tremendous amount of energy liberated during nuclear reactions, which led to the discovery of atomic bomb and hydrogen bomb. The controlled release of nuclear energy promises to lead us into a new era, in which an unlimited storehouse of energy is available to mankind. It is rightly said that we are now living in the nuclear age, and the future of humanity is at the mercy of nuclear chemists. They can annihilate the whole world within a few minutes. They are the hope of human happiness and prosperity as well.

14.2. RADIOACTIVITY

The phenomenon of radioactivity was discovered by **H. Becquerel** in 1895. He observed that when a photographic plate wrapped in black paper was exposed to certain uranium salts, it was fogged. He concluded that fogging of the plate was due to the radiation emitted from the uranium salt. Subsequently, it was shown that radiation can cause ionization of air and is not affected by factors like temperature, pressure, chemical environment or source of uranium. The spontaneous emission of radiation of this type by an element is called radioactivity and the element which exhibits this behavior is said to be radioactive. The name radioactivity was proposed by a Polish pupil of Becquerel, Marie Sklodowska, who later became the illustrious scientist Marie Curie, the recipient of two Nobel Prizes.

In 1898, Marie and her husband Pierre Curie undertook the systematic study of radioactivity of many substances. They noted that the chief source of uranium (pitchblende, U_3O_8) contains elements which had greater activity than uranium. By chemical methods, Madam Curie succeeded in isolating from this mineral two new radioactive elements, polonium and radium. At the same time Madam Curie (France) and G.C. Schmidt (Germany) independently discovered a new radioactive element, thorium. Debierne in 1899 discovered a new element actinium which was also radioactive. Since then, the systematic investigation has been brought to light about forty elements which show characteristics of radioactive elements. A large number of other elements have found to become radioactive by special methods.

In 1902, Rutherford began investigating the nature of the radiations emitted from radioactive elements. He showed that the radiations were composed of there types of rays; the alpha rays (α) the beta rays (β) and the gamma rays (γ). Characteristic properties of these three types of radiations are given below:

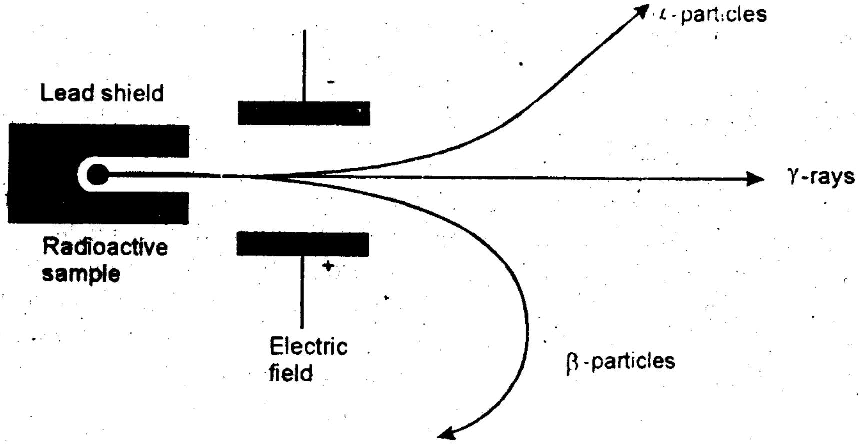


Fig. 14.1. The effect of an electric field on α, β and γ rays.

Alpha Rays

(i) *Nature.* The deflection of α-rays in an electric or a magnetic field shows that these are positively charged particles. Furthermore, it has been shown by Rutherford and T. Royds (1909) that an alpha particle carries two units of positive charge and has a mass approximately four times than that of the hydrogen atom. In other words, the α-particle is a helium nucleus consisting of two neutrons and two protons ($^4_2$He).

(ii) *Velocity.* Alpha particles generally move with a velocity ranging from 1.4 to 2.0 $\times 10^7$ ms^{-1}.

(iii) *Ionization.* Since alpha particles have large mass and move with high speeds, they have therefore, considerable kinetic energy. Due to this large energy, the alpha particles cause ionization when passed through a gas.

(iv) *Luminescence.* The α-particles cause luminescence when they strike a zinc sulphide screen, and have intense photographic activity.

(v) *Penetrating Power.* Alpha particles have smaller penetrating power and are stopped by a sheet of paper or by a thin foil of aluminum or a few cm of air at atmospheric pressure.

Beta Rays

(i) *Nature.* The deflection of β-particles in an electric or a magnetic field shows that they are negatively charged particles. Their e/m ratio is the same as that of the electron indicating that β-particles are actually fast moving electrons.

(ii) *Velocity.* The velocity of β-particles is approximately equal to that of light. The average value being 2 x 10 ms^{-1}.

(iii) Ionization. Due to smaller mass, β-particles have low ionization power than αparticles.

(iv) *Luminescence.* Due to their low kinetic energy, β-particles have very little effect on zinc sulphide plate. On the other hand, their photographic activity is greater than that of β-particles, perhaps; it is due to the production of X-rays being produced by the absorption of β-particles, by matter.

(v) *Penetrating Power.* Due to their high speed, β-particles are more penetrating than β-particles. Their penetrating power is about 100 times more than those of β-particles. β-rays are stopped by 3 mm of lead. Because of their small mass they are easily deflected from their path by an electric or a magnetic field.

Gamma Rays

(i) *Nature.* Gamma rays are unaffected by electric and magnetic fields, hence they are not charged particles. They are electromagnetic radiations analogous to X-rays. Their wavelengths lie in the range of 10^{-10} to 10^{-13} m and hence have shorter wavelengths than X-rays.

(ii) *Velocity.* They travel with extremely high velocity, which is nearly equal to that of light.

(iii) *Ionization.* They cause ionization of the gases, but have proportionally weaker ionizing power, among the three radiations.

(iv) *Penetrating Power.* Gamma rays have very high penetrating power due to very short wavelength. Their penetrating power is about 10 to 100 times more than β-rays. These rays are stopped by several centimeters of lead.

(v) *Luminescence.* Gamma rays produce very little effect on zinc sulphide and photographic plate.

2.3. DETECTION AND MEASUREMENT OF RADIOACTIVITY

Decaying of a radioactive material in unit time is called its activity. The standard unit of radioactivity is Curie (Ci), which is defined as that amount of any radioactive material which gives 3.70×10^{10} disintegrations per second. The disintegration per second is abbreviated as dps. One gram of radium-226 undergoes 3.70×10^{10} disintegrations per second and is also equal to one Curie. In practice, activities are expressed in terms of megacuries, curies, millicuries and microcuries.

1 curie (Ci) $= 3.70 \times 10^{10}$ dps

1 millicurie (mCi) $= 3.70 \times 10^{7}$ dps

1 microcurie (æCi) $= 3.70 \times 10^{4}$ dps

The SI unit of radioactivity is Becquerel (Bq) which is defined as the activity due to one disintegration per second.

1 Ci $= 3.70 \times 10^{10}$ Bq

1 Bq = 1 disintegration per second.

The activity of a radioactive material per unit mass is called its specific activity. It is measured in counts per second or counts per minute. It is a measure of relative abundance of radioisotopes, since radioisotopes occur in mixture with stable isotopes.

The detection and measurement of radioactivity of any sample is based on the detection, identification and measurement of the radiations emitted by the sample. Some methods employed for this purpose are described below:

(i) Photographic Methods.

(ii) Gas Ionization Methods.

(iii) Scintillation Methods.

1. Photographic Methods

Detection of radiation by photographic method is also known as autoradiography. Autoradiography is a photochemical process. It was the one used by Becquerel in 1896 in the discovery of radioactivity. In this method, ionizing radiation interacts with the silver halide in photographic emulsions. When a radioactive material is placed near a photographic film or plate, a blackening will be produced on development of the emulation. The blackened areas constitute a self-portrait of the activity in the material. The intensity of the blackening (as determined by an eye or with a densitometer) at a given place will be a function of exposure time and the amount of activity in the simple at that place.

The method of autoradiography is particularly suitable when the distribution of a radioactive compound in biological material is to be studied. However, precautions should be taken that there is no chemical or pressure effect of the material on the emulsion as this may also produce an image. Autoradiography is frequently applied to the determination of the components of a paper or thin layer chromatogram, but detection of radiation on a quantitative basis by this method is difficult and tedious.

2. Gas-Ionization Methods

When radiation passes through a gas, some of the energy is transferred to the gas molecules, which may be ionized into positive ions and electrons. If an electric field is applied, these ions and electrons can be collected before they have the opportunity to recombine (Fig. 14.2). The magnitude of the resulting current can be correlated with the amount of radiation initially responsible for the ionization. An ionization chamber is a device in which an electric field is applied just sufficient to collect all the ions and electrons produced in the volume of the gas between the electrodes.

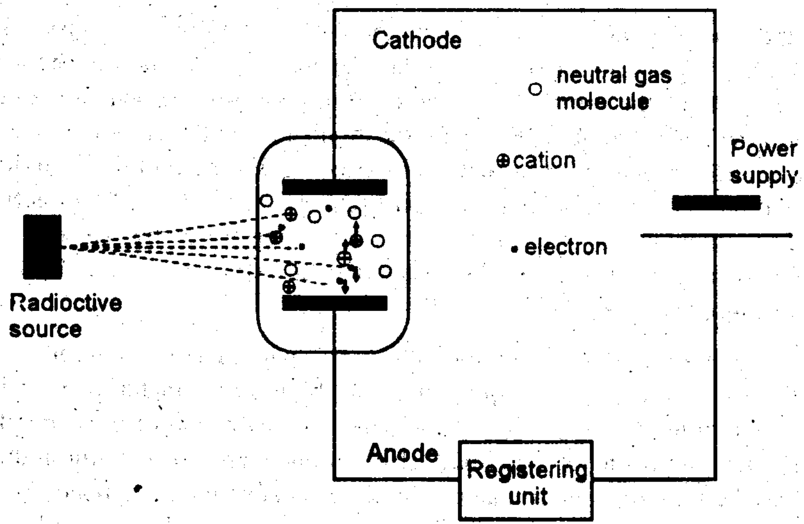


Fig. 14.2. Radiation detection by ionization.

A common gas ionization counter is the **Geiger Muller Counter** which is shown in Fig. 14.3 In fact, it is also an ionization chamber in which the cathode is cylindrical and a thin tungsten wire fixed along the axis of the cylinder or tube shell serves as anode. Radiation enters the tube through a thin window made of mica. The tube is filled with a gas, usually argon at low pressure. A working potential of about 1200 volts is applied between the inner wire and the outer tube. When ionizing radiation enters through thin mica window, interacts with the atoms of the filled gas to produce positive ions and electrons. The positive argon ions (Ar+) move to the cathode and the electrons to the anode. The counter generates a pulse due to the free electrons. Amplification of the pulse from each ionization causes a clicking sound in a loudspeaker or activates a digital counter that registers the amount of radiation entering the tube. A chart recorder may also be attached to the circuit to give a graphic display of the intensity of radiation versus time. This counter is generally employed for the detection of β and γ-rays, although its modified form could be used for à-particles, protons, neutron and X-rays photon.

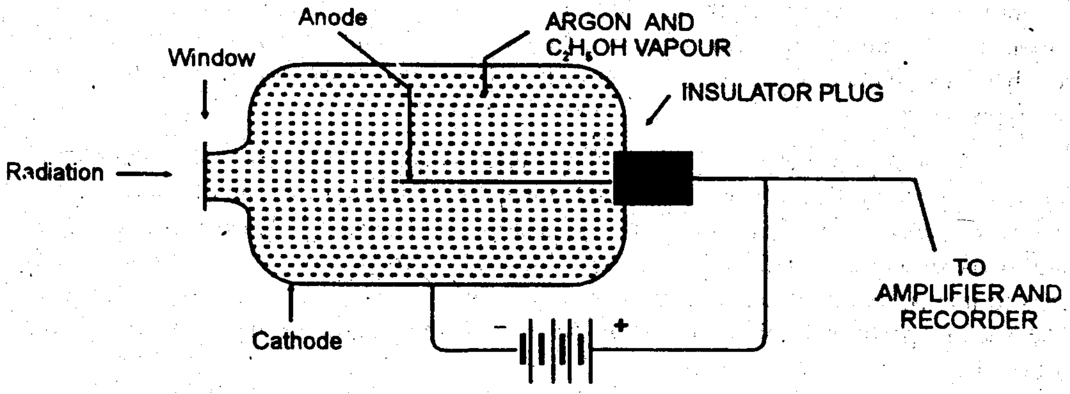


Fig. 14.3. The G.M. counter.

Merits

- (i) This technique is very sensitive.
- (ii) It produces a large pulse which requires no further amplification.
- (iii) The pulse size is independent of the nature of incident radiation.

Limitations

- (i) It is nit very sensitive for very high counting rates.
- (ii) It is unable to give information about the nature of particle detected.

3. Wilson's Cloud Chamber.

Wilson developed a cloud chamber in which the tracks of charged particles can be seen. The principle of this technique is that when a gas containing vapours at saturation pressure is expanded suddenly it gets cooled and becomes supersaturated. In presence of dust particles, droplets are formed around the dust particles. In a dust free atmosphere condensation could be produced on a negative ion present in the gas and expansion of gas is made 1.31 – 1.4 times its volume.

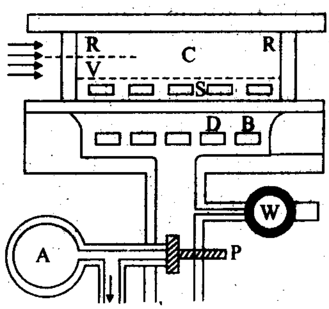


Fig 14.4. Wilson's Cloud Chamber

The Wilson's Cloud Chamber consists of a cylindrical glass chamber, C. It is provided with a glass plate cover and a perforated metal plate base. The metal plate is covered by a dark velvet cloth V. Water is sprinkled on velvet cloth to provide water vapour to saturate the air in the chamber, C. The rubber diaphragm D forms an air-tight seal between chamber C and space S below it. A is an evacuated container kept closed by a piston P Fig. 14.4.

When a piston P is withdrawn, the space S is connected to the container A. The pressure in S suddenly falls. This pulls down the diaphragm D, and the air in the chamber C undergoes expansion. After expansion, container A is closed by the piston P and air is slowly admitted into the space S through a small valve V. The diaphragm R goes to its original position. The pressure in the chamber C reverts to its original value. The second perforated plate B is kept below the diaphragm D and expansion ratio adjusted.

The water droplets are condensed on charged ions. The Chamber is illuminated and tracks can be viewed through the top glass plate and photographed. After that potential difference is adjusted to 100V and electric field sweeps the ions from the chamber. The chamber is then made ready for next operation.

Alpha-particles ionize to large extent and produce thick tracks. Beta particles ionize to less ionization and tracks are thin.

Demerits

1. It is not practicable to build Cloud Chamber large enough to show the entire path of an extremely high energy particle.
2. High energy bubble chambers or photographic emulsions have to be used to observe the tracks.
3. The Cloud Chamber is less sensitive as the duration of super saturation is of the order of one second.

4. Scintillation Methods

A scintillator is a substance which emits a small flash of light when struck by a fast charged particle. Solid scintillators are particularly suited for the detection of gamma rays because of high density and high atomic number of the crystals used. Some alkali halides, in particular sodium iodide (activated with Tl) have been the most useful.

When a gamma photon is partially or totally absorbed in the scintillation crystal, at least one fast electron is liberated (photoelectron, Compton electron or pair production electron). The electron causes ionization and excitation along its path in the crystal. When the excited atoms return to their ground state, they emit light photons, the number being proportional to the gamma photon energy that is lost in and absorbed by the crystal.

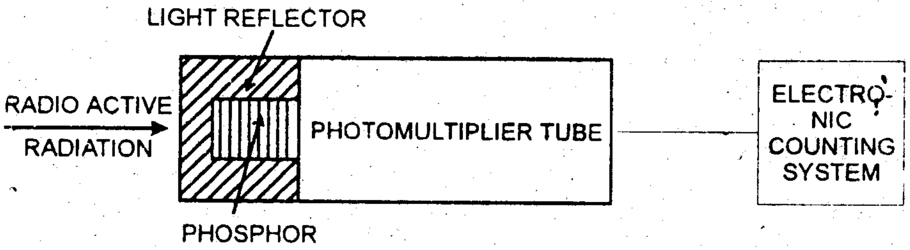


Fig. 14.5. Scintillation counter

In the so-called photomultiplier tube, a photosensitive layer or photocathode is optically coupled to the scintillation crystal. The light flashes produced in the crystal cause electrons to be liberated from the photocathode. The photocathode is followed by a series of electrode stages (dynodes), each at a potential more positive than that of the preceding one. Thus photoelectrons released from the photocathode surface will be attracted to the first dynode and will gain sufficient kinetic energy to release several secondary electrons from the surface. This multiplication process occurs at each stage and at the end of ten or more stages a very large number of electrons will arrive at the anode. The size of this pulse of electrons will be proportional to the original gamma ray energy absorbed in the crystal.

14.4. NUCLEAR TERMS

Atomic number. The number of protons in the nucleus is called the atomic number Z.

Neutron number. The number of neutrons in the nucleus is called neutron number N.

Mass number. The sum of numbers of neutrons and protons in the nucleus is called mass number A. Thus

$$A = Z + N$$

Nuclide. Any species of atoms with a definite number of protons and neutrons is called a nuclide. The composition of a nucleus is indicated by its nuclide symbol. It consists of the symbol for element (E) with atomic number (Z) written as the subscript at the lower left and the mass number (A) as the superscript at the upper left.

$^{A}_{Z}E,\ ^{4}_{2}He,\ ^{14}_{7}N$

Isotopes. Nuclides with the same number of protons are called isotopes.
For example,

Isotopes of hydrogen (Z = 1); $^{1}_{1}H,\ ^{2}_{1}H\ ,\ ^{2}_{1}H$

Isotopes of sodium (Z = 11); $^{22}_{11}Na,\ ^{22}_{11}Na,\ ^{22}_{11}Na$

Isobars. Nuclides with the same mass number are isobars.
For example,

Isobars of A = 3 ; $^{8}_{1}H\ ,\ ^{8}_{2}He$

Isobars of A = 14 ; $^{14}_{6}C\ ,\ ^{14}_{7}N$

Isotones. Nuclides with the same number of neutrons are Isotones.
For example,

$^{8}_{1}H$ *and* $^{4}_{2}He$

$^{18}_{8}C$ *and* $^{14}_{7}N$

Isomers. Nuclides having the same atomic number and mass number but differing in their energy contents or radioactive properties are called nuclear isomers. The isomers are denoted as

$^{A}_{Z}X$ *and* $^{Am}_{2}X$

$^{60}_{27}Co$ *and* $^{60m}_{27}Co$, $^{80}_{35}Br$ *and* $^{80m}_{35}Br$

The isomer of higher energy is in a metastable state and is indicated by writing m after the mass number. The metastable isomer is radioactive and decays by γ-emission into ground state isomer, which may also be radioactive.

Nucleon. Particle comprising the nucleus is called nucleon. Either proton or neutron is called nucleon.

Example 14.1. Determine the number of protons, neutrons and electrons in a $^{210}_{82}Pb^{2+}$ ion.

Solution. The atomic number of lead is 82, which means this ion contains 82 protons. Since it has a charge of +2, this ion must contain 80 electrons. Because neutrons and protons both have a mass of about 1 amu, the difference between the mass number (210) and the atomic number (82) is equal to the number of neutrons in the nucleus of atom. This ion therefore contains 128 neutrons.

Example 14.2. Classify the following sets of nuclides as examples of isotopes, isobars or Isotones.

(a) $^{12}_{8}C$, $^{13}_{6}C$, $^{14}_{6}C$

(b) $^{40}_{18}Ar$, $^{40}_{19}K$, $^{40}_{20}Ca$

(c) $^{14}_{8}C$, $^{15}_{7}N$, $^{16}_{6}O$

Solution.

(a) $^{12}_{6}C$, $^{13}_{6}C$ *and* $^{14}_{6}C$ are isotopes because they all contain six protons.

(b) $^{40}_{18}Ar$, $^{40}_{19}K$ *and* $^{40}_{20}Ca$ are isobars because they have the same mass

(c) $^{12}_{6}C$, $^{15}_{7}N$ *and* $^{16}_{8}O$ cannot be isotopes because they contain different number of protons. They cannot be isobars because they have different mass numbers. They all contain eight neutrons, however, so they are examples of Isotones.

14.5. MASS DEFECT AND NUCLEAR BINDING ENERGY

It is an experimentally observed fact that the mass of an atom is always less than the sum of the masses of its constituent particles, such as protons, electrons and neutrons. A helium atom, for example, contains two protons, two neutrons, and two electrons. The mass of a helium atom therefore should be 4.03296 amu.

2 (1.00727) amu = 2.01454 amu

2 (1.00866) amu = 2.01732 amu

2 (0.00055) amu = 0.0011 amu

Total mass = 4.03296 amu

When the mass of a helium atom is measured, we find that the experimental value is smaller than the predicted mass by 0.03036 amu.

Predicted mass = 4.03296 amu

Observed mass = 4.00260 amu

Mass defect = 0.03036 amu

The difference between the mass of an atom and the sum of the masses of its protons, neutrons and electrons is called the *mass defect*. The mass defect of an atom reflects the stability of the nucleus. It is equal to the energy released when the nucleus is formed from its constituent protons and neutrons. The mass defect is therefore also known as the binding energy of the nucleus.

The binding energy serves the function for nuclear reaction that ΔH° does for a chemical reaction. It measures the difference between the stability of the products of the reaction and the starting materials. The larger the binding energy, the more stable is the nucleus. The binding energy can also be viewed as the amount of energy that must be added to take the nucleus apart to form isolated protons and neutrons. It is therefore literally the energy that binds together the neutrons and protons in the nucleus.

The binding energy of a nuclide can be calculated from its mass defect with Einstein's equation that relates mass and energy. For example, binding energy of helium nucleus can be calculated as follows:

Mass defect $= 0.03036$ amu

or Mass defect $= 0.03036 \times 1.66 \times 10^{-27}$ kg

$= 5.04 \times 10^{-29}$ kg

($\therefore$ 1 amu $= 1.66 \times 10^{-27}$ kg)

Velocity of light $= 3 \times 108\ \text{ms}^{-1}$

$$E = mc^2 \qquad \text{---------} \qquad 14.1$$

$= 5.04 \times 10^{-29} \times (3 \times 10^{8})^2$

$= 4.53 \times 10^{-12}$ J

Binding energies are usually expressed in units of electrons volts (eV) or million electron volts (MeV) per atom.

1 eV $= 1.602 \times 10^{-19}$ J

$$\text{Hence } E = \frac{4.53 \times 10^{-12}}{1.602 \times 10^{-19}} = 28.30 \times 106 \text{ eV/atom}$$

or $E = 28.30$ MeV/atom

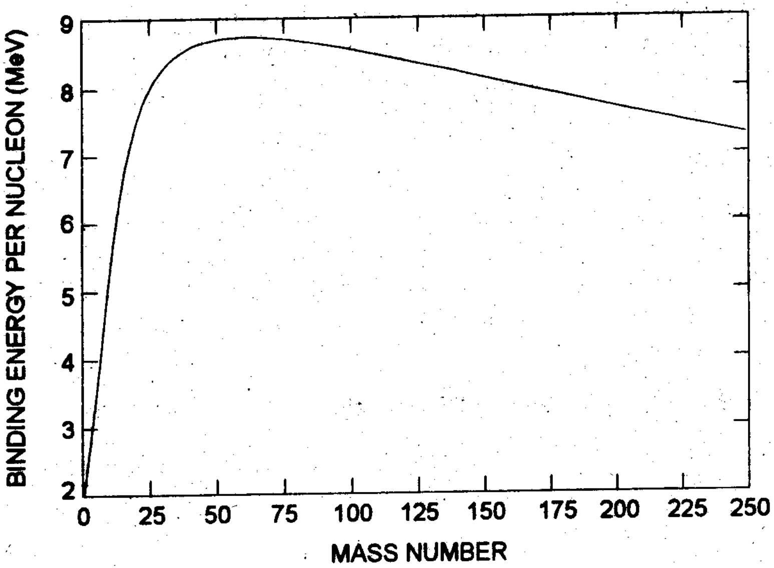


Fig. 14.6. Binding energy per nucleon as a function of mass number.

Calculations of binding energy can be simplified by using the following conversion factor between mass defect in atomic mass units and the binding energy in MeV.

$$1 \text{ amu} = 931.50 \text{ MeV}$$

Binding energy per nucleon is called average binding energy. Fig. 14.6 shows the variation of average binding energy with respect to mass number.

As is clear from figure 5.1, the average binding energy increases rapidly with increasing mass number. It reaches maximum around mass number 50 (about 9.0 MeV) and then decreases slowly. The nuclei with highest binding energies (mass number 40 to 120) are the most stable, because so much energy would be required to separate these nuclei into their component particles. The heavier nuclei possess low average binding energies and are therefore unstable. Thus a heavy nucleus may break down (fission) to intermediate masses having higher average bonding energies. Similarly higher nuclei may combine together (fusion) to form nuclei of intermediate atomic masses having high average binding energy.

14.6. NUCLEAR STABILITY

The nuclides may be classified as (*a*) stable and (*b*) unstable or radioactive nuclides. Stable nuclides are those which are permanent. Their proton and neutron contents remain unchanged for ever. Just 274 naturally occurring nuclides are considered stable.

Radioactive nuclides are intrinsically unstable and undergo spontaneous change with time forming new nuclides by one or the other way. Above 2000 nuclides including a very large number of man made ones are known to be radioactive. The question naturally arises why some nuclides are stable while others are radioactive. In other words what are the factors leading to nuclear stability? A review of the nuclear composition of various nuclides reveals the following three main rules concerning the stability of nuclides.

1. Odd-Even Rule

Most naturally occurring nuclides have even number of protons and even number of neutrons, 165 nuclides fall into this category. Nuclides with odd numbers of both are least common (5), and those with odd-even combinations are intermediate in abundance. Table 2.1 gives summary of stable nuclides along with the odd or even number of protons and neutrons in them.

Table 14.1. Frequency Distribution of Stable Nuclides

Protons	Neutrons	Number of Nuclides
Even	Even	165
Even	Odd	55
Odd	Even	50
Odd	Odd	5

2. Magic Numbers

It has been noted that a nuclide is more stable if its neutron and proton numbers are 2, 8, 20, 28, 50, 82 or 126. These numbers are called magic numbers. The nucleus is most stable, if its neutron and proton numbers both are magic numbers

e.g., $^{1}_{2}He$.

3. Neutron-Proton Ratio

Except in the case of ordinary hydrogen, all other nuclides contain both neutrons and protons. A look at the stable nuclides shows that the ratio $^{N}/_{Z}$ in them is ≥ 1. The ratio is $\cong 1$ in all the light stable nuclides upto $^{40}_{20}Ca$ and thereafter the ratio is > 1 for heavy nuclei.

A plot of the number of neutrons versus the number of protons for stable naturally occurring isotopes is shown in fig. 14.7. Several conclusions can be drawn from this figure.

The stable nuclides lie in a very narrow band of $^{N}/_{Z}$ ratio. The $^{N}/_{Z}$ ratio in stable nuclides gradually increases as the number of neutron increases.

Light nuclides, such as ${}^{12}_{6}C$, contains about the same number of protons and neutrons.

Heavy nuclides, such as, ${}^{288}_{92}U$ contain up to 1.6 times as many neutrons as protons. There are no stable nuclides with atomic number greater than 83.

This narrow band of stable nuclides is surrounded by a sea of instability.

Nuclides that lie above this line have too many neutrons and are therefore neutron rich.

Nuclides that lie below this line do not have enough neutrons and are therefore neutron poor.

So all nuclides lying above or below the stability zone would be unstable and can attain their stability by radioactive changes in the nucleus so that $^{N}/_{Z}$ ratio falls within the zone of stability.

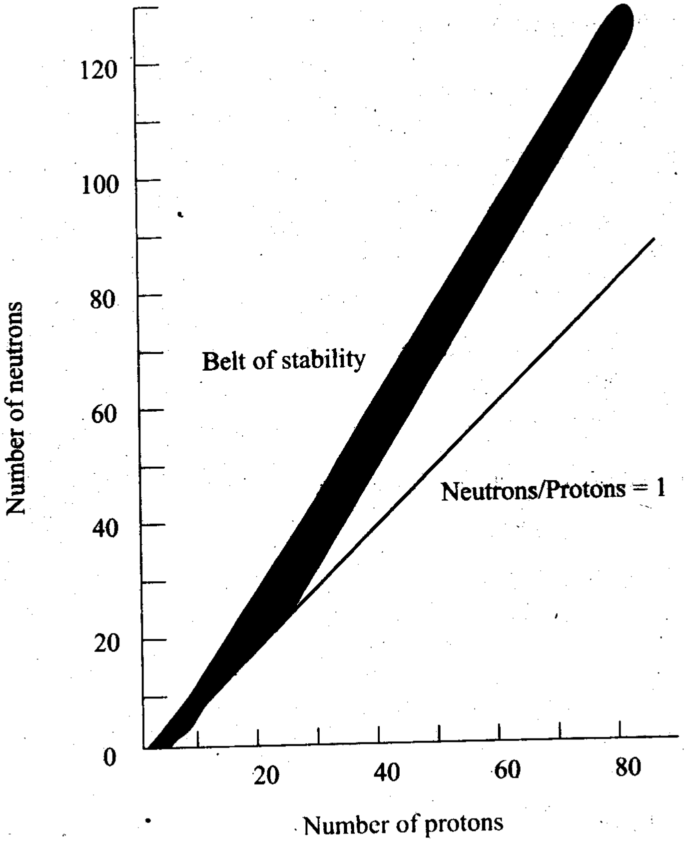


Fig. 14.7. A graph of the number of neutrons versus the number of protons for all stable nuclei.

2.7. KINETICS OF RADIOACTIVE DECAY

Radioactive nuclei decay by first order kinetics. The rate of radioactive decay does not depend on the physical or chemical state of the sample. Since radioactivity is a nuclear phenomenon, a radioactive nuclide will emit the same type of radiation at the same rate, regardless of its chemical composition, its temperature, applied pressure or the presence of electrostatic or magnetic fields. The rate of decay at any instant of time is proportional to the number of radioactive atoms present.

$$-\frac{dN}{dt} \propto N$$

or $$-\frac{dN}{dt} = \lambda N \qquad \text{.....14.2}$$

Where N is the number of atoms remaining at any time t. λ (lambda) is a proportionality constant called the decay constant and is characteristic of the given element. It represents the fraction of total number of atoms of radioactive element transformed per unit time, and is often expressed in reciprocal second (s^{-1}).

The above equation can be written as

$$-\frac{dN}{N} = \lambda dt \qquad \text{..... 14.3}$$

On integrating Eq. 2.3. we get

$$\int\frac{dN}{N} = -\lambda \int dt$$

$$\ln N = -\lambda t + Z \qquad \text{..... 14.4}$$

Where Z is constant of integration. When t = 0, then $N = N_o$, where N_o represents the initial number of atoms. So

$$Z = \ln N_o \qquad \text{..... 14.5}$$

Substituting value of Z into 14.4, we have

$$\ln N = -\lambda t + \ln N_o$$

or $$\ln N - \ln No = -\lambda t$$

or $$\ln\frac{N}{N_o} = -\lambda t$$

or $$\ln\frac{N_o}{N} = -\lambda t$$

or $$\lambda = \frac{1}{t}\ln\frac{N_o}{N}$$

or $$\lambda = \frac{2.303}{t}\log\frac{N_o}{N} \qquad \text{..... 14.6}$$

Equation 14.6 is the required kinetic expression for radioactive decay and is identical with the first order kinetic equation. Equation 14.6 can be written in the exponential form as

$$\therefore \quad In\frac{N}{N_o} = -\lambda t$$

$$\text{or} \quad \frac{N}{N_o} = -e^{-\lambda t}$$

$$\text{or} \quad N = N_o\ e^{-\lambda t} \qquad \text{...... 14.7}$$

Equation 14.7 represents the exponential form of the decay law.

Example 14.3. A radioactive element decays with a decay constant of 2.0 x 10^{-4} s^{-1}. How long will it take for 0.50 g of the substance to decay to 0.10 g ?

Solution

$\lambda = 2.0 \times 10^{-4}\ s^{-1}$

$No = 0.50$ g

$N = 0.10$ g

On applying Eq. 2.6.

$$\lambda = \frac{2.303}{t}\log\frac{N_o}{N}$$

$$\text{or} \quad t = \frac{2.303}{\lambda}\log\frac{N_o}{N}$$

$$\text{or} \quad t = \frac{2.303}{2.0\times10^{-4}}\log\frac{0.50}{0.10} = 8047.15 \text{ seconds.}$$

14.8. HALF-LIFE AND AVERAGE LIFE

According to law of radioactive disintegration, the proportion of atoms disintegrating is constant for any given period of time. This means that a certain fraction of the atoms, one third, for example, would decay in a given period of time. For convenience, the time required for one half of the atoms to decay is frequently designated. This is called the half-life. It is defined as the time in which the radioactive atoms are reduced to half of their initial amount. To obtain t½, we

substitute $N = \frac{N_o}{2}$ and t = t½ in Eq.14.6.

$$t½ = \frac{2.303}{\lambda}\log\frac{N_o}{N_o/2}$$

$$\text{or} \quad t½ = \frac{2.303}{\lambda}\log 2\ \frac{0.693}{\lambda} \qquad \text{..... 14.8}$$

Equation 14.8 shows that the time necessary for half of the quantity of a radioactive element to disintegrate, is constant, independent of the initial amount present and characteristic of the given radioactive element. Half-life period is a useful property for the identification of various radioactive species. Thus if half-life period of a radioactive element is known, its decay constant can be calculated and vice versa. The half-life periods of different radioactive elements vary widely ranging from a fraction of second to millions of years.

Table 14.2. Half Lives

Isotope	$t_{1/2}$
$^{214}_{85}At$	1×10^{-6} seconds
$^{212}_{84}Po$	3×10^{-7} seconds
$^{214}_{83}Bi$	19.7 minutes
$^{210}_{82}Pb$	19.7 years
$^{235}_{92}U$	4.5×10^{9} years

The average life of a radioactive element is equal to the sum of all possible life times divided by the total number of atom. The reciprocal of the decay constant gives the average life of the radioactive element.

$$\text{Average life } (\tau) = \frac{1}{\lambda} \qquad \therefore \quad \lambda = \frac{0.693}{t½}$$

$$\tau = 1.44\, t½ \qquad \ldots\ldots 14.9$$

The average life is frequently used to express the rate of transformation of a radioactive element. For example, the average life of radium is 2400 years.

Example 14.4. The half-life of radium is 1590 years. How long will it take for a sample of radium to decay to 10% of its original radioactivity?

Solution

$t½ = 1590$ years.

Let $N_o = a,\ N = \frac{a}{10}$

$$\lambda = \frac{0.693}{t½}$$

$$\lambda = \frac{0.693}{1590} = 4.36 \times 10^{-4}\ \text{years}^{-1}$$

$$t = \frac{1}{\lambda} \ln \frac{N_o}{N}$$

$$= \frac{1}{4.36\times10^{-4}} \ln \frac{a}{a/10}\ 5280 \text{ years.}$$

After 5280 years 10% of the original radioactivity remains.

$$N_o = 1,\ N = (1 - 0.01) = 0.99 \text{ g},\ t = 50 \text{ seconds}$$

Thus $\lambda = \frac{1}{t} \ln \frac{N_o}{N}$

or $\lambda = \frac{1}{50} \ln \frac{1}{0.99} = 2.02 \times 10^{-4}\ s^{-1}$

$$\text{Half-life} = \frac{0.693}{\lambda} = \frac{0.693}{2.02\times10^{-4}}\ 3240 \text{ seconds.}$$

and $\text{average life} = \frac{1}{\lambda} \ln \frac{1}{2.02\times10^{-4}} = 4936 \text{ seconds.}$

Example 14.6. If a radioactive substance loses 95% of its activity in 110 minutes, what is its half-life?

Solution

$$t = 110 \text{ minutes}$$

Let $N_o = 100$, then $N = 100 - 95 = 5$

$$\lambda = \frac{1}{t} \ln \frac{N_o}{N}$$

or $\lambda = \frac{1}{110} \ln \frac{100}{5} = 0.02718\ \text{min}^{-1}$

$$t½ = \frac{0.693}{\lambda} = \frac{0.693}{0.02718} = 25.44 \text{ minutes.}$$

14.9. THEORY OF RADIOACTIVE DISINTEGRATION

Rutherford and Soddy in 1903 proposed the theory of radioactive disintegration. According to their theory, nuclei of radioactive elements are unstable and decompose spontaneously by emission of an β or ß particle to form a new element of different physical and chemical properties. The α and ß particles are ejected out of the nucleus undergoing disintegrating process. The new element so formed may also be unstable and may emit radiation to form another new element. The γ-rays arise from energy rearrangements within the nuclei after an α or ß particle ejection. We can also say that γ-rays are the secondary effects of nuclear disintegration process. For example, when uranium with atomic mass 238 and atomic number 92 emits an α-particle, it yields uranium X_1 of mass 234 and atomic number 90. In the formation of new element the charge has decreased by two units, and mass by four units and the element is known as thorium.

$$ {}^{238}_{92}\mathrm{U} \longrightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He} $$

When an Ó-particle is emitted from the nucleus it must be accompanied by the loss of two electrons so that the atom remains electrically neutral. Thorium formed above is also unstable like uranium and it further emits a ß-particle from the nucleus. The new element so formed now has the same atomic mass but its atomic number is increased to 91. This new element now has an atomic mass 234 and an atomic number 91 and is called protactinium.

$$ {}^{234}_{90}\mathrm{Th} \longrightarrow {}^{234}_{91}\mathrm{Pa} + \beta^- $$

The loss of ß-particle from the nucleus should involve the gain of a planetary electron. This idea, that as a result of radioactive disintegration new elements are formed, has been verified, and is a well established fact in the field of radioactivity.

Soddy-Fajan's Group Displacement Law

The transformations brought about by the emission of an α or ß particle from the nucleus are summarized in the Group Displacement Law given by Fajan and Soddy. This law states that whenever a parent nucleus emits an Ó-particle, its atomic number is decreased by two units and the new element is shifted two positions to the left in the periodic table from that of the parent. On the other hand, when the parent nucleus emits a ß-particle, the atomic number is increased by one unit and hence the product is shifted one place to the right in the periodic table.

Examples:

polonium

$$ {}^{215}_{84}\mathrm{Po} \longrightarrow {}^{211}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He} $$

$$ {}^{211}_{82}\mathrm{Pb} \longrightarrow {}^{211}_{83}\mathrm{Bi} + \beta^- $$

$$ {}^{211}_{83}\mathrm{Bi} \longrightarrow {}^{211}_{84}\mathrm{Po} + \beta^- $$

14.10. ARTIFICIAL RADIOACTIVITY

We know that some radioelements such as uranium, thorium, radium etc. are found in nature. They are called natural radioactive elements and their disintegration is called natural radioactivity. The naturally occurring radioelements were the only ones available for study until 1934. In 1934, F. Joliot and I. Curie discovered that it is possible to make radioactive isotopes of several elements by suitable nuclear reactions. They observed that when α-particles impinge on light elements such as aluminium, magnesium and boron, there were two types of disintegrations,

(a) the main one resulting in the emission of protons, and

(b) emission of neutron and positron.

It was found that the emission of protons ceased as soon as the α-irradiation was stopped. However, the emission of positron continued after the removal of α-source. The most plausible explanation for this phenomenon is that the α-particle is first taken up by the bombarded nucleus to produce a complex which disintegrates instantaneously with the emission of the neutrons. Thus with aluminium,

$$^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}\text{n}$$

$^{30}_{15}P$ is not a stable isotope of phosphorus and decays into a stable isotope of silicon with emission of positron.

$$^{30}_{15}\text{P} \longrightarrow {}^{30}_{14}\text{Si} + \beta^{+}\ \text{(positron)}$$

This phenomenon of bombarding certain stable nuclei of elements with α-particles producing artificial radioactive elements is referred to as artificial or induced radioactivity. This conversion of an element into another is called Transmutation of an element. A few other examples of artificial radioactivity are:

(i) $^{24}_{12}\text{Mg} + {}^{4}_{2}\text{He} \longrightarrow {}^{27}_{14}\text{Si} + {}^{1}_{0}\text{n}$

$^{27}_{14}\text{Si} \longrightarrow {}^{27}_{13}\text{Al} + \beta^{+}$

(ii) $^{10}_{5}\text{B} + {}^{4}_{2}\text{He} \longrightarrow {}^{13}_{7}\text{N} + {}^{1}_{0}\text{n}$

$^{13}_{7}\text{N} \longrightarrow {}^{13}_{6}\text{C} + \beta^{+}$

Besides α-particles, the artificial radioactivity can be induced by protons, deuterons and neutrons. For examples:

(iii) $^{23}_{11}\text{Na} + {}^{2}_{1}\text{H} \longrightarrow {}^{24}_{11}\text{Na} + {}^{1}_{1}\text{H}$

$^{24}_{11}\text{Na} \longrightarrow {}^{24}_{12}\text{Mg} + \beta^{-}$

(iv) $^{27}_{13}\text{Al} + {}^{1}_{0}\text{n} \longrightarrow {}^{24}_{11}\text{Na} + {}^{4}_{2}\text{He}$

$^{24}_{11}\text{Na} \longrightarrow {}^{24}_{12}\text{Mg} + \beta^{-}$

It must be noted that induced radioactivity is just like the natural radioactivity, since it obeys the same laws. Hence the term-induced radioactivity refers to the way in which new radioactive substances are produced rather than to their decay. In each instance, the elements exhibiting induced radioactivity are the unstable isotopes of the known elements. They do not appear among the stable isotopes, because their life period is usually short, and hence it is hardly to be expected that they will be found in nature. Artificial radioactive elements behave very much like those, which are naturally radioactive. They disintegrate according to the same rate law and exhibit constant half-life periods characteristic of the element. There is, however, one aspect in which the two differ. Whereas the natural radioactivity is confined only to the very massive nuclei, induced or artificial radioactivity can be induced in light nuclei as well. Thus not only

$^{210}_{83}Bi$, $^{209}_{82}Pb$ are artificially radioactive, but also such light nuclei as $^{3}_{1}H$, $^{6}_{2}He$ *and* $^{7}_{4}Be$ etc. At least one radioactive isotope is now known for every element in the periodic table, and some elements have as many as 20 or more.

14.11. NUCLEAR REACTIONS

Nuclear Reaction is a process in which some change in the character of a nucleus takes place either spontaneously or as a result of bombardment by a particle or a ray. A nuclear reaction takes place if a particle is able to enter a target nucleus. The particle which is used to strike a target nucleus is called a projectile.

The notation used for a nuclear reaction is analogous to that in chemical reaction, with reactants on the left and products on the right hand side of the equation. A nuclear reaction is generally represented by the following equation.

$$a + X \longrightarrow Y + b$$

Table 14.3. Types of Nuclear Reactions

Type	Example	Representation
(p, γ)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{8}_{4}Be + \gamma$	$^{7}_{3}Li\,(p,\gamma)\,^{8}_{4}Be$
(p, n)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{7}_{4}Be + ^{1}_{0}n$	$^{7}_{3}Li\,(p,n)\,^{7}_{4}Be$
(p, α)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{4}_{2}He + ^{4}_{2}He$	$^{7}_{3}Li\,(p,\alpha)\,^{4}_{2}He$
(d, p)	$^{23}_{11}Na + ^{2}_{1}H \longrightarrow ^{24}_{11}Na + ^{1}_{1}H$	$^{23}_{11}Na\,(d,p)\,^{24}_{11}Na$
(d, n)	$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + ^{1}_{0}n$	$^{2}_{1}H\,(d,n)\,^{3}_{2}He$
(n, p)	$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$	$^{14}_{7}N\,(n,p)\,^{14}_{6}C$
(α, n)	$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{16}P + ^{1}_{0}n$	$^{27}_{13}Al\,(\alpha,n)\,^{30}_{15}P$
(α, p)	$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$	$^{14}_{7}N\,(\alpha,p)\,^{17}_{8}O$
(n, γ)	$^{59}_{27}Co + ^{1}_{0}n \longrightarrow ^{80}_{27}Co + \gamma$	$^{59}_{27}Co\,(n,\gamma)\,^{60}_{27}Co$

Where X	stands for target nucleus
a	for projectile
Y	for product nucleus
b	for emitted particle or ray.

A short hand notation is often used for the representation of a nuclear reaction. This is known as Bethe's notation. According to this notation, the above reaction can be represented as

$$X\ (a, b)\ Y$$

which implies that the particle `a' comes in and particle `b' goes out. The symbols `a' and `b' may stand for the neutron (n), alpha particle (α), deuteron (d), proton (p), and gamma ray (γ) etc. Some important types of nuclear reactions are shown in Table 14.3.

Comparison of Nuclear and Chemical Reactions

Nuclear reactions like chemical reactions are always accompanied by a release or absorption of energy and this is expressed by adding the term `Q' to the right hand side of the equation. For example:

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H + Q$$

The quantity `Q' is called the energy of reaction. Positive Q corresponds to energy release (exoergic reaction); negative `Q' to energy absorption (endoergic reaction). Individual particles are involved in each case, nucleons in nuclei and atoms in molecules respectively. Number of nucleons is conserved just as in chemical reactions, the number of atoms of each element is conserved. Moreover, law of conservation of energy applies to each. Some of the characteristics that differentiate between nuclear reactions and ordinary chemical reactions are summarized below:

	Nuclear Reaction	**Chemical Reaction**
1.	Elements may be converted from one to another.	No new elements can be produced.
2.	Particles within the nucleus are involved.	Usually only outermost electrons are involved.
3.	Often accompanied by release or absorption of tremendous amounts of energy.	Accompanied by release or absorption of relatively small amount of energy.
4.	Rate of reaction is independent of factors such as concentration, tempetature, pressure and catalyst etc.	Rate of reaction is influenced by external factors.
5.	The quantities are defined per particle.	The quantities are defined per mole.
6.	The quantity of matter is changed appreciably.	The quantity of matter is unchanged.
7.	Nuclear reactions are very rare.	Chemical reactions are frequent.

14.12. NUCLEAR FISSION

Nuclear fission is a process in which a heavy nucleus is broken into two intermediate nuclei with the release of energy. This process is usually accompanied by the emission of neutrons.

E. Fermi (1934) studied the bombardment of uranium nucleus with slow neutrons and observed that the products show several different types of strong ß-rays activity and some strong products of decay. At the same time O. Hahn and Strassman in Germany (1934-38) showed that when uranium (^{235}U) was irradiated with slow moving neutron, the product so formed has an atomic mass and atomic number considerably lower than that of uranium. It was shown that the products of the reaction were isotopes of barium and krypton.

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{140}_{56}Ba + ^{93}_{36}Kr + 3^{1}_{0}n + \text{Energy}$$

These results were interpreted by stating that the uranium nucleus is rendered highly unstable by capturing a neutron which then breaks up immediately into two nuclei of approximately equal size. This process is known as nuclear fission. In the process of nuclear fission the mass of the products obtained is less than the mass of disintegrating uranium atom and the projectile neutron, and considerable amount of energy is liberated. Measurements indicate that there would be a mass defect of about 0.215 amu which is equivalent to about 200 MeV per uranium atom.

The fission of each uranium nucleus is accompanied by 2-3 neutrons. These neutrons act as chain carriers and are capable of bringing about a sustaining chain reaction. If this fission chain reaction proceeds uninterrupted, a tremendous amount of energy will be released in a fraction of a second which can lead to a nuclear explosion.

Although nuclear fission can be brought about by other high speed particles in elements with atomic number 80 or above, neutrons are the only practical projectiles that result in a sustained chain reaction. The amount of fissionable material necessary for the chain reaction to sustain itself is called the critical mass. The species $^{233}_{92}U$, $^{235}_{92}U$ *and* $^{239}_{94}Pu$ are fissionable by neutrons of all energies, whereas isotopes like $^{238}_{92}U$, $^{232}_{90}Th$ *and* $^{240}_{94}Pu$ are fissionable only by high energy neutrons. The more abundant isotope $^{238}_{92}U$ (99.27%) by itself is not a nuclear fuel, it can absorb neutrons to form $^{239}_{92}U$, which is unstable and undergoes decay by successive loss of two ß⁻ particles to form $^{239}_{94}Pu$

$$^{238}_{92}U, ^{1}_{0}n \longrightarrow ^{239}_{92}U + \gamma$$

$$^{239}_{92}U \longrightarrow ^{239}_{93}Np + \beta^-$$

$$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + \beta^-$$

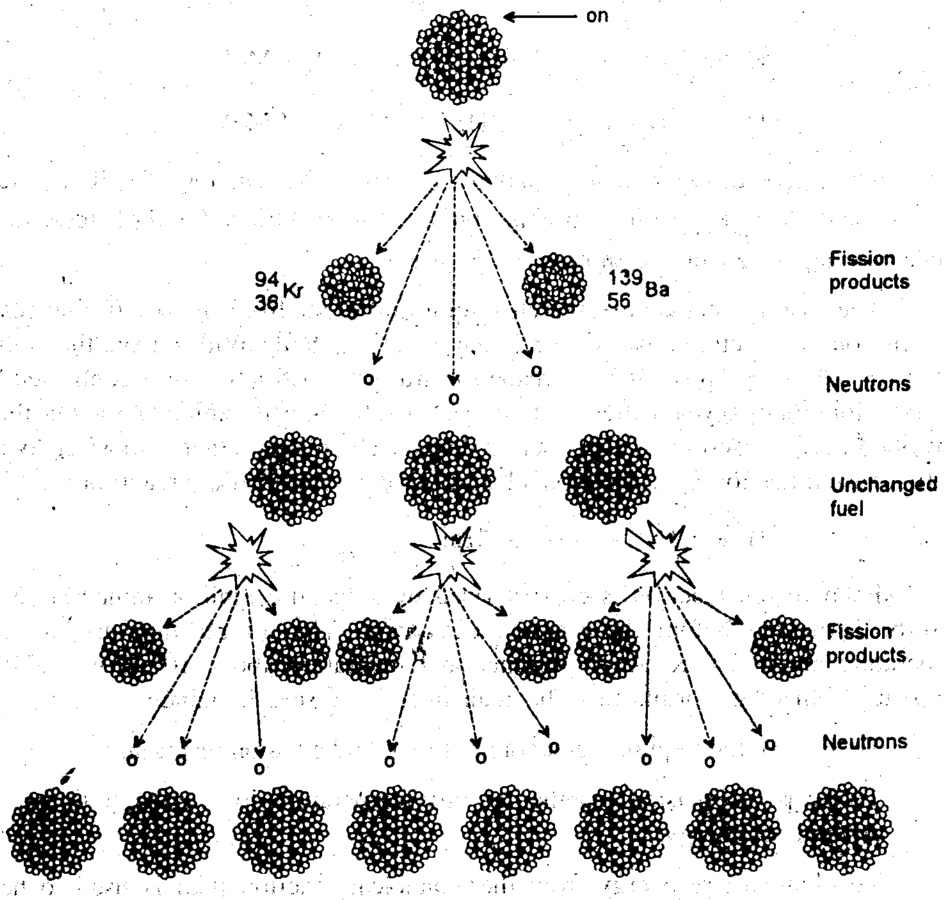


Fig. 14.8. A Nuclear fission chain reaction.

$^{238}_{92}U$ is, therefore, an example of a fertile nuclide (which produce fissile material). It does not undergo fission with thermal (slow) neutrons, but it can be converted to $^{239}_{94}Pu$, which does undergo thermal neutron induced fission.

14.13. NUCLEAR FUSION

Nuclear fusion may be considered as the reverse of fission. It may be defined as the process of combining two lighter nuclei to form a heavier nucleus with the release of energy. It has been observed that tremendous amount of energy is obtained when lighter nuclei such as hydrogen, deuterium and helium are fused to form heavier nuclei. Such reactions are also known as thermonuclear reactions, as these reactions occur at high temperature. Some examples of nuclear reactions are:

$$ {}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{3}_{2}He + {}^{1}_{0}n + 3.27 MeV $$

or $$ {}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{3}_{1}H + {}^{1}_{1}H + 4.03 MeV $$

$$ {}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6 MeV $$

$$ {}^{2}_{1}H + {}^{3}_{2}He \longrightarrow {}^{4}_{2}He + {}^{1}_{1}H + 1.8 MeV $$

The fusion of two deuteron nuclei is known as d-d reaction. It will be noted that both ${}^{3}_{1}H$ and ${}^{3}_{2}He$ are products of deuteron-deuteron reactions. Each of these reactions can be produced in a suitable particle accelerator.

The history of fusion research is quite different from that of fission research. With fission the reactor came first, and then bomb was built. With fusion, the bomb was built long before any progress was made toward the construction of a controlled fusion reactor. More than 40 years after the first hydrogen bomb was exploded, the feasibility of controlled fusion reactions is still open to debate. The reaction that is most likely to fuel the first fusion reactor is the thermonuclear d-t or deuterium-tritium reaction.

$$ {}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0} $$

Each fusion reaction is characterized by a specific ignition temperature which must be surpassed before the reaction can occur. The d-t reaction has an ignition temperature above 10^{8} K. Any substance at temperature above 10^{8} K will exist as a completely ionized gas or plasma. The goals of fusion research include:

1. To achieve the required temperature to ignite the fusion reaction.
2. To keep the plasma together at this temperature long enough to get useful amounts of energy.
3. To obtain more energy from thermonuclear reaction than is used to heat the plasma to the ignition temperature.

Thermonuclear fusion reactions are very probable in sun and stars, the temperatures of which are very high. Bethe (1939) developed the theory for the production of stellar energy in which protons, by suitable reactions, are transmuted into helium nuclei, thereby releasing, energy which is transformed into radiation. One possible series of reactions in which protons are converted into helium nuclei is one in which carbon and nitrogen act as catalyst. This series is usually referred to as the carbon-nitrogen cycle and consists of the following reactions.

$$ {}^{12}_{6}C + {}^{1}_{1}H \longrightarrow {}^{13}_{7}N + \gamma $$

$$ {}^{11}_{7}N \longrightarrow {}^{13}_{6}C + \beta^{+} + v $$

$$ {}^{13}_{6}C + {}^{1}_{1}H \longrightarrow {}^{14}_{7}N + \gamma $$

$$ {}^{14}_{7}N + {}^{1}_{1}H \longrightarrow {}^{15}_{8}O + \gamma $$

The energy released by this cycle is 26.7 MeV.

$$^{15}_{8}\mathrm{O} \longrightarrow {}^{15}_{7}\mathrm{N} + \beta^{+} + \nu$$

$$^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{H} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{4}_{2}\mathrm{He} + \gamma$$

Attempts to produce controlled thermonuclear fusion reactions have so far been unsuccessful.

Difference between Nuclear Fission and Fusion

The two controversial phenomena can be distinguished by the following points:

	Nuclear Fission	Nuclear Fusion
1.	The process occurs only in the nuclei of heavy elements.	The process occurs in the nuclei of light elements.
2.	The process involves the fission of heavy nucleus to the lighter nuclei.	The process involves the fusion of the lighter nuclei to a heavy nucleus.
3.	The process takes place at ordinary temperature.	The process takes place at high temperature (10^8 K).
4.	The energy liberated during the process is high (200 MeV per fission).	The energy liberated during the process is comparatively low (3 - 24 MeV per fusion).
5.	The process can be controlled for useful purposes.	The process can not be controlled.
6.	Atom bomb is based on the principle of nuclear fission.	Hydrogen bomb is based on the principle of nuclear fusion.
7.	Percentage efficiency of energy conversion is comparatively less.	Percentage efficiency of energy conversion is high (four times to that of fission process).
8.	Lesser amount of energy per unit mass of reacting atoms is produced.	Much larger amount of energy per unit mass of reacting atoms is produced.
9.	Fission products are radioactive and dangerous.	Fusion products are not dangerous.
10.	Fuel can be stored in fission.	Fuel cannot be stored.
11.	Solid or liquid fuel is used.	Fuel is in the plasma state.

2.14. USES OF RADIOACTIVE ISOTOPES

Radioactive isotopes find many practical applications either because they decay at known rates or, in some cases, simply because they emit radiations continuously.

1. Medical Uses

Several radioactive isotopes are used successfully in checking growth of or removing the cancerous cell. Since radioisotopes of an element have the same chemical properties as stable isotopes of the same element, they can be used to 'label' an element in a compound. A radiation detector can be used to follow the path of the element throughout the body. Salt solution containing sodium-24 can be injected into the bloodstream in order to follow the flow of blood and locate obstructions in the circulatory system. Thallium-201 tends to concentrate in the healthy heart muscle tissue, while technetium-99 concentrates in the abnormal heart tissue. Iodine-131 concentrates in the thyroid gland, the liver and certain parts of the brain, and is used to monitor goiter and other thyroid problems, as well as liver and brain tumors. Cobalt-58 is used to determine uptake of vitamin B12, while cobalt-60 is used for the radiation treatment of cancer.

2. Research Applications

Stable as well as radioactive isotopes are frequently used in tracing out the correct path of chemical and physiological reactions, some of which are described below:

(a) If radioactive sulphur-35 ion is added to a saturated solution of cobalt sulphide in equilibrium with solid cobalt sulphide, the solid becomes radioactive. This indicates that sulphide ion exchange occurs between solid and solution in solubility equilibrium.

$$CoS_{(s)} \rightleftharpoons Co^{2+}_{(aq)} + S^{2-}_{(aq)}$$

(b) Photosynthesis is the process by which green plants synthesize carbohydrates from carbon dioxide and water in the presence of light.

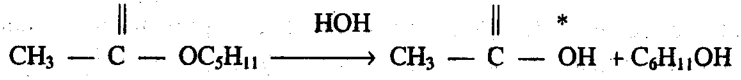
$$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_6H_{12}O_6 + 6O_2$$

In the mechanism of photosynthesis the important point is that the molecular oxygen in the product is coming from water and not from carbon dioxide molecule. By studying the reaction with labeled oxygen, the product oxygen can be identified.

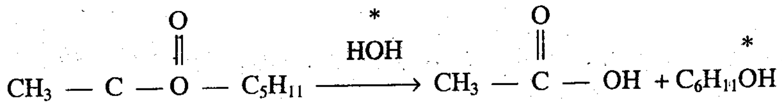
$$6C\overset{*}{O}_2 + 6H_2O \longrightarrow C_6H_{12}\overset{*}{O}_6 + 6O_2$$

(c) The mechanism of ester hydrolysis can be studied by making use of labelled water $(H_2\overset{*}{O})$. Theoretically an ester may be hydrolyzed in two different manners to form an acid and alcohol.

(i)



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OC_5H_{11} \xrightarrow{H\overset{*}{O}H} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{*}{O}H + C_6H_{11}OH$$

(i) 

$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-O-C_5H_{11}\xrightarrow{H\overset{*}{O}H}CH_3-\overset{\overset{O}{\|}}{C}-OH+C_6H_{11}\overset{*}{O}H}$$

The labeled oxygen appeared only in the acid, showing that $-OC_5H_{11}$ group is substituted by $-\overset{*}{OH}$ in the hydrolysis.

(d) Phosphorus-32 when present in the phosphate fertilizer has been used to investigate the rate and manner of the absorption of fertilizer. Moreover, by such studies we may know separately about the proportion of plant's phosphorus coming from soil and from the fertilizer, and thus about the kind of fertilizer which is best for a given soil and crop.

3. Industrial Applications

There are many applications of radiochemistry in industry and engineering, some of them will be mentioned here.

(a) Addition of a small amount of phosphorus-32 to the iron ore is used in steel industry for detecting all the phosphorus impurity present in the original ore. The disappearance of radioactivity from the molten steel indicates the removal of all the phosphorus.

(b) Radioisotopes have been used in studying the wear and lubrication of motor car engines. In practice, piston rings are made radioactive by irradiating them in a nuclear reactor; they are then assembled into an engine. Engine is allowed to run and the oil is tested regularly for the appearance of radioactivity caused by the presence of tiny bits of metal from wearing off of the piston rings.

(c) The radiation passing through a material decreases as the material gets thicker. Thus the amount of penetrating radiation can be used to estimate the thickness of various materials such as paper or plastic etc.

(d) A similar use of radioactive isotopes is made in level gauges and empty packet detectors. The level of a liquid in a closed vessel can be found by placing a source on one side of the container and detector on the other. These are then moved down, a sudden decreases in the detected radiation shows the level of the liquid. Level gauges of this type are used to measure the level of liquids in fire extinguishers and gas cylinders. Similarly empty packet detectors can be used to reject empty or insufficiently filled packets of cigarettes or biscuits.

(e) Radioactive isotopes can be used to detect leaks in pipelines of water. For this purpose sodium-24 is used. Solution containing radioisotope is injected into the pipeline and the points where the leakage into the surrounding soil has occurred can be scanned from the surface using a detector.

4. Radioactive Dating

The ages of articles of organic origin can be estimated by radiocarbons dating. The radioisotope carbon-14 is produced continuously in the upper atmosphere, as nitrogen atom captures cosmic-ray neutron.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

The $^{14}_{6}C$ atoms thus produced are rapidly oxidized to $^{14}_{6}CO_2$ which in turn is incorporated in plants as a result of photosynthesis. Thus all plants contain some $^{14}_{6}C$ and since the carbon of animals is ultimately derived from plants, the carbon of animal will contain the same ratio of $^{14}_{6}C/^{12}_{6}C$ as the carbon of plants. When the plant or animal dies, the $^{14}_{6}C$ isotope is no longer absorbed from the atmosphere (in case of plant) and plants (in case of animal). After this the amount of $^{14}_{6}C$ in the dead tissues starts decreasing due to its radioactivity.

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + \beta^-$$

To determine the age of a sample, the activity per minute per gram of carbon is measured. Now thus knowing the half life, the approximate time of the death of the plant or animal can be calculated according to the following disintegration equation:

$$T = \frac{1}{\lambda} \ln \frac{N_0}{N}$$

This technique was first used by Willard Libby (nobel laureate) to determine the age of wood or animal fossils. The carbon-14 technique is useful only for dating objects less than 50,000 years. Older objects possess too little activity to be dated accurately.

Example 14.7. The amount of $^{14}_{6}C$ isotope in a piece of wood is found to be one sixth of its amount present in a fresh piece of wood. Calculate the age of wood (half-life of $^{14}_{6}C$ = 5577 years).

Solution.

Let $N_0 = 1$ then $N = \frac{1}{6}$

$t½ = 5577$ years

$$\lambda = \frac{0.693}{t½}$$

or $\lambda = \frac{0.693}{5577}$ year^{-1}

$$t = \ln \frac{1}{\lambda} \text{in} \frac{N_0}{N}$$

or $t = \frac{5577}{0.693} \ln \frac{1}{1/6} = \frac{2.303 \times 5577}{0.693} \log 6$

or $t = 20{,}170$ years

14.15. NUCLEAR REACTOR

Nuclear reactor is a device to obtain the nuclear energy in a controlled way to be used for peaceful purposes. We can also say that a nuclear reactor is designed and operated for the purpose of sustaining a nuclear fission chain reaction at a controllable pre-determined rate.

Nuclear reactors are used for the production of heat, mechanical and electrical energy, radioactive isotopes, weapons material and nuclear research.

Working Mechanism

In any nuclear reactor, the heat generated by the controlled fission chain reaction of the nuclear fuel confined in the core of the reactor is transferred to a coolant and this heat energy is used to generate high pressure steam that turns a turbine connected to a generator, thus producing electric power. If the heat energy generated in the fission is utilized for generation of electricity, the reactor is known as a power reactor.

Components of a Reactor

A fission reactor consists of five main components.

(a) **Fuel Elements.** The material containing the fissile isotope is called the reactor fuel or nuclear fuel. Its composition can vary from natural uranium to material highly enriched in ^{235}U, ^{239}Pu or ^{233}U. The basic source materials for nuclear fuels are uranium and thorium. ^{235}U present to the extent of about 0.71 percent by weight in the natural uranium is fissile and this is the only natural material from which nuclear energy can be directly produced.

(b) **Moderators.** The function of a moderator in a nuclear reactor is to rapidly reduce (within a fraction of second) the high energy of the fission neutrons. The fast neutrons ejected during fission must be slowed by collisions with atoms of comparable mass which do not absorb them, for efficient fission reaction. The most commonly used moderator is ordinary water, although graphite is sometimes used. The most efficient moderator is helium, which slows neutrons but does not absorb them all. The next most efficient one is "heavy water" (deuterium oxide D_2O), but this is so expensive that it has been used chiefly in research reactor. However, on considerations of price and other properties, H_2O finds favor in many commercial reactors.

(c) **Coolants.** The heat generated in the core of the reactor is removed by a coolant. Both ordinary and heavy water are considered to be good coolants for thermal reactors because of their excellent heat exchange properties. They have also the advantage of serving as both coolants as well as moderators. However, due to their low boiling points, high pressures are required to prevent their boiling at high temperatures. Liquid metals such as Na and K are recommended as coolants for use at high temperatures. Various other coolants such as benzene, polyphenyles, air, CO_2, CH_4, H_2 and He are also used.

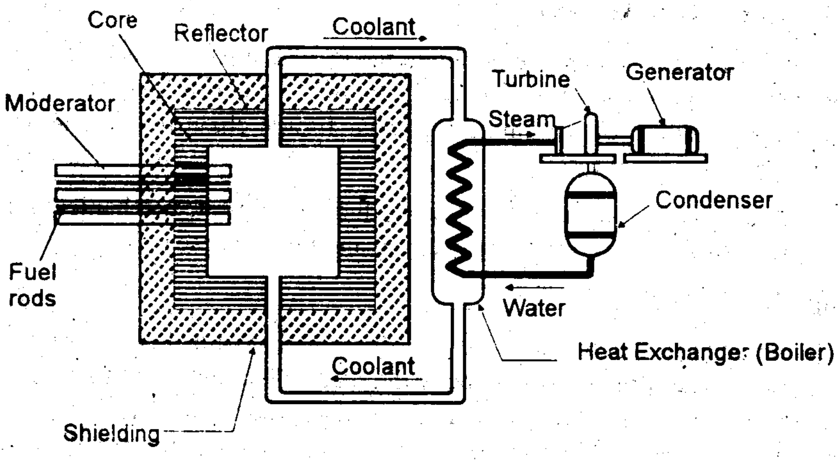


Fig. 14.9 Schematic diagram of nuclear reactor system for generating electric power.

(d) **Control Rods.** The control of power level in a reactor can be achieved by controlling the neutron flux which in turn is achieved by altering the neutron leakage rate or the quantity of fuel in the reactor core or by incorporating a suitable neutron absorbing material. Boron is the most common material used for reactor control due to its very high melting point and very large neutron absorption cross section. It is commonly employed in the form of boron steel. Besides boron, cadmium is also used.

(e) **Shielding.** It is an important component of a reactor installation, although it has nothing to do with the operation of reactor. Shielding is provided for attenuation of the gamma rays and neutrons emerging from the reactor which helps to protect the operating personnel from radiation hazards. The shield comprises of a layer of concrete (several feet thick) which surrounds the reactor core. It absorbs both gamma rays and neutrons. It is a good structural material and contains enough hydrogen to moderate the fast neutrons.

14.16 NUCLEAR HAZARDS AND SAFETY MEASURES

The ionization of atoms molecules results from the passage of nuclear radiation through matter, a single α-, β- or γ-ray producing about 100,000 ion pairs. A secondary effect of ionization in molecules is the rupture of chemical bonds causing the destruction of the chemical compounds from which living tissue is composed.

In handling radioactive materials, two distinct types of hazard should be distinguished and appreciated. These are:

(*a*) Contamination hazards involving ingestion of very small quantities of radioactive material, and

(*b*) Radiation hazards involving exposure to some external source of radiation.

(*a*) Contamination Hazards

The factors which influence the radio-toxicity of a nuclide as a contamination hazard if ingested orally, by inhalation, by absorption through the skin, or directly into the blood stream— as a result of an accident— are:

(*a*) The type of radiation emitted, α and β being the worst.

(*b*) The physical properties of the materials, for example the chances that a compound ingested orally will enter the blood stream, and so be deposited in a vital organ, will be reduced if it is an insoluble compound.

(*c*) The chemical properties of the nuclide.

(*d*) Half-life of the nuclide. A composite "effective" half-life which takes into account both radioactive and biological half-lives can be determined from:

$$\frac{1}{\text{effective half-life}} = \frac{1}{\text{radioactive half-life}} + \frac{1}{\text{biological half-life}},$$

A few examples of effective half-lives are given in Table 14.4. Because of biological retention properties associated with many nuclei there is a long term accumulative effect and, therefore, the quantities of these materials which constitute a hazard are often extremely low.

Table 14.4

Nuclide	Concentrates	Half-life (in days)		
		Radioactive	Biological	Effective
Sodium-24	Whole body	0.62	19	0.61
Iodine-131	Thyroid	8.1	180	8.1
Strontium-90	Bone	$9.1.10^3$	$3.9.10^3$	$2.7.10^3$
Radium-226	Bone	$5.9.10^5$	$1.6.10^4$	$1.6.10^4$

(*b*) Radiation Hazards

The radiation hazards associated with most chemical and tracer work will be small or negligible. They mainly arise from isotope stock storage and from sealed sources such as those used as radiation sources for radiation chemistry studies. Under no circumstances should the combined effect of all the sources of activity be permitted to involve a weekly gross exposure to any person in excess of 100 milli roentgens and, indeed, the aim should be to maintain conditions such that the total radiation dose cannot exceed a tenth of this value. Film badges can— and frequently are— worn in order to measure the accumulated weekly dose. They do, however, only measure what has already occurred, and in this respect, they are a poor substitute for careful radiation monitoring to anticipate radiation exposure.

Exposure to radiation hazards is minimized by one or more of the following methods:

(a) Using minimum necessary quantities of active material and limiting exposure time.

(b) Making full use of the inverse square by remaining at a distance and by using forceps or tongs where necessary to achieve this end.

(c) Employing adequate' shielding— particularly in the case of fixed irradiation installations.

Rules and regulations concerning the use of radioactive material can at no time substitute for anticipation of hazards, care in manipulations and "good housekeeping". With proper thought and care a radiochemical laboratory can be as safe as more conventional organic and inorganic laboratories.

Safety Measure of Nuclear Hazards

Exposure to high levels of nuclear radiation can cause sickness or death. Because people cannot see, hear, smell, taste, or feel nuclear radiation, they are unable to tell without the proper radiological instruments whether the levels of radiation around them might be harmful.

High energy radiations, coming out of radioactive substances, can cause chemical changes in biological systems. Living systems are composed of a sufficient quantity of water which gets radiolysed on interaction with alpha, beta and gamma rays of high energy and ions such as H_2O^+ are produced. When these ions interact with any negatively charged species such as an election, they generate a highly excited neutralized molecule which stabilizes itself by immediate fragmentation into a hydrogen atom and a hydroxyl radical.

$$H_2O^+ + e^- \longrightarrow H^*_2O \longrightarrow H + OH^\bullet$$

This is one of many possible reactions that my occur as a consequences of radiation interaction with water and other molecules which constitute the living organisms. The overall effect is the formation of ions, atoms and free radicals. There resulting species are highly reactive and can destroy protein and other molecules present in the living matter. Fore example, free radicals can damage the hydrogen bonds and sulphur-sulphur, pivotal in maintaining the critical conformation of protein. Such a reaction will bring about protein destruction which will curtail its role as an enzyme and thus metabolic processes and cell division swill be abnormal penetration of substances into and out of the cells can take place to such an extent that organisms are injured.

Units for Radiation Expose.

There are several units which are employed to estimate the radiation damage on biological systems s described below.

The unit of radiation dosage that was originally used in measuring biological damage is the roentgen (symbol r). One roentgen is the radiation that produces one electro static unit (esu) of pairs of positives and negative ions in 1 cm^3 of air as S.T.P (standard temperature and pressure).

The ionization efficiency and the mode of absorption vary with the nature of radiation and the corresponding exposure effects also differ. This is because an alpha article emitted within a cell will deposit its energy entirely within that cell, whereas gamma rays will be only fractionally consumed by any biological tissue. The greater the amount of energy deposited per cell the greater is the biological damage.

The dosage assigned to one rad of fast neutrons is about 10 rem, and that to one rad of alpha particles is 20 rem. It is obvious from the discussion above that there is a considerable variation in the biological effects of different kind of radiations as their penetration and ionizing capabilities are significantly different. An alpha particle having one Mev of energy produces 10^5 ion paris per centimeter in air whereas beta particles and gamma rays of the same energy generate 100 and 10 ions pairs for the same path length, respectively. Accordingly, the alpha particles lose their energy very quickly as they pass through the matter, and their penetration is limited to as little as the thickness of a sheet of paper. For penertration of the skin the alpha particles must have 7.5 Mev or more and exposure of the skin to the low energy alpha particles is a negligible hazards. However, ingestion of material emitting alpha particles can have very serious effects. The penetrating ability of beta particles info the skin is relatively high and therefore it is more hazardous as compared to alpha particles. Ingested beta emitter will be more dangerous than when it is taken externally, but less so than alpha emitters will be the smaller amount of ionizing capability. The gamma rays, like X-rays have a greater destructive potential than the alpha and beta rays. They are much more penetrating and could only be stopped by about 5 cm thickness of a lead shielding. Because of their high ionizing thrust gamma rays destroy tissues and inflict serious burns quite rapidly. Due to these hazardous consequences of radiation exposure International Commission on Radiological Protection for various types of radiations have adopted maximum permissible doses for human beings occupationally exposed to external radiations. They have adopted two different standards for whole body exposure and limited body exposure. For whole body exposure this maximum dose has been fixed at 3 rem over a period of 13 consecutive weeks for the people over the age of 18, with the additional restriction that the total accumulated dose should not exceed 5 (N—18) rem, where N is the age of the recipient in years. For the case of limited exposure the hands and forearms or feet and ankles, the corresponding figures are 25 rem and 75 (N—18) rem. However, the radiation exposure may also occur by ingestion. The most likely means of ingesting radioisotopes can be (1) inhalation of contaminated air (2) drinking of contaminated water (3) entry through open wounds. Radioactive substances when ingested or inhaled become fixed in the body for varying lengths of time. All care must therefore be taken to avoid intake of radioactive materials.

14.17 BIOLOGICAL EFFECTS OF RADIATIONS

The radiation produced by nuclear reactions interacts with living tissue in many ways depending on the type of radiation. This radiation includes high-energy, charged particles (alpha and beta), neutrons of various energies, and photons (gamma and X-rays). In addition to this primary radiation, fission also produces radioactive isotopes of many elements, which in turn can emit particles and photons, known as secondary radiation.

Many of these isotopes, such as strontium and iodine, can enter the body, where they replace non-radioactive elements and remain there emitting ionizing radiation. In many ways, the presence of these radioactive isotopes is more insidious than direct radiation from external sources that is more easily detected and reduced by proper shielding.

Living tissue contains large amounts of water and the light elements, hydrogen, carbon, nitrogen, and oxygen, with lesser quantities of phosphorous and sulfur. The abundance of these light nuclei affects the interaction of nuclear radiation with living tissue. Alpha and beta particles, (gamma and X-rays), can remove. ~~the~~ valence electrons of the elements in living materials. This process, known as ionization, changes the chemical reactivity of the affected atoms. Molecules contains ionized atoms may react to form substances that are detrimental to life. The ionizing particles and fission products may undergo thousands of collisions with the atoms before stopping thus they may cause extensive ionization in the target material.

Long-term risks of radiation exposure center on the incidence of cancer and genetic mutations. Both effects have proven difficult to determine since cigarette smoking, diet, and sunlight exposure are also known to approximately 100,000 survivors of **Hiroshima** and **Nagasaki** shows a slight increase in genetic mutations over what would be expected for a normal population, but this increase is so small that it may not be statistically significant. Hiroshima survivors who received more than 2 gray showed a slight increase in the instances of cancer over a normal population. There is a good deal of controversy over the contribution of natural background radiation and man-made radiation to the incidence of cancer in humans. The dosage threshold below which radiation has no effect is also controversial.

The rapidly dividing cancer-producing cells are most susceptible to radiation damage. Thus radiation is used to treat many types of cancer. It has, however, proven most effective against individual tumors. Focused radiation beams can shrink or eliminate cancerous tumors while doing less damage to surrounding tissue. In most cases, the benefits of radiation therapy outweigh the risks to the patient's health. Radiation is also used in medical diagnosis. X-ray imaging and radioactive tracer studies provide information useful in treating patient.

When radiation strikes complex biological molecules, such as proteins or nucleic acids, it may fracture the molecules and prevent their proper functioning. This can result in loss of cell vitality, decreased enzyme activity, initiation of cancer, and genetic mutations. The immediate effects of acute exposure to radiation are caused by free radicals rupturing the cell membranes. This rupturing causes the cells to lose their contents and die. If enough cells are killed, functions associated with the cells cease. Death occurs because of the direct loss of vital organs or because of secondary infections resulting from the breakdown of the immune system. The effect depends on the dose of radiation received.

The radiation effects on the human body are of two types, somatic effects and genetic effects. The somatic effects and confined to the actual persons exposed to radiation. (Skin rash, and cancer are examples of somatic effects). The genetic effects affect not only the person exposed to radiation but also his children and subsequent generations. The genetic effects of radiation results from radiation damage to the cells of the testes (sperm) or ovary (egg cells).Radiation causes ionization in the cell; this may break a DNA strand or alter its structure. The damaged DNA would be replicated. This would give new message to successive generations; this is called mutation of cells. Such mutations lead to birth disorders. The fast-dividing cells in the body are the ones most affected by radiation. The cells in bone marrow, blood, and gonads are some of the fast-dividing ones (Fig. 14.10)

The neutrons cause the worst radiation problems for human being. The human body contains a high percentage of H_2O which absorbs neutrons very efficiently.

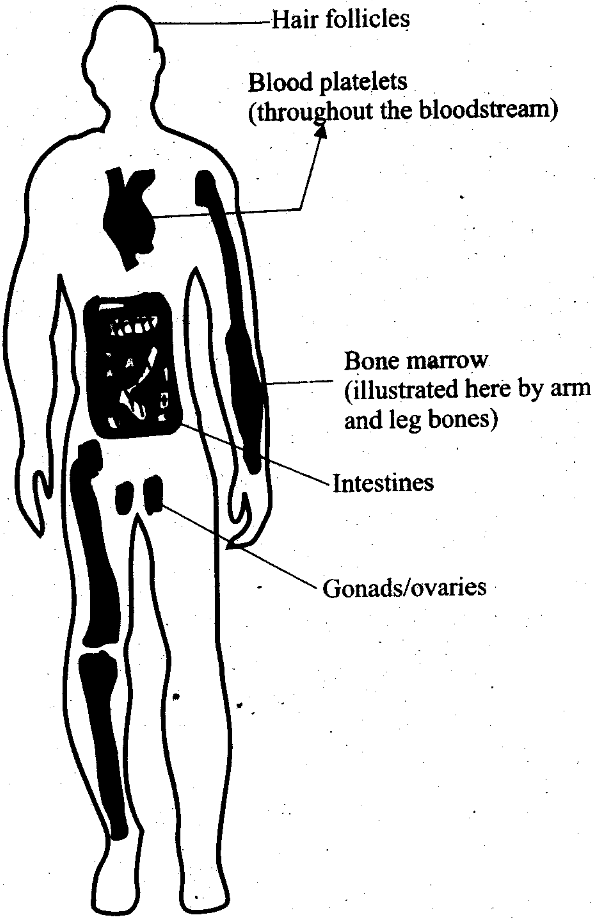


Fig. 14.10 Human organs affected by radiation

Radiation, like other aspects of nuclear science, can be both destructive and beneficial. The intelligent use of radiation for the treatment of caner, medical diagnosis, food preservation, and other useful applications requires an informed public; likewise, the solutions to the storage of nuclear waste also necessitate public understanding of the effects of nuclear radiation.

QUESTIONS

Q.1. (*a*) Explain the terms mass defect and binding energy.

(*b*) Calculate the binding energy of ${}^{6}_{3}\text{Li}$ in MeV per atom if the exact mass of this nuclide is 6.01512 amu. Calculate the binding energy per nucleon.

(Ans. 32.02 MeV/atom, 5.34 MeV/nucleon)

Q.2. Explain why some of the naturally occurring elements are stable and others are not.

Q.3. (*a*) What are the various types of radiations given off by a radioactive element? Discuss their main characteristics.

(*b*) Give an account of the methods available for the detection and measurement of radiation.

Q.4. (*a*) Discuss the kinetics of radioactive decay.

(*b*) Define half-life and decay constant. How they are related to one another?

Q.5. (*a*) The half-life of ${}^{32}_{15}\text{P}$ is 14.3 days, calculate how long would it take for 1 g of sample of ${}^{32}_{15}\text{P}$ to decay to 0.500 g of ${}^{32}_{15}\text{P}$.

(Ans. 14.3 days)

(*b*) Calculate the half-life for the decay of ${}^{39}_{17}\text{Cl}$ if 1 g of sample decays to 0.125 g in 165 minutes.

(Ans. 55 minutes)

Q.6. State and explain group displacement law.

Q.7. (*a*) What is a nuclear reaction? How do nuclear reactions differ from ordinary chemical reactions?

(*b*) Fill in the missing symbols in the following nuclear reactions:

(i) ${}^{22}_{11}\text{Na} + \longrightarrow {}^{23}_{12}\text{Mg} + {}^{1}_{0}\text{n}$

(ii) ${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + \ldots\ldots$

(iii) ${}^{1}_{1}\text{h} + {}^{7}_{3}\text{Li} \longrightarrow 2$

(iv) ${}^{10}_{5}\text{B} + {}^{2}_{1}\text{H} \longrightarrow {}^{11}_{6}\text{C} +$

Q.8. What is meant by nuclear fission? Show how nuclear fission is a chain reaction.

Q.9. How do nuclear fission and fusion differ? How are they similar?

Q.10. What is a nuclear reactor? Briefly describe its various parts.

Q.11. Explain the term radioactive dating. How the age of a plant material is determined?

Q.12. Describe how the radionuclide can be used in

(i) Research,

(ii) Industry, and

(iii) Medical Treatments?

Q.13. (*a*) What are the hazards associated with nuclear radiations?

(*b*) Discuss various safety measures for nuclear hazards.

Q.14. Write a comprehensive note on the biological effect of radiations.

Q. 15. Justify/comment on the following statements.

(*a*) The future of mankind is in the hand of nuclear chemist.

(*b*) Curie is SI units of radioactivity.

(*c*) Stable nuclei have more binding energy.

(*d*) Radionuclides are intrinsically unstable.

(*e*) All nuclear decay follow first order kinetics.

(*f*) A nuclear reaction is similar to chemical reaction.

(*g*) A nuclear fusion is a sustainable reaction.

(*h*) Water is used as moderator on atomic pile.

(*i*) Alpha-rays have more penetrating power.

(*j*) Beta-rays have more ionization power,

(*k*) Radiations can cause somatic effects.

(*l*) Radiations can be used as diagnostic purposes.

(*m*) Radiations can damage human skin.

Chapter Fifteen

SOLVENT EXTRACTION

15.1. BASIS OF SOLVENT EXTRACTION

Solvent extraction is a technique for separating a mixture of substances, by selective transfer between two immiscible liquid phases. The purpose of an extraction technique is physically to separate components of a mixture (solutes) by exploiting differences in their relative solubility in two immiscible liquids or between their affinities for a solid sorbent. Substances reach an equilibrium distribution through intimate contact between the two phases, which are then physically separated to enable the species in either phase to be recovered for completion of the analysis. An equilibrium distribution of the solutes between the two phases is established by dissolving the sample in a suitable solvent, then shaking the solution with a second, immiscible, solvent or by passing it through a sorbent bed or disk. Where the equilibrium distributions of two solutes differ, a separation is possible. The principal factors that determine how a solute will distribute between two phases are its polarity and the polarities of each phase. Degree of ionization, hydrogen bonding and other electrostatic interactions also play a part.

Most solvent-extraction procedures involve the extraction of solutes from an aqueous solution into a nonpolar or slightly polar organic solvent, such as hexane, methylbenzene or trichloromethane, although the reverse is also possible. Readily extractable solutes, therefore, include covalent neutral molecules with few polar and no ionized substituents; polar, ionized or ionic specific will remain in the aqueous phase. A wide range of solid sorbents with different polarities are used in solid phase extraction making this a very versatile technique, but the factors affecting the distribution of solutes are essentially the same as in solvent extraction. Two examples illustrate these points.

Example 1 If an aqueous solution containing iodine and sodium chloride is shaken with hydrocarbon or chlorinated hydrocarbon solvent, the iodine, being a covalent molecule, will be extracted largely into the organic phase, whilst the completely ionized and hydrated sodium chloride will remain in the aqueous phase.

Example 2 If an aqueous solution containing a mixture of weakly polar vitamins or drugs and highly polar sugars is passed through a hydrocarbon-modified silica sorbent which has a nonpolar surface, the vitamins or drugs will be retained on the surface of the sorbent whilst the sugars pass through.

15.2. DISTRIBUTION LAW AND DISTRIBUTION CO-EFFICIENT

Solvent extraction is governed by the Nerst Distribution or Partition law. This law may be stated as follows:

"When a solute distributes itself between two non-miscible phases in contact and in equilibrium with each other, ratio of the concentrations of the substance in the two phases is constant at constant temperature, provided the molecular state of the distributed solute is same in both the phases."

It should, however, be noted that if a solute associates to from double molecules in one solvent but not in the other, the equilibrium cannot exist between double molecules present in one phase, and single molecules present in the other. Thus the law holds good only when the ratio of concentration of single molecules in the two phases is considered.

Distribution Coefficient - The ratio of the equilibrium concentrations (strictly their activities in the two phase defines a distribution or partition coefficient, K_d, given by the expression

$$K_d = \frac{[S]_{org}}{[S]_{aq}} = \frac{C_1}{C_2} \qquad 15.1$$

where [ ] denotes concentrations (activities) of the distributing solute species, S and the value of K_d is independent of the total solute concentration.

The apparatus used for solvent extraction is the separatory funnel, illustrated in Figure 15.1. Most often, a solute is extracted from an aqueous solution into an immiscible organic solvent. After the mixture is shaken for about a minute, the phases are allowed to separate and the bottom layer (the denser solvent) is drawn off in a completion of the separation.

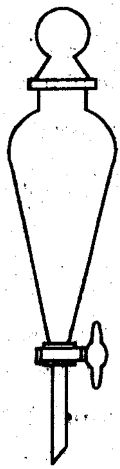


Fig. 15.1 Separatory Funnel

Many substances are partially ionized in the aqueous layer as weak acids. This introduces a pH effect on the extraction. Consider, for example, the extraction of benzoic acid from an aqueous solution. Benzoic acid (HBz) is a weak acid in water with a particular ionization constant K_a. The distribution coefficient is given by

$$K_d = \frac{[HBz]_e}{[HBz]_a} \qquad 15.2$$

where e represents the ether solvent and a represents the aqueous solvent. However, part of the benzoic acid in the aqueous layer will exist as Bz^-, depending on the magnitude of K_a and on the pH of the aqueous layer, hence, quantitative separation may not be achieved.

Applications of Distribution Law - According to Nernst, there are various limitations of this law and it is applicable only:

(1) When temperature remains constant

(2) When dilute solutions are employed. The ratio C_1/C_2 will not remain constant if the concentration of the distributed substance is high in the two solvents. Generally speaking, the higher the concentration, the larger the deviation. In an extreme case, if both of the solvents are saturated with solute, then the partition coefficient is given by,

$$K = \frac{C_1}{C_2} = \frac{[S]_{org}}{[S]_{aq}} = \frac{S_1}{S_2} \qquad 15.3$$

where S_1 and S_2 represent the solubilities of the solute in the solvent. The above equation holds only when S_1 and S_2 are small. In other words, it will not be amiss to say, that this equation is strictly valid when the solute is sparingly soluble in both the phase

(3) When the molecular state of the solute is same in the two solvents. In case the solute associates in a solvent, where its concentration is C_2, the law is modified to

$$K = \frac{C_2}{\sqrt[n]{(C_2)}} \qquad 15.4$$

where n is the number of molecules associating to give a suitable large molecule.

In case the solute dissociates, then the law is modified as,

$$\frac{C_1}{C_2(1 - x)} = K \qquad 15.5$$

where x-represents the degree of dissociation of the solute.

(4) When the two solvents are mutually insoluble or only very sparingly soluble, and their mutual miscibility is not altered by the addition of solute to them.

Distribution Ratio It is more meaningful to describe a different term, the distribution ratio, which is the ratio of the concentrations of all the species of the solute in each phase. In this example, it is given by

$$D = \frac{[HBz]_e}{[HBz]_a + [Bz^-]_a} \qquad 15.6$$

We can readily derive the relationship between D and K_d from the equilibrium involved. The acidity constant K_a for the ionization of the acid in the aqueous phase is given by

$$K_a = \frac{[H^+]_a[Bz-]_a}{[HBz]_a} \qquad 15.7$$

Hence, $[\mathrm{Bz}^-]_a = \dfrac{K_a[\mathrm{HBz}]_a}{[\mathrm{H}^+]_a}$ 15.8

From equation 15.2

$$[\mathrm{HBz}]_e = K_d[\mathrm{HBz}]_a \qquad 15.9$$

Substitution of Equations 15.8 and 15.9 into Equation 15.6

$$D = \frac{K_d[\mathrm{HBz}]_a}{[\mathrm{HBz}]_a + K_a[\mathrm{HBz}]_a/[\mathrm{H}^+]_a} \qquad 15.10$$

$$D = \frac{K_d}{1 + K_a/[\mathrm{H}^+]_a} \qquad 15.11$$

This equation predicts that when $[\mathrm{H}^+]_a >> K_a$ D is nearly equal to K_d and if K_d is large, the benzoic acid will be extracted into the ether layer; D is maximum under these conditions. If, on the other hand, $[\mathrm{H}^+] << K_a$, then D reduces to $K_d[\mathrm{H}^+]_a/K_a$ which will be small, and the benzoic acid will remain the aqueous layer. That is, in alkaline solution, the benzoic acid is ionized and cannot be extracted, while in acid solution, it is largely undissociated. These conclusions are what we would intuitively except from inspection of the chemical equilibria.

Equation 15.11 like Equation 15.3 predicts that the extraction efficiency will be independent of the original concentration of the solute. This is one of the attractive features of solvent extraction; it is applicable to tracer (e. g. radioactive) levels and to macro levels alike a condition that applies only so long as the solubility of the solute in one of the phrases is not exceeded and there are no side reactions such as dimerization of the extracted solute.

Of course, if the hydrogen ion concentration changes, the extractions efficiency (D) will change. In this example, the hydrogen ion concentration will increase with increasing benzoic acid concentration, unless an acid-base buffer is added to maintain the hydrogen ion concentration constant.

In deriving Equation 15.11 we actually neglected to include in the numerator of Equation 15.6 term for a portion of the benzoic acid that exists as the dimer in the organic phase .The extent of dimerization tends to increase with increased concentration, and by Le Chatelier's principle, this will cause the equilibrium to shift in favor of the organic phase with increased concentration. So, in cases such as this, the efficiency of extraction will actually increase at higher concentration.

15.3. PERCENT EXTRACTED

The distribution ratio D is constant independent of the volume ratio. However, the fraction of the solute extracted will depend on the volume ratio of the two solvents. If a larger volume of organic solvent is used, more solute must dissolve in this layer to keep the concentration ratio constant and to satisfy the distribution ratio.

The fraction of solute extracted is equal to the millimoles of solute in the organic layer divided by the total number of millimoles of solute. The millimoles are given by the molarity times the milliliters. Thus, the percent extracted it given by

$$\%E = \frac{[S]_o V_o}{[S]_o V_o + [S]_a V_a} \times 100\% \qquad 15.12$$

where V_o and V_a are the volumes of the organic and aqueous phases, respectively. It can be shown from this equation that the percent extracted is related to the distribution ratio by

$$\%E = \frac{100D}{D + (V_a/V_o)} \qquad 15.13$$

If $V_a = V_o$ then

$$\%E = \frac{100D}{D + 1} \qquad 15.14$$

Example 15.1 Determine whether nickel dimethylglyoxime will be extracted completely or not from 10 cm^3 of an aqueous solution at pH 8 after shaking twice with 5 cm^3 of chloroform. The distribution coefficient is 410.

Solution

$$E\% = \frac{100}{1 + (V_1/DV_2)} = \frac{100}{1 + (50/5 \times 410 \times 5)} = 98.5\%$$

Thus nickel dimethyl glyoxime will be extracted nearly completely.

Example 15.2 Twenty milliliters of an aqueous solution of 0.10M butyric acid is shaken with 10 cm^3 ether. After the layers are separated, it is determined by titration that 0.5 mol butyric acid remains in the aqueous layer. What is the distribution ratio, and what is the present extracted?

Solution

We started with 2.0 mmol butyric acid, and so 1.5 mmol was extracted. The concentration in the ether layer is 1.5 mmol/10 cm^3 = 0.15 M. The concentration in the aqueous layer is 0.5 mmol/20 cm^3 = 0.025 M. Therefore,

$$D = \frac{0.15}{0.025} = 6.0$$

Since 1.5 mmol was extracted, the percent extracted (1.5/2,0) × 100% = 75%. Or

$$\text{Percent Extracted } (\%E) = \frac{100 \times 6.0}{6.0 + (20/10)} = 75\%.$$

15.4. EXTRACTION SYSTEMS

(a) Simple Extraction System It is one of the simplest, cleanest and most rapid methods of performing a separation. The mixture dissolved in one solvent is shaken with another immiscible-solvent and the phase allowed to settle. Usually one solvent is water and other is organic solvent. The ionic species prefer to be remaining aqueous layer and natural species in organic phase.

(b) Double and Multiple Extraction System When the separation is not completely obtained in one extraction step, complete extraction may be achieved by separated extractions.

1. Take a series of tubes (0, 1, 2, 3) containing a fixed amount of an aqueous solution of known pH.
2. Place the mixture in aqueous solution to be separated in tube 0 and add a fixed amount of chloroform.
3. Shake the tube 0 to achieve distribution and allow the layers to separate.
4. Transfer the chloroform layer to tube 1 and add a fresh aliquot of chloroform to tube 0.
5. Shake tube 0 and 1 and allow the layers to separate.
6. Transfer the chloroform layer of tube 1 to tube 2 and that of tube 0 to tube 1 and add a fresh aliquot of chloroform to tube 0.
7. Continue the cycle until separation is complete.

This process is known as Craig counter-current multistage extraction.

15.5. TECHNIQUES FOR SOLVENT EXTRACTION

Solvent extraction may be made use of analytically for concentrating or rejecting a particular substance, or for the separation of mixtures. The extraction may be accomplished by the following two limiting processes.

1. Batch extraction (Single, Double and Multiple Extraction) This is the simplest and most widely used method. This method is used where a large distribution ratio for the desired separation is readily available. In this method, the solute is extracted from one layer by distributing it with a second immiscible layer until partition equilibrium has been attained. The two layers may be shaken in a separatory funnel. The layers are then allowed to settle out and the layer containing the desired constituent is removed.

In general, in a batch extraction, a given volume of a solution containing the ion under analysis is shaken with a given volume of the organic solvent in pear-shaped separatory funnel. The extent of extraction can be determined by adjusting the experimental conditions in the aqueous layer. When equilibrium is reached, which can be hastened by vigorous agitation, the two layers are separated by draining off one layer at a time.

It should be noted that micro as well as macro pear type separtory funnel are available, of which some are designed to drain off the top layer rather than the bottom layer. This type of separatory funnel is used for those systems where the organic layer is less dense than the aqueous layer, and hence appears at the top.

2. Continuos Extraction This method of extraction is applicable when the distribution ratio is low. This method makes use of continuous flow of immiscible solvent through the solution to be extracted. Although partition equilibrium may not be achieved during the time of contact, solute is being removed continuously with the spent extracting solvent. If the extracting solvent is volatile, it is recycled by distillation and condensation and is dispersed in the aqueous phase with the help of a sintered glass disc or any other suitable device.

For separation of mixture, discontinuous counter current extraction using a number of separating funnels, a Craig apparatus, or some form of mixer settler equipment is suitable for laboratory work.

The removal of extracted solute from the organic phase for further preparation for the detailed analysis is known as stripping. The impurities present in the organic phase may be removed by back washing.

There are a large number of batch as well as continuous counter current extractors in commercial use. The feed preparations can be carried out either in stainless steel or concrete tanks provided with eating as well as cooling coils, a suitable mixing arrangement and a man hole Vertical or horizontal extracting vessels, known respectively as columns and mixer settlers have commonly been used. In continuous operation, using mixer settlers, the liquids are pumped continuously through the mixture in parallel files and the resulting dispersion is continuously settled or decanted in a separate vessel, known as settler. Each mixture settler constitutes one stage of extraction. Multistage effects can be done by arranging them in desired number of mixer settlers.

Rotary columns, pulsed counter current columns, pumper decanters, centrifugal extractor or hydrocyclones have also been used occasionally. The principal object of the extractor of any type is to achieve close contact between the phase in order to ensure rapid as well as efficient transfer of solute to the desired phase. This can be achieved by using a number of columns such as spray columns, scheible columns, perforated plate columns and rotating disc columns etc.

Example 15.3 An aqueous solution contains 100 g of solute per dm^3. When 1 dm^3 of the solution is shaken with 100 cm^3 of ether, 6g. of the solute are extracted. How much more of the solute would be extracted from the aqueous solution by a further 100 cm^3 ether. The molecular state of the solute is assumed to be the same in ether and water.

Solution

Conc. in ether $C_{\text{ether}} = 6/100$

Conc. in water, $C_{\text{water}} = (10 - 6)/1000 = 4/1000$

$$K = \frac{C_{\text{ether}}}{C_{\text{water}}} = \frac{6/100}{4/1000} = \frac{6 \times 1000}{100 \times 4} = 15$$

Suppose x g. of the substance gets extracted with a further 100 cm^3 of ether. Then

$$C_{ether} = \frac{x}{100} \text{ and } C_{water} = \frac{4-x}{1000}$$

Hence, $\dfrac{C_{ether}}{C_{water}} = \dfrac{x/100}{(4-x)/1000} = 15$

or $10x = 15(4-x) = 60 - 15x$

or $x = 2.4$ g.

Example 15.4 The solubility of a substance is twice as great in ether as in water. Compare the amounts percent extracted from 100 cm^3 of an aqueous solution (a) By using 100 cm^3 ether in a single operation, and (b) 50 cm^3 ether in two successive extractions.

Solution

Let S_1 and S_2 are solubilities of the substance in ether and water. Then

$$K_d = \frac{S_1}{S_2}, \text{ but } S_1 = 2S_2$$

so $K_d = \dfrac{2S_2}{S_2} = 2$

(a) Suppose x_1 be the percentage of the substance extracted when 100 cm^3 of ether is used in a single lot. Thus

$$K_d = 2 = \frac{x_1/100}{(100-x)/100} = \frac{x_1}{100-x_1} \text{ or } x_1 = \frac{200}{3} = 66.7\%$$

(b) Suppose x_2 percent of the substance is extracted when 50 cm^3 of ether is used in two successive extractions. Here $K = 1/2$, $V = 100$ cm^3, $v = 50$ cm^3 and $n = 2$. Thus $KV = \frac{1}{2} \times 100 = 50$.

Thus $x_2 = \left[1 - \dfrac{50}{50+50}\right]^2 100 = \left[1 - \dfrac{50}{100}\right]^2 100 = 25\%$

Hence, $x_1 : x_2 = 66.7\% : 25\%$

15.6. CHOICE OF SOLVENT

It should be noted that the choice of solvent for extraction is governed, generally by the following considerations.

(i) A high distribution ratio for the solute i.e. distributed substance, and a low distribution ratio for undesired impurities.

(ii) Low solubility in the aqueous phase.

(iii) Low toxicity and inflammability.

(iv) Sufficiently low viscosity.

(v) Sufficient density difference from the aqueous phase in order to avoid the formation of emulsions.

(vi) It must be selective.

(vii) It should be chemically inactive.

(viii) It should be cheaply available.

(ix) It should be blast resistant.

(x) It should exhibit low oxidizability.

(xi) It should be easy to recover.

(a) Extractants lighter than water Examples are benzene, toluene, alcohols such as butanol, pentanal, isopentanol etc. ethers such as diethyl ether, isopropyl ether, dichloroethyl ether etc.

(b) Extractants heavier than water Examples are chloroform, carbondisulphide, carbon tetrachloride etc.

For analytical separations and determinations of a number of metals such as Ni, Co, Zn, Cd, Cu, Te, TI, Se etc. other effective extractants such as cation exchange reagents (synthetic carboxylic acids of the fractional composition C_7 — C_9, C_{10} — C_{13}, C_{13} — C_{16}; high molecular weight amines, ammonium bases, esters and acid mono and di-esters of phosphoric acid etc.)

A qualitative estimation of miscibility of two solvents can also be carried out by comparing their position in mixotrophic series. the more separated the solvents are in the series, the less miscible they are. An example of the mixotrophic series is the series; Water, formic acid, acetic acid, phenol, aniline, acetone, pyridine, ethyl acetate, ethyl ether, chloroform, dichloroethane, benzene, carbon tetra chloride, carbon disulphide.

The rate and selectivity of an extraction process is promoted by the following important factors:

(a) By proper choice of extractant.

(b) By adjusting the pH of the solution.

(c) By regulating the temperature.

(d) By masking the interfering ions.

(e) By changing the concentrations of the components.

(f) By the duration of the extraction process.

(g) By the effect of the processes that occur in extractors (acid-base, precipitation, oxidation-reduction etc.)

15.7. FACTORS AFFECTING EXTRACTION

(a) Salting out agents. The extraction of metals may be enhanced by adding high concentrations of inorganic salts to the aqueous phase. This process is known as salting out effect and is due to the pronounced effect of the added salt on the activity of the disturbing species by the common ion effect and also due to strong ability of these ions to bind water around them (depleting the aqueous phase of water molecules for use as a solvent).

(b) pH value The process of liquid extraction is largely influenced by pH. Two metals may be extracted at different pH values. In some cases, effective stripping of the loaded organic phase may be achieved by simply bringing in contact with another aqueous phase at a different pH value.

(c) Oxidation state The selectivity of extraction may sometimes be increased by modifying the oxidation state of metal or the impure. For example, extraction of Fe from chloride solutions can be prevented by reducing Fe (III) to Fe(II), which does not extract. Variation of the valence states of some elements in the organic extract is also useful as a method of stripping.

(d) Masking agents. These agents, which are metal complexing agents prevent particular metals from taking part in their usual reactions and in this way they remove their interference without requiring an actual separation. These agents, also known as sequestering agents, are used to prevent certain metals from forming extractable complexes in solvent extraction and thus greatly increase the selectivity of the extraction methods. For example, aluminium can be extracted in presence of iron with 8-quinolinol by masking iron with an alkali cyanide to form stable ferrocyanide ion. Cyanide, tartrate, cirate, fluoride and EDTA are commonly used as masking agents.

(e) Modifiers. Modifiers are the additives to the organic phase to increase the solubility of the extractant in diluent. High molecular weight alcohols (e. g. capryl alcohol) are commonly used as modifiers.

(f) Synergistic agents. Synergistic agents are added to the organic phase in order to enhance the extraction. They form complexes which are taken up by the extractant, event if the extractant does not form suitable complexes directly with the desired metallic species. Neutral organophosphourus compounds added to acidic organophosphorus compound exert synergistic effects.

Advantages of Solvent Extraction

Extraction as a physicochemical separation and concentration method, has a number of advantages.

(a) Low time taken in the process.

(b) A more complete separation of ions than in the precipitation process, because a small inter phase area and the absence of precipitates preclude coprecipitation and other processes that may complicate separation of the components.

(c) Great opportunities for concentration, which ensure a significant increase in the sensitivity of analysis.

(d) Extractants can be selected in such a manner that the removal and separation of substances related in their chemical properties and solubilities become possible. Moreover, removal and separation of components possessing close boiling points or which can not be separated at all by other chemical or physicochemical methods, is also possible.

(e) Separation of the components is combined with their quantitative determination (extraction spectral analysis, extraction-polarography, extraction-flame photometry etc.).

(f) In a number of cases, the extract contains more stable forms of compounds than water.

(g) The operation is carried out at low temperature.

(h) The process can be automatically controlled.

(i) The selectivity of reactions can be appreciably increased.

15.8. APPLICATIONS OF SOLVENT EXTRACTION

This technique is mainly used for selective extraction and spectroscopic determination of metals in geological samples, petroleum products, food stuffs, body fluids, plants and animal tissues.

When extraction is used to separate elements the process is often characterized by the degree of extract in, which represents what percent of the total amount of a substance has been extracted into the organic phase. The degree of extraction is the ratio of the analytical concentration of the substance in the organic phase to its original concentration.

Applications in Chemistry

(i) The greatest use in analytical chemistry has been found by the extraction, separation of elements in the form of chelates.

(ii) Extraction in often carried out to concentrate an element, which enables us to lower its detection limit at the same probability.

(iii) Extraction concentration is generally combined with subsequent photometric analysis of the coloured organic extract. Such methods are known as extraction photometric methods of analysis.

(iv) Determination of uranium as 8-hydroxy quinolate.

(v) Determination of nickle as dimethyl glyoxime complex.

(vi) Extraction of precious metals such as gold, palladium platinum etc.

(vii) Separation of impurities.

(viii) Extraction of trace metals in seq.

(ix) Determination of iron chloride extraction.

(x) Determination of lead by dithizone method.

(xi) Determination of copper as diethyl dithiocarbamate complex.

(xii) Determination of copper as neo cuperion complex.

(xiii) Determination of beryllium as acetyl-acetone complex.

(xiv) Determination of molybdenum by thiocyrnate method.

(xv) Determination of iron as 8-hydroxy quinolate.

Applications in Industry

(i) Extraction of metal from leach liquors obtained from low grade or complex ores.

(ii) Separation of metals that are either chemical similar or occur in combined state in ore deposits.

(iii) Purification in order to obtain a very pure starting material for further metallurgical processing.

(iv) Study of effect of K, Cr, Mg on tomato crop.

(v) In nuclear technology for the separation of nuclear fuel poisons.

(vi) In oil and fat industry.

(vii) Separation of geological samples.

(viii) Separation and analysis of petroleum products.

(ix) Quality control of food stuffs.

(x) Analysis of plants, animals and body fluids.

(xi) Lanthanides can be separated by the extraction of nitrates with ether or cyclopentane as a solvent.

(xii) Hf and Zr has been separated using this techniques.

(xiii) Purification of thorium nitrate has also been carried out by solvent extraction techniques.

(xiv) Extraction of beryllium from low grade beryllium ores has been made possible by this technique.

(xv) Boric acid can be obtained by solvent extraction techniques from locally occurring low grade brines.

Questions

Q.1. What is distribution law? Give its applications.

Q.2. What is the basis of solvent extraction process? Give its principle and techniques.

Q.3. What do you mean by distribution ratio and distribution coefficient?

Q.4. What is percent extracted? How is it helpful to calculate the extraction efficiency?

Q.5. What are simple, double and multiple extraction systems? Explain with examples.

Q.6. Solvent extraction may be made use of analytically for concentrating or rejecting a particular substance. Discuss.

Q.7. Give salient features of the process of solvent extraction.

Q.8. On what factors solvent extraction depends?

Q.9. Briefly discuss the advantages of solvent extraction.

Q.10. Batch extraction is helpful in single double and multiple extraction system.

Q.11. Discuss briefly the application of solvent extraction in the field of chemistry and industry.

Q.12. Justify/comment on the following statements.

(a) Solvent extraction is based on distribution law.

(*b*) Solvent extraction is used to separate mixture of substances.

(*c*) The ratio of the concentration of the substance remains constant in two immiscible solvents.

(*d*) Degree of association/dissociation can be found from distribution law.

(*e*) Continuous extraction is used when the distribution ratio is low.

(*f*) pH can affect solvent extraction.

(*g*) Solvent extraction finds application in quantitative analysis

Chapter Sixteen

CHROMATOGRAPHY

16.1 INTRODUCTION

Chromatograpy is a technique which achieves the separation of similar components by a process of differential migration. This technique was invented by the Russian botanist Mikhali Tswett (1903) who used this technique to separate pigments like chlorophylls and xanthophylls of green plant leaves by passing a solution (green coloured) of these pigments in petroleum ether through a vertical glass tube packed with powdered calcium carbonate. The separated components (e. g. pigments) appeared as coloured bands or zones on the column of packing material and different pigments separated into different bands. This column was taken out of the tube and the different bands were cut out. Each pigment was then extracted with suitable solvent. Since different coloured bands appeared on the column, the name chromatography (chroma means *colour*; graphy means *writing*), i.e., colour writing, was given by the inventor of this technique. But, the name, chromatography, included a group of closely related separation methods and finds its application to both coloured and colourless mixtures.

Because of extensive application of chromatographic techniques for separation of complex mixtures, A. J. P. Martin and R. L. M. Synge were awarded Nobel Prize in 1952 for their work.

16.2. PRINCIPLE OF CHROMATOGRAPHY

Separation of the components in sample has been the centre of attention so far. In chromatography, the components to be separated are distributed between two phases. One of the phases is a stationary phase of large surface or bulk area, which is either a solid, or a liquid held immobile by a solid, and the other, a mobile phase, either liquid or gas. The sample for separation is in the mobile phase that flows past the stationary phase. Separation of the sample components is based on difference in the rates of migration among the components. It may well be asked at this point: How justifiable is it to think of differences in the migration rates among the components to be separated?

A general answer can easily be put forward. There are two conditions under which one can consider differences in the migration rates. The first condition is that of equilibrium, the removal of a component from the mobile phase by the stationary phase is an equilibrium process. When the mobile phase containing the sample components passes through the stationary phase, the rate of travel of an individual component is directly related to the partition (i.e. distribution) of that component between the mobile phase and the stationary phase. The equilibrium involved can be described quantitatively by means of a partition coefficient, K, which for chromatography is defined as,

$$K = C_s/C_m \qquad (16.1)$$

where C_s is the analytical concentration of the component in the stationary phase and C_m is that in the mobile phase. At the low concentration, the partition coefficient becomes approximately constant, and under these conditions a linear relationship between C_s and C_m exists, and chromatography, is, therefore, termed linear chromatography.

Separation of two or more sample components takes place when the partition coefficients of these components between the two phases vary. It may be recalled that the components in a sample differing only slightly in their physical and chemical properties exhibit different partition coefficients between the two phases. However, the essence of separation of two or more components lies in the fact that the component which interacts strongly with the stationary phase will pass very slowly through the phase whereas the components which do not interact strongly will pass through more rapidly. Thus, because of difference in the extent of interaction between the component and the stationary, phase, which causes differences in the migration rates among the components, the components are separated in different regions in form of bands in the stationary phase.

The second condition is that of time period, the duration of which tells about the retention or retardation of a component by the stationary phase. The retention means that the overall time spent by the component is more in the stationary phase than in the mobile phase, and hence separation of this component takes place. Separation of two or more components is possible when these components pass through the stationary phase at different time intervals. This again points to differences in the migration rates among the sample components.

Description of Chromatographic Separation So far we have discussed the principles of chromatography. For practical purpose, let us consider a general procedure for chromatographic separation. In this procedure, a small quantity of the sample is placed on the top of the column packed with some powdered solid, and a liquid is allowed to flow through the column at a constant rate. When the mobile phase (e. g. liquid) passes over the sample, the more soluble component dissolves in it. The mobile phase along with the dissolved component moves down the column and gets adsorbed.

As the mobile phase is poured down the column, the mobile phase comes in contact with the adsorbed component on the solid phase (i.e. stationary phase) and again dissolved off the component and moves down the column. There, it again gets adsorbed by the fresh solid phase. The removal for the component from the mobile phase by the solid phase and the subsequent dissolution of the component into the fresh mobile phase continues a number of times until the component passes through the entire chromatographic column and gets separated. Greater the solubility of the component in the mobile phase, the faster the component will move down the column. The individual components tend to move down the column at different rates and leave the chromatographic column at different times. The components which is not soluble in the mobile phase remains as such at the top of the column, no mater how much mobile phase is poured down. For efficient separations, very small quantities of the sample are used.

16.3. CLASSIFICATION OF CHROMATOGRAPHIC METHODS

As stated earlier, in chromatography, the components to be separated are distributed between two phases. Depending on the nature of the two phases as well as on the nature of the stationary phase alone, classification of chromatographic methods has been made in different ways. As the components interact with the stationary phase in the process of separation, a classification of the technique has been made according to the type of interaction, i.e. the physical properties of the component utilised for separation. Different types of classification of chromatographic methods are described below:

(i) Difference in the Nature of the Two Phases It has been stated earlier that the mobile phase is either a liquid or a gas, and the stationary phase is either a solid or a liquid. Depending on the nature of the mobile and stationary phases, a general classification of chromatography has been made in terms of various combinations, such as, liquid-liquid, liquid-solid, gas-solid, and gas-liquid.

(ii) Difference in Physical Properties of the Components in the Stationary Phase The components to be separated must be soluble in the mobile phase. When the mobile phase carrying the dissolved components percolates through or along the stationary phase, the components interact with the stationary phase in different manners:

(a) When the components dissolves in the stationary phase (e.g. liquid) i.e., the component is partitioned between two liquid phase (one, stationary and the other, mobile), the process is called *partition chromatography*.

(b) When the component is adsorbed on the stationary phase, the process is called *adsorption chromatography*.

(c) When the ionic components in the mobile phase react chemically with the ionic components in the stationary phase, the process is called *ion-exchange chromatography*.

(iii) Types of Stationary Phases As stated earlier, the stationary phase may either be a solid or a liquid (immiscible with the mobile phase) held immobile by a solid. Depending on the nature of the stationary phase, different names are given to chromatography. These are:

Column chromatography. In this type, stationary phase (powdered solids) is packed in a long narrow glass or metal tube, and the mobile phase (a fluid, e.g., a gas or a liquid) percolates through or along the column of powdered solids.

Paper chromatography. Filter paper is used as a support medium where water is adsorbed between the fibres of paper and forms the stationary hydrophilic phase.

Thin-layer chromatography. Finely divided solid coated with a thin layer of liquid held in a metal or glass tube is the stationary phase and the mobile phase flows or percolates through the stationary phase.

Exclusion chromatography. Molecular sieves are used as the stationary phase. The components are separated on the basis of differences in their size by passing through a column containing the molecular sieves. This type is referred to as gel-permeation chromatography (by polymer chemists), or as gel filtration (by biochemists). Table 16.1. gives the classification of the chromatographic methods.

Table 16.1. Classification of Chromatographic Methods

Physical property	Mobile phase	Stationary phase	Name of chromatography
Partition	Liquid	Liquid	Partition or liquid chromatography (column, paper chromatography)
Partition	Gas	Liquid	Gas-liquid chromatography
Adsorption	Liquid	Solid	Adsorption chromatography (column). Thin-layer chromatography. Ion-exchange chromatography
Adsorption	Gas	Solid	Gas-solid chromatography

16.4. PAPER CHROMATOGRAPHY

Paper partition chromatography was introduced in 1944 by Consden, Gordon and Martin. Cellulose in the form of paper sheets makes an ideal support medium where water is adsorbed between the cellulose fibres and forms the stationary hydrophilic phase. The mobile phase (flowing solvent) which is immiscible or slightly miscible with water percolates within the porous structure of the paper. The technique is based on the different partition coefficient of the components between the two phases. Although separation is effected mainly by partition, but adsorption effects also occur to certain extent (when the stationary phase is not completely inert).

On a strip of filter paper (about 30 × 5 cm) a pencil line is drawn at a distance of 5 cm from one end. A minute drop of the test solution is placed at the centre of this line. It is called the original line (Fig. 16.1(a)). The solvent is then evaporated and the strip is then suspended from the other end in a tall vessel (Fig. 16.1(b)) containing the developing solvent (i.e. the mobile phase-a solvent mixed with water-to prevent dehydration of the paper during the flow of solvent) so that the pencil line end dips in the solvent to a depth of 1-2 cm. The top of the vessel is closed with a cardboard so that the suspended paper strip is in an atmosphere of the vapours of both solvents.

Upon standing, the solvent rises over the strip by capillary action, carrying the components of the sample at different rates according to their partition coefficients. When the solvent reaches almost the top edge of the paper strip, the strip is removed and the solvent front is marked. The strip is then dried and the positions of the components are visualised by a suitable staining reagent. The dry paper strip is called *chromatogram.*

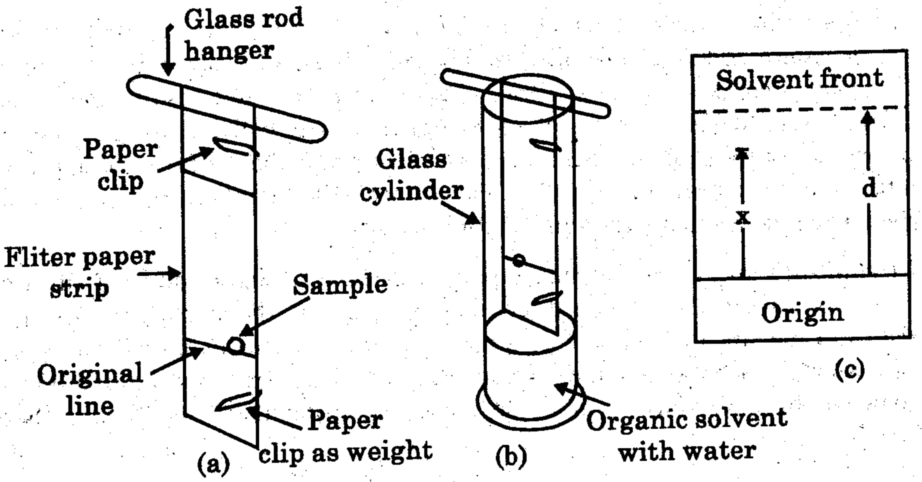


Fig. 16.1 ***(a) Strip prepared for Chromatographic analysis,***
(b) Paper Strip Suspended in a Container and Dipping into a Solvent, and
(c) Determination of the Therefore Value.

The distance of he solvent front and the separated spots (corresponding to different sample components) marked on the strip are measured from the original line [Fig.16.1(c)]. The ratio of the distance moved by a component to that moved by the solvent is known as the R_f value, i.e. $R_f = x/d$, and is more or less constant for particular compound, solvent system, and paper under carefully controlled conditions of solute concentration, temperature, the direction of flow of the solvent (i.e. ascending, descending, or radical) and pH.

It may be noted that paper chromatography is particular, useful for the qualitative as well as quantitative separation of he components of the mixture. This technique does not provide a means of separating the sample in pure form. But, it helps to know the purity of the sample.

(i) *Choice of Paper* As stated earlier, the value depends upon the natures of the paper used. Since a paper strip serves as a stationary support to hold a polar solvent stationary and the mobile phase percolates within the porous structure of the paper, it is necessary to select a paper which satisfies these conditions. Some of the types of papers used in this technique are described below.

Whatman No. 1 is the paper most frequently used for analytical-purposes. Whatman 3 MM is a thick paper and is best used for separating large quantities of material; the resolution is, however, inferior to Whatman No.1 For rapid separation, Whatman Nos. 4 and 5 are convenient, although the spots are less well defined. The paper may be treated with a buffer solution before use or chemically modified by acetylation. Ion-exchange papers are also available commercially.

For the separation of lipids and similar hydrophobic substances, pure cellulose paper treated with silica, alumina, etc. and kieselghur filter papers are used.

Pure Cellulose Papers. Ordinary filter paper is a somewhat random arrangement of fibres. But, pure cellulose paper is a systematic arrangement of fibres. Cellulose is a fibre network of polymeric carbohydrate chains of molecular mass up to 500,000. It is hydrophilic in nature and is cross-linked by hydrogen bonding system. Each fibre is a packet of oriented smaller units called fibrils. These fibrils have regions of a high degree of order called crystallites and regions of a low degree or order called amorphous regions. The stationary liquid phase is not uniformly distributed over these fibrils but appears to be concentrated in the amorphous regions. The surface and amorphous regions that hold the absorbed water are mutually responsible for retention.

Modified Cellulose Papers. Pure cellulose paper treated with highly purified silica gel, alumina, etc. is called the modified cellulose paper. In these papers, adsorptive characteristics of the silica or alumina dominate over those normally associated with the supporting cellulose material. By these treatments, the paper exhibits the hydrophobic nature. Hydrophobic substances can be separated by using these modified cellulose papers.

(ii) *Choice of Solvent.* In paper chromatography, the components to be separated are partitioned between two solvents. So this technique is a liquid-liquid partition in which the paper serves as a support for the solvent system. However, the choice of solvent, like that of the paper, is largely empirical and depends on the sample investigated. If the compounds move close to the solvent front, in a solvent (say A) then they are too soluble, while if they are crowded around the origin in another solvent (say B) then they are not sufficiently soluble. A suitable solvent for separation would, therefore, be an appropriate combination of two solvents, A and B (provided that they are not infinitely miscible with one another), so that the R_f values of the components of the mixture are spread across the length of he paper. The pH may also be important in a particular separation, and may solvents contain acetic acid or ammonia to create a strongly acidic or basic environment.

In terms of the stationary phase, the solvent systems used are:

(a) *Aqueous stationary phase.* Water is used for strongly polar or ionic components. Water is held stationary on the paper and the mobile phase passes through the stationary phase. The aqueous stationary phase is attained by hanging the strip of paper in an air-tight container containing a solvent (mobile phase, usually n-butanol or higher alcohols) saturated with water. If an aqueous buffer solution or a salt solution is to be used as the stationary phase, the paper is drawn through the solution, allowed to dry and then exposed to an atmosphere saturated with water vapour.

(b) *Stationary hydrophilic organic solvent* When a hydrophilic organic solvent is adsorbed by the paper to form the stationary phase, the method used depends upon the volatility of the stationary phase.

(i) When the stationary phase is sufficiently volatile, the paper strip is suspended in a saturated atmosphere until equilibrium is attained.

(ii) If the stationary phase is not sufficiently volatile, the paper strip is drawn through a solution of the liquid in a volatile diluent (e.g. a mixture of two solvents, viz, chloroform-benzene, benzene-cyclohexane, etc. then suspended in air to evaporate the diluent. Formamide is a suitable hydrophilic organic solvent.

(c) *Stationary hydrophobic solvent* The paper may be chemically modified by acetylation or by treating with vapours of dimethyl dichloro silane or by treating with the hydrophobic solvent dissolved in a volatile diluent followed by evaporation of the diluent.

(iii) *Mechanism of Paper Chromatography* As stated earlier, the paper chromatographic separation is effected partly by partition and partly by adsorption. A solution of the mixture of compounds to be separated is prepared by dissolving in water (if soluble) or in an aqueous solution of a suitable organic solvent (if not soluble in water) and a minute drop is placed on a strip of chromatographic paper. The developing solvent (mobile phase) taken in a container is allowed to travel along the strip suspended in the container. The cellulose in the paper serves as a support for the stationary phase with adsorbed water.

The compounds of the mixture partition between the two phases. Because of the difference in the partition coefficient of the compounds, the rate of the travel of each compound is different. As the result, the separation of the compounds of the mixture occurs on the strip of paper.

(iv) *Types of Paper Chromatography* Essentially, the paper chromatography apparatus consists of a sheet of paper supported on a frame so that one edge is dipped into the solvent taken in a container. Depending upon the separation of the components being carried out in one direction or two directions, there are one dimensional, or two dimensional paper chromatography.

One-dimensional Paper Chromatography As stated earlier, when a sheet of paper is suspended in a container containing the solvent (i.e. mobile phase), the later travels along the sheet of paper. Depending upon the direction of flow of mobile phase, three different experimental procedures for one dimensional are known. These are:

(a) *Ascending method* The procedure outlined in the beginning of the section is known as ascending paper chromatography. As stated, on a strip of filter paper (about 30 × 5 cm), a pencil line (called the base line) about 5 cm from one end is drawn along the width of the paper strip. If the mixture to be separated contains four compounds (A, B, C, and D), then mark five points on the base line on the filter paper. A minute drop of the solution of the mixture is put on one point and similar drops of solutions of each of known compounds (A, B, C, and D) are placed in the remaining four points. After allowing the solvent to dry, the strip is then suspended by means of a glass rod tied with paper clips in an air-tight glass tank above the developing solvent called eluting solvent (i.e. the mobile phase so that the pencil line end dips in the solvent.

Because of the capillary action, the solvent rises up. The solvent dissolves the compound and flows up until the force due to capillarity is counter balanced by the downward force to gravity. When the solvent reaches a suitable height or the top, the paper is taken out of the tank, the solvent front is marked with a pencil and the paper is allowed to dry.

Note: It may be noted here that when the solvent front reaches the top of the filter paper, the paper should be removed. If the paper strip is left dipped in the solvent for any length of time, the compounds tend to diffuse on the paper and cause the spots to diffuse on the developed chromatogram.

Different compounds in the mixture travel through different heights on the filter paper and corresponds to the heights travelled by known compounds [Fig. 16.2(a)]. Thus, different compounds in a mixture are separated as well as identified.

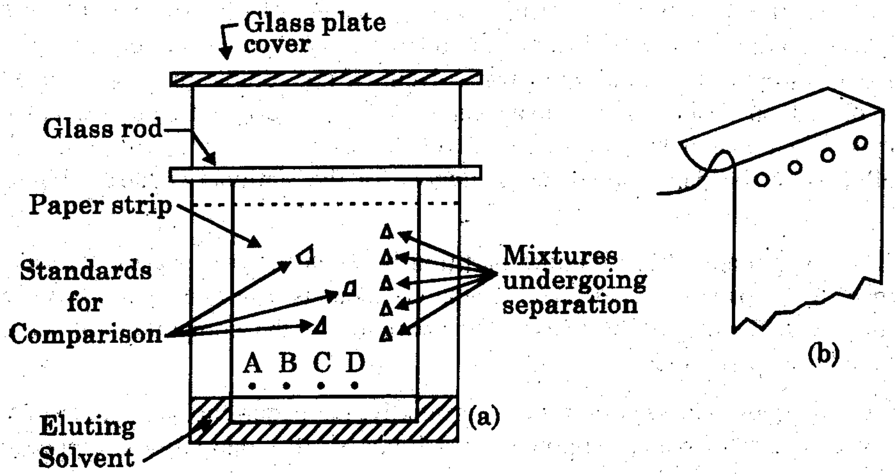


Fig. 16.2 (a) Ascending Chromatography, and (b) Descending Chromatography

The R_f value for a compound can be determined as described earlier. If in the place of strip of filter paper, a whole sheet is used, then multiple separations (hence, multiple chromatograms) may be carried out simultaneously under the same conditions of solvent and temperature.

(b) *Descending method* In the preceding discussion we described the ascending method in which the mobile phase ascends upwards during the process. Although this method is the most suitable and convenient it is of little use for the separation of the slow moving compounds, i.e. with low R_f values, because the distance travelled by the solvent front is limited. For this purpose, the descending method is of particular use in which the mobile phase (solvent) moves downward [shown in Fig. 16.2(b)].

Thus, the descending method is convenient for compounds which have similar or low R_f values. Since the solvent drips off the bottom of the paper, the effective length of the paper is increased thus giving a wider separation. In this case, of course, the R_f values cannot be measured, and the compounds are compared with a standard reference compound, such as glucose, for example, in the case of sugars:

$$R_f = \frac{\text{Distance travelled by compound}}{\text{Distance travelled by glucose}}$$

(c) *Radial or Horizontal method* This is a convenient method for rapid separation of mixtures. In this method, a circular filter paper is taken and a thin strip is cut along its radius. This thin strip or tongue is termed a wick for solvent.

The circular filter paper with its thin strip bent downwards at right angles is kept over a petri dish containing the solvent in such a way that the strip is dipped into the solvent. A drop of the solution of the mixture of the compounds is placed near the centre of the circular paper. The petri dish is covered with a circular glass plate to prevent evaporation of solvent.

As the solvent spreads through the filter paper by capillary action, the various compounds of the mixture are separated in the form of semi-circular bands by radial development.

Two dimensional Paper Chromatography This technique is convenient for the separation of the compounds which have similar R_f values. Two dimensional paper chromatography of the separated mixture at right angles to the first direction of development using a different solvent for the second development.

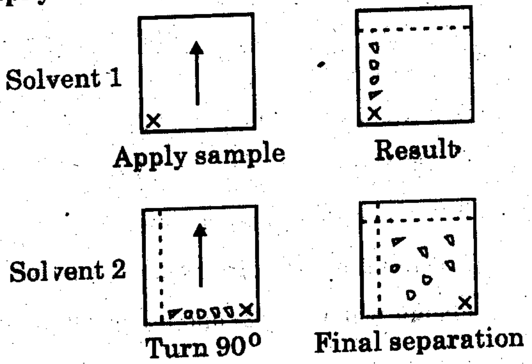


Fig. 16.3 Two Dimensional Paper Chromatography

The mixture is separated by ascending chromatography in one direction with a solvent, which should be volatile, then after drying, the paper is turned through a right angel and separation is carried out in the second solvent. After locating the spots, a map is obtained and compounds can be identified by comparing their positions with a map of known compounds developed under the same conditions. Fig.16.3 shows the separation of a mixture by two-dimensional paper chromatography.

(v) *Drying the Paper Chromatogram* So for we have described the development of chromatogram. Now, the question is: How do we dry the paper chromatogram? As stated earlier, after the development of the chromatogram, the paper is removed from the glass tank and the solvent front is marked with a pencil. If the solvent (i.e. the mobile phase) is sufficiently volatile, the paper can be dried in a fume-cup-board. In case of less volatile solvents, the paper can be dried by a hot-air blower or by a drying oven.

(vi) *Detection of Spots* In case of coloured compounds, the separated spots can readily be detected. But, spots of colourless compound are to be detected by specific reagents. The location regent is applied by sparing the paper or by rapidly dipping the paper in a solution of h location regent in a volatile solvent, viewing under UV light is also useful for locating the spots.

(vii) *Factors on which R_f Value Depend* As stated earlier, the R_f value of a compound is more or less constant. Nevertheless, the R_f value depends upon the conditions of chromatography, such as the nature of the solvent, nature of the compound, quality of paper, direction of flow of solvent, and temperature. Since fluctuation of temperature causes uneven movement of he solvent, the R_f undergoes a change. However, it is a physical constant for a given compound provided the conditions of chromatography are specified. If the method is standardised for known compounds, the R_f values can be used for identification of individual compounds.

How do R_f values change with the change of solvent can be known from their values for some amino acids in different solvents.

R_f Values of Amino Acids in Different Solvents

Amino acid	1	2	3
β-alanine	0.10	0.22	0.66
Arginine	0.02	0.17	0.89
Aspartic acid	0.01	0.21	0.19
Glutamic acid	0.02	0.20	0.31
Glycine	0.07	0.24	0.41

1: Amyl alcohol saturated with water.

2: 2, 6-Lutidine-collidine-water (1 : 1 : 1)

3: Phenol-water (10: 2) in presence of 3% NH_3 or 1: 1 acetic acid.

(viii) *Applications* Some of the applications of paper chromatography are given below:

(a) Separation of organic acids

Organic acids: oxalic, malonic, succinic, tartaric, adipic, malic, fumaric and citric.

Chromatographic Paper: Whatman No. 1

Preparation of Solution: In 10% iso-propanol-water, about 1% of individual acid is prepared, so also of the mixture.

Development solvent: n-Butyl formate-formic acid-water (10: 4: 1).

Procedure: Ascending paper chromatography.

Detection of spots: Different acids are detected as yellow spots on a blue black background.

(b) Separation of amino acids

Amino acids: Glycine, arginine, Aspartic acid, and histidine.

Chromatographic Paper: Whatman No.1

Preparation of solution: Solutions of each acid and of the mixture in 10% aqueous iso-propanol with addition of one drop of Conc. HCl are prepared.

Developing solvents Solvent-1: Ethanol-water-ammonia (80:10:10). Solvent-2: n-Butanol-water-acetic acid (60: 15: 25).

Procedure: One dimensional ascending chromatography (using solvent-1),Two-dimensional chromatography (using both solvents 1 and 2), Location reagent: 0.5% solution of ninhydrin in absolute alcohol.

Detection of spots: Amino acids are detected by purple spots on a white background.

(c) Separation of sugars

Sugars: lactose, glucose, fructose, and galactose.

Chromatographic Paper: Whatman No.4.

Preparation of solution. Aqueous solution

Development solvent: n-Butanol-water-acetic acid (60: 15: 25).

Procedure: Descending paper chromatography.

Location reagent: Aniline hydrogen phthalate in acetone.

(d) Separation of cations and anions

Paper chromatography is also useful for separation of cations and anions.

16.5. COLUMN CHROMATOGRAPHY

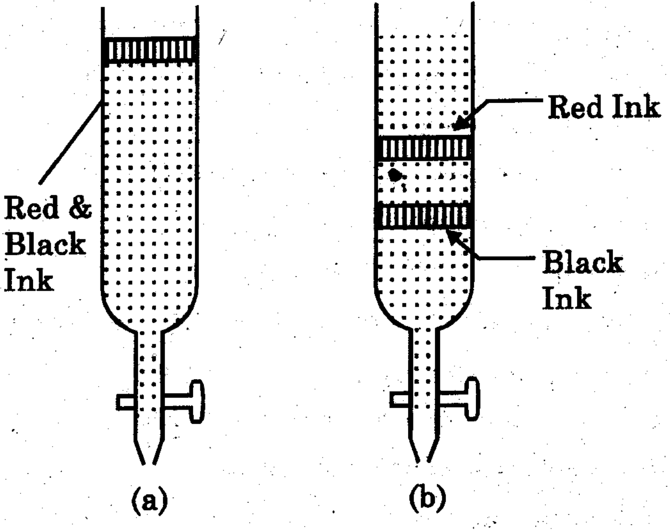
The idea of column chromatography was coined for the first time by an American petroleum chemist D. T. Davy (1897). He used this method for the study of the differences in chemical compositions of different natural petroleum products. The important use of column was soon realised by other workers who were confronted with the problems in petroleum fields. Since then, a number of workers were involved with this technique for more complicated cases. The advantage of this method lies in the fact that it is very simple to carry the experiment; even a small glass tube or burette is enough in which the experiments can be carried out.

What is column chromatography?

Column chromatography is defined as the uniform percolation of a liquid through a column of finely divided substances. The selected substance selectively retards certain components of the liquid.

The interaction of a substance with the stationary phase may occur in several ways.

1. There may be direct interaction between the substance and the surface of the phase.
2. The stationary phase may merely hold a second fluid phase so that the distribution involves a partition between two liquid phases.



(a) (b)

Fig. 16.4

When the solution containing definite proportions of red and black inks is allowed to pass through a column filled with the adsorbent like alumina, at the top of the column, there is no distinction in these two types of inks (Fig. 16.4a). This happens because the two inks are adsorbed in the same region. Now if pure solvent is added at the top and the stop-cock is opened at the bottom, the solvent flows through and while flowing it takes away the inks with it. The coloured zones start moving down the column. With the progress of the time and flow of solvent, the inks are separated from each other. Finally, after some time it is seen there is a division into two parts and colourless zones appear between them (Fig. 16.4b). When the basic idea of the separation is achieved further flow of the solvent is stopped and adsorbents containing each ink are separated form which the inks are taken out after dissolving in water. This is what is known as column chromatography.

This method has been used successfully in many complicated systems and is not limited to coloured solutions only. For each type there are definite disciplines which are taken into considerations and which will be discussed later on.

The important things which must be taken into consideration at the offset are the types of solvents, adsorbents, design of the apparatus and the nature of the substance to be identified. As the case may be, depending upon the viscosity and other factors of the solvent the rate of flow may be increased or decreased.

Adsorbents There are many adsorbents which can be used in the columns like cellulose, silica gel, alumina, magnesium oxide, $BaSO_4$, ZnO, ThO_2, BeO, etc. But the selection cannot be made arbitrary because there are many factors which guide about their choice. They are as follows:

1. The adsorbent should be so selected such that there is no reaction wit the substance to be separated.
2. The adsorbent should not catalyse the decomposition of the substances.
3. The adsorbent should be insoluble in the solvent to be used.
4. As far as possible the adsorbent should be colourless more especially in those cases where the zones with coloured substances are to be separated.

5. The properties of the adsorbent should remain the same throughout, irrespective of the experiment operation.

6. Particle size of the adsorbent should be uniform. Amongst all, the question of particle size is of fundamental importance. It has been seen that the adsorbents with fine particles are most helpful in giving rapid separation of the components. But this has one serious problem which is of the slow rate of filtration through the column. On the other hand the use of the large particle size adsorbent or coarse powder is generally avoided. This leads to the formation of irregular zones and also cause slow attainment of the equilibrium between the, substances which are adsorbed and not adsorbed in the solution.

For most practical purposes, alumina is generally used for chromatographic work. Before use alumina is heated for 4-6 hrs. which is then cooled in the desiccator This alumina can be used over and over again after recovering in alcohol. This product is then heated strongly for several hours. Besides, magnesia is another useful adsorbent which can also be successfully used. The sample of magnesia is made active by dehydrating the hydroxide, by heating or rotating the carbonate. The properties of magnesia is very much similar to alumina. Other substances like Na_2SO_4, $MgSO_4$, $Ca_2(PO_4)_3$ can also be used.

Due to the solubility relationship of many adsorbents with the organic solvents their extensive use have been limited. However, sucrose, starch have proved to be very successful for the separation of chlorophylls.

Charcoal is another adsorbent which is very cheap. But it is rarely used simply because of its intense colour and general dirtiness. But in certain cases it has proved of extreme importance.

There is no simple guideline between the chemical structure and adsorptive affinity. Still some generalisation have been made, e. g. olefinic linkages increases the adsorptive affinity. Likewise the phenolic and ketonic groups also increase adsorptive affinity. It has been found that aromatically attached halogen atoms make the substances more strongly adsorbed.

Based on the strength and other properties the adsorbents have been classified as given in the following table.

Classification of the Adsorbents

Weak adsorbent	Sucrose, inulin, starch, talc, etc.
Intermediate adsorbent	Calcium carbonate, calcium phsophate, magnesia, slaked lime etc.
Strong adsorbent	Alumina, charocoal, etc.

Developers There are substances which are used to produce colour with the colourless solution. These are known as developers. The developers should have less affinity for the adsorbent than the ions which are under examination. The standard reagents used as developers are hydrogen sulphide, ammonium sulphide, potassium thiocyanate, and potassium ferrocyanide.

Solvents There are many types of solvents that can be used in column chromatography. The choice is determined by factors like polarity and solubility relationship. In this method there are three methods of separation. They are

(i) Adsorption

(ii) Partition

(iii) Ion exchange

Adsorption depends upon the nature of both solid and liquid phases. In those cases where only one type of adsorbent is used a number of solvents can be used. In this method it is the purity of the solvent which plays very significant role. The development may be affected considerably by the presence of impurities. The strength of adsorption increases with increasing polar nature of materials. The substances are always added in solvent of non-polar in nature. This is because the OH groups present in water and ethanol would lead to desorption process.

In the partition process of separation, the same type of solvents are used as in paper chromatography. But in the ion exchange process of separation, the sample is poured on ion exchanges where the eluant gives the separated substances by the exchange of ion.

In general, it can be said that the solvents have many important roles. Firstly they put the mixture on the column, secondly they bring the separation of the substances into different zones and thirdly and finally they elute the contents of each separated zones. For all these processes, sometimes, same solvents may be used but it is always advantageous to use different solvents for different process.

The solvents which are used follow the sequence given as:

Petrol ether
Carbon tetrachloride
Cyclohexane
Carbon-disulphide
Ether
Acetone
Benzene
Alcohols
Water
Pyridine
Acetic acid
Mixture of acids or bases with water
Alcohol or pyridine
Organic esters

Amongst the solvents given in the above table, the solvents which are on the top are generally used for preparing solutions which are ultimately poured on the adsorbent. Alcohols are used for eluting the final fractions for developing the chromatogram. Very often the same solvent is used both for making the solution as well as for development. A wide range of solvents are used for complex substances.

In some cases volatile solvents are used which have boiling points in the range of 40 — 80°C. As far as possible the use of volatile solvents are avoided especially in those cases where the use of suction pump is made for increasing the flow rate. In this case boiling of the solvents may take place which will spoil the whole set-up.

Viscosity of the solvent is another important factor and therefore the proper combination of adsorbent and solvent is very important. In standard cases, there stands no difficulty but the problem arises with unknown cases. In such cases the only solution is to take resort to trial experiments with some solvents and adsorbents which after a careful study gives the proper solution.

Columns The columns used are very simple. The simplest is a length of the glass tube which is drawn at one end to form a narrow tube. The opening of the tube is closed by putting a cotton or glass wool. This serves the purpose of retaining the absorbent. In cases when large volume of solvent is to be used a large reservoir is fixed at the top of the column. In the collecting flask a side arm is provided which serves the purpose of suctioning for increasing flow rate.

In those cases where the substances are oxidised in the presence of air, a flow of an inert gas like nitrogen is maintained. The geometry of the column depends very much on the form and size of the zones to be separated. Generally a length breadth ratio of 5: 1 or 8: 1 is satisfactorily used. Narrow columns are used where very narrow zones are to be separated.

Packing of the Columns It is not the question about the column which is important but what matters very much is the packing of the column. While packing, careful attention has to be paid. There are two methods of packing the columns which are

(i) Wet packing

(ii) Dry packing

1. Wet Packing The column is clamped in the vertical position and its lower end is plugged. The plug is wet by pouring some amount of the solvent into it. Now a slurry of the adsorbent and the solvent is made which is then introduced into the column slowly through the side of the column and in the presence of the solvent. In case if there is some air bubble in the plug or at bottom of the column the case is removed by pushing with a glass rod. The pouring of slurry is continued until the column of desired height is obtained. The bottom of the column is opened to remove excess of solvent.

The adsorbent is allowed to settle down and is ready for use.

This type of packing is very common with adsorbent like alumina, and magnesia, magnesia, etc. It is to be carefully noted that the top of the column is nerver in a dry position.

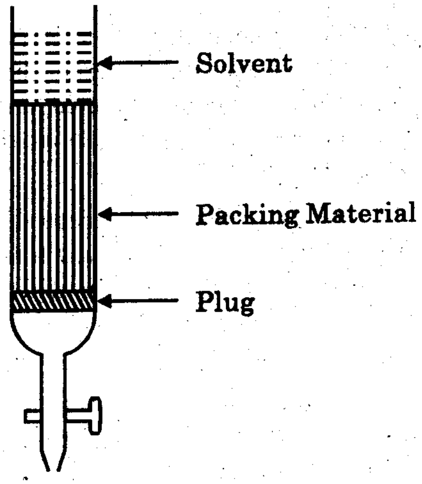


Fig. 16.5

2. Dry Packing A small amount of powder is taken which is then sprinkled in the column filled with the solvent. In actual sense the adsorbent is sprinkled to a depth of 1.2 cm. A rod with a sticking cork is selected so that its diameter is slightly less than the diameter of the column. The hole is then tampered with the rod so that the adsorbent goes down (Fig. 4). While doing this type of tampering, care is needed to avoid packing layers of which some are tight and some are not. Alternatively the column is tapped with fingers so that the adsorbent settles down at the bottom. Likewise adsorbents are added to the extent so that it covers the height of the column required for the purpose. When such height is achieved, the column is ready for use. Air which is trapped in is removed by the tapping technique.

Method of Separation The mixture which is to be separated is dissolved in the solvent to give a concentrated solution. This solution is then introduced into the column in a stepwise manner by means of a pipette. The stop cock at the bottom is opened and solvent is allowed to run down. The eluting solvent is then added and allowed to flow through the medium. This flow is continued until the mixture is completely separated into components.

This separation can be done in two ways. In first method the solvent is passed through the column until the zones are washed out completely. The eluted solvent is collected in a separate vessel. The second method is the one in which the addition of eluting solvent is continued till different zones are obtained separately. The adsorbent with the zones is taken out and each zone is separated with the help of a knife. After that each zone is dissolved in suitable solvent and then estimated by usual standard methods.

Identification of Compounds The applicability of chromatography is not limited to coloured solution only but can be equally used with the colourless solution as well. When the samples used in the column are coloured there stands no difficulty in ascertaining the position and also in its identifications. But the situation is complicated with colourless solutions. When direct visual methods are not applicable, the handling of such solutions involves some devise by which their position can be located on the chromatogram.

One of the methods is to carry out the elution for sufficient length of time and then taking out the packing material out of the column. The column is then cut into small pieces which is then extracted and identified. But this method suffers from many disadvantages. It is not easy to cut the column material equally at all the times with the help of the knife.

The most commonly method is to divide the eluted solvent into many fractions. Thus a large number of small fractions are collected and then analysed by suitable methods. On analysing it would be seen that some of the fractions contain the compounds, whereas some of them do not. The fractions which do not have any components are rejected.

But the collection of large number of fractions is very tedious and unmanageable .Apart from this, it is very time-consuming. Now-a-days apparatuses are available by which the collection of fractions can be done automatically. This is know as automatic fraction collector.

There are other methods like the use of UV lamp, which is generally used. There are many substances which are just colourless in ordinary light but fluoresce strongly in UV light. The columns are directly examined under UV lamp. The colour and intensity of the compound which fluoresce depend upon factors like nature of solvent and adsorbent. The use of UV light is advantageous when using dark adsorbent like charcoal. But there are limitations with the use of UV lamp. There are substances like silver salts and sterols which are so sensitive to UV light that they cannot be exposed directly.

For those substances which are not fluorescent, some other devices have been employed. In certain cases reagents known as developers are added which form coloured products, e. g., vitamin A is located with antimony tetrachloride in chloroform where it gives blue colour. In these cases where these methods are also not suitable helps, are taken of the knowledge of viscosity, refractive index, and density, etc. which are compared with the standard literature values.

Questions

Q. 1. What is chromatography? Give its historical background.

Q. 2. Classify chromatography on the basis of various phenomenon.

Q. 3. Explain the following terms with suitable examples.

(*a*) Stationary phase.

(*b*) Mobile phase.

(*c*) Partition chromatography

(*d*) Ion exchange chromatography

(*e*) Eluent

(*f*) Chromatogram

Q. 4. What is paper chromatography? Discuss its various types.

Q. 5. Choice of a paper and solvent are main back bones of paper chromatography techniques. Comment.

Q. 6. What is column chromatography? Explain it with suitable examples.

Q. 7. What types of methods are involved in packing of column?

Q. 8. How would you discuss method of separation and identification of compounds in column chromatography?

Q.9. Justify/comment on the following statements.

(*a*) Chromatography is a separation technique.

(*b*) Chromatography is based on partition principle.

(*c*) Chromatography is based on adsorption principle.

(*d*) Chromatography is used to separate only color compounds.

(*e*) Paper chromatography is a type of partition chromatography.

(*f*) Column chromatography is a type of adsorption chromatography.

(*g*) The adsorbent should be insoluble in the solvent.

(*h*) Compound can be identified by chromatography.

(*i*) The R_f value is 1

(*j*) Chromatography is only a qualitative technique.

Chapter Seventeen

SPECTROSCOPY

17.1. ELECTROMAGNETIC RADIATION

The nature of light and other radiation was the subject of much investigation since Newton's experiments in the 17th Century. It is a form of energy and may be considered either as a continuous wave travelling through space, or as discrete photons of the same energy. For many spectrometric techniques, the wave approach is more useful. Figure 17.1 shows a representation of an electromagnetic wave as an oscillating electric field of amplitude E and a magnetic field of amplitude H at right angles to each other.

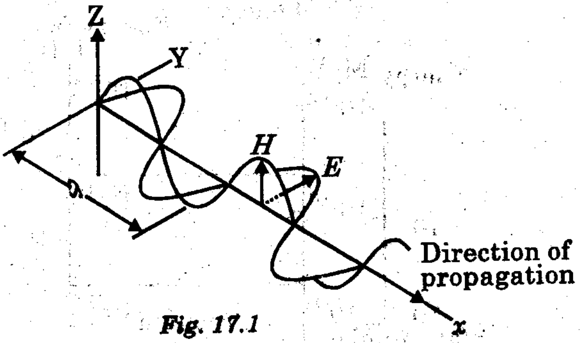


Fig. 17.1

In a vacuum, this wave travels at a fundamental constant speed, c

$$c = 2.997925 \times 10^8 \text{ ms}^{-1}$$

The wave is characterized in three ways, as shown in Figure 17.1.

The *wavelength*, λ, is the distance between equivalent points on the wave train, for example, between two consecutive positive crests, or two points where the wave increases through the zero value. The wavelength has been expressed in a variety of units, but these should now all be related to the metre, as shown in Table 17.1.

Table 17.1. Wavelength units

Name	Units
femtometer	10^{-15} m = 1 fm
micrometer	10^{-6} m = 1μm
nanometer	10^{-9} m = 1 nm

Older units such as the Angstrom (Å) are used in earlier work.

$1\text{Å} = 10^{-10}$ m.

The *frequency*, ν, is the number of cycles of radiation passing a point in space per second. It is expressed as s^{-1}, or hertz (Hz).

The above definitions show that the relation between thse quantities is

$$\nu = c/\lambda$$

Sometimes the wave number, $\bar{\nu}$, is used where

$$\bar{\nu} = 1/\lambda$$

The *wave number* is frequently given in cm^{-1}, especially in infrared spectrometry, and it should be noted that $100\ m^{-1} = 1\ cm^{-1}$. (Note that if there are 100 per metre, there is 1 every centimeter).

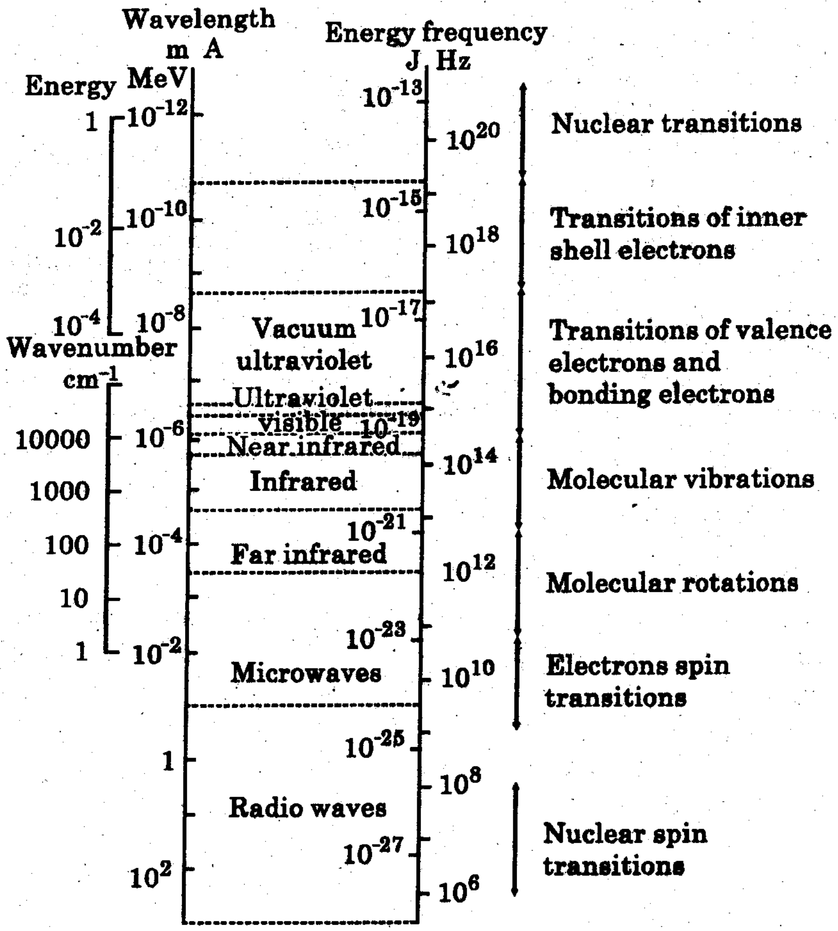


Fig. 17.2. **The electromagentic spectrum from γ-ray to radiowave.**

The *energy*, ε, of the radiation is most important, since it defines the molecular or atomic processes which are involved. For a single photon,

$$\varepsilon = h\nu = hc/\lambda = hc\ \bar{\nu}$$

where h is the Planck constant, 6.62608×10^{-34} Js^{-1}.

Occasionally, the *electron-volt* is used as a unit for energy, where

$$1\text{eV} = 1.602 \times 10^{-19}\text{J}$$

Thus, a wavelength of about 5.00 μm is equivalent to a frequency of 5.996×10^{13} Hz, a wave number of 2000 cm^{-1}, and energy 3.973×10^{-20}J. This corresponds to molecular vibrational energy. It is sometimes an advantage to consider 1 mole of photons. For the above example the molar energy will be

$$N_A\varepsilon = 6.022 \times 10^{23} \times 3.973 \times 10^{-20} = 23.9 \text{ kJ mol}^{-1}$$

Table 17.2 shows the very wide range of wavelengths and energies that relate to spectrometric techniques and Figure 17.2 relates this to the electromagnetic spectrum.

When electromagnetic radiation is directed at an atom or molecule, the atom or molecule can absorb photons whose energy corresponds exactly to the difference between two energy levels of the atom or molecule. This gives rise to an absorption spectrum. It must be noted, however, that when large change occurs (e.g. due to an alternation in the electronic structure of a molecule) the less energetic changes, such as the vibration of bonds and rotation of the molecule, will happen as well, leading to more complex spectra.

Table 17.2. The regions of the electromagnetic spectrum

Wavelength range	Frequency (Hz)	Region	Spectra
100 – 1 m	$3 - 300 \times 10^{6}$	Radiofrequency	Nuclear magnetic resonance
1 – 0.1 m	$0.3 - 3 \times 10^{9}$	Radiofrequency	Electron spin resonance
100 – 1 mm	$3 - 300 \times 10^{9}$	Microwave	Rotational
1 – 0.02 mm	$0.3 - 15 \times 10^{12}$	Far infrared	Vibrational
20 – 2 mm	$15 - 150 \times 10^{12}$	Infrared (IR)	Vibrational
2 – 0.8 mm	$150 - 375 \times 10^{12}$	Near infrared	Vibrational
800 – 400 nm	$375 - 750 \times 10^{12}$	Visible	Electronic
400 – 150 nm	$750 - 2000 \times 10^{12}$	Ultraviolet (UV)	Electronic
150 – 2 nm	$2 - 150 \times 10^{15}$	Vacuum UV	Electronic
2 – 0.1 mm	$150 - 3000 \times 10^{15}$	X-ray	Inner shell electronic
0.1 – 0.0001 nm	$3 - 3000 \times 10^{18}$	γ-ray	Nuclear reactions

The regions overlap considerably, and the range is approximate.

17.2. ATOMIC ENERGY LEVELS

Quantum theory shows that atoms exist only in the discrete states, each of which possesses a characteristic energy, defined by quantum numbers, which characterize the atomic state. Transitions may occur only between these levels, and even then some transitions are unfavorable. Electrons occupy atomic orbitals with characteristic spatial distributions around the nucleus.

The discrete energy levels arise naturally as the allowed solutions of the wave equations for the system under consideration. Electronic energy levels in atoms may be accounted for by solving the schrodinger wave equation.

Atoms have electronic energy levels and atomic orbitals that are defined by three quantum numbers that can have integer values.

n	principle quantum number
l	orbital angular momentum quantum number
m	magnetic quantum number, and
m_S	electronic spin quantum number which ca be +1/2 or −1/2 only.

The energy of an orbital is mostly dependent on its principal quantum number n. In fact, for hydrogen, the energy depends only on n. There are only certain allowed values of the other quantum numbers. For example, l may take integer values from 0 to $(n - 1)$; m values form $+1$ to -1 and m_S + 1/2 or −1/2.

The different orbitals are described by symbols:

s(sharp)	for $l = 0$
p(principal)	for $l = 1$
d(diffuse)	for $l = 2$
f(fundamental)	for $l = 3$

For atoms other than hydrogen, the other quantum numbers modify the energy slightly. For example, the 3p level where $n = 3$, $l = 1$ has a higher energy than the 3s with $n = 3$, $l = 0$. These are often referred to as subshells.

The atoms of the various elements are built up by adding electrons into the next empty level with the lowest energy, remembering that each level may contain two electrons with opposite spins ($m_S = \pm 1$). This is called the *Aufbau principle*. An example may be used to illustrate this. The

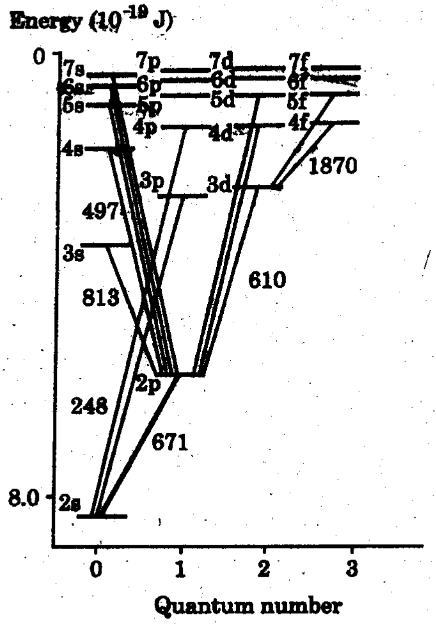


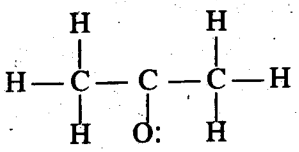
Fig. 17.3. Energy level diagram for the lithium atom showing the wavelength in nm for a number of transitions. Note: the transition at 671 nm is used in flame emission spectrometry.

element lithium, atomic number 3, has 3 electrons. In the unexcited or ground state, these must occupy the lowest energy levels, which are the 1s and 2s levels. Two electrons fill the 1s level and one goes into the 2s.

Figure 17.3 shows the sets of atomic energy levels with $n = 2, 3, 4, 5, 6$ and 7 and $l = 0, 1, 2$ and 3. The diagram also shows that the most favorable transitions occur when l changes by ±1. It is worth noting that the transition shown in bold is used to measure lithium in atomic emission spectrometry (see Topic E4). In an excited state, the electron population is altered. In transition elements there are many low-lying energy levels and excited states with similar energies.

17.3 MOLECULAR ENERGY LEVELS

Molecules also possess energy levels defined by quantum numbers. When atoms combine into molecules, their orbitals are changed and combined into molecular orbitals. As an example the atomic orbitals of carbon, hydrogen and oxygen combine in the molecule of propanone, C_3H_6O so that the three carbons are linked in a chain by single (σ) bonds, the two outer carbons are each linked by σ bonds to three hydrogens, while the central carbon is linked by a double bond to the oxygen, that is by both a σ and a π bond. Additionally, the oxygen still has unpaired or nonbonded n electrons.



$$\begin{array}{ccccccccc} & & \mathrm{H} & & & & \mathrm{H} & & \\ & & | & & & & | & & \\ \mathrm{H} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{H} \\ & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{O}: & & \mathrm{H} & & \end{array}$$

This results in a set of bonding and corresponding antibonding electronic orbitals or energy levels as shown schematically in Figure 17.4. Transitions may occur selectivity between these levels, for example between the π and π^* levels.

In addition, molecules may vibrate, and the vibrational energy levels are defined by the vibrational quantum number, v. In the gaseous state, molecules may also rotate freely, and the rotational energy levels are defined by the rotational quantum number, J, In the condensed states of solid and liquid, rotation is restricted. With nuclear spin, the nuclear spin quantum number, I, is important.

In more complex molecules, additional rotational, vibrational, electronic and nuclear energy levels are possible, and some simplification is usually employed in interpreting their spectra, as described in the later topics in this section (Fig. 17.4).

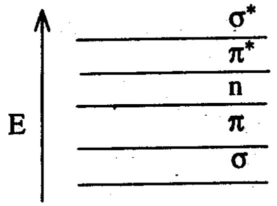


Fig 17.4. Schematic of molecular orbitals or energy levels.

Although the technique of mass spectrometry does not normally involve electromagnetic, radiation, molecules or atoms are ionized and dissociated by the removal of electrons using high-energy techniques. The ions are then dispersed, detected and displayed as mass spectrum. The information given by measurements using mass spectrometry is helpful both in combination with atomic emission spectrometry and in molecular structure elucidation, where it is used in conjunction with other molecular spectrometric techniques.

17.4 POSSIBLE TRANSITIONS

For a given set of energy levels, defined by their quantum numbers, there are several possible types of transition (Fig. 17.5). Consider just two energy levels, the upper with energy E_u and the lower, E_L separated by an energy difference $\Delta E = E_u - E_L$

There is a definite statistical probability of transitions between these levels, which depends on the structure and population of the energy levels and also on ΔE. If energy is supplied to the sample, for example, by passing electromagnetic radiation through it, the sample atoms or molecules may absorb energy and the promoted into the higher energy. The radiation emerging from the sample will be less intense. If the sample is activated in another way, for example thermally, then atoms or molecule are promoted to the higher energy level and emit energy in falling back to the lower level.

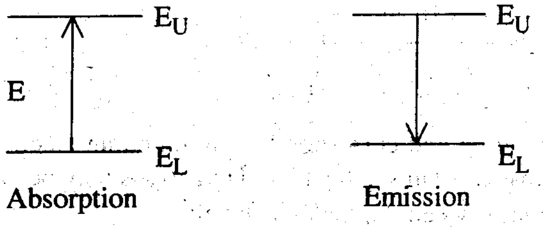


Fig. 17.5 Absorption and emission of radiation.

If a sample absorbs energy, and the at more molecules then drop back to an intermediate level, before returning to the lowest level, emitting radiation, this is called fluorescence. The energy of the fluorescent emission is generally lower than that initially absorbed.

17.5. QUANTITATIVE SPECTROMETRY

In emission spectrometry, the intensity of the spectral line is related to the number of emitting species present in the emitting medium and to the probability of the transition. If there are N_o atoms in the ground state, then the number of excited atoms capable of emission, N_E is given by the Boltzmann distribution law.

Therefore, the emitted intensity, I, is given by an equation of the form

$$I = A \cdot N_o \exp(-\Delta E/kT)$$

where A is a constant for a particular transition, incorporating the transition probability, the degeneracies and any reduction due to other unwanted transitions, such as ionization in atomic spectra. Under constant temperature and other excitation conditions, this may be written

$$I = k'c$$

where k′ is a constant and c the concentration.

The constant, k′, may vary in a complex way as c varies, and calibration, plus the use of an internal standard must be used to obtained reliable quantitative results.

Beer-Lambert absorption law For absorption spectrometry the intensity of the incident (exciting) radiation is reduced when it interacts with the atoms or molecules, raising them to higher energy levels. In order to interact, the radiation must come into contact with the species. The extent to which it does this will depend on the concentration of the active species and on the path length through the sample.

As the radiation of a particular wavelength passes through the sample, the intensity decreases exponentially, and Lamberd showed that this depend on the path length, *l*, while Beer showed that it depended on the concentration, c.

The two dependencies are combined to give the Beer-Lambert absorption law:

$$I_t = I_0 \exp(-k'cl)$$

where I_0 and I_t are the incident and transmitted intensities, respectively. Converting to the base 10 logarithmic equation.

$$\log(I_0/I_t) = A = \varepsilon\, c\, l$$

where A = the absorbance and ε = the molar absorptivity.

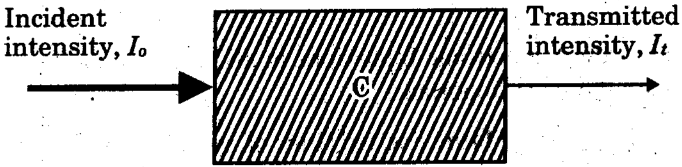


Fig. 17.6(a). The absorption of radiation by a sample.

The value of ε (sometimes incorrectly referred to as the 'extinction coefficient') is most usually quoted for a concentration of 1 *M* and a path length of 1 cm. However, if the concentration is expressed in mol m^{-3} (= 1000 × M) and *l* is expressed in meteres (= cm/100) then the units of ε are m^2 mol^{-1}, suggesting that the absorptivity depends on the effective capture area of the species. This indicates that ε combines the transition probability and the nature of the absorbing species. (Note that ε in $m^2\ mol^{-1}$ = ε in $(\text{cm}\ M)^{-1}/10$.

Very high values of ε, for example over 10 000 for the UV, π – π* absorption of conjugated polyenes, indicate a favored transition. Lower value, for example, ε is less than 100 for the n – π* absorption of ketones, show that the transition is lessfavoured or 'forbidden'.

The Beer-Lambert law applies equally to infrared absorption spectra. Spectra are plotted either a absorbance, A, or as the transmittance, T, against wavelength, frequency or wavenumber, where

$$T = (I_t/I_o)$$

or sometimes as percentage transmittance = 100 T

If the relative molecular mass is unknown, comparison may be made using $E_{1\%}^{1cm}$ representing the absorbance of a 1% solution in a 1 cm cell. It is worth noting the range of values which each of these parameters may take. A can have any value from 0 to infinity. T must between 0 and 1, and ε usually has values from about 1 to 10^6.

17.6. FLAME ATOMIC EMISSION SPECTROMETRY

Principle When the atoms of samples are excited to higher electronic energy levels in flames they emit radiation in the visible and UV regions of the electromagnetic spectrum. Emission intensities may be measured to analyze for metals, especially alkali and alkaline earth elements.

When the salts of some metals are introduce into a flame, they impart characteristic color to it. For example, sodium salts give an intense yellow-orange color. This is the basis of the 'flame test' used in qualitative analysis. The thermal energy of a gas-air flame is quite low, since the temperature is usually less than 2000 K and only those transitions of low energy are excited.

Early atomic emission instruments used electric arc or spark excitation. The higher energy of these sources produced a very great number of emission lines throughout the visible and UV regions. However, simultaneous measurement of a large number of elements possible,

With flame excitation, electronic transitions in alkali and alkaline earth metals, as listed in Table 17.3 are the most important.

Table 17.3 Flame excited lines of some metals

Metal	Wavelength/nm	Color
Lithium	670	Red
Sodium	589[a]	Orange-yellow
Potassium	766[a]	Red
Rubidium	780[a]	Dark red
Magnesium	285	UV
Calcium	622[b]	Orange
Strontium	461	Red
Barium	554	Green
Thallium	535	Green
Copper	513	Green

a. These lines are doublets. b. This line is due to emission from a calcium hydroxide band.

Table 17.4 Gas mixture used in flame atomic emission spectrometry

Fuel	Oxidant	Maximum flame temperature (K)
Neutral gas	Air	1800
Propane	Air	1900
Hydrogen	Air	2000
Acetylene	Air	2450
Acetylene	Nitrous oxide	2950
Acetylene	Oxygen	3100

The flame may be produced by burning various gas mixtures, some of which are listed in Table 17.4.

The structure of the flame comprises an inner cone, which is the primary reaction zone for combustion, and the outer cone or mantle where secondary reactions occur. For the best results, the optical axis is arranged to pass through the flame at the junction of the inner and outer cones. The supply of fuel and oxidant is adjusted to give an optimum burning velocity.

The process that occur to transfer the sample to the flame may be summarized as follows:

(i) Production of an aerosol from solution (nebulization)

(ii) removal of solvent $MA(aq) \rightarrow MA(solid)$.

(iii) vaporization of sample $MA(solid) \rightarrow MA(vapour)$

(iv) atomization $MA \rightarrow M^{\bullet} + A^{\bullet}$

(v) excitation $M^{\bullet} \rightarrow M^{*}$

(vi) emission $M^{*} \rightarrow M^{\bullet}$

Ionization may also occur to give the M^{+} ion.

These stages each depend on the experimental parameters used in the instrument. For example:

- the viscosity of the solvent, which affects the aerosol production;
- the nature of the solvent, which may affect the vaporization
- the rate of fuel flow, which can change the nebulization and the time the atoms spend in the flame;
- the flame temperature, which controls the evaporation, the atomization and the extent of ionization; and
- the nature of the flame.

Because of the chemical reactions taking place in the flame, various species such as OH radicals, CO, water and other combustion products are present, and may give a background emission throughout the UV-visible range. Compensation for this background must be made.

Instrumentation. Flame atomic emission spectrometers have similar optical systems to those of UV-visible spectrometers, but the source of radiation is provided by the sample itself. A flame photometer is a simpler instrument employing narrow band pass optical filters in place of a monochromator Fig. 17.6(b). The sample is prepared s a solution, which is drawn into a nebulizer by the effect of the flowing oxidant and fuel gases. The fine droplets produced ;pass into the flame where sample atoms are progressively excited. The emitted radiation passes through the monochromator or filter and is detected by a photocell or photomultiplier tube.

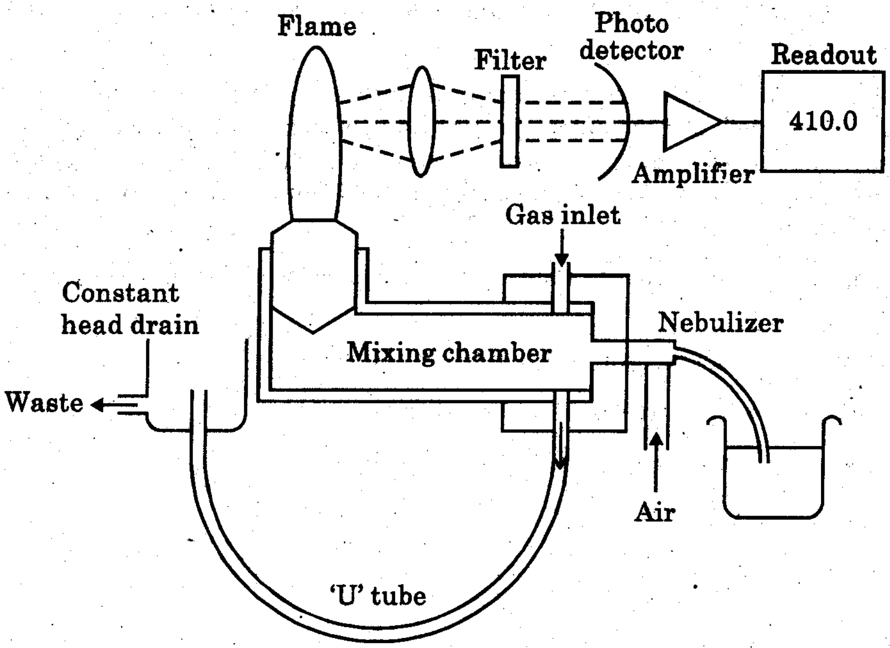


Fig. 17.6(b). Schematic of a flame photometer. Reproduced with permission from Sherwood Scientific Ltd.

Applications Flame atomic emission spectrometry (FAES) and flame photometry are used widely for the determination of alkai and alkaline earth metals. The rapid determination of Na, K an Ca in biological and clinical samples is one of the most important applications; for example, calcium in beer, milk or biological fluids. The usual solvent is water; but organic solvents may be used to enhance the intensity, since they produce smaller droplets, and have a smaller cooling effect on the flame.

The instrument is calibrated with standard solutions of the elements to be determined and the intensity of the emission recorded at each characteristic wavelength. A calibration graph is constructed after correcting for background (blank) emission.

The advantages of FAES and flame photometry are that the instrumentation is relatively simple and measurements can be made quickly. A disadvantage is the sensitivity of the emission intensities to changes in flame temperature due to variations in gas flow, or cooling by the solvent.

17.7. ATOMIC ABSORPTION SPECTROMETRY

Principles The energy levels of atoms are specific and determined by the quantum numbers of the element. If ground state atoms are excited as described earlier, some will be promoted to higher energy levels, the transitions being characteristics of the element involved. Atoms may be excited by incident UV or visible electromagnetic radiation, and if the wavelength (or frequency) corresponds to that of the transition, it will be absorbed. The degree of absorbance will depend on concentration, in the same way as with other spectrometric techniques. This techniques is known as *atomic absorption spectrometry* (AAS).

The sample is generally volatilized by a flame or furnace. The temperature is not usually sufficient to produce ionization, so that the vapor contains largely atoms. These atoms absorb the characteristic incident radiation resulting in the promotion of their electrons to an excited state. They may then undergo transitions to other energy levels and re-emit radiation of another, but sill characteristic, wavelength as fluorescence. This allows determination by a *atomic fluorescence spectrometry* (AFS).

Ideally, the lines of an atomic spectrum should be very narrow, of the order of 10^{-5} nm. However, thermal movement causes Doppler shifts and pressure broadening due to collisions among the atoms, and also electrical and magnetic fields in the sample vapor all tend to broaden the lines slightly to about 10^{-2} nm.

If a source emitting a broad band of wavelength were used, the fraction absorbed by a narrow line would be small. It is therefore important to use a source producing a sharp emission line characteristic of the element to be analyzed, for example, a zinc source lamp to determine zinc. These are called resonance line sources, and may be a hollow cathode lamp (HCL) or a electrodes discharge tube. Continum source instruments require very high-resolution monochromators.

In a similar way to the flame emission spectrometers described in earlier, a flame may be used to volatilize the sample. Nonflame atomizers, particularly the graphite furnace, are very useful especially when only small volumes of sample are available.

Instrumentation The source is often a hollow cathode lamp (HCL). This has a glass envelope with a quartz window and contains a gas such as argon, which is excited by an electric discharge. The excited argon atoms bombard the cathode, which is made of the element to be determined and the atoms of that element are then excited in the discharge too. The excited atoms decay back to their ground state, emitting the characteristic radiation. a turret with several lamps allows multi-element determinations.

Electrodeless discharge lamps have a small, sealed cavity containing a minute amount of the element to be measured, or its salt. The cavity is excited by a radio frequency signal passed through a coil, and turned to resonate at a chosen frequency. This excites the atoms to produce the desired emission spectrum.

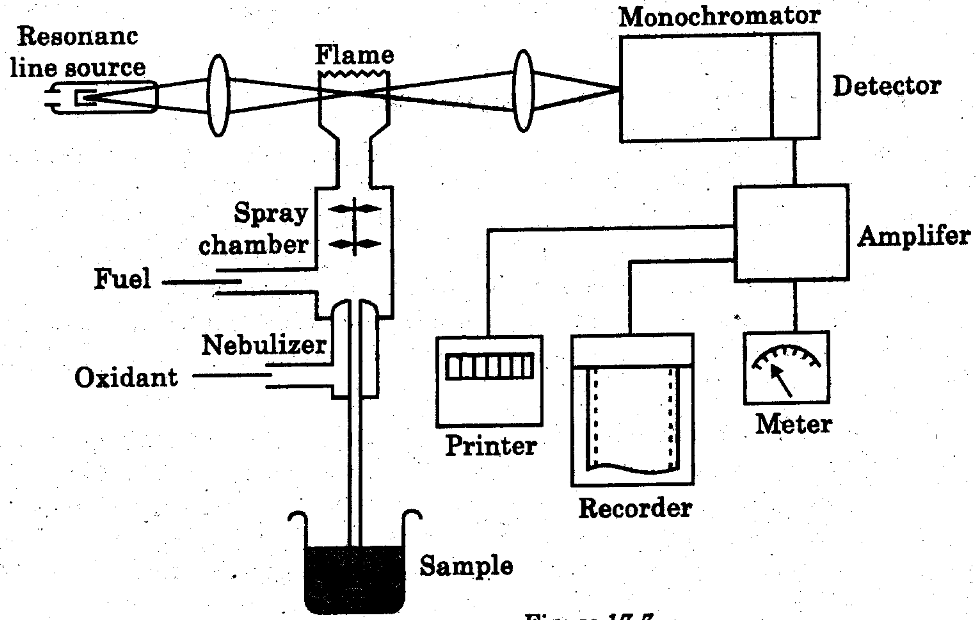


Figure 17.7

For flame vaporization, the sample is usually prepared as a solution that is sprayed into the burner. A flow spoiler removes large droplets, and the sample undergoes a similar sequence of a events to that described in atomic emission, converting it into gaseous atoms. The signal reaches a constant value proportional to the concentration of the analyte element in the sample.

The flame is generally produced using one of the gas mixtures given in Table 17.4. Air-acetylene gives a flame temperature of about 2400 K while air propane is cooler (1900 K) and nitrous oxide-acetylene hotter (2900 K). An alternative vaporization method is it use a graphite furnace, which is an open-ended cylinder of graphite placed in a electrically heated enclosure containing argon to prevent oxidation. Temperature in the region of 2500 K are achieved, and the heating program is designed to heat the sample, deposited on a smaller tube or L'Vov platform, by radiation. The graphite furnace produces a peak signal whose area is proportional to the total amount of vaporized element in the sample.'

The use of graphite furnace atomic absorption (GFAA) has a number of advantages:

- it avoids interactions between the sample components and the flame since atomization takes place in an inert gas steam;
- it gives increased sensitivity because of the longer residence time of the sample in the beam from the source;
- the sensitivity is further increased because a higher proportion of atoms are produced;

- it has the ability to handle small volumes of samples, down to 0.5 – 10 μl, such as clinical specimens;
- the results are more reproducible than flame AA.

One disadvantage is that it is rather slower that flame AAS.

Interferences may be troublesome in AAS. Background absorption by smoke particles or solvent droplets may be removed as detailed above.

Matrix interference, such as any reaction that prevents the sample getting into the flame, may reduce the sensitivity. It is always preferable to run the standard in the same matrix, or to use standard addition procedures (Topic B4).

Chemical interference due to the production of thermally stable compounds, such as involatile phosphates of calcium, may sometimes be dealt with by adding a releasing agent such as EDTA, or by using a hotter flame or a reagent that preferentially forms stable, volatile compounds.

Ionization interference due to the production of ions is most troublesome with alkali metals because of their low ionization potentials. Occasionally, ionization suppressors such as lithium or lanthanum salt, which are easily ionized, are added.

Spectral interference is rare because of the sharpness of the atomic elemental lines, but is difficult to overcome. For example, the zinc line at 21.856 nm is too close to the iron line at 213.856 nm, but the iron line at 271.903 nm could be used to determine iron instead.

In atomic fluorescence spectrometers the detector is placed so that no radiation from the lamp reaches it, often right angles to the incident radiation path. Both HCL and high intensity continum sources, such as mercury lamps, may be used since the fluorescence intensity depends on the intensity of the primary radiation.

Applications The spectrometer should be calibrated by using standard solutions of the element to be determined, prepared in the same way as the sample solution. Usually, acidic aqueous solutions are used; for example, many elements are commercially available as 1000 ppm certified standards in dilute perchloric acid. Organic solvents, such as white spirit (C_{10} alkanes) or methyl isobutyl ketone, may be used if the sample is insoluble in water (e.g. a lubricating oil) Standards can then be made of metal complexes soluble in the organic solvent .The standard solutions should be chosen to 'bracket' the concentration to be determined and, ideally, the calibration curve should be linear in the region.

Multi-element standard stock solutions are useful and permit more rapid determination of several elements of interest.

The techniques are used for many industrial and research purposes, especially:

agricultural samples, particularly the analysis of soils-metal pollutants in solid and water samples are often determined by AAS;

- clinical and biochemical determinations, e.g., the measurement of sodium, potassium lithium and calcium in plasma and serum, and of iron and lead in whole blood;
- metallurgical samples may be assayed to measure impurities;
- oils and petrochemical samples can be analyzed for metals in feed stocks and to detect metals in used oils due to corrosion and wear,
- water samples are extremely important, since pollution may be a health hazard. Nickel, zinc, mercury and lead are among the metals determined.

Atomic fluorescence ha the advantage, compared to AAS, that with a continuous source, several elements may be determined simultaneously. There are, however, problems due to scattered radiation and quenching, but detection limits are lower than for AAS.

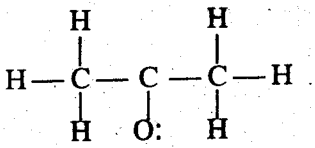
It is particularly suitable for elements that are volatile, such as mercury, or form volatile hydrides, such as arsenic or bismuth, or for elements forming stable volatile organic derivatives.

17.8. ULTRAVIOLET AND VISIBLE SPECTROSCOPY

The ultraviolet (UV) and visible region of the electromagnetic spectrum covers the wavelength range from about 100 nm to about 800 nm. The vacuum ultraviolet region, which has the shortest wavelengths and highest energies (100–200 nm), is difficult to make measurements in and is little used in analytical procedures. Most analytical measurements in the UV region are made between 200 and 400 nm. The visible region occurs between 400 and 800 nm.

The energy levels involved in transitions in the UV-visible region are the electronic levels of atoms and molecules. For example, although light atoms have widely spaced energy levels, some heavy atoms have their outer orbitals close enough together to gives transitions in the visible region. This accounts for the colors of iodides. Transition metals, having partly occupied d or *f* orbitals, often show absorption bands in the visible region and these are affected by the bonding of ligands. For example, iron(III) reacts with the thiocyanate ion to produce an intense red color due to the iron(III) thiyanate complex, which may be used to determine iron(III) in the presence of iron(II).

Organic molecules contain carbon-carbon bonds, and bonds between carbon and other elements such as hydrogen, oxygen, nitrogen, sulfur, phosphorus and the halogens. Single bonds correspond to the bonding σ orbital, which has an associated antibonding σ^* orbital. Multiple bonds may also be formed and corresponds to the π bonding and π^* antibonding orbitals. Bonding orbitals have lower energy, while antibonding orbitals have higher energy. Lone pair electrons on atoms such as oxygen are little changed in energy. Thus, a molecule such as propanone (acetone) has the structure:



$$H-\underset{H}{\overset{H}{C}}-\underset{\ddot{O}:}{C}-\underset{H}{\overset{H}{C}}-H$$

The Single C — H and C — C bonds relate to σ orbitals, the carbonyl double bond to π orbitals and the unpaired electrons on the oxygen to the nonbonding n-levels. The energy levels may be grouped approximately as shown in Figure 1. Transitions between σ and σ* and between π and π* are favored, and those of the n electrons to the higher levels also occur.

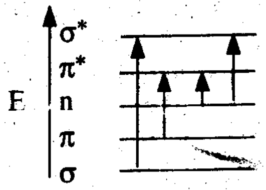


Fig. 17.8.. Typical transitions for organic molecule.

Figure 17.8 shows that σ – σ* transitions require the largest energy change and occur at the lowest wavelengths, usually less than 190 nm, which is below the wavelengths measurable with most laboratory instrumentation. The π – π* transitions are very important, as they occur in all molecules with multiple bonds and with conjugated structures, such as aromatic compounds. The transitions occur around 200 nm but the greater that extent of the conjugation, the closer the energy levels and the higher the observed absorption wavelength. Transitions involving the lone pairs on heteroatoms such as oxygen or nitrogen may be n – σ*, which occur near 300 nm. These values are considerably altered by the specific structure and the presence of substitutents (auxochromes) in the molecules.

Since electronic transitions may occur between states with many vibrational and rotational sublevels, and since these may also be affected by sample solvent interactions, UV and visible spectra of solutions do not generally give sharp lines, but broad bands, as shown in Fig. 17.9. Generally, the peak wavelength λ_{max}, is specified for analytical purposes. The absorbances obey the Beer-Lambert law, which is described earlier.

Instrumentation The source of visible light (400 — 800 nm) is generally a tungsten filament lamp or a tungsten halogen bulb. For the UV (200 — 400 nm) region, the source most often used is a deuterium lamp and arrangements are made to switch between these sources at an appropriate wavelength, often around 380 nm . Xenon arc lamps may also be used.

The sample is generally a dilute solution of the analyte in a solvent with a low absorbance in the region of interest. The nature of the solvent may alter the position of the spectral peaks, as discussed in the next section. The sample solution is contained in a thin-walled silica glass cell, usually with a path of 1 cm, while a matched reference cell contains the solvent alone or a blank of solvent and reagents. If measurements are restricted to the visible region, ordinary glass or plastic cells may be used, but these should be used, but these should not be used for UV work. Occasionally, reflectance measurements are used on opaque surfaces, such as thin layer chromatography plates or material with surface coatings.

The sample should be positioned in the spectrometer after dispersion of the radiation to avoid UV photochemical decomposition. Suitable solvents for UV and visible spectrometry are listed in Table 1.

Dispersion of the spectrum is achieved using silica glass prisms or diffraction gratings. Occasionally, filters are used to select a narrow band of radiation for quantitative analysis. An example of a filter system is a modern fibre-optic photometer. Light from a tungsten lamp passes down the quartz fiber and into the sample solution. A mirror set a fixed short distance away reflects the light back up the fibre through a suitable interference filter set to the wavelength of interest and onto a photodiode detector. This type of system may be used for continuous on-line analysis of sample.

Table 17.5. Solvents for UV-visible spectrometry

Solvent	Minimum usable wavelength (nm)
Acetonltrile	190
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
Ethanol	204
Diethylether	215
Dichloromethane	220

For detection in the UV-visible region, photomultipliers or other photo electric devices are used. Some instruments may use a multi-channel diode array detector. An array of typically 300 silicon photodiodes detects all the wavelength simultaneously with a resolution of about ±1 nm. This provides a great saving in time and improved signal/noise ratio.

The recorded spectrum is generally displayed by plotting absorbance against wavelength, as shown in Figure 17.8. This allows direct quantitative comparison of samples to be made.

For practical purposes, it is important that the sample solution is dilute and that it contains no particulate matter. More concentrated samples may reabsorb the emitted radiation, either due to the sample itself or due to the presence of some other quenching agent. Particles will cause the radiation to be scattered.

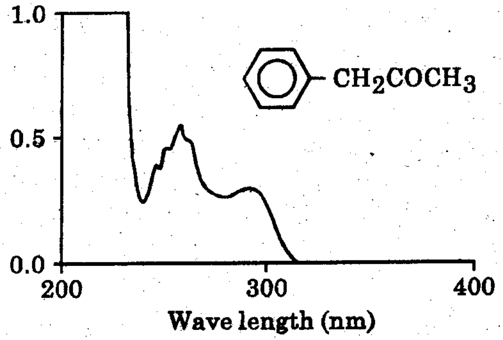


Fig. 17.9 UV absorption spectrum of phenyl propanone.

Applications of UV-Visible Spectrometry

Structure Effects The structures of organic molecules may be classified in terms of the functional groups, which they contain. Where these absorb UV or visible radiation in a particular region they are called chromophores. Some of the chromophores important for analytical purposes are listed in Table 17.6. This shows that the absorption by compounds containing only σ bonds such as hexane, or with lone pairs, such as ethanol, will occur below 200 nm. These compounds are therefore useful solvents.

The effects of conjugation, that is, the interaction of the molecular orbitals between alternate single and double bonds in a chain or rings, greatly affects the absorption characteristics of the chromphore. Since each isolated double bond has a π-bonding energy level and a higher energy π*-antibonding level, when two double bonds are separated by one single bond, the molecular orbitals overlap, and there are two π levels and two π* levels. the separation in energy between the highest filled π level and the lowest empty π* level is smaller and hence the wavelength of that absorption is greater.

Table 17.6. Absorption of simple unconjugated chromophores

Chromophore	Transition	Approximate wavelength (nm)
σ-bonded		
>C—C< / >C—H	σ – σ*	150
Lone pair		
O:	n – σ*	185
>N:	n – σ*	195
>C=O:	n – σ*	195
	n – π*	300
—N=N—	n – π*	340
π-bonded		
>C=C< (isolated)	π – π*	– 180

Thus, ethene $CH_2 = CH_2$ absorbs at about 180 nm (ε = 1500 m^2 mol^{-1}), whereas butadiene, $CH_2 = CH - CH = CH_2$ absorbs at 210 nm (ε = 2100). Long-chain conjugated polyenes; such as the carotenes absorb in the visible region with a very high ε. There is a general rule that states the longer the chromophore, the longer the wavelength at which is absorbs'. It is also generally true that molecules possessing extended conjugation have more intense absorption bands and more complex spectra. Similar arguments apply to conjugation between carbonyl double bonds and carbon-carbon double bonds.

Solvent effects are important, both in considering the position of the absorption maximum and also the nature of the spectral transition involved. For $\pi - \pi^*$ transitions, the excited state is more polar than the ground state, so it will tend to form dipole-dipole bonds with a polar solvent, such as water or ethanol. This will lower the transition entry and raise the absorption peak wavelength. This is called a *red shift (or a bathochromic shift).* Tables of solvent corrections are available in specialist texts.

For $n - \pi^*$ transitions, the ground state is often more polar and may form hydrogen or dipole bonds with polar solvents. This increase the transition energy and lowers the peak wavelength, causing a *blue shift (or hypsochromic shift).* pH will affect the structure of compounds with acidic or basic groups, and may cause considerable wavelength shifts.

Substituents that alter the wavelength or absorptivity of a chromophore significantly are called *auxochromes*, and tables of the effect of substituents plus rules for their application in particular structure are to be found in specialist texts. For example, an unsubstituted, unsaturated ketone would have a peak maximum at about 215 nm. Substitution of a hydroxyl group on the carbon next to the carbonyl (α) raises the peak to 250 nm, and two alkyl groups on the next (β) carbons would raise it to 274 nm.

Table 17.7 lists a few of the substituent effects for aromatic compounds. It should be noted that the phenoxide ion ($\_O^-$), which is present in alkaline solutions of phenols, absorbs at a considerably longer wavelength than the parent phenol (–OH). Generally electron donating and lone-pair substituents cause a red shift and more intense absorption. More complex shifts arise when there is more than one substitutent present, and tables are given in standard spectrometry texts listing these.

Table 17.7 Absorption maxima for some monosubstituted benzenes Ph-R (in methanol or water)

R	Maxima/nm	
–H	204	54
$-CH_3$	207	261
–Cl	210	264
–OH	211	270
$-OCH_3$	217	269

$-CO_2^-$	224	271
$-COOH$	230	280
$-NH_2$	230	280
$-O^-$	235	287

Identification of unknown organic samples can be considerably aided by considering the UV-visible absorption spectra. The following general rules may be used as a guide.

Observation	**Possible Conclusion**
No UV absorption present	σ bonds or lone pairs only
Isolated double bond	
Strong absorption between 200 and 250 nm (ε ~ 1000)	Aromatic ring
Weak absorption near 300 nm (ε ~ 1)	carbonyl compounds

Metal complex involving organic or inorganic ligands are important in analytical determinations.

The transitions which are responsible for visible and UV absorption by complexes may be classified as follows:

(i) d-d transitions due to transition metal ion. These give rise to the color of many compounds of transition metals and are modified by changing the ligands that are bound to the central atom. The spectrochemical series relates the increasing strength of the ligand field to the shift the absorption band towards the UV. However, these transitions often have low absorptivity concentrations of metals.

(ii) The absorption bands of an organic ligand may be modified when it is complexed wit ha metal. The complexes formed with dyes such as eriochrome black T, used in complexometric titrations as in indicator, and metals such as magnesium, have high absorptivities. Complexing agents such as dithizone $(C_6H_5 \cdot NH \cdot NH \cdot CSN{=}N \cdot C_6H_5)$ form highly colored complexes with several metals.

(iii) Charge-transfer bands arise because of transitions between the levels of an electron donor, often the σ or π orbitals of the ligand, and electron acceptor levels, such as the empty orbitals of a transition metal. The intense red color of the iron(III) thiocyanate complex and the purple color of the permanganate ion both arise as a result of such transfers.

Quantitative Analysis Many organic compounds and inorganic complexes may be determined by direct absorptiometry using the Beer-Lambert Law. It is important to recognize that for the most accurate work, or determination of trace amounts, three criteria must be observed.

(i) The absorptivity of the species to be determined must be reasonably large. While it is possible to determine metals such as copper or cobalt in water as the aquo complex, this will give accurate results only down to about 1% since $\varepsilon \sim 10\ m^2\ mol^{-1}$. However, for anthracence, $C_{14}H_{10}$, which has three fused aromatic rings, $\varepsilon = 18\ 000\ m^2\ mol^{-1}$ and, thus, even a solution of about 0.5 ppm will give an absorbance of approximately 0.1 in a 1 cm cell.

(ii) The species must be stable in solution. It must not oxidize or precipitate or change during the analysis (unless the analysis intends to study that change).

(iii) Calibration must be carried out over the range of concentrations to be determined. Agreement with the Beer-Lambert law must be established.

(iv) In complex matrices, it is not possible to analyze for all the species present using a few spectra. It is necessary to separate the components using one of the technique, or to use combined method.

It should be noted that it is possible to determine two (or more) species in an analytical sample by measuring the absorbance at several wavelength.

Applications of UV-Visible Spectroscopy

1. The UV spectra helps in detection of conjugation between two or more C — C double or triple bonds, C — C and C — O double bond.
2. UV-spectrum can also reveal the number and location of substituents attached to the carbons of the conjugated system.
3. The geometric isomers can be identified by U.V. spectroscopy as the trans isomers exhibit λ_{max} at slightly lower wavelength and have larger extinction coefficient than the cis-isomers.
4. UV spectrum is also used in qualitative analysis and purification control in dye stuff and pharmaceutical industries.
5. The quantitative determination of those compounds is possible which absorbs UV radiations.
6. Spectrophotometrically determination of molecular weight is possible for those compounds whose derivates could be prepared.
7. Calculation of dissociation constants of acids an bases can be done by U.V spectrum.
8. It is possible to study the kinetics of very fast chemical reaction using U.V. spectroscopic technique.
9. Change transfer transition can be studied well with the help of U.V. spectroscopy.

10. The %age of keto and enol-form present in tautomers equilibrium can also be determined using U.V. spectroscopy.
11. Actual chloral structure was confirmed by UV spectroscopy.
12. Characteristic intense absorption band of lanthanide can be appear in UV region and can be used to determine them.
13. UV is one of the best method for detecting impurities is organic compounds.
14. The halid complexes of metals are the main inorganic compounds absorbing UV radiations.
15. The UV spectra in the elucidation of structure of vitamins.

17.9. INFRARED SPECTROSCOPY

Principles The vibrational levels of molecules are separated by energies in the infrared (IR) region of the electromagnetic spectrum. That is, in the wave number range from 13·000 to 10 cm^{-1}, or between 0.8 and 1000 μm on the wavelength scale. For convenience, this large region is divided into near IR, or NIR (13 000 — 4000 cm^{-1}), mid IR (4000 — 400 cm^{-1}) and far IR (400 — 10 cm^{-1})

Molecules contain bonds of specific spatial orientation and energy. These bonds are seldom completely rigid, and when energy is supplied, they may bend, distort or stretch. A very approximate model compares the vibration to that of a harmonic oscillator, such as an ideal spring. If the sprig has a force constant, k, and masses m_A and m_B at the ends, then the theoretical vibration frequency ν is given by:

$$\nu = (1/2\pi)\sqrt{(k/\mu)}$$

where $\mu = m_A \cdot m_B/(m_A + m_B)$ is called the reduced mass.

Each type of molecular vibration is characterized by vibrational quantum number, v. For a simple stretching vibration, there is a series of levels whose energy is given approximately by

$$E = h\nu \cdot (v + 1/2)$$

This means there is a set of levels spaced in energy by $h\nu_0$ or in wave number by $\bar{\nu}_0$. The selection rule for an ideal harmonic oscillator allows transitions where $\Delta v = \pm 1$, giving a single, fundamental vibrational absorption peak.

However, when bonds are stretched they weak, so a better model takes this into account, and the molecules are treated as anharmonic oscillators. Thus, where high energies are involved, larger energy transitions may occur, where $\Delta v = +2, +3$ etc. giving the first overtone at a wavenumber approximately double that of the fundamental, and so on.

The electrical field associated with the electromagnetic radiation will interact with the molecule to change its electrical properties. Some molecules (for example, HCl) have a dipole moment due to charge separation and will interact with the field. Others may acquire a dipole when they vibrate. For example, methane, CH_4, has no dipole, , but when one of the CH bonds stretches, the molecules will develop a temporary dipole.

Even if the molecule does not have a dipole, the electric field ,E may distort the electron distribution and polarize the molecule:

$$\mu_{ind} = \alpha E$$

where μ_{ind} is the dipole induced by the field, E , and α is the polarizability of the molecule.

The rules governing transitions in the infrared region of the spectrum require that, in order to absorb, the dipole moment of the molecule must change during the vibration. Such vibrations are said to be IR active. For transitions to be active in the Raman region, it is required that the polarizability must change during the vibration. The transitions are then Raman active, or R active.

Consider two simple diatomic molecules, nitrogen and carbon monoxide. These molecules have only one fundamental vibration frequency, ν_0. For nitrogen it is 2360 cm^{-1} and for carbon monoxide 2168 cm^{-1}.

As molecules become more complex, the number of possible vibrations increases. For example, carbon monoxide, CO_2 has three atoms arranged in a line: $O{=}C{=}O$. This molecule does not have a dipole and may vibrate in three ways.

(i) The symmetric stretch, denoted by ν_1, is where both oxygen are equidistant from the central carbon, but the C — O bonds lengthen and contract together. The dipole does not change, but the polarizability does, so this vibrations is IR inactive, but R active.

(ii) The antisymmetric stretch, ν_3, has one C — O bond stretching, while the other contracts. The carbon atoms moves as well so that the centre of mass of the molecules remains stationary. The dipole changes, but the polarizability does not, so this is IR active but R inactive.

(iii) The bending vibrations, ν_2, may be resolved into two identical and mutually perpendicular components corresponding to two transitions of the same energy (degenerate). It is necessary to think in three dimensions: considering the page as a plane, then if the two oxygens go equally down the page', while the carbon goes 'up the page' to balance, this is in-plane bending. If the oxygens go 'into the page' and the carbon 'out of the page', this is out-of-bending. These changes will be reversed as the vibration progresses. This vibrations is IR active and R inactive.

The triangular molecule of water, H_2O, also has three different vibrations, corresponding to the same vibrational types. However, each involves a change in dipole so all three are IR active. The Raman spectrum shows only one line due to the symmetric stretch. These vibrations are shown schematically in Figure 2.

It is possible to extend these arguments to more complex molecules, but this is only of value of studies of structural parameters such as the length and strength of bonds and their interaction. For analytical purposes, it is sufficient to note that there are 3N — 6 fundamental vibrations for a molecule with N atoms (or 3N — 5 if the molecule is linear). If the molecules has a centre of symmetry (e.g. CO_2, ethyne, $CH \equiv CH$ or benzene, C_6H_6) then those bands that are IR active are not R active, and vice versa.

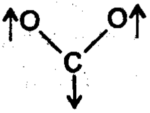
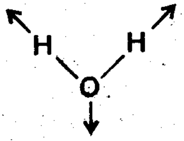
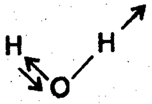
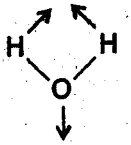
Schematic	Dipole	Polarizability	Activity	Wave number (Cm^{-1})
$\leftarrow O{=}C{=}O\rightarrow$	No change	Change	R active	1320
$O\leftarrow:\rightarrow C{=}O\rightarrow$	Change	No change	IR active	2350
	Change	No Change	IR active	668
	Change	Change	IR & R active	3650
	Change	No change	IR active	3756
	Change	No change	IR active	1600

Fig. 17.10 Schematic of the vibration of the CO_2 and H_2O molecules.

Besides the fundamental vibrations, it is important to note that some IR absorptions may corresponds to combinations of vibrations and also to overtones.

For example, for HCl, which has a fundamental stretching band around 2800 cm^{-1}, there is a first overtone at just below 5600 cm^{-1} in the NIR. Carbon dioxide, whose fundamentals are listed above, has overtones of ν_1 at 6980 and 11500 cm^{-1} in the NIR and several combination vibrations such as $(\nu_2 + \nu_1)$ at 2076 cm^{-1}.

In complex molecules, the structure is dominated by functional groups. For example, a large number of compounds contain the carbonyl group, $C{=}O$. These include aldehydes, ketone, acids, esters, amides and quinines. Almost every organic compounds has C — H bonds, although they may differ considerably in their behavior. Alcohols, acids and phenols contain the —OH group. These groups and also aromatic rings and other larger structural units may be considered as giving rise to characteristic group frequencies.

Group Frequencies

There are three main type of functional group that give rise to absorption in IR (and R) spectra which are highly characteristics.

(i) The stretching of bonds between a heavier atom and hydrogen, H — X —. Relating these bonds to the harmonic oscillator model, the reduced mass depends chiefly on the mass of the H atom, because this has such a low mass compared to all the other atoms, and the force constant is high because the bonds connecting the hydrogen and other atoms are strong. This accounts for the H — X —stretching vibrations, which almost all occur in the region between 2000 and 4000 cm^{-1}. The X-atoms and the structure to which they are attached will determine the exact frequency, as shown in Table 17.8. It should be noted that hydrogen bonding, which occurs with electronegative atoms such as oxygen or nitrogen, but not with carbon, will make the H — X — bond both weaker and more variable. Consequently, whereas the free OH stretch of gaseous alcohols has a sharp absorption at 3600 cm^{-1}, liquid alcohols show a very broad band nearer 3200 cm^{-1}.

(ii) Double and triple bonds; aromatic systems. Because these are bonds with high bond energies, they are less affected than single bonds by the structures to which they are attached. It is worth noting that the higher the bond order, the higher the IR absorption frequency or wave number, as shown for C — C and C — N bonds as shown in Table 17.9.

(iii) The bending vibrations of organic molecules also give characteristic group frequencies. A general 'rule of thumb', it is usually found that the bending vibrations occur at the lowest frequency or wave number, the symmetric stretch next and the antisymmetric stretch at the highest value. Table 17.10 give a selection of the most useful group frequencies in the mid-IR and NIR regions respectively.

Raman spectra have similar group frequency correlations, but two features are of special interest. The R spectrum of water is much less intense than the IR spectrum, and therefore aqueous solutions may readily be studied. Overtones and combinations vibrations occur less often. Vibrations of symmetrical structure, such as $R - C \equiv C - R$, which are weak in the IR, appear as strong bands in the R.

Table 17.8 H—X group frequencies

X	Wavenubmer (cm^{-1})	Comment
H—C (aliphatic)	2960—2900	Strong
H— C (aromatic)	3050—3000	Strong
H—C (alkyne)	3300	
H—O	3600	Free OH
H—O	3500—2500	H-bonded
H—N	3500—3300	Broad
H—S	2600—2500	Weak

Table 17.9 Multiple bonds

Bond		Wavenubmer (cm^{-1})	Comment
Single	C—C	Approx. 1200	Variable
Aromatic	C :::: C	1660, 1500	
Double	C═C	1650	
Triple	C≡C	2200	Weak
Single	—C—N	1100	Variable
Double	—C═N—	1670	
Triple	—C≡N	2250	Strong

Table 17.10 Selected group frequencies in the NIR region

Frequency	Group
A Combination bands 5000 to 4000 cm^{-1}	
5300, 4500	Water
4700—4600	RNH_2
4650—4150	CH
4700—4600	CC
B First overtone region 7500—5000 cm^{-1}	
7300	
5500—5100	Water, ROH
5400—4800	RCOOR, RCOOH
	CONHR, $CONH_2$

7500 — 5700	CH, CH_2, CH_3
C Higher overtone region 14 000 to 8000 cm^{-1}	
13 500, 10 700	ROH, ArOH
14 000	ArCH
14 000 — 11 000	CH, CH_2, CH_3

Vibrations that appear in the near infrared (NIR) regions are the overtones and combination vibrations of those in the mid-IR. They are generally less intense, and are useful in quantitative measurements. For example, water has fundamental vibrational vibrations at 3700, 3600 and 1600 cm^{-1}. In the NIR of water, combination bands occur at 5300, and overtones around 7000, 11 000 and 13 500 cm^{-1}.

For compounds with an — OH group, overtones at 7000, 10500 and 13 600 occur, while for aliphatic hydrocarbons, there are absorptions at 4200 – 4700, 5700 – 6300, 7000 – 7500 and so on.

Instrumentation For mid-IR, NIR and Raman spectrometry, the instrumentation is different, but the main components are all required.

The sources used for mid-IR are heated rods, such as a nichrome ribbon or a 'globar', which is a rod of silicon carbide. The Opperman source is a rhodium heater in an alumina tube packed with alumina and zirconium silicate. When heated to above 1000°C, these sources emit energy over a wide range, resembling a black-body radiator with a maximum intensity at about 1000 cm^{-1}. For NIR, tungsten or tungsten halogen lamps are used.

In Raman spectrometry, a high intensity source is required, since Raman scattering yields low intensity lines. Laser sources such as the Ar^+ laser give strong, sharp lines at 488.0 nm and 514.5 nm. One disadvantage is that these wavelengths may cause fluorescence. This is avoided by using NIR laser sources. A schematic of an FT-Raman spectrometer is shown in Figure 17.11.

Sampling for vibrational spectroscopy is an extensive subject. Only thee basic methods will be discussed here. Since glass and polymers absorb strongly in the IR region, it is necessary to use ionic materials to contain samples. Typical examples are listed in Table 17.11.

The types of samples that may be analyzed by IR are very varied and will be considered in turn.

For gases, because they are present at much lower concentrations than pure liquids or solids (e.g., 0.04 M for nitrogen in air, 17.4 M for liquid ethanol), longer path lengths are required. The gas-phase spectrum of HCl at 0.2 atm may be studied in a 10 cm glass cell with NaCl windows. Low concentrations of exhausted gases may need a 10 m cell, which reflects the IR beam to achieve the long path length.

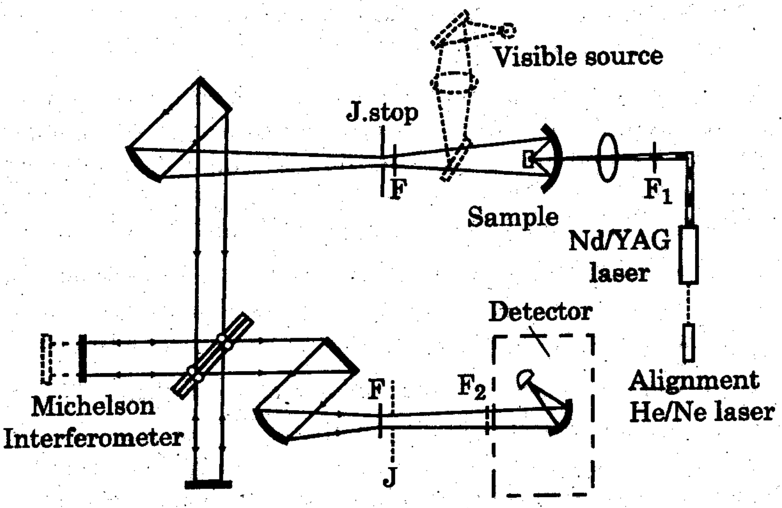


Fig. 17.11. Schematic of an FT-laser Raman spectrometer.

Table 17.11 Window material for infrared spectrometry

Material	Range (cm^{-1})	Comment
NaCl	40 000 — 625	Soluble in water
KBr	40 000 — 385	Soluble in water
TlBr/I (KRS-5)	16 600 — 250	Slightly soluble
ZnSe (Irtran-4)	10 000 — 515	Insoluble

Two points should be stressed if gas phase spectra are to be studied.

(i) The fine structure of the IR stretching band of HCl shows many lines. These are due to rotational transitions superimposed onto the vibrational one. The vibration-rotation spectrum of water vapor shows a complex pattern of lines across much of the IR region. With heavier molecules, the moments of inertia of the molecule are larger, and therefore the rotational lines are closer together. For gaseous CO_2, one vibration-rotation band occurs at about 2300 cm^{-1} and, at low resolution, shows two lobes only. It is therefore important to exclude water vapor and carbon dioxide from the spectrometer as far as possible, and this is usually done by purging with dry nitrogen.

(ii) The second cautionary point is that, with gas-phase spectra, hydrogen bonding is much less important. For the —OH stretch in ethanol, therefore, instead of the broad band between 3500 and 3000 cm^{-1} seen in the spectrum of a liquid, a single sharp peak occurs at 3600 cm^{-1} when the gaseous spectrum is recorded.

Liquids or melts are more concentrated, and may be studied directly as a thin a film between NaCl plates. For more quantitative work, accurately prepared solutions in solvents which do not absorb in the region of analytical interest, such as CCl_4 or CS_2 in

NaCI cells, with a known path length provided by a spacer, may be used. Most of these are also applicable to NIR, and short path length silica cells may also be used there.

If a solid organic powder sample is placed in an IR beam, the particles scatter the light, and little is transmitted. Therefore, for routine analysis, the sample is usually ground to a fine powder and mixed with paraffin oil ('Nujol') to form a paste or mull. This reduces the scattering at the powder surface and gives a good spectrum, with the disadvantage that the bands due to the oil (at approximately 2900, 1450, 1380 and 750 cm^{-1}) are superimposed on the spectrum. Alternatively, the fine powder may be mixed with about 10 — 100 times its mass of dry powdered KBr and the mix pressed in a hydraulic press between smooth stainless steel dies to give a clear KBr disk.

Solutions of solids may also be used, and tetrachloromethane, CCl_4 is often used as solvent, since it has few IR-active bands, mostly at the low wave number end of the spectrum. These must be ignored when the spectrum is interpreted. Thin films of solids such as polymers may be supported directly in the IR beam. Polystrene is a useful calibration sample to check the performance of an IR spectrometer.

Applications of IR Spectrometry

Structural Identification Comparison of the infrared (or Raman) spectra of related compounds illustrates the importance of the group frequency concept. The following examples will illustrate this.

Example 1 The spectrum of compounds containing, aliphatic chains exhibit bands due to CH_3 —, — CH_2 — and ═ CH — groups, both in their stretching and bending modes. The IR spectrum of a liquid paraffin, or Nujol, used as a mulling agent is shown in Figure 17.12. The — CH stretching vibrations all absorb just below 3000 cm^{-1}, and provide at least four peaks. The bending vibrations of — CH_3 — and — CH_2 — absorb around 1450 cm^{-1} whereas the characteristic band at 1380 cm^{-1} is due to the methyl groups. With long chains a weak band around 750 cm^{-1} is due to rocking of the (— CH_2 —$)_n$ groups. A similar spectrum is observed with polyethylene film.

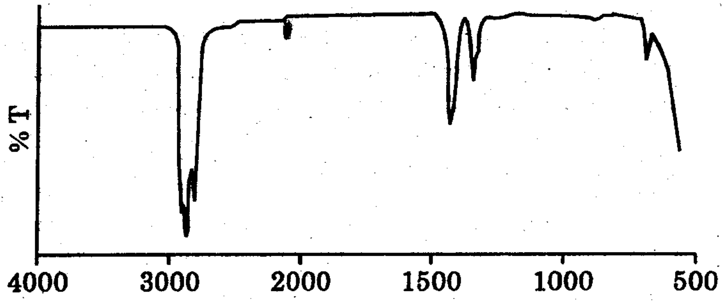


Fig. 17.12 Liquid paraffin: (Nujol).

If the compound has no methyl groups, for example cyclohexane, the spectrum is simplified, as only the methylene absorptions are observed. If hydrogens are substituted by halogens; peaks corresponding to the halogen occur at about 700 cm^{-1} for — C — CI, 600 cm^{-1} for — C — Br or 500 — C — Br or 500 cm^{-1} for — C — I.

Example 2 Aromatic compounds, especially those derived from benzene, show bands characteristic of their structure and substitution. A thin film of polystyrene, (C_6H_5 — CH — CH_2)n shows in Figure 2 is often used for calibrating the wave number scale of an IR spectrometer.

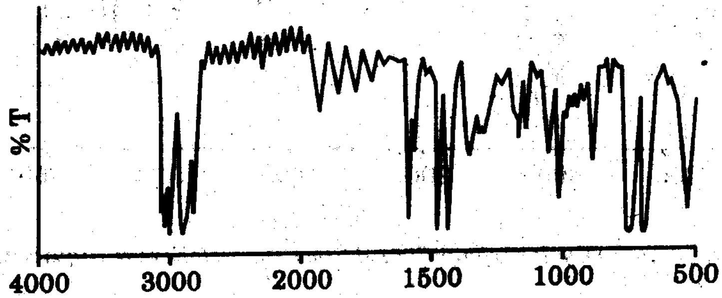


Fig. 17.13 Polystyrene film.

The aromatic — CH — stretch occurs just above 3000 cm^{-1} and the aliphatic just below.

The weak absorptions due to overtones in the 2000 — 1800 cm^{-1} region are typical of a mono substituted benzene, as are the bands in the 800 — 600 cm^{-1} region due to out-of-plane (OOP) bending of the C — H bonds. Ring vibrations give bands between 1600 and 1500 cm^{-1} whereas the rest of the spectrum can be regarded as a "fingerprint" of the entire structure.

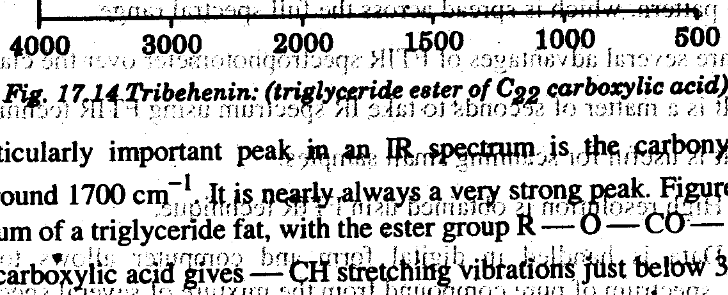


Fig. 17.14 Tribehenin: (triglyceride ester of C_{22} carboxylic acid).

A particularly important peak in an IR spectrum is the carbonyl, > C = O absorption around 1700 cm^{-1}. It is nearly always a very strong peak. Figure 17.14 shows the IR spectrum of a triglyceride fat, with the ester group R — O — CO — R′. The long-chain of the carboxylic acid gives — CH stretching vibrations just below 3000 cm^{-1} and chain rocking at 720 cm^{-1}. The prominent peak near 1750 cm^{-1} clearly shows the presence of the carbonyl group.

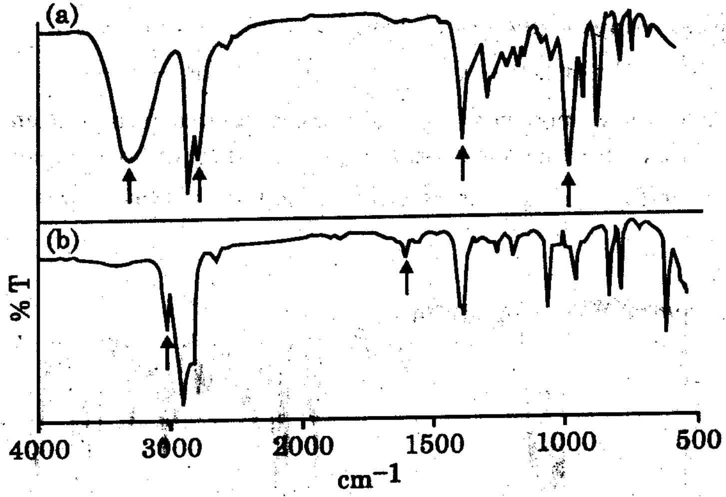


Fig. 17.15 (a) Cyclohexanol (liquid film); (b) cyclohexene (liquid film).

The changes that may occur during a reaction are readily studied. For example, the dehydration of an alcohol to an alkene is observed by the disappearance of the strong, broad —OH bands at 3300 and 1350 cm^{-1} and the —C—O— stretch near 1100 cm^{-1}, arrowed in the spectrum of cyclohexanol in Figure 17.15(a) and the appearance of the —C═C— bands, especially around 1600 cm^{-1} as shown in the spectrum of cyclohexene shown in Figure 17.15(b).

Fourier Transform Infra Red (FTIR) Spectrophotometry

Untill about 1900, IR spectrophotometer use wavelength dispersive systems with a scanning monochromators. However, the performance of these scanning IR systems was severely limited by the performance capabilities of the thermal IR detectors available at that time, which were slow in comparison to photo detectors and had poor signal to noise ratio. The development of faster IR detectors, plus the use of Fourier Transform (FT) system has permitted the use of a totally different method of collecting the data.

A typical FTIR- spectrophotometer uses a Michelson Interferometer instead of monochromators. A monochromator only transmits a very narrow band of wave numbers at any given setting of diffraction grating, In contrast, the interferometer has a sinusoidal transmittance pattern, which is spread across the full spectral range.

There are several advantages of FTIR spectrophotometer over the classical one:

(i) It is a matter of seconds to take IR spectrum using FTIR technique.

(ii) It is useful for scanning small samples.

(iii) High resolution is obtained usin FTIR technique.

(iv) Data is handled in digital form and computer allows to subtract the spectrum of pure compound from the mixture of several spectra.

Quantitative Measurements The use of IR and NIR spectrometry for qualitative measurements is extensive and wide ranging, and for this purpose transmission spectra are conventionally recorded as a function of wavenumber. In order to make quantitative measurements, it is necessary to convert the transmittance readings to absorbance, A, the relation between the two being.

$$A = \log(100/T\%)$$

This also allows any absorbance by solvents or other components of the sample to be subtracted from the analyte peak.

$$A(\text{total}) = A(\text{sample}) + A(\text{background})$$

This also allows the proper subtraction of solvents or other components. For example, if the spectrum of a machine oil without additives is measured in a 0.1 mm NaCI cell, and then the same procedure is followed for a sample with small amount of additives, subtraction of the absorbance spectra will give the spectrum of the additives in absorbance form. Gas analysis by IR spectrometry using long path length cells has been used to measure concentrations of anaesthetic gases. For example, nitrous oxide, N_2O, shows a strong absorbance at 2200 cm^{-1} at which the wave number for neither water vapour nor carbon dioxide interfere. Measurement of the concentrations between 2 and 50 ppm is possible with a 15 m path length gas cell. Trichloromethane (chloroform) give a strong, sharp peak at 770 cm^{-1} and may be measured down to 0.1 ppm.

In addition, IR spectrometry has been used to measure the mineral contents of rocks, asbestos and to study residual solvents in pharmaceuticals. Mixtures can be analyzed directly, although chromatographic methods are normally preferred.

NIR spectrometry has been used widely for the analysis of agricultural, food and pharmaceutical products. It is a rapid technique and may be adapted to the quality control of process streams as, using fiber optics, remote sampling in industrial environments is possible. One of the most useful NIR methods uses diffuse reflectance to analyze solid materials. The sample, usually as a powder, is placed in an integrating sphere and illuminated from an NIR source that directs radiation onto it. A typical use of this type of instrument is the measurement of starch proteins, water and oil components of wheat.

Questions

Q. 1. What is spectroscopy? Briefly discuss its importance in structure elucidation.

Q. 2. What are electromagnetic radiations? Classify them on the basis of wavelength.

Q. 3. What is Lambert-beer law? Discuss its significance in quantitative analysis.

Q. 4. What is flame photometry? Discuss working mechanism of a flame photometer with the help of suitable diagram.

Q. 5. Describe various application of flame photometry.

Q. 6. What do you mean by AAS? Draw a block diagram of AAS and label its various components.

Q. 7. Briefly describe the principle of atomic absorption spectrophotometer. What are different types of interferences encountered in AAS? Describe various applications of AAS.

Q. 8. What is the principle of UV visible spectroscopy? Describe various types of transitions studied in this technology.

Q. 9. Draw a block diagram of UV visible spectrophotometer.

Q. 10. Discuss application of UV visible spectroscopy in structure elucidation.

Q. 11. What is the basis of IR spectroscopy? Write some important characteristics group absorption frequencies.

Q. 12. Give an account of FTIR spectrophotometer with its working mechanism.Also mention some of its advantages over the classical technique.

Q. 13. What are the applications of IR spectroscopy in structure identification and quantitative measurement?

Q. 14. Justify/comment on the following statements.

(*a*) Spectroscopy is a useful technique for structure determination

(*b*) Interaction of electromagnetic radiation with matter is useful.

(*c*) All electromagnetic radiation has same speed.

(*d*) All quantitative measurements are based on Lambert,s law.

(*e*) Electronic transitions take place in UV-Visible region of the spectrum.

(*f*) Conjugation increases the wave length of absorption.

(*g*) Electronic spectroscopy is useful for quantitative analysis.

(*h*) IR-spectroscopy is useful for functional group determination.

(*i*) FTIR-spectrometer is more useful as compared to classical IR spectrometer.

Chapter Eighteen

CHEMICAL INDUSTRIES

18.1. SOAP

History

The washing industry is also known as soap industry. It has roots over 2000 years in the past. Soap itself was not discovered, but gradually evolved from crude mixtures of alkaline and fatty materials. Both hard and soft soap was manufactured in the first century up to the early 1800's soap was considered as a mechanical mixture of fat and alkali. Later on, a French chemist showed that soap formation was actually a chemical reaction. Now, it has been accepted its importance in the daily life. The per capita use of toilet soap is a reliable guide to the standard of living for any country.

Sodium or potassium salt of fatty acids mainly oleic, palmitic, stearic, lauric and myristic is known as soap.

Raw Materials

(i) **Tallow** is the principal fatty material in soap-making. It contains the mixed glycerides obtained from the solid fat of cattle. This solid fat is digested with steam. The tallow forms a layers above the water and is easily removed. to increase the solubility of soap, tallow is usually mixed with coconut oil.

(ii) **Greases** are the second most important raw material in soap-making. These are important source of glycerides of fatty acids. They are refined by steam digestion or by solvent extraction.

(iii) **Oils.** A large yield of soap is attained from cotton seed oil, corn oil, coconut oil, palm oil, palm kernel oil, castor oil and olive oil etc. The soap from coconut oil is firm and lathers well.

Besides raw materials some other chemicals such as soda ash, caustic potash, sodium silicate, sodium bicarbonate, etc. are also required.

Builders. Inorganic chemicals add to soap are called builders. e.g. soda ash, tetra sodium pyrophosphate, sodium tripolyphosphate.

Manufacture

Soap is obtained by the reaction between oils or fats and caustic soda solution. This chemical reaction is called saponification, which is given below

$$(C_{17}C_{35}COO)_3C_3H_5 + 3NaOH \longrightarrow 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

Glyceryl stearate Caustic Sodium Glycerin
(fat) soda stearate

There are different methods by which soap can be made which are enlisted as

1. Twitchell Process
2. Kettle Process
3. Continuous countercurrent process. Only last process is described here briefly.

Continuous Counter Current Process

It is a modern method of soap making. In this process the fat is hydrolyzed. After this, the fatty acid is neutralized by caustic soda solution to form soap, and glycerin is separated from it.

$$(C_{17}H_{35}COO)_3C_3H_5 + 3H_2O \longrightarrow 3C_{17}H_{35}COOH + C_3H_5(OH)_3$$

GlycerylStearic acid Glycerin
stearate

$$C_{17}H_{35}COOH + NaOH \longrightarrow C_{17}H_{35}COONa + H_2O$$

Sodium stearate

In countercurrent splitting the fatty oils is deaerated under a vacuum to prevent darkening by oxidation during processing. It is charged at a controlled rate to the bottom of the hydrolyzing tower, which breaks the fat into droplets. These towers are about 20 m high and 60 cm in diameter and are made of stainless steel. At the same time deaerated, demineralized water is fed to the top of contacting section to separate the glycerin from the fatty phase. The fatty acids are discharged from the top of splitter or hydrolyzer to a decanter, where the water is separated. In a high vacuum still, the fatty acids are distilled from the bottom and rectified. The soap is formed by continuous neutralization with 50% caustic soda.

The neat soap is discharged at 93°C into blending tank and extruded, milled, flaked or spray-dried depending upon the product desired. At this point the neat soap analysis shows that 0.002 to 0.10% NaOH, 0.3 to 0.6% NaCl and approximately 30% H_2O. The neat soap is heated to 200°C at high pressure in a high pressure steam exchanger. Then the soap is cooled by brine from 105°C to about 65°C and cut into bar lengths. Further cooling, staming and wrapping complete the operation. The entire process completed in 6 h, as compared to kettle process which take over a weak.

The main classes of soap are toilet soap and industrial soap. All soaps contain 10 – 30% water. If soaps are anhydrous, they would be too hard to dissolve. Toilet soaps contain 10 – 15% moisture and have perfume and o fraction of a percent of titanium dioxide as a whitening agent. Shaving soaps contain potassium soap and an excess of stearic acid. "Burshless" shaving creams contain stearic acid and fats with much less soap.

18.2. SODIUM CARBONATE (SODA ASH)

The manufacture of soda ash is one of the most important heavy chemical industries. It is used for the production of soap, detergents, fibers, glass, petrochemicals, pulp and paper, fertilizers, explosives and other chemicals. Sodium carbonate can be manufactured by four methods.

(i) Leblanc Process

(ii) Electrolytic process.

(iii) Solvay process

The first three processes are usually used and would be discussed over here.

1. The Leblanc Process

This is an obsolete method and described here just for knowledge. According to this method following three stages are involved to prepare soda ash.

(a) Sodium chloride is treated with solphuric acid to produce sodium sulphate.

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

(b) The salt cake of Na_2SO_4 is converted into black ash ($CaS + Na_2CO_3$) by heating at high temperature in the presence of lime stone and coke in revolving furnaces.

$$Na_2SO_4 + CaCO_3 + 2C \longrightarrow Na_2CO_3 + CaS + 2CO_2$$

(c) The sodium carbonate is extracted from black ash by leaching with water. The solution is filtered and crystallized to get the sodium carbonate in solid form. The calcium sulphide can be used to prepare the sodium thiosulphate. The Leblane process is not used due to high fuel cost, labour cost and extra necessities to run the process.

2. Electrolytic Process

Sodium carbonate is also prepared by the electrolytic process by using the Hargreaves – Bird diaphram cell. Caustic soda solution formed in the cathode compartment is carbonated by passing requisite amount of CO_2 gas in the compartment. The resultant solution is concentrated to remove NaCl and then the solution is evaporated to form soda ash.

$$2NaOH + CO_2 + 2H_2O \longrightarrow Na_2CO_3 + 2H_2O$$

The electrolytic process is very suitable where there is an avenue for the utilization of the evolved chlorine to prepare bleaching powder and hydrochloric acid.

3. Ammonia Soda or Solvay Process

Sodium carbonate is now principally manufactured by the ammonia soda or the Solvay process. The principle of the process is that when an excess of carbon dioxide is bubbled through nearly saturated solution of NaCl containing ammonia, ammonium bicarbonate is produced. It reacts with NaCl producing sparingly soluble sodium bicarbonate and NH_4Cl. The sodium bicarbonate is separated by filtration and heated to get sodium carbonate and carbon dioxide.

$$NH_3 + CO_2 + H_2O \rightleftharpoons NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow[\Delta]{} Na_2CO_3 + H_2O + CO_2\uparrow$$

The NH_4Cl in the filterate is treated with lime to regenerate ammonia, which is used again to saturate the fresh brine.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3\uparrow + 2H_2O + CaCl_2$$

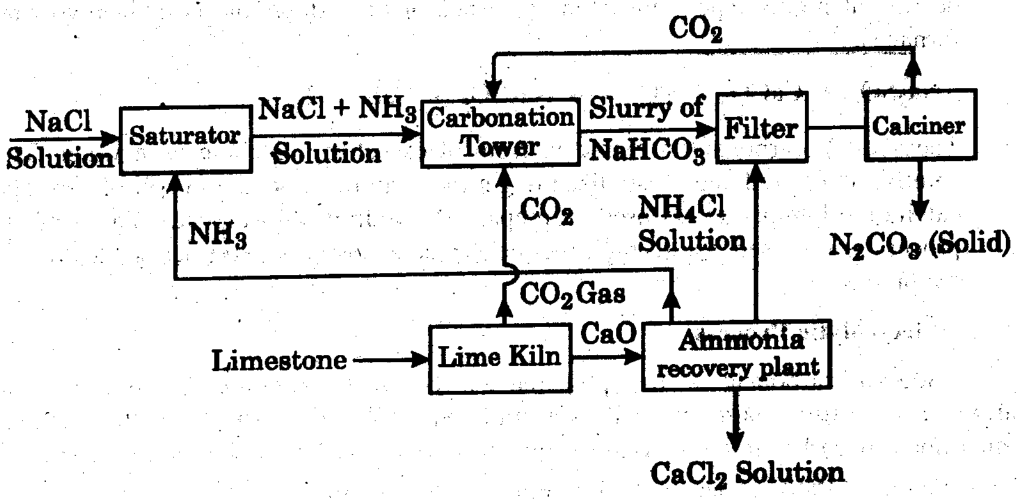


Fig. 18.1. Flow sheet of Solvay process

The process will be discussed with respect to the various parts of the plant.

(i) Saturator

Brine is a saturated solution of NaCl. Before saturating with ammonia the impurities like Ca and Mg salts are precipitated by CO_2 along with NH_3 from ammonia recovery plant in a saturator. Saturator is a saturating tank of cylindrical shape (15 × 12 feet) with conical bottom. The absorption of ammonia is an exothermic reaction and hence the saturator is fitted with cooling coils.

$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3\downarrow + 2NH_4Cl$$

$$MgCl_2 + (NH_4)_2CO_3 \longrightarrow MgCO_3\downarrow + 2NH_4Cl$$

The saturated brine is allowed to stand in setting tank where precipitates of impurities are settle down.

(ii) Carbonation Tower

Ammonical brine is carbonated in carbonation tower fitted with partitions and cooling coils. The CO_2 gas is formed by burning of $CaCO_3$ in a lime kiln. This gas is compressed and passed through the bottom of the tower while ammonical brine is trickled from the top of the tower. They react with each other according to counter current principle. As a result of this ammonium bicarbonate is formed which precipitates $NaHCO_3$. The solution is filtered to get $NaHCO_3$. The solid sodium bicarbonate is heated in rotary furnace to get solid sodium carbonate (Na_2CO_3). During this process CO_2 is evolved which is recirculated to carbonation tower.

(iii) Lime Kiln

About 45% carbondioxide is formed by burning of $CaCO_3$ and the reaction is

$$CaCO_3 \rightleftharpoons CaO + CO_2\uparrow$$

CO_2 is sent to carbonation tower. While lime is slaked by water an sent to ammonia recovery plant to regenerate NH_3 from NH_4Cl.

(iv) Ammonia Recovery Tower

The filterate from carbonation tower containing NH_4Cl is treated with slaked lime to regenerate the NH_3. This is circulated to the saturator.

The following reactions take place in ammonia recovery tower.

$$NH_4HCO_3 \longrightarrow NH_3 + H_2O + CO_2$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3$$

Advantages of the Solvay Process

(a) The Solvary process produces soda of highest purity.

(b) The process is less expensive.

(c) The operation is continuous, and clean.

(d) The consumption of fuel is less.

(e) The efficiency of the process is high.

Recent Improvements in the Solvay process

Solvay process has been improved recently by coupling with synthetic ammonia process. In this case there is no need for ammonia recovery. The bicarbonate mother liquor is agitated with dry common salt, when NH_4Cl precipitate, and is filtered; the filterate which now contains sodium chloride is made into ammonical brine and carbonated as usual. The conversion of salt into soda is 96% and Cl_2 is completely utilized as NH_4Cl.

QUESTIONS

Q. 1. How would you prepare soda ash by Solvay process?

Q. 2. Describe briefly the LeBlane Process for soda ash production.

Q. 3. Describe briefly the Electrolytic process for soda ash production.

Q. 4. Why do we prefer the Solvay process over LeBlanc process?

Q. 5. Draw the flow sheet diagram of Solvay process.

Q. 6. What are soaps and describe the continuous counter current process for manufacturing the soap.

Q. 7. Explain the following briefly
Tallow, greases, oil, builders.

Short Questions

(i) How is soda ash is prepared by electrolytic process?

(ii) Define soap and give three names atleast for the manufacturing of Soap?

(iii) Draw the flow sheet diagram of Solvay.

(iv) Describe the theory of Solvay process.

(v) Advantages of the Solvay process.

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