# NATIONAL OPEN UNIVERSITY OF NIGERIA

**COURSE CODE: CHM 303**

**COURSE TITLE: INORGANIC CHEMISTRY III**

**NATIONAL OPEN UNIVERSITY OF NIGERIA**

National Open University of Nigeria

Headquarters

14/16 Ahmadu Bello Way

Victoria Island

Lagos

Abuja Annex

245 Samuel Adesujo Ademulegun Street

Central Business District

Opposite Arewa Suites

Abuja

**CHM 303 INORGANIC CHEMISTRY III**

**DR HD ALIYU**

**DEPARTMENT OF CHEMISTRY**

**UNIVERSITY OF ABUJA**

**Introduction**

Inorganic Chemistry III course (CHM 303) is one of the core courses for the Bachelor of Science degree programe in Chemistry. It is a three credits course at 300 level of the National open University of Nigeria, designed for students with a fair background knowledge in inorganic Chemistry II course. This course gives an over view of the physical and chemical properties of the elements of the periodic table.

The chemical properties of the representative elements were highlighted along side some of their important compounds, and their industrial applications. The transition and inner transition elements are discoursed, including some of their features. One of the most significant property of the transition elements is its ability to form coordination compound. The theories behind this will be examined. The instability of some heavy elements which leads to radioactivity will be introduced.

**What You Will Learn in This course**

This course of inorganic chemistry III, deals with the study of the elements of the periodic table and the compounds formed from their elements with exception of those formed between carbon and hydrogen. The differences and similarities between the main groups will be examined. The chemical properties of the transition and inner transition elements will be discoursed, with emphancies on its coordination property. Thus the nature of bonding in coordination compounds will be treated. An introduction to the nature of radioactivity is also been presented. The course is made up of six units. You will find several Self Assessment Exercise (SAE) as well as **Tutor Marked Assignments)** (TMA) in each units, with answers provided at the end of the course.

This course guide introduces you to the course material, of its usage for study. It suggest how much time to be spent on each unit of the course and on your TMA

**Course Aims**

This course aims at the understanding of the chemistry of the noble gases and the halogens. It also discourses the differences and similarities of the main group elements, and the chemistry of transition elements with an introduction to coordination compound and radioactivity.

**Course Objectives**

In order to achieve the aim of this course as set above, at the beginning of each units are some objectives, which you should read before working the unit, during your study and after completing a unit. In this you would have achieved the aims of the course as a whole.

On successful completion of the course you should be able to

-list the elements of the noble gas, group IA, IIA, VIIA and transition elements.

-describe the chemistry of the noble gas, halogens, groups IA and IIA elements.

-discuss the similarities and differences between carbon and silicon, nitrogen and phosphorous, and oxygen and sulphur.

-discuss the chemistry and extraction of transition and inner transition elements

-explain the valence bond, molecular orbital and crystal field theories.

-describe the nature of radioactivity

**Working through this Course**

In order to be able to successfully complete this course, you are required to carefully study each unit along with recommended textbooks and other materials that may be provided by the National Open University. You may also need to exploit other e-reading such internet for further useful information on the course.

Each unit contains self assessment exercise and at certain points in the course you would be required to submit assignment for grading and recording purposes. You are also to participate in the final examination at the end of the course. It is recommended that you devote an abundant time for reading and comprehension. It is highly necessary that you avail yourselves the opportunity of attending the tutorial sessions where you will be able to compare your understanding of the course contents with your colleagues.

**The Course Materials**

The main components of this course are:

1. The Course Guide
2. Study Units
3. Self Assessment Exercise
4. Tutor Marked Assignments
5. Further Readings

**Study Units**

**Module 1        Noble Gases**

Unit 1        Chemistry of the Noble Gases

Unit 2        Compounds of the Noble Gases

**Module 2        Chemistry of the Representative Elements**

Unit1        Hydrogen Element

Unit 2        Group III, IV, VI and VII

**Module 3        Transition Elements**

Unit1        Nature and Chemistry of Transition Elements

Unit 2        General Reactivity

Unit 3        Inner-Transition Elements

**Module 4        Isolation and Purification of Metals**
Unit 1        Metallurgy
Unit 2        Purification of Metals

**Module 5        Coordination Chemistry and Field Theory**

Unit 1         Introduction to Coordination Chemistry

Unit 2        Field Theories

This course consists of five Modules. In Module 1 the chemistry of noble gases were described including their electronic configurations. Module 2 deals with the chemistry of group IIA to VIIA and other representative elements. The similarities and differences in their chemical properties were highlighted.

In Modules 3 we considered the chemistry of the transition and inner transition elements, while Module 4 deals with isolation and extraction of metal.

The Module 6 introduces the chemistry of the coordination compounds and that of the radioactivity.

Each of the unit is made up of one or two weeks' work consisting of introduction, objectives, reading materials, self assessment exercise, conclusion, summary and Tutor marked Assignment (TMA), suggestion for further reading and source materials. The unit directs you to work on exercises related to the required reading. Together with the TMAs, they are meant to test your basic understanding and comprehension of the course materials, which is a prerequisite for the achieving the stated aims and objectives of the course.

**Presentation Schedule**

The course materials have important dates for the timely completion and submission of your TMAs and tutorial lessons. You are vividly reminded of the need to promptly submit answers to tutorials and assignments as at when due.

**Assessment**

The course assessment consists of three aspects namely the self assessment exercise, the tutor marked assignment and the written examination/end of course examination.

It is essential that you attempt all exercises and assignments and submit appropriately to the course facilitator for grading. Let your answers be concise and as accurate as possible. You are expected to consult other material course in addition to your course materials in order to be able to present accurate answers to the questions. Kindly note that the tutor marked assignment covers only 30% of the total marked for the course.

**Tutor Marked Assignment (TMA)**

The TMA is a continuous assessment component of your course. It accounts for 30% of the total score. You will be given a number of TMAs to answer. Nearly all of them must be answered before you are allowed to sit for the end of the course examination. The TMAs will be given to you by your facilitator and returned after you have done the assignment. Note that these assignments are already contained in the assignment file to be given to you. You may do yourself good by reading and researching well before you attempt to answer the questions.

You are warned to submit these assignments to the facilitator at the stipulated time as could be seen in the assignment file. However, if for any reason you are unable to meet the deadline, you are highly required to intimate the facilitator of your problem before the due date and seek for an extension which may be granted or not.

**Final Examination and Grading**

The end of the course examination for Physical Chemistry III will be for about 3 hours with maximum score value of 70% of the total course work. The examination will be made up of questions which normally reflect on what you have learnt in the course materials/further reading. In addition, they may be prototype of the self assessment exercises and the TMAs. The end of the course examination is intended to cover information from all parts of the course.

Avail yourself the opportunity of the time-lag between the completion of the course content and the beginning of the examination to revise as much as possible the whole course materials, the exercise and assignments.

**Course Marking Scheme**

| Assignment | Marks |
|---|---|
| Assignments | The best three marks of the submitted assignments count at 10% each i.e. 30% of the course marks |
| End of course Examination | 70% of overall course marks |
| **Total** | 100% of the course materials |

**Facilitators/Tutors and Tutorials**

There are few hours of tutorials provided in support of this course. You will be informed appropriately of the name, telephone number and e-mail address of your facilitator. In addition, the time, dates and location of the tutorial lessons will be communicated beforehand. You are required to mail or submit your Tutor Marked Assignment to your facilitator, at least two working days, before the schedule date. Note that all the submitted assignments will be duly marked by the facilitator with further comments that can improve on your performances. The facilitator will from time to time takes track record of your comprehension, progress and difficulty in the course.

Be kind enough to attend tutorial lessons at the fixed appointment. It is probably the only avenue to meet face to face and discuss with you facilitator. There, you will be able to ask question or seek clarification on seemingly grey area in the course material. You may as well have prepared questions and comments for your facilitator before the due date. An active participation during the tutorial lessons will be an added advantage to boost confidence level.

In case any of the situations listed below arises, do not hesitate to intimate your facilitator using his or her telephone number or via e-mail address;

. You do not understand any part of the study or the assigned readings
. You are not skill enough to attempt the self assessment exercise
. The questions in the TMAs are not clearly understood

Accept my best wishes in the course and I do hope that you benefit considerably from its application.

**Module 1      Noble Gases**

**UNIT 1           Chemistry of the Noble Gases**

1.0      Introduction

2.0      Objectives

3.0      Discovery of Noble Gases

4.0      Position of Noble Gases in the Periodic Table

5.0      Occurrence, Isolation and Uses of Noble Gases

6.0      General Characteristics

## 1.0      INTRODUCTION

In the Modular year, you have learnt about the chemistry of a group of highly reactive elements, viz., the halogens. This unit deals with the chemistry of a group of elements which were considered to be rather inert till recently. These elements are helium, neon, argon, krypton, xenon and radon. These elements constitute Group 18 of the modern periodic table. If you compare Mendeleev's periodic table of 1871 with the modern periodic table, you will see that it is remarkably similar in its coverage to the modern periodic table, with the exception that the Group VII (18) is missing. Elements of Group 18 were not known at that time and have been discovered only about a hundred years back. Since these elements have very low reactivity, they were called inert. However, the term inert is no longer applicable to the group as a whole, as the heavier elements of this group form compounds and, thus, are not inert. These elements have also been called the rare gases, but as

argon forms nearly 1 % of the atmosphere, and the gases can be readily isolated by the fractional distillation of liquid air at low temperatures, this name is also not very appropriate. They are now called the noble gases by analogy with the noble metals, like gold and platinum which are not very reactive. The unique chemical inertness of the noble gases is well reflected in the history of their discovery which was followed by a long gap of a few decades before xenon could be made to combine with only the most electronegative elements, fluorine and oxygen. In this unit you will study the discovery, isolation, uses, general characteristics and the compounds of noble gases.

## 2.0 Objectives

After studying this unit, you should be able to:

- describe the discovery of noble gases,
- discuss their electronic configuration and position in the periodic table,
-  enumerate the properties of the noble gases and their uses, and

## 3.0    REDISCOVERY OF NOBLE GASES

The story of the discovery and investigation of one noble gases is one of the most brilliant and interesting chapters in the history of science. Their discoveries can be traced back to 1785, when Henry Cavendish investigated the composition of air. He mixed excess oxygen with air and then passed electric sparks through the mixture. The oxides of nitrogen thus formed, were removed by dissolving in alkali solution and the excess of oxygen was removed with potassium sulphite. The residual gas, which was always left behind, was neither nitrogen nor oxygen. It did not form more than 1/120th part of the original volume of air. Time was not yet ripe for the discovery of noble gases. What Cavendish had actually isolated was, of course, a mixture of the noble gases, but he could not characterise them. It would be interesting for you to know that his figures about the volume of residual gas are remarkably close to the proportion of the noble gases in the atmosphere as

we now know it. It was almost a century after the investigation of the composition of air by Cavendish that advances in spectroscopy, periodic classification and the study of radioactive elements made possible the discovery of all six noble gases.

Of all the noble gases, first came the **discovery of helium**, which is unique in being the first element to be discovered extra-terrestrially before being found on the earth. In 1868 the French astronomer Pierre Janssen came to India to study the total eclipse of the sun. Using a spectroscope he observed a new yellow line close to the sodium D lines in the spectrum of the sun's chromosphere. This led two Englishmen, chemist E. Frankland and astronomer Sir J. Norman Lockyer to suggest the existence of a new element, which, appropriately, they named helium, from the Greek word helios meaning the sun. The terrestrial existence of helium was established by Sir William Ramsay in 1895. He showed that a gas present in trace amounts in the uranium mineral, cleveite, has a spectrum identical with that of helium. Five years later, he and Travers isolated helium from air. Cady and McFarland discovered helium in natural gas in 1905 when they were asked to analyse a sample of natural gas that would not burn.

Most developments in noble gas chemistry date from Lord Rayleigh's observations in 1894. In order to test Prout's hypothesis, that the atomic weights of all elements are multiples of that of hydrogen, Rayleigh made accurate measurements of the densities of common gases and found, to is surprise that the density of nitrogen obtained from air by the removal of $O_2$, $CO_2$ and $H_2O$ was consistently about 0.5% higher than that of nitrogen obtained chemically from ammonia. He observed that a litre of nitrogen obtained from air weighed 1.2572 grams while a litre of nitrogen obtained from ammonia weighed only 1.2506 grams under the same conditions. This small difference of 0.0066 gram in a gram and a quarter made Rayleigh to suspect an undiscovered element in the atmosphere. This reflects not only the extraordinary experimental skill of Lord Rayleigh but also his scientific and objective method of thinking and working which led to the discovery of a whole new group of elements.

Ramsay treated atmospheric nitrogen repeatedly with heated magnesium and found that a small amount of a much denser gas was left behind which would not combine with any other element. Lord Rayleigh and Sir W. Ramsay found that the residual gas showed spectral lines which were not observed earlier in the spectrum of any other element. In 1894, they announced the isolation of the noble gas which they named **argon**, from the Greek word argos meaning idle or lazy, because of its inert nature. They also realised that argon could not be put with any of the other elements in the groups already identified in the periodic table.

In 1898, Sir William Ramsay and his assistant Morris W. Travers isolated **neon** (from the Greek word meaning new) by the fractional distillation of impure liquid oxygen. Shortly thereafter, they showed that the less volatile fractions of liquid air contain two other new elements, **krypton** (from the Greek word meaning hidden) and **xenon** (from the Greek word meaning stranger).

Element 86, the last member of the group is a short lived radioactive element. It was isolated and studied in 1902 by Rutherford and Soddy and has been named as **radon** as it is formed by radioactive decay of radium.

## 4.0　　Position of Noble Gases in the Periodic Table

Due to their almost inert chemical nature, the noble-gases occupy a peculiar position in chemistry. Mendeleev had not left any vacant spaces for the noble gases in his periodic table although he had left such spaces for several other elements which were not known at that time. The reason was that he could not imagine the existence of a whole group of elements devoid of all chemical reactivity under ordinary conditions. Therefore, the discovery of the noble gases at the outset seemed to upset Mendeleev's scheme of classification of elements.

After studying the chemical nature of the noble gases, Ramsay introduced a new group in. Mendeleev's periodic table to accommodate these elements. He placed

this group after the halogens and before the alkali metals in the periodic table. As you have studied in Unit 1, in the long form of the periodic table, the noble gases occupy the last column of the table. The inclusion of the noble gases has actually improved the periodic table because it provides a bridge between the strongly electronegative halogens and the strongly electropositive alkali metals.

As you have studied in CHM 121 initially the group consisting of noble gases used to be termed as the Group zero or the Group VIII A. But according to the latest IUPAC convention, number 18 has been assigned to this group. However, the position of the group in the periodic table remains unchanged, that is, after the halogens at the end of each period.

In the next section, you will study the occurrence, isolation and uses of noble gases. Before that you may like to try the following SAQ.

**Self Assessment Exercise 1**
a)      What were the reasons for late discovery of noble gases?
b)      What made Lord Rayleigh suspect that there may be an additional element in air?

**5.0     OCCURRENCE, ISOLATION AND USES OF NOBLE GASES**
The noble gases constitute about 1.18% by volume of the dry air at sea level. Of all the noble gases, argon is the most abundant constituting 0.93% by volume of the dry air. As shown in Table 1.1, He, Ne Ar and Rn are also found occluded, though in very minute quantities, in igneous rocks. Certain natural spring waters contain small amounts of dissolved He, Ne and Ar. Large reserves of helium have been recently discovered in hot water springs of Bakreswar and Tantloi in West Bengal. The gas coming out of these springs contains about 1.8% of helium. Natural gas in certain parts of the world, particularly in U.S.A., contains as high as 7% of helium.

The principal source of Ne, Ar, Kr and Xe is air. Due to the difference in their boiling points (Table 1), these gases are separated by fractional distillation of liquid air. Although the concentration of helium in the air is five times that of Kr and sixty times that of Xe, recovery of He from this source is uneconomical. The main source of helium is natural gas which consists predominantly of hydrocarbons and nitrogen. These arc liquefied by cooling under pressure. The residual helium is purified by passing it over activated charcoal cooled with liquid air. The charcoal absorbs traces of heavier noble gases, leaving pure helium. Radon is obtained by allowing radium or any of its salts to decay for some weeks in a sealed vessel.

Helium, being very light and non-inflammable is used to lift weather balloons and to inflate the tyres of large aircrafts, thereby increasing their payload. A mixture of 80% He and 20% $O_2$ is used in place of air for breathing by deep-sea divers. Because He is much less soluble in blood than $N_2$, it does not cause sickness by bubbling out when the pressure is released as the diver comes to the surface. Boiling point of helium is the lowest of any known substance. Hence, it is extensively used in cryoscopy as a cryogen. You must have heard of **superconductivity** which is expected to bring revolutionary changes in our life. So far, helium provides the only practical means of studying and utilising such low temperature phenomena as superconductivity, though intensive research is going on and claims have been made of achieving superconductivity in some materials at 125 K. Again, heat generated in the high temperature reactor (HTR) must be extracted by means of a suitable coolant. Helium serves as an excellent coolant in these reactors. It is also used as a flow gas in gas liquid chromatography and in microanalysis.

Helium and argon are used to provide an inert atmosphere in some chemical reactions, in welding operations of Mg, Al, Ti and stainless steel and in zone-refining of silicon and germanium. Argon is extensively used in place of nitrogen in incandescent electric bulbs and radio tubes to prevent the oxidation and

evaporation of the metal filament. Neon, argon, krypton and xenon are used in discharge tubes—the so called neon lights for advertising, the colour produced depending upon the particular mixture of gases used. Radon finds a limited use in cancer treatment.

**Table 1.1 : composition of dry air**

| Gas | % by volume | B.P. (K) |
|---|---|---|
| $N_2$ | 78.03 | 77.2 |
| $O_2$ | 20.99 | 90.1 |
| Ar | 0.93 | 87.2 |
| $CO_2$ | 0.033 | 194.7 |
| Ne | 0.0018 | 27.2 |
| $H_2$ | 0.0010 | 20.2 |
| He | 0.0005 | 4.2 |
| Kr | 0.0001 | 119,6 |
| Xe | 0.000008 | 165.1 |

Superconductivity is a phenomenon in which the material offers no resistance to the flow of electricity. It would, therefore, allow transmission of electrical energy with practically no loss.

## 6.0    GENERAL CHARACTERISTICS

All the noble gas elements are colourless, odourless and tasteless monoatomic gases. Indeed, they are the only elements that exist as uncombined gaseous atoms at room temperature and one atmosphere pressure. Each atom, behaves as if it is effectively isolated. Some properties of noble gases are summarised in Table 1.2

**Table 1.2 : Some properties of the noble gases**

| Property | Helium He | Neon Ne | Argon Ar | Krypton Kr | Xenon Xe | Radon Rn |
|---|---|---|---|---|---|---|
| Atomic number | 2 | 10 | 18 | 36 | 54 | 86 |
| Electronic configuration | $1s^2$ | $[He]2s^2 2p^6$ | $[Ne] 3s^2 3p^6$ | $[Ar]3d^{10} 4s^2 4p^6$ | $[Kr] 4d^{10}5s^2 5p^6$ | $[Xe]4f^{14} 5d^{10}6s^2 6p^6$ |
| Atomic weight | 4.0026 | 20.183 | 39.948 | 83.80 | 131.30 | (222) |
| van der Waals radius (pm) | - | 131 | 174 | 189 | 210 | 215 |
| Boiling point (K) | 4.2 | 27.2 | 87.2 | 119.6 | 165.1 | 211 |
| Melting point (K) | 1 at 26 atm | 24 | 84 | 116 | 161 | 202 |
| Density of liquid at b.p. ($10^3 \times kg\,m^{-3}$) | 0.126 | 1.20 | 1.40 | 2.6 | 3.06 | 4.4 |
| Ionisation energy ($kJ\,mol^{-1}$) | 2372 | 2081 | 1520 | 1350 | 1170 | 1037 |
| Electron affinity ($kJ\,mol^{-1}$) | 54 | 99 | - | | | |
| Abundance in dry air (ppm by volume) | 5.2 | 18.2 | 93.40 | 1.14 | 0.087 | 0 |
| Abundance in igneous rocks (ppm by weight) | $3 \times 10^{-3}$ | $7 \times 10^{-5}$ | $4 \times 10^{-2}$ | | | $1.7 \times 10^{-10}$ |

You can see from the Table that all the noble gases have eight electrons in their valence shell except helium which has only two electrons. Till 1962, the noble gases were considered to be inert as their compounds were not known. Lewis and Kossel in formulating their electronic theory of Valence in 1916 stipulated that a grouping of eight electrons or an octet in the valence shell represents a very stable configuration. Hence, they proposed the octet rule. According to this, the

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reactions of elements can be explained in terms of their tendency to achieve stable electronic configuration of the nearest noble gas, $ns^2np^6$, by gaining, losing or sharing of electrons.

As all the noble gases have the stable $1.s^2$ or $ns^2$-$np^6$ configuration, they have the highest ionisation energies compared to other elements in their periods. This reflects their reluctant for chemical reactivity. Analogously, the electron affinity of these elements is either zero or has a small positive value. Therefore, they are unable to accept electrons to form unions. As we go down the group, the ionisation energy of the noble gases decreases. Thus, there is an increase in chemical reactivity of the noble gases as we go down the group from helium to radon.

Since, there are no usual electron pair interactions between the noble gas atoms, the only interactions are weak van der Waals forces. Therefore, they have very low melting and boiling points in comparison with those of other elements of comparable atomic or molecular weights. In fact, melting and boiling points of helium are the lowest of any known substance. The van der Waals attraction between the molecules atoms increases with the increase in the number of electrons per molecule or atom, Heavy molecules containing more electrons attract one another more strongly than the lighter molecules. Thus, the van der Waals forces between the noble gas atoms increase as we move down the group from helium to xenon. Consequently, melting and boiling points increase with the increase in atomic number.

Helium has two isotopes, 'He and $^4$He. The latter constitutes almost 100% of atmospheric helium. While $^3$He behaves normally, $^4$He has strange properties. When cooled below 2.2 K at one atmosphere pressure, ordinary liquid $^4$He, called helium-I. changes to an abnormal form called helium-II. The temperature at which this transition of He-I to He- II takes place is known as Lambda point.

Below this temperature, its thermal conductivity increases a million fold and the viscosity becomes effectively zero, hence it is described as a superfluid.

All the noble gases, especially helium, have tremendous ability to diffuse through almost all types of glass, rubber, PVC, etc.

**Self Assessment Exercise  2**

You have read above that boiling point is related to the binding forces in atoms/molecule:  In noble gases, the atoms are held by van der Waals forces. Can you now explain in the space given below as to,

a)      What is the relationship between the boiling point and van der Waals forces?

b)      Why there is a steady increase in boiling points from He to Rn?

**Further Readings**

*Chemistry: Facts, Patterns and Principles,* W.R. Kneen, M J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

*Comprehensive Inorganic Chemistry,* F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 9th reprint, 1986.

*Principles of Inorganic Chemistry,* B.R. Pun and L.R. Sharma, Shohan Lal Nagin Chand & Co., New Delhi. 19th ed., 1986.

*Theoretical Inorganic Chemistry,* M.C. Day, Jr and J. Selbin, Affiliated East-West Press Pvt. Ltd. 1985.

*Advanced Chemistry (physical and industrial)* Philip Mathews Cambridge university press 2003
*Theoretical principles of inorganic chemistry* GS Manku Tata McGraw-Hill 1981
*Modern Inorganic Chemistry*: GF Liptrot ELBS 1971

**Module 1        Noble Gases**

**Unit 2            COMPOUNDS OF NOBLE GASES**

1.0      Introduction

2.0      Objectives

3.0      Compounds of Xenon

4.0      Clathrates of Noble Gases

5.0      Structure and Bonding in Xenon Compounds

6.0      Molecular Shapes of Noble Gas Compounds and Valence
         Shell Electron Pair Repulsion (VSEPR) Theory

**1.0 Introduction**

Xenon difluoride, $XeF_2$ can now be made by a simple reaction of xenon and fluorine gases in a pyrex bulb in sunlight. But still the compounds of the noble gases were unknown until 1962. Is it not surprising that a compound which can be prepared so easily eluded the world of science for so long? One reason for this is that most of the reactions were carried out on argon, which was the most readily available, and the results of experiments on argon, wire thought to apply to all noble gases. Moissan, in 1986, found that argon would not react with fluorine under any conditions. Secondly, attempts at reacting xenon with fluorine using electric discharge methods did not meet with success, although Pauling had predicted that some noble gas fluorides should be stable Chemists were discouraged by these failures and also by the preconceived notion that the noble gases must be inert because of their stable configuration.

The first breakthrough in the noble gas compounds was achieved in l960 by an English chemist Neil Banlett. He was trying to make the newly discovered compound $PtF_6$, instead he obtained a deep red compound containing oxygen. The X-ray diffraction picture of the red solid showed it to be the first known salt of dioxygennyl cation, i.e. $|O_2|+|PtF_6|^-$. This showed that $PtF_6$ oxidises the oxygen molecule. Hurtled realised that xenon should form an analogous compound because the ionisation energy of xenon, 1170 kJ mol$^{-1}$, is slightly lower than that of the oxygen molecule, 1180 K.J mol$^{-1}$. When he brought xenon and $PtF_6$ together, he obtained an orange yellow solid, xenon hexafluoroplatinate, $(Xe)^+[PtF_6]^-$. This opened the field for the study of the chemistry of noble gases.

True chemical bonding in the noble gases seems to be restricted to krypton, xenon and radon with fluorine or oxygen as ligands. None, however, combines with oxygen directly.

The oxides are made from the fluorides when they react with water. Krypton chemistry is limited to the difluoride, $KrF_2$, which is stable only below 353 K, and one or two complexes with fluorine bridges between krypton and another element. Radon is known to form at least one Chloride, but its formula has not yet been established because of the vigorous disintegration of the nucleus. Thus, the noble gas chemistry is effectively limited to the compounds of xenon.

2.0    **Objectives**

At the end of this unit, you should be able to;
•       describe the important compounds of the noble gases, particularly xenon, especially the bonding in these compounds.
    -   Enumerate the structure and bonding in Noble gases
    -   Predict the VSEPR theory in noble gases

**3.0    Compounds of Xenon**

The chemistry of xenon is the most extensive in this group and the known oxidation states of Xe range from +2 to +8. Structural details of some of the more important compounds of Xe are listed in Table 1.4

Xenon reacts directly with fluorine on heating the gases in a nickel vessel. The products depend upon the amount of fluorine present and the reaction conditions:
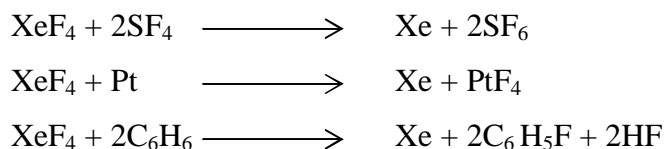
$$Xe + F_2 \xrightarrow[\text{700 K, sealed vessel}]{\text{2:1 mixture}} XeF_2$$

$$Xe + 2F_2 \xrightarrow[\text{700 K, 6 atmosphere}]{\text{1:5 mixture}} XeF_4$$

$$Xe + 3F_2 \xrightarrow[\text{500-600 K, 50-60 atmosphere}]{\text{1:20 mixture}} XeF_6$$
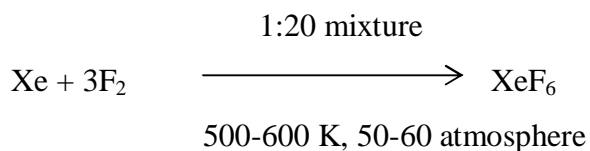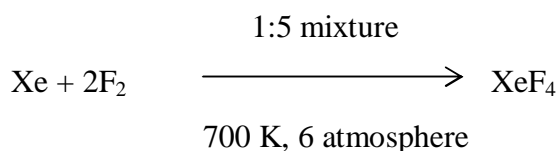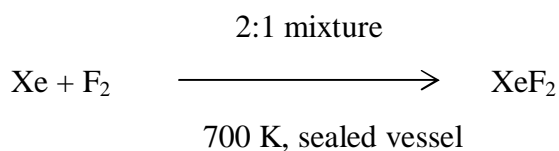
The compounds $XeF_2$, $XeF_4$ and $XeF_6$ are white solids which can be sublimed at room temperature. The lower fluorides react with fluorine on heating under pressure forming higher fluorides. The fluorides are extremely strong oxidising and fluorinating agents. They react quantitatively with hydrogen.

$$XeF_2 + H_2 \longrightarrow 2HF + Xe$$
$$XeF_2 + H_2 \longrightarrow 4HF + Xe$$
$$XeF_2 + H_2 \longrightarrow 6HF + Xe$$
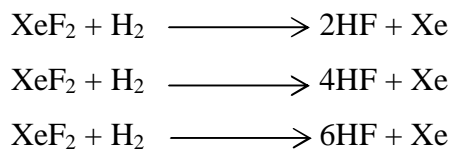
They oxidise chlorides to chlorine, iodides to iodine, cerium (III) to cerium (IV), Ag(I) to Ag(II), Cr(III) to Cr(VI) and Br(V) to Br(VII):

$$XeF_2 + 2HCl \longrightarrow Xe + 2HF + Cl_2$$

$$XeF_4 + 4Kl \longrightarrow Xe + 4HF + 2l_2$$

$$XeF_2 + BrO_3 + \longrightarrow Xe + BrO_4 + 2HF$$
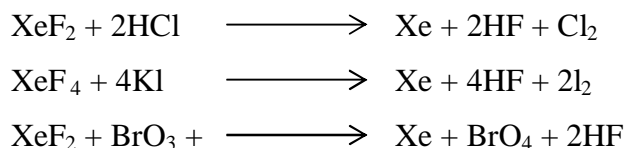
They fluorinate many compounds as well as elements:

$$XeF_4 + 2SF_4 \longrightarrow Xe + 2SF_6$$

$$XeF_4 + Pt \longrightarrow Xe + PtF_4$$

$$XeF_4 + 2C_6H_6 \longrightarrow Xe + 2C_6H_5F + 2HF$$

The fluorides differ in their reactivity with water. $XeF_2$ dissolves unchanged in water or acidic solutions, but on standing, decomposition occurs slowly. Decomposition is more rapid with alkali.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$
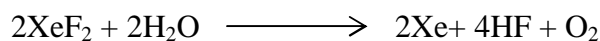
Reaction of XeF, with water is violent since xenon trioxide, $XeO_3$, formed is highly explosive:

$$3XeF_6 + 6H_2O \longrightarrow 2Xe + XeO3 + 12\ HF + \frac{3}{2}\ O_2$$
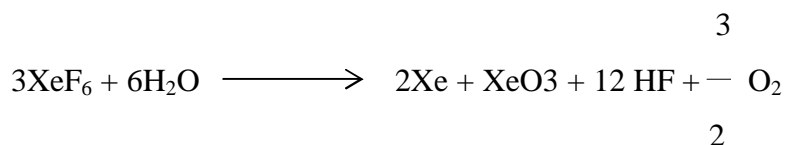
$XeF_6$ also reacts violently with water and hydrolysis by atmospheric

$$2XeF_6 + 6H_2O \longrightarrow 2XeO_3 + 12HF$$
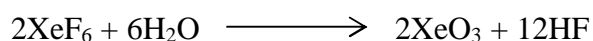
With small quantities of water, partial hydrolysis occurs giving a colourless liquid xenon oxofluoride, $XeOF_4$. The same product is formed when $XeF_6$ reacts with silica or glass. Because of the stepwise reaction which finally produces the dangerous $XeO_3$, $XeF_6$ cannot be handled in glass or quartz apparatus.

$$XeF_6 + H_2O \longrightarrow XeF_4 + 2HF$$

$$2XeF_6 + Si_2O \longrightarrow 2XeF_4 + SiF_4$$

$$2XeOF_6 + Si_2O \longrightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_6 + Si_2O \longrightarrow 2XeO_3 + SiF_4$$
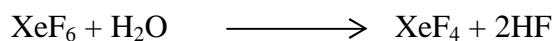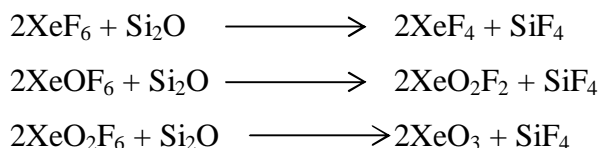
$XeO_3$ does not ionise in aqueous solution, but in alkaline solution above pH 10.5, it forms the xenate ion $HXeO_4$,

$$XeO_3 + NaOH \longrightarrow 2XeO_3 + SiF_4$$
$$\text{sodium xenate}$$
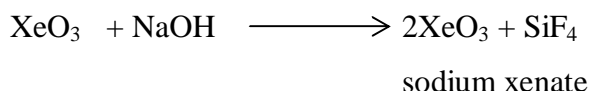
Xenates slowly disproportionate in alkaline solution to form perxenates and Xe gas:

$$2HXeO_4 + 2OH^- \longrightarrow XeO_6 + Xe + O_2^- + 2H_2O$$
$$\text{Perxenate ion}$$
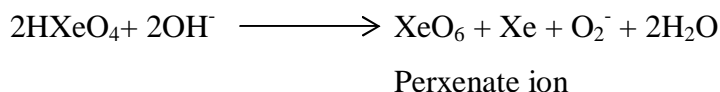
Alkaline hydrolysis of $XeF_6$ also forms perxenates

$$2XeF_6 + 16OH^- \longrightarrow XeO_6 + Xe + O_2^- + 12F^- + 8H_2O$$
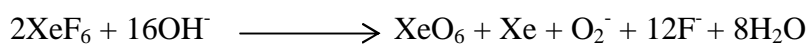
Perxenates are extremely powerful oxidising agents, and can oxidise HC1 to $Cl_2$ $H_2O$ to $O_2$ and Mn(II) to Mn(VH). With concentrated $H_2SO_4$, they give xenon tetroxide $XeO_4$, which is volatile and explosive:

$$Ba_2XcO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaS0_4 + 2H_2O$$
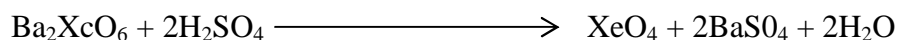
$XeF_2$ acts as a fluoride donor and reacts with pentafluorides such as, $PF_5$, $AsF_5$, $SbF_5$, $TaF_5$, $RuF_5$, $RhF_5$, $IrF_5$ and $PtF_5$ to form salts of the types $[XeF]^+|MF_6]^-$ , $[XeF]^+ [M_2F_{11}]$- and $[Xe_2F_3 [MF_6]^-$. $XeF_4$ is much less reactive in this respect and reacts only with the strongest $F^-$ acceptors such as $SbF_5$ and $BiF_5$. But $XeF_6$ combines with pentafluorides to yield 1: 1 complexes such as, $[XeF_5]^+[AsF_6]^-$ and $[XeF_5]^+lPtF_6]^-$.

Before proceeding to clathrates of noble gases, try the following SAQ related to xenon compounds.

**Self Assessment Exercise 1**

Complete the following reactions by writing the reaction conditions/products in the blank spaces given for each reaction.

i) $Xe + F_2$ $\xrightarrow{\quad ? \quad}$ $XeF_2$

$\qquad\qquad$ 1:20 ratio of Xe: F2

ii) $Xe + F_2$ $\xrightarrow{\qquad}$ $\underline{\qquad ? \qquad}$

$\qquad\qquad$ Nickel crucible

iii) $XeF_2 + H2O$ $\xrightarrow{\qquad}$ $Xe +$ $\underline{\qquad ? \qquad}$ $+$ $\underline{\qquad ? \qquad}$

## 4.0 Clathrates of Noble Gases

Crystalline clathrates or inclusion complexes of noble gases have long been known. In these complexes the noble gas atoms are trapped in cavities in the crystal lattice of certain other 'compounds such as quinol or water. The formation of clathrates seems to depend on relative molecular dimensions rather than on any particular chemical affinity. The atoms or molecules of any substance, which are of a suitable size to fit in the cavities in the host lattice, can form clathrates. Thus, $O_2$, $SO_2$, $H_2S$ and MeOH are examples of other substances which form clathrates with quinol.

When quinol is crystallised from its aqueous solution in the presence of heavier noble gases like Ar, Kr or Xe under a pressure of 10-40 atmosphere, crystals of clathrates of the composition G.3Quinol are obtained. The crystals are quite stable and can persist for several years. However, when heated or dissolved in water, the gas escaped leaving behind quinol. Similarly, when water is allowed to freeze in the presence of Ar, Kr or Xe under pressure, atoms of noble gas get trapped in the crystal lattice of ice giving clathrates corresponding to the composition, $8G.46H_2O$. These clathrates are also known as the noble gas hydrates. You can

see the hydrates may not be stoichiometric since the degree to which the cavities are filled depends on the partial pressure of the guest material.

The hydrates increase in thermal stability down the group as the noble gases become more polarisable. With xenon, at a partial pressure of one atmosphere, the hydrate is stable up to 275 K. Because of their very low polarisability, small size and low boiling points, no hydrates of helium and neon have been prepared. Clathrates provide a means of storing noble gases and of handling the various radioactive isotopes of Kr and Xe which are produced in nuclear reactors.

> The crystal lattice with cavities is called the host, substance entrapped in it is called guest.

## Self Assessment Exercise 2

Explain briefly:
i)      Why no compounds of He and Ne are known?
ii)     Why noble gas compounds are formed only with $O_2$ and $F_2$?
iii)    Why does the tendency to form clathrates increase down the group?

## 5.0    Structure and Bonding in Xenon Compounds

You would recall that prior to 1962, it was widely believed that the noble gases are chemically inert because of the stability of their electronic configurations. However, the discovery that their compounds could be prepared made it necessary that some description be given of the nature of bonding in the compounds they form. The nature of the bonds and the orbitals used fur bonding in the compounds of noble gases is of great interest. It has been the subject of considerable controversy as will be evident from the discussion of bonding in some individual xenon compounds.

### Xenon   Difluoride

It is a linear molecule. Bonding in $XeF_2$ may be explained with the help of Valence Bond Theory (cf. Unit 4, Block 1, Atoms & Molecules course). An electron from the 5p level of Xe is promoted to the *5d* level, followed by *sp³d* hybridisation.



*sp³d*–hybridisation
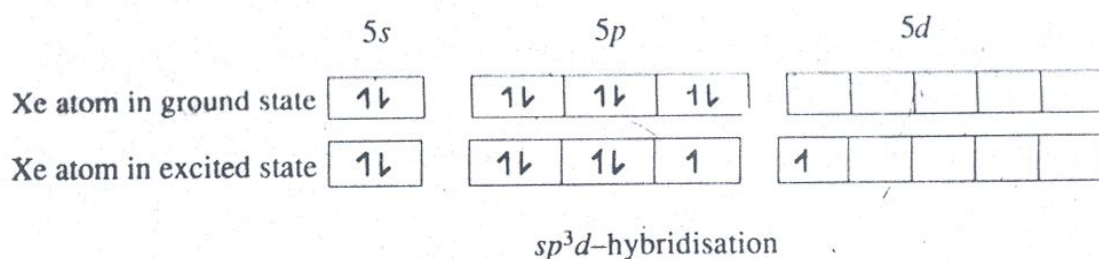
The two Unpaired electrons in axial orbitals form bonds with two fluorine atoms and three lone pairs occupy the equatorial positions of the trigonal bipyramid giving rise to a linear molecule as shown in Fig. 1.1
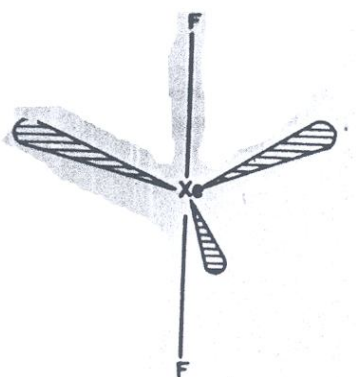
Figure 1.1 Linear structure of $XeF_2$

The objection to this model is that the $5d$ orbital of Xe appears to be too large and too high in energy to participate in hybridisation. However, it has been suggested that the highly electronegative atoms like fluorine cause a large contraction in the size of the $d$ orbitals enabling them to participate in bonding.

Molecular orbital approach involving three-centre four electron bonds has been found more acceptable. The outer electronic configuration-of the atoms involved in bonding are:

| | $5s$ | | $5p_x$ | $5p_y$ | $5p_z$ | | | $2s$ | | $2p_x$ | $2p_y$ | $2p_z$ |
|----|------|--|--------|--------|--------|--|--|------|--|--------|--------|--------|
| Xe | ⇅ | | ⇅ | ⇅ | ⇅ | ; | F | ⇅ | | ⇅ | ⇅ | ↑ |
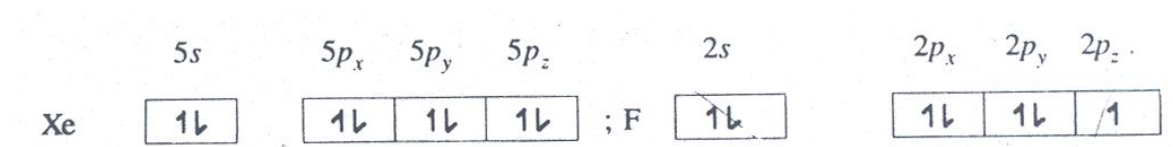
It is assumed that the $5p_z$ orbital of xenon and the $2p_z$ orbital of the two fluorine atoms are involved in bonding. These three atomic orbitals combine to give three molecular orbitals, one bonding, one nonbonding and one antibonding which can be represented as shown in Fig. 1.2

F          Xe          F

antibonding    (orbitals have wrong symmetry for overlap).

nonbonding    (5pz orbitals of Xe has no contributing, since the bonding effects in one half is cancelled by the antibonding effects in the other half).

bonding    (orbitals have correct symmetry for overlap).
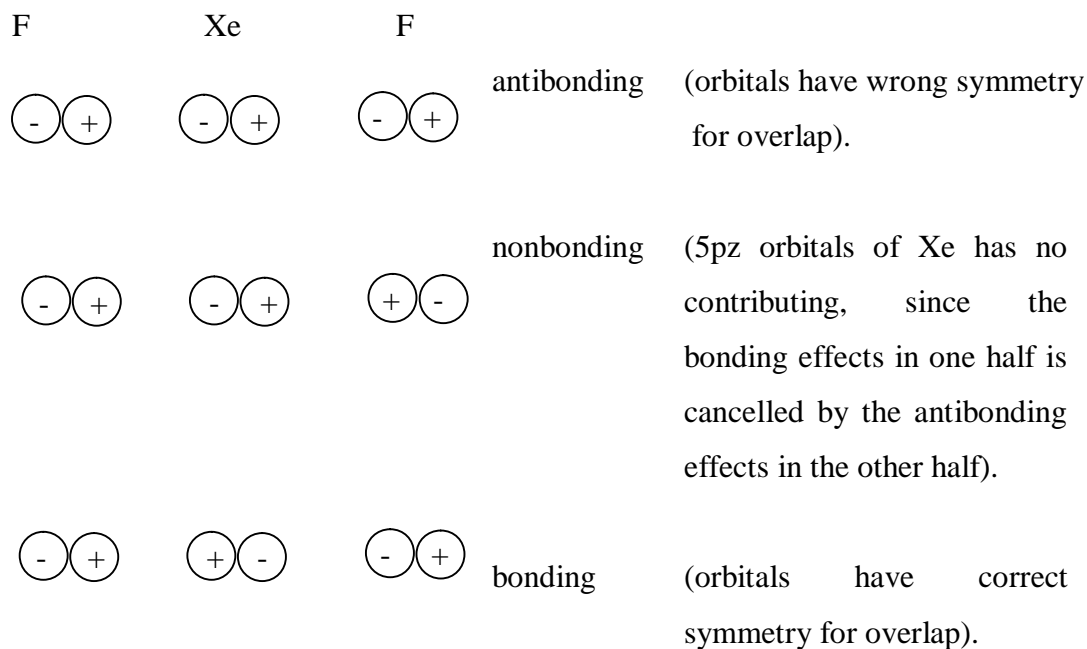
Fig. 1.2 Molecular orbital representation of the 3- centre 4-electron bond in $XeF_2$

The three original atomic orbitals contained four electrons. These occupy the molecular orbitals of lowest energy as shown in Fig. 1.3
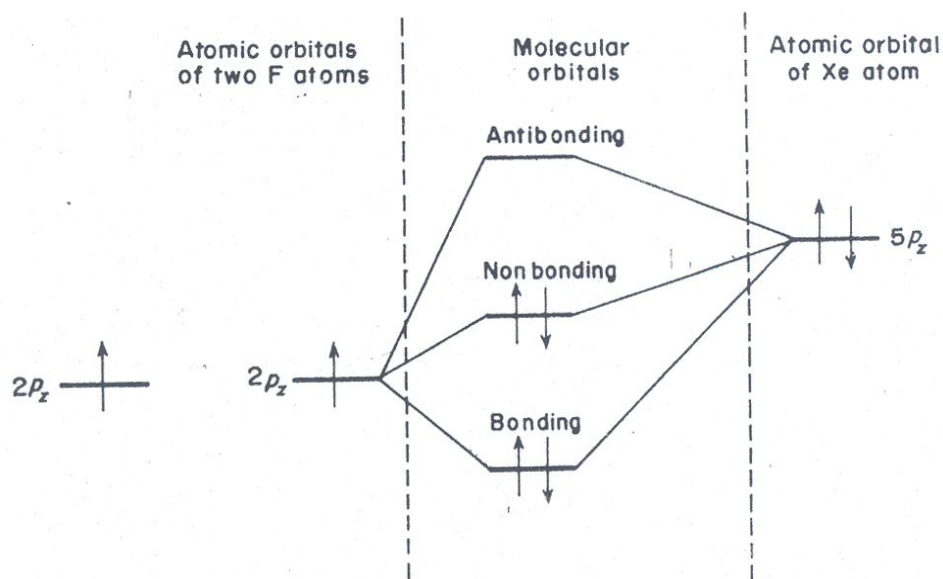


**Fig. 1.1: Molecular orbital energy level diagram for $XeF_2$ molecule**

A linear arrangement of the atoms gives the best overlap of orbitals, in accordance with the observed structure. The situation is similar to that in the boron hydrides where there are three-centre B-H-B bonds (refer CHE 121 except that in $XeF_2$ there are four electrons involved compared with two electrons in the boranes.

**Xenon Tetrafluoride**

The structure of $XeF_4$ is square planar (Fig. 1.4). The Valence Bond Theory explains this by promoting two electrons resulting in $sp^3d^2$ hybridisation. Two of the positions on the octahedron are occupied by two lone pairs. This gives rise to a square planar structure.
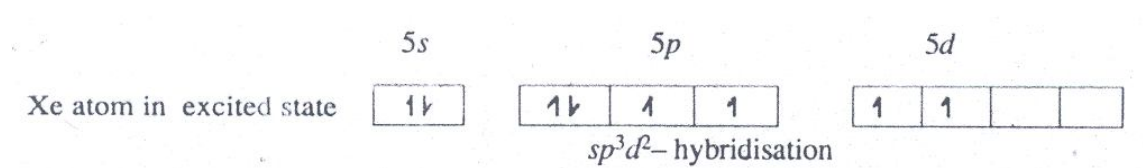


The alternative explanation is that in $XeF_4$. the Xe atom binds to four F atoms by using two of its $p$ orbitals to form two three-centre molecular orbitals at right angle to each other, thus giving a square planar shape.
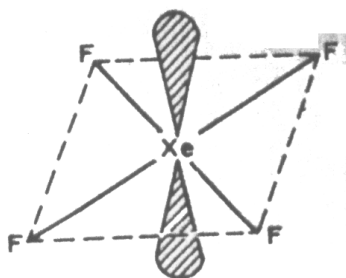


**Fig. 1.2 Structure of XeF₄**

**Xenon Hexafluoride**

According to Valence Bond approach, 3 electrons are promoted and the hybridisation is $sp^3d^3$ which predicts a pentagonal bipyramidal or capped octahetral structure as shown in Fig. 1.5
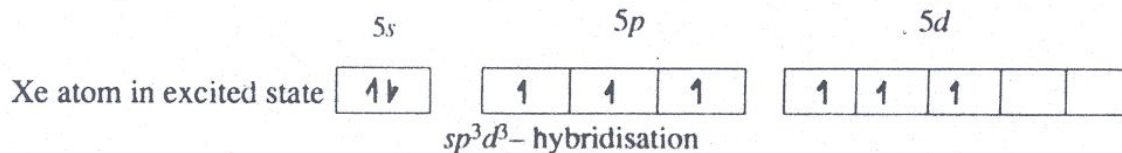
According to M.O. theory, the structure of $XeF_6$ can be explained by considering three three-centre molecular orbitals mutually at right angles and giving a regular octahedral shape. Thus, M.O. theory fails here to predict the correct structure. A more detailed discussion regarding this can be found in higher courses in the subject.
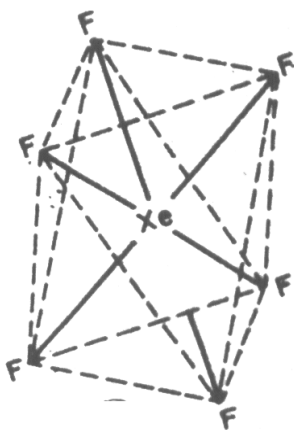


**Fig. 1.3: Structure of XeF$_6$**

## 6.0    Molecular Shapes of Noble Gas Compounds and Valence Shell Electron Pair Repulsion (VSEPR) Theory

Thus, we have seen above that neither the Valence Bond approach nor the Molecular Orbital theory is able to explain the bonding in all the noble gas compounds. The approach which has given the most rational explanation about the stereochemistry of noble gas compounds and provided the most readily visualised description of their shapes is the Valence Shell Electron Pair Repulsion Theory (VSEPR) of Gillispie and Nyholm. You may have come across this in

CHM 101. To recollect, this theory assumes that stereochemistry is determined by the repulsions between valence shell electron pairs, both bonding and nonbonding, and that the latter exert the stronger effect. Thus in $XeF_2$, the valence shell of Xe atom has ten electrons, eight from the Xe atom and one each from the two F atoms. These are distributed in five pairs, two bonding and three nonbonding, which are directed to the corners of a trigonal bipyramid. Because of their greater mutual repulsion, the three nonbonding pairs are situated in the equatorial plane at 120° to each other, leaving the two bonding pairs perpendicular to the plane and so producing a linear F-Xe-F molecule.

In the same way, $XeF_4$ with six electron pairs is considered as pseudo-octahedral with its two nonbonding pairs opposite to each other leaving the four F bonds in a plane around Xe.

More distinctively, the seven electron pairs around Xe in $XeF_6$ suggest the possibility of a non-regular octahedral geometry and imply a distorted structure based on either monocapped octahedral or a pentagonal pyramidal arrangement of electron pairs, with the Xe-F bonds bending away from the protruding nonbonding pair.

It will be interesting to devise similar rationalisations for the xenon oxides. Three electron pairs of the Xe atom can be used to complete the octet of three oxygen atoms, leaving on lone pair on xenon. This gives a trigonal pyramidal shape to $XeO_3$ molecule (Fig. 1.6 Similarly in xenon tetroxide, four electron pairs from xenon can coordinate with each of the lour oxygens forming a tctrahedral molecule (Fig. 1.7). Such coordination, however, leaves a rather high positive charge on the central atom. The tetrahedral silicate, phosphate and sulphate ions, which are isoelectronic with $XeO_4$, are stabilised by $p\pi$-$d\pi$ back bonding in which lone-pair electrons on oxygen spend some time in $d$ orbitals on the central atom. This helps to even out the charge distribution. But $5d$ orbitals of xenon are ill-matched with $2p$ orbitals of oxygen, thus weak Xe-O bond is consistent with

rather little $p\pi$-$d\pi$ bonding and considerable polar character. Structural details of some xenon compounds based on VSEPR theory are given in Table 1.5. Although chemists were taken by surprise by the noble gas compounds but as you can see, these were soon found to be readily accommodated by current bonding theories.
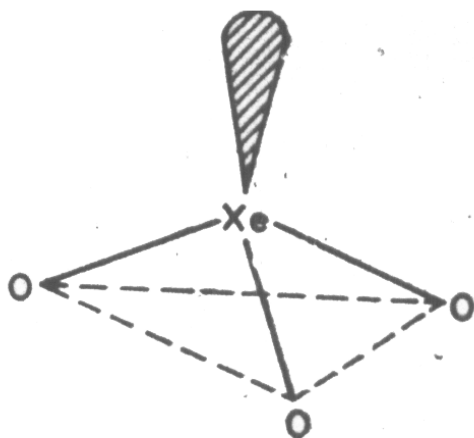


**Fig 1.6: Structure of XeO₃**
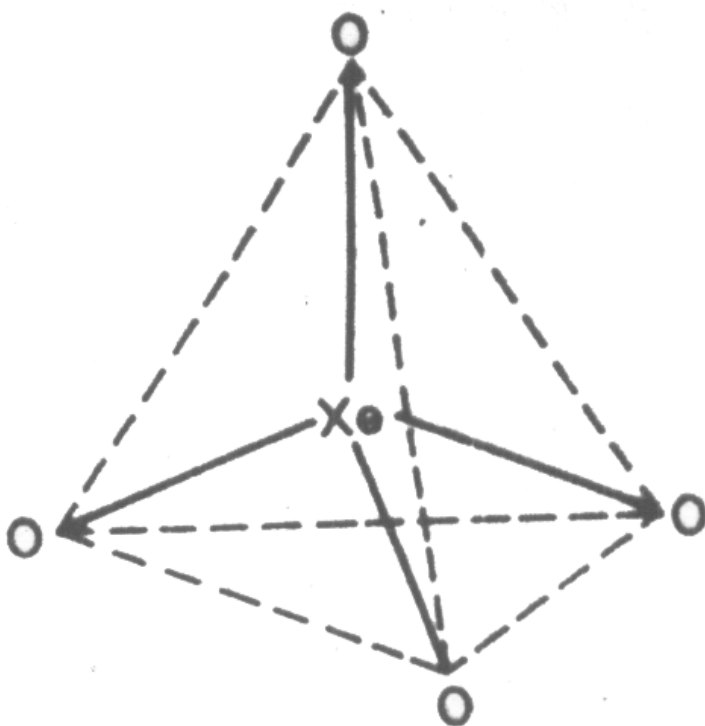


**Fig. 1.4: Structure of XeO₄**

Table 1.5 : Structure of some of Xenon compounds

| Compound | Oxidation State of Xe | No. of electron pairs around Xe | | | Structure | Remarks |
|---|---|---|---|---|---|---|
| | | Bond pairs | Lone pairs | Total | | |
| $XeF_2$ | +II | 2 | 3 | 5 | Linear | Lone pairs occupy equatorial positions of trigonal bipyramid |
| $XeF_4$ | +IV | 4 | 2 | 6 | Square planar | One lone pair above and the other below the plane of molecule |
| $XeF_6$ | +VI | 6 | 1 | 7 | Distorted octahedral | Lone pair either at the centre of a face or at the midpoint of an edge |
| $XeO_3$ | +VI | 6 | 1 | 7 | Trigonal pyramidal | Bond pairs are in three double bonds, lone pair protruding from the apex of the pyramid |
| $XeO_4$ | +VIII | 8 | — | 8 | Tetrahedral | Bond pairs are in four double bonds |
| $XeO_2F_2$ | +VI | 6 | 1 | 7 | see-saw | Four bond pairs in two Xe=O bonds, two bond pairs in two Xe–F bonds, lone pair occupying one equatorial site |
| $XeOF_4$ | +VI | 6 | 1 | 7 | Square pyramidal | Two bond pairs in Xe=O bond, four bond pairs in four Xe–F bonds, lone pair protruding from the base |
| $XeOF_2$ | +IV | 4 | 2 | 6 | 'T' shaped | Two bond pairs in Xe=O bond, two bond pairs in two Xe–F bonds, lone pairs occupying two equatorial sites of trigonal bipyramid. |

**Self Assessment Exercise 3**

Given below in Column I are the few expected compounds of noble gases. Write down in Column II the shapes of these compounds on the basis of VSEPR theory.

| Column I | Column II |
|---|---|
| (i)   $XeF_4$ | (i)   ………………………………… |
| (i)   $XeOF_4$ | (ii)  ………………………………… |
| (i)   $XeO_4$ | (iii) ………………………………… |
| (i)   $XeF_6$ | (iv) ………………………………… |

**SUMMARY**

Let us now recall what you have learnt in this unit:

- The atmosphere surrounding the earth is a mixture of gases consisting of nitrogen (78%), oxygen (21%), noble gases (1%), some other gases like $CO_2$ and air pollutants.

- Noble gases were discovered in the order: helium in 1868, then neon, argon, krypton and xenon in the 1890s and finally radon in 1902.

- The characteristic stable electronic configuration of noble gases is $.Is^2$ or $ns^2np^2$
  They have the highest ionisation energies and the lowest electron affinity, melting and boiling points and heat of vaporisation in their periods.

- Noble gases have various applications like as coolants and for providing inert atmosphere. Their chemistry is limited due to the exceptional stability of their closed valence shells. Only xenon reacts directly with fluorine forming fluorides. Oxides may be prepared by the reaction of water with fluorides.

- The shapes of xenon compounds can usually be explained with the help of Valence Shell Electron Pair Repulsion Theory.

**Further Readings**
*Chemistry: Facts, Patterns and Principles,* W.R. Kneen, M J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

*Comprehensive Inorganic Chemistry,* F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 9th reprint, 1986.

*Principles of Inorganic Chemistry,* B.R. Pun and L.R. Sharma, Shohan Lal Nagin Chand & Co., New Delhi. 19th ed., 1986.

**Module 2    CHEMISTRY OF REPRESENTATIVE ELEMENTS**

**UNIT 1 :    Hydrogen Element**

**1.0    INTRODUCTION**

During the course of CHM 101 and CHM 205, you were introduced to the properties of the Group IA to Group IVA elements. The representative elements are made of S and P block elements of the periodic table, in which their valence shell is either S or P orbitals

In this unit, you we will focus our attention on Chemistry of Hydrogen. Group IA and Group IIA elements, Boron, and compare between the chemistry of  carbon and silicon, nitrogen and phosphorus and oxygen and sulphur.

**2.0  Objectives**

- Describe the electronic configuration of the elements.
- Chemical properties of the element.
- Comparative study of the chemistry of the elements.

**3.0    HYDROGEN**

Lavoister gave the name hydrogen to inflammable gas colleted by reacting iron with sulphuric acid. Hydrogen occurs in the free state, in some volcanic gases and in the outer atmosphere of the sun. Other stars are composed almost entirely of hydrogen. The main source of hydrogen are water, and petroleum and natural gas, where it occurs in combination with carbon. The element is an essential ingredient in all living matter, being found in proteins and fats.

The hydrogen atom consists of one proton and one electron, with electronic configuration of $1S^1$. Most of the chemistry of hydrogen can be explained in terms

of its tendency to acquire the electronic configuration of the noble gas helium, this it can do by gaining an additional electron to give the hydride ion, $H^-$, by sharing its electron and accepting a part share of an electron from atom as in the hydrogen molecule $H - H$, and by accepting a lone pair of electrons, which it does as a proton when combined with, for example water and ammonia to give the hydroxonium $H_3O^+$ and ammonium $NH_4^+$ ions respectively.

Hydrogen can readily be obtained by the action of certain metal on water or steam and dilute acids. Nitric acid and concentrated sulphuric acid must be avoided.

$$Na + H_2O \rightarrow 2NaOH + H_2(g)$$

and by action of steam on coke or hydrocarbon.

$$C(s) + H_2O \rightarrow 2NaOH + CO(g) + H_2(g)$$
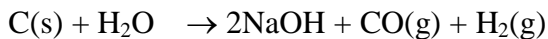
There are three isotopes of hydrogen of relative masses, 1, 2 and 3. They are called ordinary hydrogen, deuterium and tritium respectively and differs in that whereas ordinary hydrogen has no neutrons, deuterium has one and tritium has two neutrons in the nucleus. Tritium is the only one that is radioactive. The ratio of ordinary hydrogen to deuterium in hydrogen compounds is about 6000:1, tritium occurs in even smaller amounts.

Deuterium is slightly less reactive than ordinary hydrogen but otherwise its properties are almost identical. Deuterium is used as a tracer for elucidating a wide range of reaction mechanisms, and so are its compounds. Many of these compounds can be readily obtained from deuterium oxide ($D_2O$-heavy water), for example DCl, an equivalent of hydrogen chloride.

## 3.1 Properties of Hydrogen

Hydrogen is a colourless gas without taste or smell. It can be liquefied by compression and cooling in liquid nitrogen, followed by sudden expansion. Liquid hydrogen boils at $-25^{\circ}C$ and becomes solid at $-259^{\circ}C$.

Hydrogen burns in air and, under certain conditions, reacts explosively with oxygen and the halogens e.g.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(1)}$$
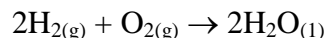
It reacts partially with boiling sulphur to give hydrogen sulphide.

$$H_2(g) + S_{(l)} \rightleftharpoons H_2S_{(l)}$$
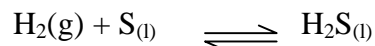
and with nitrogen at elevated atmosphere and pressure in the presence of a catalyst to form ammonia. It forms ionic hydrides with most metals of Group IA and 2A. It form covalent hydrides with the elements from Group 4B and 7B in the periodic table, and are gaseous at ordinary temperature, with exception of a few, and with transition metals a series of rather ill-defined compounds – interstitial hydrogen- is formed.

## 3.2    Active Hydrogen

Atomic hydrogen can be generated by dissociating hydrogen molecules into atoms using high energy sources, such as discharge tube containing hydrogen at low pressure, or a high current density arc at high temperature. Thus, dissociation is highly endothermic

$$H_2(g) \rightarrow 2H(g) \; \Delta H^\ominus \; (298k) = +435.9 Kjmol^{-1}$$
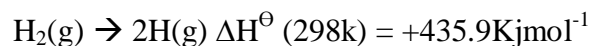
Many metals are able to catalyse the recombination of hydrogen atoms e.g. platinum and tungsten, which results in liberation of the same quantity of energy as is needed to effect the dissociation. This effect is used in the atomic hydrogen blowlamp for welding metals. Hydrogen is a powerful reducing agent e.g. it will reduce metallic oxides and chlorides to metals, and oxygen to hydrogen peroxide.

The nascent hydrogen is a hydrogen at the instant of formation. Nascent hydrogen can reduce elements and compounds that do not readily react with normal hydrogen.

## 3.3    Uses of Hydrogen

Before now, only small quantities of hydrogen were required as a fuel in the form of town gas and water gas, for filling balloons and in the oxy-hydrogen blowlamp for welding. Recently, however, large quantities of the gas are employed in the process listed below:
- Manufacture of ammonia by Harber process.
- Manufacture of hydrogen chloride and hydrochloric acid.
- Manufacture of organic chemicals e.g. methanol.
- Manufacture of margarine.

- Extraction of some metals from their oxide.
- Liquid hydrogen has been used as a rocket fuel.

## 4.0     CONPARATIVE STUDY OF Group IA and Group IIA ELEMENTS

The elements of Group IA includes $L_1$, Na, k, Rb, Cs, and Fr, the first four are metals. Indeed, from a chemist point of view, they made an excellent set because they have a large number of properties in common. Lithium is the only member of the group that is not completely typical.

They are all highly electropositive metals. Indeed, the tendency for them to lose their outermost electron and change into a positive ion is the most important feature of their chemistry. This is due to the fact that the outer S electron is very well shielded by the inner electrons. The S electron feels only a fraction of the nuclear charge. As we do down the group, shielding wins over the effect of the increasing numbers of protons in the nucleus. Caesium, for example is a much more powerful reducing agent than sodium. The metals are so reactive that in nature they are always found combined with other elements. They do exist as chlorides, nitrogen, sulphates and carbonise.

It is difficult to convert Group IA metal ions into neutral atoms, so if we need to obtain the pure metal we have to use electrolysis. The pure metals are silvery white and apart from Li, soft and easy to cu. However, they rapidly tarnish in air giving a layer of oxide, peroxide, or sometimes super oxide. They will also react violently with water. For both reasons they are kept under a layer of oil.

The elements of Group IIA; Be, Mg, Ca, Sr and Ba are all metals. They show the properties we would expect, e.g. they are good reducing agents, they give ionic compounds, their oxides and hydroxides are basic, and they give hydrogen with acids. The alkaline nature of the elements is responsible for them being known as the alkaline earth metals. The exception of the common pattern is the first member, beryllium. One reason why beryllium is different is that its elements are not strongly shielded from its nucleus. The radius of $Be^{2+}$ ion is extremely small, and it represents a very dense centre of positive charge with an immense

polarising power. This ability to draw electrons towards itself is responsible for the covalence of many of its compounds. Another feature of chemistry of beryllium is that in solution its compounds tend to suffer from hydrolysis, and some are amphoteric rather than completely basic. Like the Group IA metals, the reaction of the elements makes it difficult to extract them by chemical means.
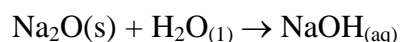
## 5.0    Chemistry of Group IA.

a.    **Reaction with oxygen**

Lithium oxidises less rapidly than the other metals, but they all give ionic oxides and peroxides. In a plentiful supply of oxygen the reactions can be violent.

$$2K(s) + O_2(g) \rightarrow K_2O_2(g)$$
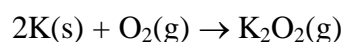
They are all basic. They dissolve in water to give strongly alkaline solutions containing hydroxide ions for example

$$Na_2O(s) + H_2O_{(1)} \rightarrow NaOH_{(aq)}$$

b.    **Reaction With Water**

Li, Na and K all float on water. Li reacts only slowly, but Na and K reacts more quickly. Hydrogen is given off and the solution remaining is alkaline. The reactions of Rb and Cs with water should not be attempted, because of explosions.

$$2Na(s) + 2H_2O_{(1)} \rightarrow 2HaOH_{(aq)} + H_2(g)$$
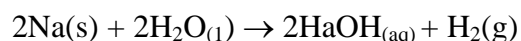
c.    **The Hydroxides**

The hydroxides of the Group IA metals are among the strongest bases known. They exist as ionic solids and are very soluble in water. With exception of LiOH, which is slightly soluble, it and is also the only one that will convert to an oxide on heating.

d.    **The Carbonates and Hydrogen Carbonates**

The carbonates are all soluble in water, and their hydrogen carbonates exist as solids. The exception once again is lithium, which does not give a hydrogen carbonate.

Sodium carbonate is useful substance; it is sold as washing soda crystals $Na_2CO_3.10H_2O$. In water it gives a slightly alkaline solution owing to salt hydrolysis.

$$Na_2CO_3 + H_2O \rightarrow NaHCO_{3(aq)} + NaOH_{(aq)}$$

The case with which hydrogen carbonates give all carbon dioxide is made use of in fire extinguishers and baking powders.

2 SAQ what would you expect to happen if you heated washing soda crystals

e.   **The Halides**

All the metals give fluorides, chlorides, bromides, and iodides. Apart from caesium they have the same crystal structure as sodium chloride.

f.   **The Nitrogen and Nitrides**

Sodium nitrate, $NaNO_3$, and sodium nitrites, $NaNO_2$ are the most important salts. In common with all other nitrates, sodium nitrate is soluble in water. Chemically, the Group IA nitrates are a little different to those of other metals. In particular, when they are heated, they give off oxygen and change into a nitrite.

$$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$$

Most nitrates are energetically stable. However, the nitrogen in a nitrate ion is in a high oxidation state (+5) and the ions contain a high percentage of oxygen. With the right chemicals, the ions will show a considerable ability to act as oxidising agents. Especially, $KNO_3$ mixed with sulphur and carbon is used as a gun powder. Sodium nitrite is used in the manufacture of dyes and in increasing the shell life of raw meat sold in supermarkets.

g.   **The Sulphates, Hydrogen Sulphases and Sulphites**

All the members of the group gave sulphates and hydrogen sulphates. They are all soluble in water.

Sulphites, such as sodium sulphite, $Na_2SO_{2}$**(3 please check and correct)**, are more reactive than either sulphates or hydrogen sulphates e.g. if you warm a sulphite with an acid, you will find sulphur dioxide is given off.

$$Na_2SO_{3(aq)} + 2HCl \rightarrow 2NaCl + SO_2(g) + H_2O_{(1)}$$

Sodium thiosulphate is produced by boiling a solution of sodium sulphate with powdered sulphur. Sodium thiosulphate is used as hypo in photography. In the laboratory it is used in iodine titrations.

h.   **The Hydrides**

All the hydrides of the group are ionic, with the metal being positive and the hydrogen being negative.

**6.0    Chemistry of Group IIA**

a.    Beryllium oxide, BeO, is more like the oxide of aluminium in Group III rather than the oxides of the other element in Group II. It has a high degree of covalence, which is lacking in the other oxides. It is insoluble in water and it will dissolve only with great difficulty in acids. The reactivity of BeO depends on its treatment. If it is heated to a high temperature (above $800^oC$) it becomes almost completely inert

The other oxides will dissolve in water with increasing ease down the group. The resulting solutions are slightly alkaline owing to reactions between the oxides and water e.g.

$$MgO(s) + H_2O_{(1)} \rightleftharpoons MgOH\ (aq)$$
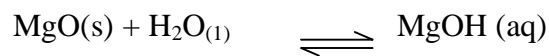
b.    **The Halides**

The elements all give fluorides, bromides and iodides as well as chlorides. They are all soluble in water, but the fluorides are much less soluble than the others.

c.    **The Carbonates and Hydrogen Carbonates**

The Group IIA carbonates are different to those of the alkali metals of Group IA in two major respects. First they are only very slightly soluble in water, with the solubility decreases down the Group. Secondly they are decomposed by heat, giving off $CO_2$ and leaving an oxide.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

d.    **The Sulphates**

The solubilities of the sulphates decrease down the group. Be, Mg, and Ca sulphates are often found as hydroxide crystals, e.g. $BeSO_4.4H_2O$, $MgSO_4.7H_2O$, $CaSO_4 .2H_2O$. The crystals of magnesium sulphates have a rather unfortunate reputation. They are better known as epsom salts (used as laxative). Crystals of $CaSO_4.2H_2O$ are found in nature as the mineral gypsum. Anhydrous calcium sulphate also occurs naturally as anhydrite. When gypsum is heated to about $100^oC$, it looses three quarters of its water of crystallisation. The powder remaining is plaster of paris.

**FURTHER READING**

1    *Comprehensive Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3rd ed., 1986.

2    *Principles of Inorganic Chemistry*, B.R. Puri and L.R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 19th ed., 1986.

**Module 2     CHEMISTRY OF REPRESENTATIVE ELEMENTS**

**Unit 2     Group III, IV, VI and VII**

## 3.0     BORON

Boron belongs to Group IIIB, elements which marks, the beginning of the P-block elements. All these elements exhibits a group valency of three, but because of the very large input of energy that is necessary to form the 3-valent ions – the sum of the first three ionisation energies – their compounds when anhydrous are either essentially covalent or contain an appreciable amount of covalent character.

Boron never forms a $B^{3+}$ ion since the enormous amount of energy required to remove three electrons from a small atom cannot be repaid with the formation of a stable crystal lattice, even with the most electronegative fluorine atom.

Boron occurs principally, as borates e.g. sodium borate in which the boron storm is part of an anionic complex. Boron can be obtained as an amorphous brown powder by treating borax with hydrochloric acid, igniting the baric acid $H_3BO_3$, to give the oxide, $B_2O_3$, and finally reducing the latter with magnesium at a high temperature.

$$B_2O_3(s) + 3Mg(s) \rightarrow 2B(s) + 3MgO(s)$$
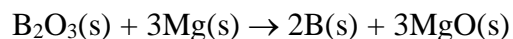
It is used in the construction of high impact resistant steel and, since it absorbs neutrons, in reactor rods for controlling atomic reactions.

A crystalline form of boron can be obtained by the thermal decomposition of boron trioxide on a tantalum filament.

$$2BI_3(s) \rightarrow 2B(s) + 3I_2(s)$$

## 3.1    Chemical Properties

Amorphous boron is a very reactive element combining directly with oxygen, sulphur, nitrogen and the halogens to give respectively an oxide, sulphide, nitride and halide with covalent bonds running completely through the structure.

### a.    Halides of Boron

The volatility of the halides decreases with increasing relative molecular mass, thus $BF_3$ and $BCl_3$ are gases, $BBr_3$ is a liquid and $BI_3$ is a white solid. They are covalent and exist as $BX_3$ molecules, their structures being planar.

The halides react vigorously with water to give the halogen hydride, with exception of boron trifluoride which gives fluoroboric acid, $HBF_4$, which in solution contains the tetrahedral $BF_4^-$ ion, boric acid is also formed, e.g.

$$BCl_3(g) + 3H_2O(1) \rightarrow H_3BO_{3(aq)} + 3HCl(g)$$

$$4BF_3(g) + 3H_2O(1) \rightarrow 3BF_4(aq) + H_3BO_{3(aq)}$$
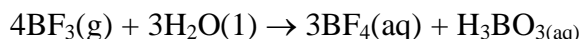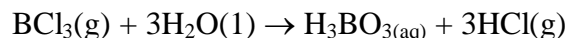
Boron trifluoride is used as a friedel-crafts catalyst in organic chemistry, particularly for polymerisation reactions.

### b.    Diborane

This compound, which is an inflammable and very reactive gas, is the simplest hydride of boron. It can be produced by the reduction of boron trichloride with Lithium aluminium hydride and must be handled in vacuum systems which employ mercury valves, since it attacks tap-grease

$$4BCl_3(g) + 3LiAlH_4 \rightarrow 2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$$

Physical evidence shows that the structure can be considered to involve something resembling boron – boron double bonds, the extra two electrons required for this being provided by two of the six hydrogen atoms which bridge the boron atoms as protons.
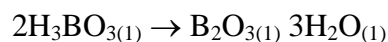
H      H$^+$      H

   \              /

```
      B  ═══  B
    /            \
   H     H⁺     H
```
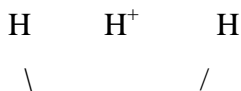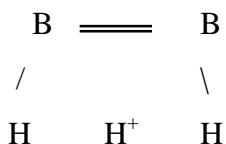
Other hydrides of boron are $B_4H_{10}$, $B_3H_9$, $B_5H_9$, $B_5H_{11}$ and $B_{10}H_{14}$, they are all electron deficient.

c. **Boron Trioxide**

Boron trioxide can be obtained by burning boron in oxygen or by fusing orthoboric acid.

$$2H_3BO_{3(l)} \rightarrow B_2O_{3(l)} \, 3H_2O_{(l)}$$

It is usually obtained as a glassy material whose structure consist of randomly orientated three-dimensional networks of $BO_3$ groups, each oxygen atom uniting two boron atoms.

```
                    |
     (½)O      O(½)
          \   /
            B
            |
            O
       (½) \
```
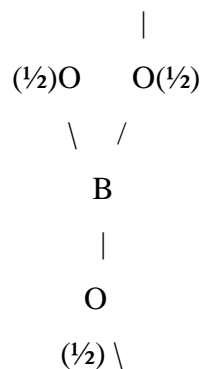
Boron trioxide is an acid oxide and slowly reacts with water, forming orthoboric acid. When fused with metallic oxides it forms borate glasses which are often coloured, this in the basis of borax based test in qualitative analyses.

3 SAQ Is BeO ionic

d. **Orthoboric Acid**

Orthoboric acid is formed when the boron halides are hydrolised or when dilute hydrochloric acid is added to a solution of borax.

$$B4O_5{}^{2-}(aq) + 2H^+(aq) + 5H_2O_{(l)} \rightarrow 4H_3BO_3(aq)$$
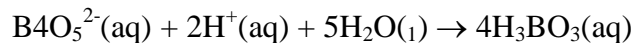
It is obtained as a white solid on subsequent crystallisation. Orthoboric acid is a weak monobasic acid and in aqueous solution the boron atom completes its octet by removing OH from water molecule.

$$B(OH)_{3(aq)} + 2H_2O_{(1)} \rightarrow B(OH)_{2(aq)} + H_3O^+(aq)$$
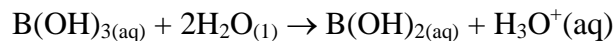
It therefore functions as a lewis acid and not as a proton donor.

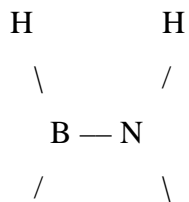The structure of orthoboric acid is based on the planar $B(OH)_3$ unit.

e.      **Borates**

Boron, like silicon, has a great affinity for oxygen and a multitude of structures exist containing rings of alternating boron and oxygen atoms. The single $BO_3^{3-}$ ion is rather uncommon but does occur in $(Mg^{2+})_3$ $(BO_3^{3-})$, the ion, as expected, has a planar structure.

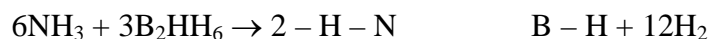The more complex borates are based on triangular $BO_3$ units e.g. $(Na+)_3B_3O_6^{2-}$ has the structure as given below

```
    –O    O     O–
     \  /  \  /
       B    B
       |    |
       O    O
        \  /
         B
         |
         O–
```
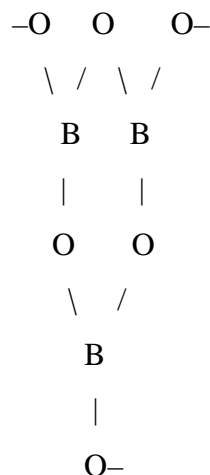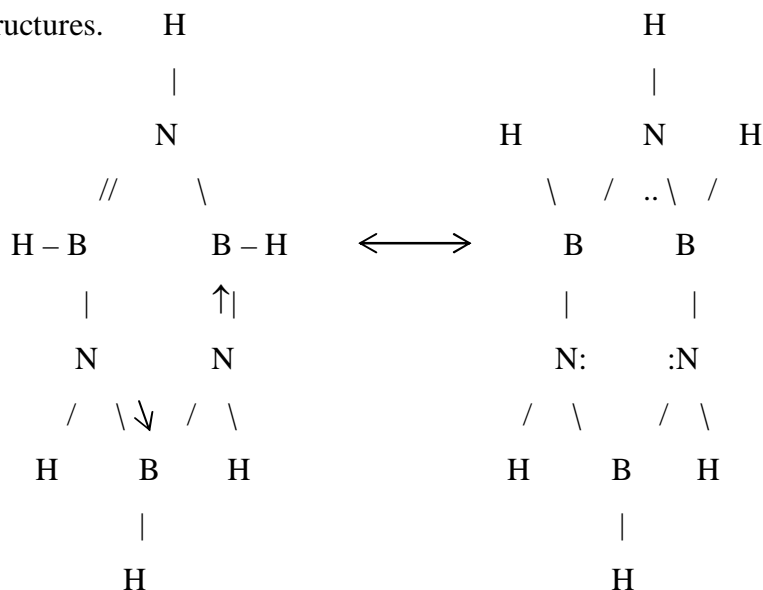
f.      **Borazine and Boron Nitride**

When ammonia and diborane, in the ratio of two molecules to one, are reacted together at high temperature the volatile compound borazine is formed, the molecule has a cyclic structure reminiscent of benzene

```
        H          H
         \        /
          B — N
         /        \
```

$$6NH_3 + 3B_2HH_6 \rightarrow 2 - H - N \qquad\qquad B - H + 12H_2$$

```
                        \        /
                         B —— N
                        /        \
                       H          H
```
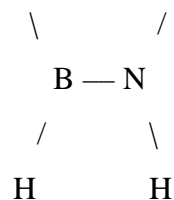
The structure of the borazine is considered to be a resonance hybrid of the two structures.

```
        H                              H
        |                              |
        N                   H          N        H
      //    \                 \    /  .. \    /
   H – B        B – H    ⟷        B        B
     |        ↑|                   |        |
     N        N                   N:       :N
    / \↓ / \                     / \      / \
   H    B   H                   H    B    H
        |                            |
        H                            H
```

It is isoelectronic with benzene and resembles the latter in some of its physical and chemical properties; its boiling point is $55^{o}C$ and forms addition compounds more readily than benzene e.g. it forms addition compound with hydrogen chloride, whereas benzene is unreactive towards this reagent.

Boron nitride (BN) is formed by direct union of boron and nitrogen at white heat, it has a structure similar to that of graphite and is thus a giant molecule but differ from graphite in only being a semiconductor of electricity.

**Self Assessment Exercise 1**.

In what respect is the chemistry of boron similar to that of silicon.

**4.0    CARBON AND SILICON**

Carbon and silicon belongs to Group IVA elements. They show many of the properties that are characteristic of non metals, but as we move down the group, the metallic nature of the elements increases.

The normal valency of the elements is four, but apart from carbon, the elements can make more than four bonds. This is because they make use of a set of d orbitals in bonding, that is the empty d orbitals of the outer electron shell, e.g. the 3d set for silicon. The availability of the d orbitals is responsible for the ability of silicon to make complex ions such as $SiF_6^{2-}$, with exception of carbon. Another feature of the chemistry of the Group IV is that some carbon compounds are less reactive than the corresponding compounds of the outer members of the group.

## 4.1     Chemistry of Carbon and Silicon

a.     **The hydrides:**

Carbon and silicon gives a variety number of hydrides such as $CH_4$, $C_2H_2$, $S_1H_4$, $S_{12}H_6$, etc. The geometries of the hydrides follow those of methane and are based on a tetrahedral arrangement around the central atom.

The carbon hydrides will not ignite in air unless a flame is put to them. Apart of silicon, $SiH_4$, the silicon hydrides are less well behaved. For example, $S_{13}H_8$ is spontaneously flammable in air.

$$Si_3H_{8(1)} + 5O_2(g) \rightarrow 3SiO_2(s) + 4H_2O_{(1)}$$
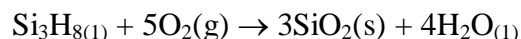
Like the carbon hydride, silicon hydrides are not hydrolysed by water alone. However, traces of alkali will convert them into hydrated silica, $SiO_2nH_2O$ and hydrogen gas. Carbon hydride are not hydrolysed by alkali.

b.     **The Halide**

Carbon and silicon forms various halides such as $CCl_4$, $SiCl_4$, $SiF_6^{2-}$. There is a tendency for the elements to make four bonds, and with a tetrahedral arrangement. As with the hydrides there is a tetrachloromethane and silicon tetrachloride. $CCl_4$ will not react with water but $SiCl_4$ is immediately converted into silica

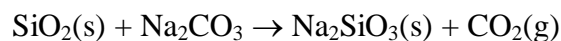$$SiCl_4(1) + 2H_2O(1) \rightarrow SiO_2(s) + 4H+(aq) + 4Cl^-(aq)$$
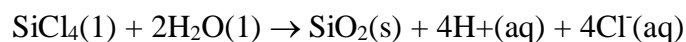
c.     **The Oxides**

The oxides of carbon and silicon are predominantly covalents, but the chief oxide of silicon, $SiO_2$, unlike the small gaseous molecules CO and $CO_2$, has a giant molecular structure that is better represented by the formula $(SiO_2)n$.

Carbon and silicon oxide are definitely acidic. For example, silica behaves like $CO_2$ when it reacts with hot and concentrated alkali

$$SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O_{(1)}$$
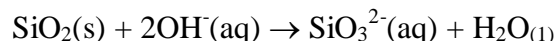
Silica will also react with metal carbonates giving off $CO_2$.

$$SiO_2(s) + Na_2CO_3 \rightarrow Na_2SiO_3(s) + CO_2(g)$$

Silica are not destroyed by hydrogen ions as are carbonates. Rather if you add dilute acid to sodium silicate solution, the solution will turn to a gel. It is a colloidal and an example of hydrosed silica, $SiO_2.2\ H_2O$.

c.      **Organic Compound**

Carbon and silicon form many interesting organic compounds, made up of chains of representing units e.g. organo-silicon compounds

  $-(Si(CH_3)_2–O)_n-$
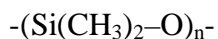

## 5.0    NITROGEN AND PHOSPHORUS

As a member of Group VA elements, nitrogen and phosphorus show the typical properties of non-metals. For example, they are poor conductors of heat and electricity and give acidic oxides. Their compounds are predominantly covalent. Phosphorus have allotrope.

**5.1    Chemistry of Nitrogen and Phosphorus**

a.    **The Hydrides**

Both of them form hydrides with unpleasant sources. They have pyramidal shape, but the bond angle in hydrocarbon and the hydrides of group IV differ from that of ammonia.

Like ammonia, phosphine, $PH_3$, can accept a proton out its lone pair and give the phosphorium ion $PH_4^+$ and it will combine to make phosphornium iodide, $PH_4I$. Like the analogous ammonium salts it is ionic.
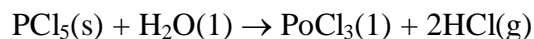
However, phosphine will not accept protons as readily as ammonia.

b.    **The Halides and Oxohalides**

Nitrogen and phosphorus form trihalide with F, Cl, Br and I and pentahalides such as $PF_5$, $PCl_5$, $PBr_5$, while those of nitrogen do not  exist.

Phosphorus penta chloride fumes in air. It reacts in water to gives the oxochloride

$$PCl_5(s) + H_2O(1) \rightarrow PoCl_3(1) + 2HCl(g)$$

and in excess of water it gives

$$PCl_5(s) + 5H_2O(1) \rightarrow H_3PO_4(aq) + 5HCl(g)$$
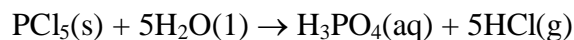
c.    **The Oxides**

Nitrogen form various oxides such as $N_2O$, $NO$, $N_2O_3$, $NO_2$, $N_2O_4$ and $N_2O_5$. The oxides of phosphorus are $P_4O_6$ and $P_4O_{10}$, which was once given as $P_2O_3$ and $P_2O_5$ respectively, before their structure, were found by x-ray diffraction.

d.    **The Oxoacides**

Phosphorous forms various oxoacids like $H_3PO_4$, $H_3PO_3$, $H_3PO_2$, $H_3PO$, etc. The structure of phosphoric(V) acid is shown below

```
        O
        ||
        P
      /   \
   HO   |  OH
        OH
```
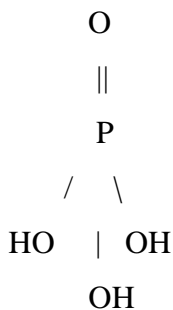
d.      **The Sulphides**

The sulphides of nitrogen is $N_4S_4$, while those of phosphorus are $P_4S_3$, $P_4S_5$, $P_4S_7$ and $P_4S_{10.}$ Particularly $P_4S_3$, have been used in making matches. To make the match head the sulphide is mixed with an oxidising agent, e.g. potassium chloride (v), and a little ground glass, and the mixture is bound together with a glue. The match boxes usually have a strip of sand paper along the side.

## 6.0    OXYGEN AND SULPHUR

Oxygen exists as diatomic molecules, $O_2$. It has three isotopes, $^{16}_8O$ or the main one, and the others are $^{17}_8O$ and $^{18}_8O$, both of about 0.3%. Oxygen also exist in triatomic molecules as ozone, $O_3$ with a triangular shape.

The one chemical property that dominates the chemistry of oxygen is its ability to combine with both metals and non-metals to make oxides. Oxides can be of four types: neutral, basic, acidic or amphoteric.

The Group I and II metals combine directly with oxygen to give basic oxides. Especially, Na and K have to be kept under oil in order to stop them converting into oxides. The reactivity of Group II metal is less marked, but a coating of oxides will soon give the otherwise shiny metal surfaces a dull grey appearance.

The oxides of sulphur and phosphorus are typical acidic oxides in that they all react with $H_2O$ to give acidic solutions e.g.

$$P_4O_{10} + 4H_2O \rightarrow H_3PO_4(aq) \rightleftharpoons 2PO_4^{3-}(aq) + 6H^+(aq)$$
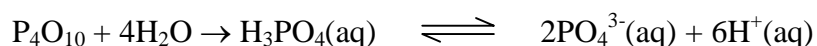
The most important peroxide is hydrogen peroxide, $H_2O_2$. When pure, it is a colourless liquid, but it is too dangerous to use in this form in the laboratory, instead, it is kept in solution with water.

Sulphur posses allotropes and another major difference to oxygen comes about through the use of d orbitals in bonding. In many sulphur compounds the bond to sulphur are shorter than expected. This sudjects a degree of double character, which can occur if sulphur makes use of its empty 3d orbitals as well as its S and P orbitals. Unlike oxygen, sulphur and other Group VI elements can make up to six covalent bonds by using d orbitals e.g. $SF_6$.

## 6.1 Chemistry of Sulphur and Oxygen

The majority of sulphur is used to make sulphuric acid. Sulphuric acid is regarded as a strong acid in water. It dissociates in two stages:

$$H_2SO_4(aq) + H_2O_{(1)} \rightarrow HSO^-_4(aq) + H_3O^+(aq)$$

$$HSO_4^-(aq) + H_2O \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$
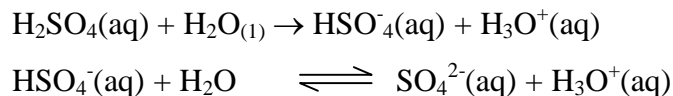
The acid shows its oxidising nature when it is concentrated, for example

### a. The Hydrides

Of the hydrides of Group VI, water is by far the most important, and is not typical of the others. Water is liquid at room temperature, due to hydrogen bonding, while others are gases.

Hydrogen sulphide is very poisonous, with a rotten egg smell. The gas can be made by mixing hydrochloric and with a metalsulphide, often iron (II) sulphide.

$$FeS(s) + 2HCl(sq) \rightarrow FeCl_2(aq) + H_2S(g)$$
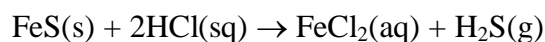
Unlike water, but like ammonia, hydrogen sulphide can be a good reducing agent.

### b. The halides and Oxohalides

Oxygen forms halide with all the halogens, while sulphur forms halides with all the haloogens with exception of iodine.

Fluorine brings out the highest oxidation state as in $SF_6$. The fact that these atoms can actually make six bonds is due to their use of d orbitals in bonding.

Of the oxohalides, the most important are those of sulphur, e.g. thionylchloride, $SOCl_2$ and sulphurylchloride, $SO_2Cl_2$. The former is a colourless liquid that is easily hydrolysed.

$$SOCl_{(1)} + 2H_2O_{(1)} \rightarrow H_2SO_3(aq) + 2HCl(aq)$$
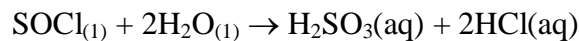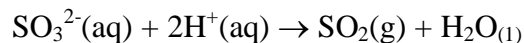
### c. The Oxides

$SO_2$ and $SO_3$ are gaseous. They are both highly soluble in water, with the reaction between $SO_3$ and water being explosive.

### d. Sulphides, Sulphates and Other Oxoanions

Sulphates contain the $SO_3^{2-}$ ion. Most sulphides are soluble in water, and act as reducing agents. When they are warmed with acid, $SO_2$ is given off.

$$SO_3^{2-}(aq) + 2H^+(aq) \rightarrow SO_2(g) + H_2O_{(1)}$$

Sulphates contain the $SO_4^{2-}$ ion. The sulphates of Group II metals tend to be insoluble e.g. $CaSO_4$. Sulphates usually decomposes when heated to a sufficiently high temperature

$$Fe(SO_4) \rightarrow FeSO_3(s) + 3SO_3(g)$$

Thiosulphates contain the ion, $S_2O_3^{2-}$. The structure of the ion is like that of a sulphate ion, except that one of the oxygen atoms is replaced by a sulphur atom. Sodium thiosulphate solution is widely used as a fixing agent in photography. It has the ability to dissolve the silver salts that have not been affected by light. In the laboratory, thiosulphate solutions are used in iodine titrations.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$
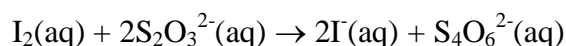
peroxodisulphates have the ion $S_2O_8^{2-}$ and are found in salts such as $K_2S_2O_6$. They are oxidising agents and behave according to the half-equation

$$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$$
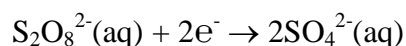
They will for example, oxidise iodide to iodine and Iron (II) to iron (III).

e.      **The Sulphides**

The sulphides of Group I metals are ionic, e.g. $(Na^+)_2S^{2-}$. The sulphides of other metals, especially the B metals are covalent to a lesser extent.


## 7.0      THE HALOGENS

The halogens are members of Group VIIA elements, and includes; fluorine, chlorine, bromine, iodine. Fluorine and dioxide are gas, Bromine is a liquid, while iodine occurs as a solid at room temperature.


## 7.1      The Chemistry of the Halogens

Fluorine has the lowest energy as a result it reacts more readily than the other halogens. Reactively decreases down the group.

a.      **Halogens as Oxidising Agents**

All the halogens have a tedency to accept electrons. The only type of negative ion they all give is the halide ion $X^-$.

They all readily form alkalihalides with group IA metals. The alkali metals towards the bottom of Group I can react violently with fluorine and chlorine.

They reaction readily with hydrocarbon, producing carbon

$$C_{10}H_{22}(s) + 11Cl_2(g) \rightarrow 10C(s) + 22HCl(g)$$
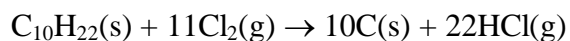
b.      **Reactions With Water and Alkali**

Both fluorine and chlorine are able to oxidise water. Fluorine can give a mixture of oxygen and trioxygen
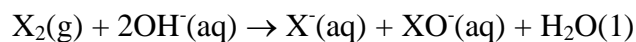
$$2F_2(g) + 2H_2O(1) \rightarrow O_2(g) + 4HF(aq)$$
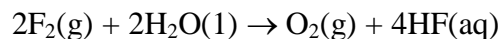
Chlorine does not release oxygen, instead, solution containing a mixture of hydrochlorous and chloric (1) acid (hypochlorous acid) is produced
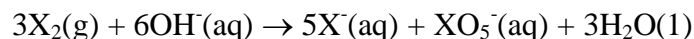
$$Cl_2(g) + H_2O(1) \rightarrow \quad HCl(aq) + HC1O(aq)$$

Chlorate (1) ions, $C1O^-$, in a solution of chlorine are responsible for its bleaching action.

The halogens reacts with cold dilute alkali as given below

$$X_2(g) + 2OH^-(aq) \rightarrow X^-(aq) + XO^-(aq) + H_2O(1)$$

and when heated with concentrated alkali as

$$3X_2(g) + 6OH^-(aq) \rightarrow 5X^-(aq) + XO_5^-(aq) + 3H_2O(1)$$

c.      **The Halide Ions**

Often, when a halogen reacts, each atom gains an electron to give a halide ion. It is possible to distinguish between chloride, bromide and iodide ions. The simplest test involves adding silver nitrate solution to a solution of the halide. This should be done in the presence of dilute nitric acid, otherwise other ions may give precipitates. Silver ions react with halide ions to give precipitate. These in turn can be identified by their colour, or by their reaction with ammonia solution. Chloride ions, is white.

   **SUMMARY**

− The Group IA and IIA metals are all good reducing agents (highly electro positive), with reducing power increasing down the group. With an exception of Li & Br due to the very small size of their ions.

− Group IA and IIA form ionic compounds with non metals.

− Group IA react vigorously with water giving off hydrogen gas.

− The Group IA sulphate are all soluble in water

- The Group IA metals oxides and hydroxide that are less soluble in water than those of Group I.

- Boron is amphoteric and it forms many electron deficient hydrides, e.g. $B_2H_6$.

- Boron form basic oxides that are insoluble in water.

- Carbon and silicon are non metal.

- Carbon and silicon forms compounds with oxygen and chlorides.

- Nitrogen and phosphorus forms compounds with oxygen, halides and hydrochloride.

- Both oxygen and sulphate are non metallic. They combine with hydrogen, halogens to give interesting compounds.

- All the halogens are oxidising agents, fluorine being the most vigorous.

- The halogens exist as diatonic molecules.


**FURTHER READING**

1    *A New Concise Inorganic Chemistry*, J.D. Lee, ELBS, London, 3rd ed., 1977.

2    *Chemistry: Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

3    *Comprehensive Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3rd ed., 1986.

4    *Principles of Inorganic Chemistry*, B.R. Puri and L.R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 19th ed., 1986.

**Module 3       TRANSITION ELEMENTS**

**UNIT 1          Nature and Chemistry of Transition Elements**

1.0      Introduction

2.0      Objectives

3.0      Electronic Configuration

4.0      General Characteristics

5.0      Periodic Trends in Properties

5.1      Atomic Radii, Atomic Volume and Density

5.2      Melting and Boiling Points

5.3      Ionisation Energy

5.4      Electrode Potential

5.5      Electronegativity

## 1.0      INTRODUCTION

As you already know, elements are classified on the basis of their electronic configuration into s-block, *p*-block, *d*-block and *f*-block elements. The *s*- and p-block elements together represent one of the major groups of the elements and are called main group elements. The *d*-block and the *f*-block elements represent the transition and the inner-transition elements respectively. Most of the discussion so far has centered around the chemistry of main group elements having valence electrons in s and/or *p* orbitals only. From this unit onwards, we will start the study of rest of the elements of the periodic table, namely, the *d*-block or transition elements and the *f*-block or inner-transition elements. The name transition is given to the elements on the basis of their position in the periodic table and their properties, that is, they occupy a position between the highly electropositive elements on the left and the electronegative elements on the right. Their properties are also intermediate of the *s*- and *p*-block elements. Thus, in this

unit we will describe the general features of the transition elements with the emphasis on the *3d* series and also the periodic trends in their properties.

Here we would like to draw your attention to the fact that some chemists consider as transition elements only those which, either as neutral atoms or in any of their common oxidation states, have partly filled d-orbitals. According to this definition, the elements Zn, Cd and Hg are excluded from the list of transition elements. However, for the sake of completion of discussion on the *d*-block elements, the elements *Zn,* Cd and Hg will also included in the discussion on transition elements in this unit.

## 2.0    Objectives

After studying this unit, you should be able to:
•         describe the electronic configuration of transition elements and their ions,
•         outline the general properties of transition elements,
•         describe the periodic trends in the properties of transition elements,

## 3.0    ELECTRONIC CONFIGURATION

Electronic configuration of the elements has been discussed in detail in Unit 1 of this course. Hence, we will concentrate here only on the features relevant to transition elements. You already know that the electronic configuration of the argon atom is $ls^2 2s^2 sp^6 3p^6$. In atoms of the successive elements from potassium to zinc, electrons can enter either $3d$ or $4s$ levels. In potassium and calcium atoms the differentiating electrons enter the 4.v level, so the electronic configuration of calcium can be written as $[Ar]4s^2$. At scandium the *3d* level begins to fill instead of *4p* and the resulting configuration of the atoms of transition elements is shown in Table 3.1 The electronic configuration of the ions can be obtained by removing first the outer *s* electrons of the atom and then the outer *d* electrons until the total number of electrons removed is equal to the charge on the ion. For example Mi the configuration as $[Ar]3d^8$ .

**Table 3.1. Electronic configurations of the free atoms and dipositive ions of the first transition series**

| Element | Free atom | Free $M^{2+}$ ion | Element | Free atom | Free $M^{2+}$ ion |
|---------|-----------|-------------------|---------|-----------|-------------------|
| Sc | $[Ar]3d^1\,4s^2$ | $[Ar]3d^1$ | Fe | $[Ar]3d^6\,4s^2$ | $[Ar]3d^6$ |
| Ti | $[Ar]3d^2 4s^2$ | $[Ar]3d^2$ | Co | $[Ar]3d^7 4s^2$ | $[Ar]3d^7$ |
| V | $[Ar]3d^3 4s^2$ | $[Ar]3d^3$ | Ni | $[Ar]3d^8 4s^2$ | $[Ar]3d^8$ |
| Cr | $[Ar]3d^5 4s^1$ | $[Ar]3d^4$ | Cu | $[Ar]3d^{10}4s^1$ | $[Ar]3d^9$ |
| Mn | $[Ar]3d^5 4s^2$ | $[Ar]3d^5$ | Zn | $[Ar]3d^{10}4s^2$ | $[Ar]3d^{10}$ |

Now you may ask as to why the electrons in potassium enter *4s* level rather man *3d* and then later (from Sc to Cu) why *3d* levels are filled prior to *4p* level.

The radial dependence of the *d* orbitals is responsible for this order of filling of electrons in these elements. Fig. 3.1 shows the plot of radial probability functions introduced in Unit 2 **of Atoms and Molecules** course for a *3d* and *4s* electron in the hydrogen atom. Let us assume that the radial probability functions for *3d and 4s* electron in a multi electron atom follow the same pattern as in the hydrogen atom.
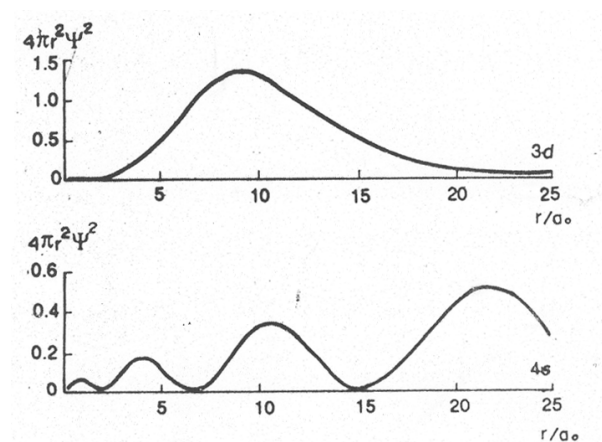


**Fig. 3.1 Radial probability functions for *3d* and *4s* orbitals in hydrogen atom. $a_0$, the radius of first Bohr orbit is 53.9 pm.**

You can see from Fig. 3.l that significant humps in the *4s* probability function occur close to the origin, and well inside the maximum of the *3d* probability function. This suggests that the *4s* electron penetrates significantly into the argon core and spends an appreciable portion of its time close to the nucleus. The average nuclear charge experienced by the 4*s* electron is, therefore, higher than that experienced by the *3d* electron and thus after argon, in potassium and calcium the electrons enter the *4s* orbital rather than the 3*d.* As these two electrons are added the nuclear charge is also increased by two units. As the *3d* orbitals penetrate the *4s* orbital more than the *4p* orbitals can penetrate the 4*s* orbital, the net result is that the effective nuclear charge for the *3d* orbitals increases abruptly and they now drop well below the *4p* orbitals to about the level of the *4s* orbital. Moreover, as the atomic number increases, the *3d* probability maximum progressively moves closer to the core and they continue to drop in energy. The next electron, therefore, enters the *3d* orbital prior to the *4p* orbital. The variation .of the energies of the orbitals with increasing atomic number is shown very clearly in Fig. 3.2.
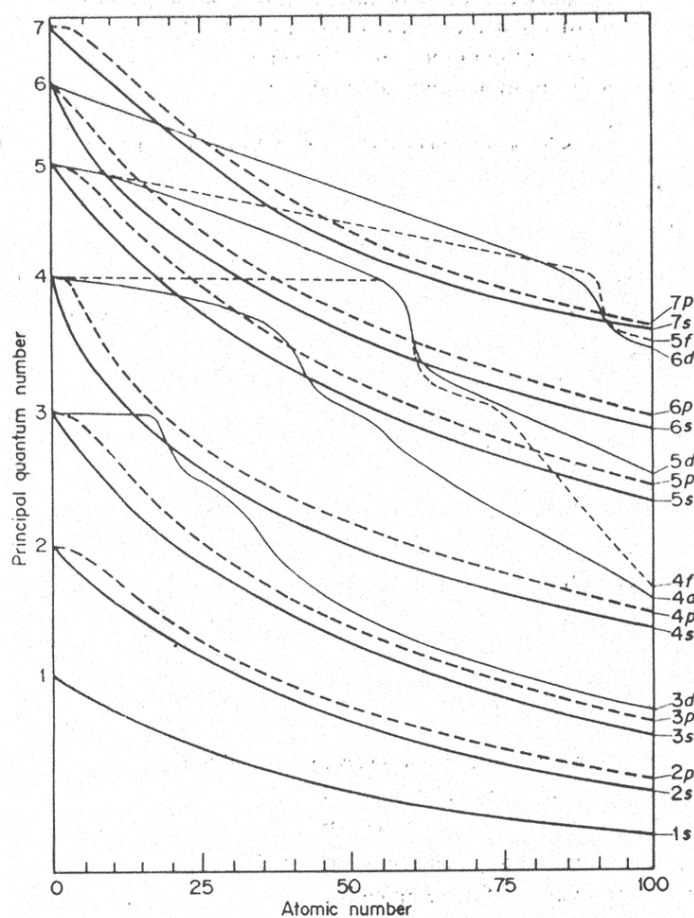
**Fig. 3.2: The variation of the energy of atomic orbitals with increasing atomic number in neutral atoms**

This process continues until the entire *3d* shell is filled. Thus at Zn we have the configuration [Ar]4s$^2$ *3d*$^{10}$. Thereafter, the next lowest available orbitals are 4*p* which get filled in the next six elements. This same sequence of events for the filling of 5*s* and 4*d* orbitals is repeated again in the elements following krypton in the second transition series. This series starts with Y and is completed at Cd having the configuration [Kr]4*d*$^{10}$5*s*$^2$. After xenon, (Kr)4*d*$^{10}$5*s*$^2$5*p*$^6$ , the next available orbitals are 4*f*, 5*d*, 6*s* and 6*p* orbitals. The 4*f* orbitals are so slightly penetrating with respect to the xenon core that they have scarcely gained any stability, while the more penetrating 6s and 6*p* levels have gained a good deal of stability. Hence, in the next two elements, electrons are added to 6*s* orbitals giving

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Cs and Ba, respectively. However, the $6s$ electrons do not shield the $4f$ orbitals effectively, so the latter abruptly feel an increase in effective nuclear charge and thus suffer a steep drop in energy (Fig. 2.2). At the same time, with the addition of electrons in the $6s$ orbital, the $5d$ orbitals also drop in energy in the same manner as the $3d$ ones. This creates a situation in which $5d$ *and* $4f$ orbitals are of almost the same energy. The next electron in lanthanum thus enters the *5d* orbital, but in the following element cerium, the electronic configuration is [Xe]$6s^2$ *5d*$^1$ *4f*$^1$. The electrons then continue to be added to the $4f$ orbital till we reach ytterbium which has the configuration [Xe]$6s^2$ *4f*$^{14}$. Now with the 6s and 4f shells full, the next lowest levels are the *5d's*. Hence from lutecium onwards, the electrons enter the *5d* orbital. This continues till we reach mercury which has the configuration [Xe]$6^2$ *4f*$^{14}$ *5d*$^{10}$. The electronic configurations of transition elements of *4d* and *5d* transition series are given in Table 3.2.

Table 3.2 : Electronic configuration of 4d and 5d transition elements

| Elements of second transition series | | Elements of third transition series | |
|---|---|---|---|
| Y | [Kr]$4d^1 5s^2$ | La | [Xe]$5d^1 6s^2$ |
| Zr | [Kr]$4d^2 5s^2$ | Hf | [Xe]$4f^{14} 5d^2 6s^2$ |
| Nb | [Kr]$4d^4 5s^1$ | Ta | [Xe]$4f^{14} 5d^3 6s^2$ |
| Mo | [Kr]$4d^5 5s^1$ | W | [Xe]$4f^{14} 5d^4 6s^2$ |
| Tc | [Kr]$4d^6 5s^1$ | Re | [Xe]$4f^{14} 5d^5 6s^2$ |
| Ru | [Kr]$4d^7 5s^1$ | Os | [Xe]$4f^{14} 5d^6 6s^2$ |
| Rh | [Kr]$4d^8 5s^1$ | Ir | [Xe]$4f^{14} 5d^7 6s^2$ |
| Pd | [Kr]$4d^{10} 5s^0$ | Pt | [Xe]$4f^{14} 5d^9 6s^1$ |
| Ag | [Kr]$4d^{10} 5s^1$ | Au | [Xe]$4f^{14} 5d^{10} 6s^1$ |
| Cd | [Kr]$4d^{10} 5s^2$ | Hg | [Xe]$4f^{14} 5d^{10} 6s^2$ |

If the filling of the orbitals in transition elements takes place through the above scheme, then you may wonder why in the case of some elements e.g., Cr & Cu (belonging to the first transition sends) and Mo & Ag (belonging to the second transition series) the electronic configuration is written as [Ar]$3d^5 4s^1$ & [Ar]$3d^{10}$ $4s^1$ and [Kr]$4d^{10} 5s^1$, respectively. This is because these configurations are considered to give more stability to the elements, rather than [Ar] $3d^4 4s^2$ & [Ar] $3d^9 4s^2$ and [Kr] $4d^9 5s^2$, respectively. This apparent stability can be associated

with the high stability of exactly half filled and completely filled orbitals. Half-filled and completely-filled orbitals have an exchange energy considerably greater than the exchange energies associated with any other configuration. This exchange energy is the driving force for these configurations to take an electron out of turn in order to achieve or maintain the half-filled or completely-filled configuration. Also these configurations provide the most symmetrical distribution of electrons which suffer the minimum mutual repulsion.

**Exchange Energy**

The exchange energy for any configuration is proportional to the total number of possible pairs of electrons with parallel spin in any orbital, i.e., $E_e x = K \times P$, where $K$ *is* a constant and $P$ is the number of possible pairs of electrons with parallel spin. If n is the number of electrons with parallel spin for any configuration, $P$ will be equal to $^nC_2$. Accordingly values of $P$ for different values of n are given below :

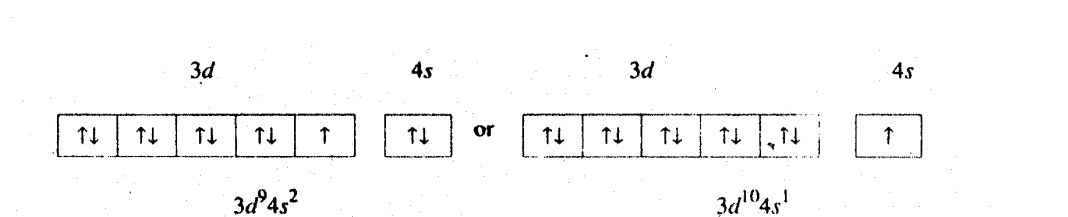| n | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| p | 0 | 1 | 3 | 6 | 10 | 15 | 21 |

Let us compare the exchange energy for two possible configurations $3d^4 4s^2$ and $3d^5 4s^1$ for chromium.
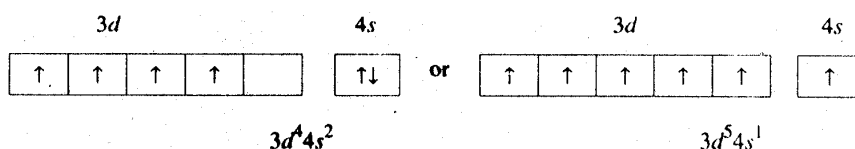


Electrons present in 4$s$ orbital in two configurations contribute nothing to exchange energy as they do not constitute any pair with parallel spin. Four unpaired $d$-electrons in first configuration can make six pairs of electrons with parallel spin and thus contribute $6K$ towards exchange energy whereas five unpaired $d$-electrons in second configuration contribute $10K$ towards exchange energy because they can constitute 10 combinations of pairs of electrons with

parallel spin. This gain of $4K$ in exchange energy would favour the $3d^54s^1$ configuration for chromium. But, you should remember that in achieving this configuration, there would be loss of energy in promoting an electron from $4s$ to $3d$ orbital. In case of chromium the gain in exchange energy is more than the loss in energy and therefore, $3d^5 4s^1$ is the favoured configuration.

Similarly you can compare the exchange energies for two possible configurations $3d^94s^2$ and $3d^{10} 4s^1$ for copper.

| 3d | | | | | 4s | | 3d | | | | | 4s |
|----|----|----|----|----|----|----|----|----|----|----|----|----|
| ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ | ↑↓ | **or** | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑ |

$3d^94s^2$                    $3d^{10}4s^1$

The former configuration has two sets of electrons with parallel spin — one set has five electrons represented by upward arrows and the other has four electrons represented by downward arrows.

These two sets of electrons will contribute $10K$ and $6K$ i.e. a total 16K towards exchange energy. On the other hand, the latter configuration has two sets of live electrons each with parallel spin which will contribute a total $20K$ towards exchange energy. Thus, there is a net gain of $4K$ in exchange energy if copper has the configuration $3d^{10}4s^1$. However, in achieving this configuration, there will again be a loss in energy in promoting an electron from $4s$ orbital to $3d$ orbital, which happens to be less than $4K$, the gain in exchange energy. Hence, the $3d^{10}$ $4s1$ configuration becomes more stable than $3d^9 4s^2$.

It is also worth mentioning here that though the $4s$ orbitals are occupied before $3d$ orbitals, we cannot say that they are always more stable. In fact, the ionisation of the transition elements takes place by the loss of $ns$ electrons first. What happens actually is that when the electron is ionised from any transition element, say the one from $3d$ series, the effective nuclear charge experienced by the $3d$ electrons is

greatly-enhanced over that of any *4s* electron as a direct consequence of the greater stability attained by the *3d* orbitals in the due course of filling (cf. Fig. 2.2). Consequently, the *3d* orbitals are expected to drop significantly in energy below the 4*s* orbital. Thus, ionisation of two or more electrons from an atom of a transition element will take place with the removal of *s* electrons in preference to the d electrons.

Thus, we sec that it is the net effect of all the forces, comprising nuclear-electronic attraction, shielding of one electron by others from the nuclear charge, inter-electronic repulsion and exchange forces, that determines the stability of the electronic configuration.

**Self Assessment Exercise   1**

In the given space explain :

a)      Why a transaction series contains ten elements.

b)      Which of the two orbitals. 3*d* and 4*s* has higher energy at potassium.

**4.0      GENERAL CHARACTERISTICS**

In the preceding section you have learnt the electronic configuration of the transition elements and their position in the periodic table. Based on these two, the transition elements have certain common properties, which are given below:

•        All are metals and form alloys with one another and with other metallic elements.

•        They art hard, strong, ductile, malleable, high melting and high boiling. They are good conductors of heat and electricity.

- Many of them are sufficiently electropositive to dissolve in mineral acids although a few are noble — that is, they have such low electrode potentials that they are unaffected by simple acids.

- They usually exhibit multiple oxidation states.

- They form coordination compounds/ions. In fact, the chemistry of the transition elements is mainly associated with the use of $d$ as well as 5 and $p$ orbitals in forming coordination compounds.

- The transition metal complexes are usually coloured.

- Most of their compounds are paramagnetic.

- Many of these elements and their compounds act as catalysts for chemical reactions.

Let us now study sonic of these properties and their periodic trends in detail.

## 5.0    PERIODIC TRENDS IN PROPERTIES

In the previous section you have studied the important properties of transition metals in general. As you know the transition metals are an integral part of the periodic table, like the main group elements, the transition metals are also expected to exhibit periodicity in their properties. Let us see how their properties vary from one group to another and from one period to another.

Some of the important properties of the elements of $3d$ - series arc listed in Table 2.3. If you study the data in the Table carefully, you will notice that along a period, these properties vary much less from one element to the other as compared to the main group elements. Although, the horizontal similarity amongst the $d$-block elements is well marked, yet the chemistry of the elements of first transition

series differs considerably from that of the elements of the second and third transition series, which are incidentally more similar to each other. This difference in the trends in the properties of d-block elements from those of *s*-and *p*-block elements arises from a basic difference in their electronic configuration. While in the building up of elements from lithium to fluorine, the electrons are added to the outermost shell, in the case of transition metals, the electrons are added to inner (n-1)*d* subshell. Let us see how this contributes to the variation in the properties of the elements.

Table 3.4 : Properties of 3d elements

| Property | Scandium Sc 21 | Titanium Ti 22 | Vanadium V 23 | Chromium Cr 24 | Manganese Mn 25 | Iron Fe 26 | Cobalt Co 27 | Nickel Ni 28 | Copper Cu 29 | Zinc Zn 30 |
|---|---|---|---|---|---|---|---|---|---|---|
| Atomic weight | 44.956 | 47.90 | 50.942 | 51.996 | 54.938 | 55.847 | 58.933 | 58.710 | 63.54 | 65.37 |
| Metallic radius (pm) | 164 | 147 | 135 | 130 | 135 | 126 | 125 | 125 | 128 | 137 |
| *Ionic radius (pm) | 81 (3+) | 76, 68 (3+)(4+) | 74, 60 (3+)(4+) | 84, 69 (2+)(3+) | 80, 66 (2+)(3+) | 76, 64 (2+)(3+) | 74, 63 (2+)(3+) | 72, 62 (2+)(3+) | 96, 69 (1+)(2+) | 74 (2+) |
| Covalent radius (pm) | 144 | 132 | 122 | 118 | 117 | 117 | 116 | 115 | 117 | 125 |
| Boiling point (K) | 3000 | 3533 | 3673 | 2753 | 2370 | 3273 | 3173 | 3005 | 2868 | 1180 |
| Melting point (K) | 1812 | 1948 | 2173 | 2163 | 1517 | 1808 | 1768 | 1726 | 1356 | 692 |
| Density $10^3 \times$ kg m$^{-3}$ | 3.0 | 4.5 | 6.11 | 7.2 | 7.44 | 7.86 | 8.86 | 8.90 | 8.92 | 7.13 |
| Electronegativity (A/R) | 1.2 | 1.3 | 1.45 | 1.55 | 1.6 | 1.65 | 1.7 | 1.75 | 1.75 | 1.65 |
| Ionisation 1st | 633 | 659 | 650 | 653 | 717 | 762 | 759 | 736 | 745 | 906 |
| energy 2nd | 1235 | 1309 | 1414 | 1591 | 1509 | 1561 | 1644 | 1751 | 1958 | 1732 |
| (kJ mol$^{-1}$) 3rd | 2388 | 2648 | 2866 | 2992 | 3259 | 2978 | 3230 | 3391 | 3556 | 3828 |
| Electrode Potential (V)+ | (III) -2.1 | (III) (IV) -1.2 -1.63 | (II) (III) -1.2 -0.86 | (II) (III) -0.91 -0.74 | (II) (III) -1.18 -0.28 | (II) (III) -0.44 -0.04 | (II) (III) -0.28 +0.4 | (II) -0.25 | (I) (II) +0.52 +0.34 | (II) -0.76 |

 **\*Values in parentheses refer to oxidation states of the metal, + (III) refers to couple M$^{3+}$ /M.etc.**

## 5.1    Atomic Radii, Atomic Volume and Density

From Table 3.3, you can see that there is a gradual decrease in atomic radius across a row of transition elements. On passing from left to right, additional positive charges are placed on the nucleus and correspondingly electrons are added to the (n-1)*d* orbitals. As the electrons in the *d* orbitals shield the *ns* electrons and also themselves from the nuclear charge incompletely, effective nuclear charge felt by them increases and hence a contraction in size occurs.

65

However, it is important to emphasise here that shielding of the outer *ns* electron(s) by (n-l)*d* electron(s) is more efficient than the shielding of an *ns* electron by another *ns* electron (or that of an *np* electron by another *np* electron). This is why the decrease in atomic radius from sodium to chlorine is greater than that from scandium to copper. The elements which occur immediately after the transition elements are smaller than expected from simple extrapolation from the group elements. This is due to the cumulative effect of incomplete shielding provided by (n-1)$d^{10}$ electrons and therefore, the effective nuclear charge fell by the outer electrons of the elements from gallium to krypton is greater than that if the *d*-orbitals had not been gradually filled in transition elements.

The rate of decrease in size along the lanthanide series is even less than that in the transition series since in the lanthanides the electrons are added to the penultimate [(n-2)*f*] shell and these shield the outer electrons much more effectively. The presence of 4/electrons in the lanthanides affects the atomic size and therefore, the chemistry of the elements following the lanthanides. The atomic radii of the elements of third transition series are much smaller than expected. This is due to the effect of the greater than expected effective nuclear charge felt by the electrons of the elements of the third row transition series, hafnium to gold, owing to the insertion of lanthanides.

**Table 2.4 metallic radii (pm) of some elements of Groups 1-13**

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga |
| 235 | 197 | 164 | 147 | 135 | 130 | 135 | 126 | 125 | 125 | 128 | 137 | 141 |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In |
| 248 | 215 | 178 | 160 | 146 | 139 | 136 | 134 | 134 | 137 | 144 | 154 | 166 |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl |
| 267 | 222 | 188 | 160 | 149 | 141 | 137 | 135 | 136 | 139 | 146 | 157 | 171 |

This trend in the variation of the metallic radii in alkali, alkaline earth and transition metals is shown in Fig. 3.3. You can see in Fig. 3.3 that as we move from alkali metals to alkaline earth metals and from alkaline earth metals to the transition elements, the radii decrease steeply but within transition elements this rate of decrease is less. However, the data in Table 3.4 and Fig. 3.3 show that the general trend of decreasing size is reversed towards the end of the series. This could be due to an increase in inter-electronic repulsion after the addition of sufficient number of electrons in the *d* orbitals leading to the gradual increase in size.
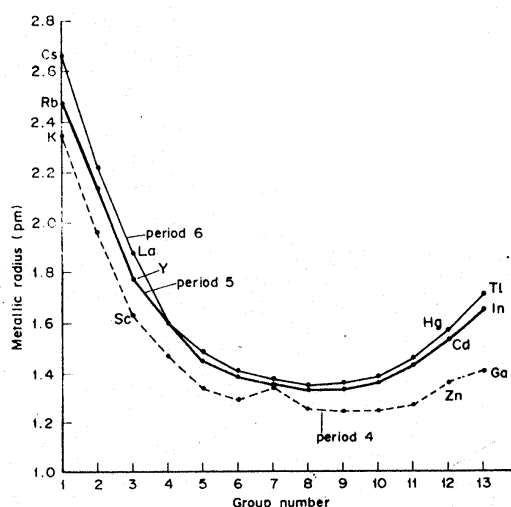


**Fig. 3.3: Trend in metallic radii of alkali, alkaline earth and transition metals of fourth, fifth and sixth.**

The group trends in atomic radii of the transition elements are parallel to those observed in *s*- and *p*-block elements. As we go down the group, there is an increase in atomic size up to the second transition series. This is not unexpected in view of the fact that electrons enter the *4d* orbital in the second transition series. However, the size of the elements of third transition series is almost similar to that of the elements of second transition series because of the filling in of 4/orbitals in the lanthanides.

Atomic volume of an element is directly related to its size and, therefore, atomic volumes follow the same trend as the atomic size. Similarly density is also related to the size of the element. The smaller the size, the higher is the density of the

element. Thus there is a general trend of increasing density across the elements of a transition series. This is well represented in Fig 2.4 which gives the variation of the densities of alkali, alkaline earth and the transition metals of the fourth, fifth and sixth periods. For *4d* and *5d* elements, this increase is not that regular as the increase in densities for *3d* elements. Along the group also, the density increases (Fig. 3.4). The increase in density within the *d* block groups is greater than that within the 5 and *p* block groups.
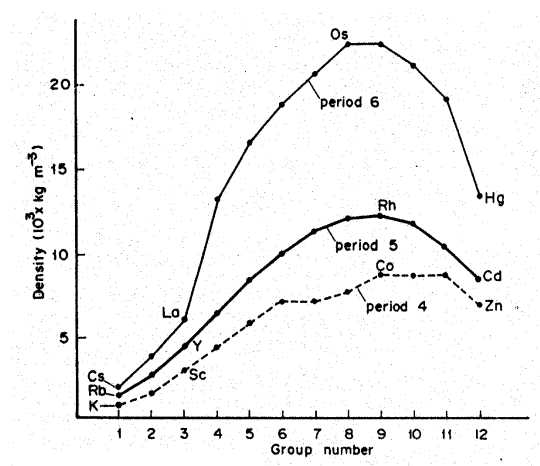


**Figure 2.4 : The variation of the density of alkali, alkaline earth and transition metals**

**Self Assessment Exercise 2**

Of the following pairs, tick or mark the element which is larger in size:

      (i)     Calcium or scandium

      (ii)    Vanadium or titanium

      (iii)   Chromium or molybdenum

      (iv)   Iron or osmium

**5.2     Melting and Boiling Points**

The melting and the boiling points of the transition elements are usually high. The melting points of the elements depend upon the strength of the metallic bond. As we know, the transition metals crystallise in the metallic lattices. The strength of the metallic bond increases with the availability of the electrons to participate in the bonding by delocalisation. Notice that between calcium and scandium (where $d$ electron first appears), there is a jump of nearly 700 K in the melting point. The presence of one or more unpaired $d$ electrons thus leads to higher interatomic forces and therefore, high melting and boiling temperatures. Thus, we can think that with the increasing availability of the unpaired $d$ electrons, the strength of the metallic bond increases, resulting in higher melting points. But, we cannot generalise the argument because when we move across any period in the periodic table, the melting point increases upto the middle of each transition series and then it decreases with the beginning of electron pairing. For the elements of first transition series.
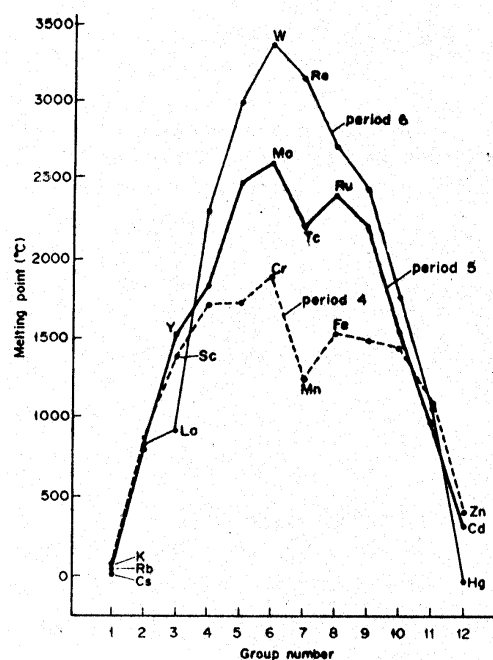


**Fig. 3.5: Trend in melting points of alkali, alkaline earth and transition metals of the fourth, fifth and sixth periods.**

there is a sharp decrease of melting point at manganese, which has five unpaired $d$ electrons. However, the softness and low melting point of Zn, Cd and Hg (Hg is a liquid) in which all the electrons are paired up can tentatively be explained on the above basis. The melting points of the elements of the first transition series are comparatively lower than those of the elements of-the second and third transition series. This trend is very well illustrated in the Fig. 3.5

The periodic trends in the boiling points are similar to those in the melting points. As the process of boiling requires almost complete breaking of bonds and such metallic bonding exists in the liquid state to some extent, high temperatures are necessary. Therefore, the boiling points "f the metals are much higher than their melting points.

**Self Assessment Exercise 3**

Explain briefly in the space given below, why zinc and cadmium are soft metals.

**5.3    Ionisation Energy**

You have already learnt about the concepts of ionisation energy and how it varies with the atomic size in Unit 2 on periodicity. In the case of transition metals also, the variation of ionisation energy across the periods and down the groups parallels quite closely the trend in atomic size. This is shown nicely in the Figure 2.6

As we move across a period, the effective nuclear charge experienced by $ns^2$ electrons goes on increasing causing the shells to shrink in size and thus making it difficult to remove the electrons. Thus along a period, the ionisation energy increases. This can be checked from the values of the first ionisation energy of these elements given in Table 3.3. The second and the third ionisation energies follow the same pattern, except for the second ionisation energies of Cr and Cu which arc comparatively higher due to the extra stability of $3d^5$ and $3d^{10}$ configurations. The ionisation energies of the elements of the second and the third transition series also follow the same trend along the period. As the decrease in the size of the transition metals is less than that of the main group elements along

a period, the ionisation energies tend to increase along the series only slightly as compared to the main group elements (Fig. 3.6). Since $s$ and the $d$ electrons do not differ much in energy, the difference in the successive ionisation energies is relatively small.
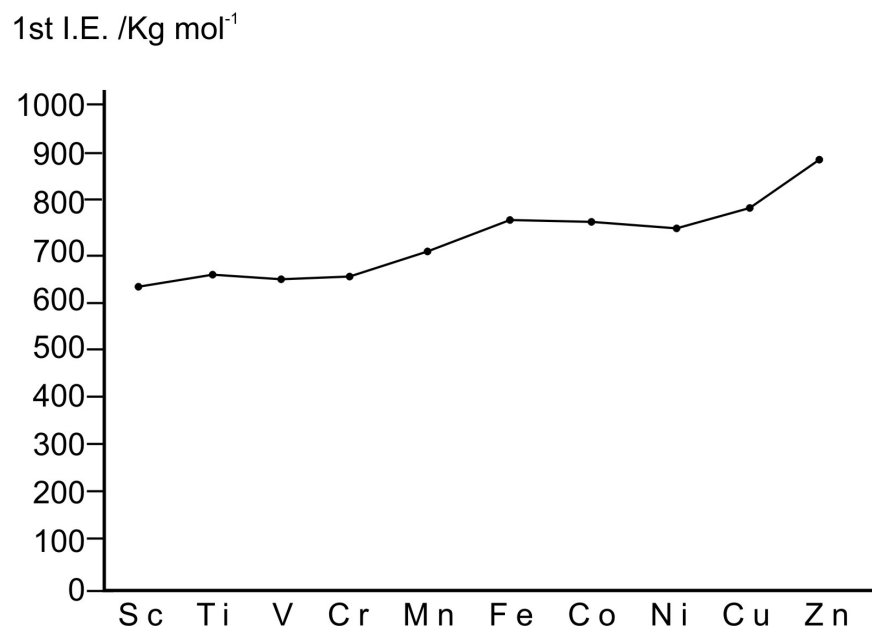
1st I.E. /Kg mol$^{-1}$



Fig 3.6        The ionisation energies of the elements of the second and the third transition series

As we move down a group from the elements of first transition series to those of the second, there is a decrease in the ionisation energy. But it again increases when we move further down the group from second to the third transition series. This trend is consistent with relatively small size of the atoms of elements of the third transition series. This is due to the insertion of the lanthanides which causes the third row transition elements to have greater than expected effective nuclear charge.

## 5.4    Electronegativity

Transition elements have fairly low values of electronegativity. It increases from Sc to Cu with a fall at Mn and Zn. However, this increase in electronegativity is much slower because the additional electron is being added to an inner shell which provides relatively good shielding to the outer electrons from the nucleus. The increasing electronegativity from Sc to Cu means that the elements become slightly less metallic and this is reflected in the increasing positive electrode potentials of their ions $M^{2+}$ and $M^{3+}$ (Table 3.3).

## 5.5    Electrode Potential

Before going into the details of the variation in the electrode potential of the transition elements, let us discuss the concept of electrode potential first. When a metal is placed in a solution of its ions a potential difference is set up between the metal and the solution. There is a tendency for the metal ions' to leave the metal lattice and go into the solution thus leaving an excess of electrons and hence a negative charge on the metal; there is also a reverse tendency for the metal ions from the solution to deposit on the metal leading to a positive charge on the metal. In practice one of these effects is greater than the other, bringing about a potential difference between the metal and the solution. The value of this potential difference for a particular metal depends upon the nature of metal, the concentration of the metal ions in solution and the temperature. By convention, the potential difference set up in a IM solution of metal ions at 298K is called the **standard electrode potential**. It is not possible to measure standard electrode potentials absolutely. Standard electrode potentials, therefore, have to be measured against some reference standard, the one adopted is the hydrogen electrode. This consists of hydrogen gas at one atmosphere pressure in contact with a 1M solution of its ions at 298 K.

In general, we can say that more negative the value of the electrode potential for the couple $M^{n+}/M$, more is the reducing power of the element. Similarly, more positive is the value of electrode potential for the couple $M^{n+}/M$, more is the

oxidising power of the element. The values of some standard electrode potentials for the elements of first transition series are given in Table 2.3. Electrode potential is a measure of the electropositive character and the reactivity of the metals. In general along a period, there is a decrease in electropositive character. The reactivity of metals also decreases along a period and down a group. As you can see from Table 2.3, all the elements of the first transition series, except copper, have" negative values and can react with acids ($H^+$) producing hydrogen. A plot of variation of the electrode potential of the transition elements of *3d* series is shown in Fig. 2.7
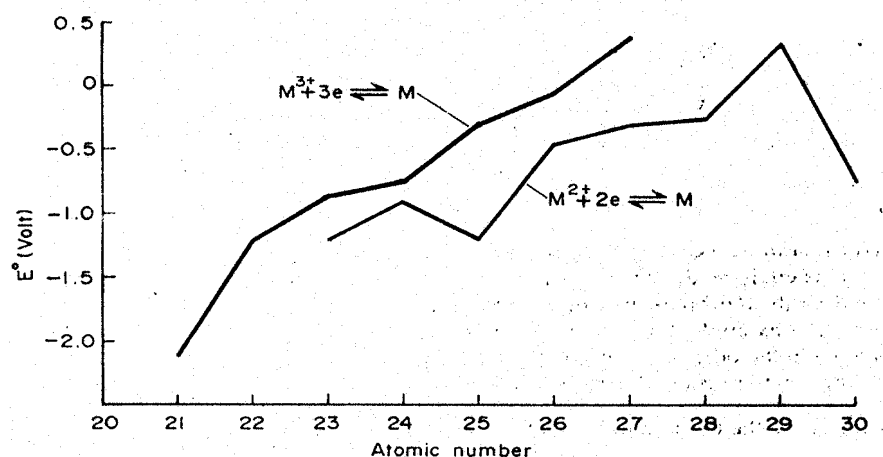


**Fig. 3.7: Trends in electrode potentials of transition metals of 3*d* series**

## FURTHER READING

1      *A New Concise Inorganic Chemistry*, J.D. Lee, ELBS, London, 3rd ed., 1977.

2      *Chemistry: Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

3      *Comprehensive Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3rd ed., 1986.

**Module 3        Transition Elements**

**Unit 2            General Reactivity**

**2.0 Objectives**

At the end of the unit, you should be able to

- Predict the nature of complexes in transition metals

- Identify the colour of each of the transition metals

- Have an overview of the general reactivity in transition metals

**3.0        General Reactivity**

Except in the unusual circumstances, metals act only as reducing agents. Generally, the    reactivity of the- transition metals as reducing agents tends to decrease as you go across the periodic table from left to right. The trend in their reactivity can be related to their electrode potentials. Group 3 metals including lanthanides and actinides are strong reducing agents. The metals of Groups 4-7 are moderately reactive as are iron, ruthenium, osmium, cobalt and nickel of Groups 8-10. The remaining metals of Groups 8-10, rhodium, (iridium, platinum and palladium, as well as silver and gold have low reactivity. Because of this relative inertness, they are called **noble metals**.

**3.1        Oxidation States**

The concept of oxidation state has already been introduced in the earlier unit of this course. Therefore, here we will consider the oxidation states exhibited by transition metals only. Transition elements exhibit a wide range of oxidation states differing usually by units of one. This is due to the fact that (n-1)$d$ electrons may get involved along with $ns$ electrons in bonding, as electron in (n-l)$d$ orbital are in an energy state comparable to $ns$ electrons. From Table 3.5 you can see that there exists a general trend of lesser number of oxidation states at each end of the series and a higher number in the middle. The lesser number of oxidation states in the beginning of the series can be due to the presence of too few electrons to lose or share, towards the end of series it can be ascribed to the presence of too many electrons and thus fewer empty orbitals to share electrons with the ligands.

Oxidation states of transition dements of $d$-block (the most common oxidation states are in bold type)

Table 3.5: Oxidation states of transition elements of $d$-block (the most common oxidation states are in bold type)

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| +3 | +2 | +1 | +2 | +2 | +2 | +2 | +2 | +1 | +2 |
|  | +3 | +2 | +3 | +3 | +3 | +3 | +3 | +2 |  |
|  | +4 | +3 |  | +4 | +4 | +4 | +4 |  |  |
|  |  | +4 | +6 | +6 | +6 |  |  |  |  |
|  |  | +5 |  | +7 |  |  |  |  |  |

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

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

Another feature is the reduced tendency of higher oxidation states towards the end of the series. This could be due to steady increase in the effective nuclear charge along the series thus pulling the $d$orbitals into the electron core and not making them readily available for bonding. For example, the only oxidation state for Zn is Zn(II) where no $d$ orbital is 'involved. On the other hand, early in the series, it is difficult to form species that do not utilise the $d$electrons i.e., Sc(II) is virtually unknown and Ti(IV) is more stable than Ti(II).

Now let us see the trend in the oxidation states as we go down the group. A full range of oxidation states of the transition elements is shown in Table 3.5. The trend in the stability of oxidation states with in the groups is different for the transition elements and the main group elements *(s* and *p* block elements). For the main group elements, the higher oxidation state becomes less-stable going down a group because of inert pair effect. However, for the transition elements the stability of the higher oxidation states increases going down a group.

To illustrate this trend, let us first look at Group 6. It is composed of Cr, Mo and W. We have seen that chromium in +*6* oxidation state as in K$_2$CrO4 is a good oxidising agent forming Cr as the product. This means that in many instances Cr(III) is more stable than Cr(VI). In contrast, molybdenum and tungsten are not easily reduced when they are in +6 oxidation stile in K$_2$MoO4 and K$_2$WO$_4$. This implies that lower oxidation states, e.g., Mo(III)-and W(III) are not as easy to form as Cr(III), making the +6 oxidation state more stable. Thus the stability of the +6 state for Group 6 elements will be $W^{6+} > Mo^{6+} > Cr^{6+}$. We find the same trend in Group 4 which is composed of Ti, Zr and Hf. For all the three elements, most Stable oxidation state is +4. However Ti(II) and Ti(III) can be formed from Ti(IV) by the use of good reducing agent but lower oxidation states of Zr and Hf are extremely difficult to prepare. Table 3.6 snows how various oxidation states of some elements of period-4 tend to react with respect to oxidation and reduction.

Going from left to right across period 4, $M^{2+}(aq)$ ions are known for the last seven elements from V to Cu and $M^{3+}$ $(aq)$ ions are known for the first seven elements from Sc and Co. Thus, there is an overall increase in stability of $M^{2+}(aq)$ with respect to oxidation as one moves across the series. However, in the case of iron, $Fe^{2+}$ $(aq)$ is less stable than $Fe^{3+}(aq)$ because of the extra stability associated with half-filled $(d^5)$ orbitals in the case of $Fe^{3+}(aq)$.

The highest oxidation, states are often stabilised in the oxide and fluoride compounds, e.g., $MnO_4^-$, $CrO_4^{2-}$ $VO_2^+$, $VF_5$, etc. in these compounds $O^{2-}$ and $F^-$ are difficult to be oxidised by the central metal because O and F are strong oxidising agents.

**Table 3.6 Reactivity of some oxidation states of first transition series elements in aqueous solution**

| Reducing agents ⟶ | Most stable | ⟵ Oxidising agents |
|---|---|---|
| | $Sc^{3+}$ | -- |
| $Ti^{2+}$, $Ti^{3+}$ | $Ti^{4+}$ | -- |
| $V^{2+}$, $V^{3+}$ | $V^{4+}$ | $V^{5+}$ (slightly) |
| $Cr^{2+}$ | $Cr^{3+}$ | $Cr^{6+}$ |
| -- | $Mn^{2+}$ | $Mn^{3+}$, $Mn^{4+}$, $Mn^{7+}$ |
| $Fe^{2+}$ | $Fe^{3+}$ | -- |
| -- | $Co^{2+}$ | $Co^{3+}$ |
| -- | $Ni^{2+}$ | -- |
| $Cu^+$ | $Cu^{2+}$ | -- |

**Self Assessment Exercise 1**
Explain, briefly in the space provided below, the existence of $OsO_4$ in terms of trends in oxidation states.

**4.0     FORMATION OF COMPLEXES**
By now you must be familiar with the word 'complexes'. The chemistry of the transition metals is dominated by their tendency to form complex ions. This is because the transition elements form small, highly charged ions which have vacant orbitals of suitable energy to accept lone pairs of electrons donated by other groups or ligands. In case of transition metals in high oxidation states,

highly charged ions can strongly bind electrostatically a wide variety of negative or polar ligands. In the case of transition metals in low oxidation states, the electrons in the *d* orbitals become involved in $\pi$ bonding with ligands. The majority of transition metal ion complexes contain six ligands surrounding the central ion octahedrally. Some elements contain four ligands which are either arranged tetrahedrally or less frequently at the corners of a square. Besides these geometries, other geometries like trigonal bipyramid, pentagonal bipyramid, etc., are also present occasionally. The bonding between the ligand and the transition metal ion can either be predominantly electrostatic or covalent or in many cases intermediate between the two extremes. Some of the typical complexes of the transition metals are $[Fe(CN)6]^{3-}$ $[Ni(NH3)4]^{2+}$, $[Cu(CN)4]^{3-}$, $[Cu(NH3)_4]^{2+}$, etc. The nature of these complexes and the important theories of bonding related to them are discussed in Unit 14 of this block.

## 4.1    COLOUR OF TRANSITION METAL COMPOUNDS

Compounds of transition elements are usually markedly coloured, in contrast to compounds of *s-* and *p-* block elements which are mostly white or colourless unless the anion is coloured. As you know, substances appear coloured when they absorb light of a particular wavelength in the visible region of the spectrum and transmit light of other wavelengths. The colour which we see is the colour of the transmitted wavelengths. In other words, the colour of the compound observed by us is the complementary colour of the colour absorbed by the compound. You know that the transition metals as such or in the form of ions have partly filled *d*-orbitals which are degenerate, i.e., they are of equal energy. You will study in Unit 14 that in transition metals complexes the *d* - orbitals do not remain degenerate, but these split into sets of orbitals of different energies. By absorbing energy, electrons can move from a *d*-orbital of lower energy to that of higher energy. This transition of electron from one *d*-orbital to another corresponds to a fairly small energy difference; therefore, light is absorbed in the visible region of spectrum. For example, the aqua ion $Ti(H2O)_6^{+3}$. Which has one electron in the *3d* orbital absorbs light of wavelength in the yellow-green region of spectrum and

therefore, appears reddish violet in colour. Table 3.7 gives the relationship between the colour and the wavelength of light.

**Table 3.7:  Relationship between the colour and wavelength**

| Wavelength absorbed in nm | Colour absorbed | Colour observed |
|---|---|---|
| <400 | UV region | White/colourless |
| 400–435 | Violet | Yellow-green |
| 435–480 | Indigo | Yellow |
| 480–490 | Green-blue | Orange |
| 490–500 | Blue-green | Red |
| 500–560 | Green | Purple |
| 560–580 | Yellow-green | Violet |
| 580–595 | Yellow | Indigo |
| 595–605 | Orange | Green-blue |
| 605–750 | Red | Blue-green |
| >750 | Infra-red | White/colourless |

Whenever the *d*-orbitals are completely filled or empty, there is no possibility of electronic, transitions within the *d*-orbitals. In such cases, the ions will not show any colour. For example, the compounds of $Sc^{3+}$, $Ti^{4+}$, $Cu^+$ and $Zn^{2+}$ are white or colourless. Table 3.8 gives the colour and oxidation states of the metal ions present in some hydrated ions of transition elements.

**Table 3.8 Oxidation states and observed colours for some aqua species**

| Element | +2 | +3 | +6 | +7 |
|---------|-----|-----|-----|-----|
| Sc | | Colourless $[Sc(H_2O)_6]^{3+}$ | | |
| Ti | | Violet $[Ti(H_2O)_6]^{3+}$ | | |
| V | Violet $[V(H_2O)_6]^{2+}$ | Green $[V(H_2O)_6]^{3+}$ | | |
| Cr | Blue $[Cr(H_2O)_6]^{2+}$ | Violet/green $[Cr(H_2O)_6]^{3+}$ | Orange/yellow $Cr_2O_7^{2-}$, $CrO_4^{2-}$ | |
| Mn | Pink $[Mn(H_2O)_6]^{2+}$ | Red $[Mn(H_2O)_6]^{3+}$ | Green $MnO_4^{2-}$ | Purple $MnO_4^{-}$ |
| Fe | Pale green $[Fe(H_2O)_6]^{2+}$ | Yellow/brown $[Fe(H_2O)_6]^{3+}$ | | |
| Co | Pink $[Co(H_2O)_6]^{2+}$ | Blue $[Co(H_2O)_6]^{3+}$ | | |
| Ni | Green $[Ni(H_2O)_6]^{2+}$ | | | |
| Cu | Blue $[Cu(H_2O)_6]^{2+}$ | | | |
| Zn | Colourless $[Zn(H_2O)_6]^{2+}$ | | | |

In the *s*- and *p*- block elements there cannot be any *d-d* transitions and the energy needed to promote *s or p* electron to a higher level is much greater and may correspond to ultraviolet region, in which case the compound will not appear coloured to the eye.

**Self Assessment Exercise 2**

Explain briefly why $CuSO_4$ is blue while $ZnSO_4$ is white

**4.2 MAGNETIC PROPERTIES**

When you place an iron piece near a magnet, you will see that it is immediately drawn towards the magnet. However, some elements are repelled by the magnets. The property of an element to be attracted or repelled by a magnet differs from

element to element. Substances which are weakly repelled by a magnetic field are called **diamagnetic,** while the substances which are weakly attracted by the magnetic field and lose their magnetism when removed from the field are called **paramagnetic**. If the force of attraction is very large and the permanent magnetisation is retained, the substance is said to be **ferromagnetic,** e.g., iron and some iron compounds.

Electrons determine the magnetic properties of matter in two ways. From the pre-wave mechanical view point, the electron may be regarded as a small sphere of negative charge spinning on its axis. Then from the completely classical considerations, the spinning of charge produces a magnetic moment. Secondly, an electron travelling in a closed path (orbit) around a nucleus, again according to pre-wave mechanical picture, will also produce a magnetic moment. The magnetic properties of any individual atom or ion will result from some combination of these two properties, that is, the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus.

The magnetic moment is usually expressed in units called **Bohr magnetons** (BM). The general equation for the magnetic moment is given by:

$$\mu s_{+L} = \sqrt{4S(S+1) + L(L+1)}$$

In the above expression, $S$ is the sum of the spin quantum numbers and $L$ is the sum of orbital angular momentum quantum numbers of all the electrons. In many compounds including those of the first row transition elements, the orbital contribution is quenched out by the electric fields of the surrounding atoms and as an approximation, the observed magnetic moment may be considered to arise only from unpaired spins. Putting $L=0$ in the above expression, you can get the spin-only magnetic moment $\mu s$.

Thus, $\mu s = \sqrt{4S(S+1)}$

The spin-only magnetic moment, $\mu s$ can also be related to the number of unpaired electrons, n, in any species, as the total spin quantum number $S = n/2$.

Hence, $\mu s = \sqrt{4S(S+1)} = \sqrt{4n/2\,(n/2 + 1)}$

$$= \sqrt{n(n+2)}$$

Above expression gives the value of magnetic moment in Bohr magnetons which can be converted into SI unit of Ampere square meter $(Am^2)$ by the following relationship:

1 BM = $9.274 \times 10^{-24}$ A m$^2$

The magnetic moment is measured by weighing the sample in the presence and absence of magnetic field using a magnetic balance called Gouy balance (Fig. 3.8)



(a)
Loss in weight
(diamagnetic)

(b)
Increase in weight
(paramagnetic)
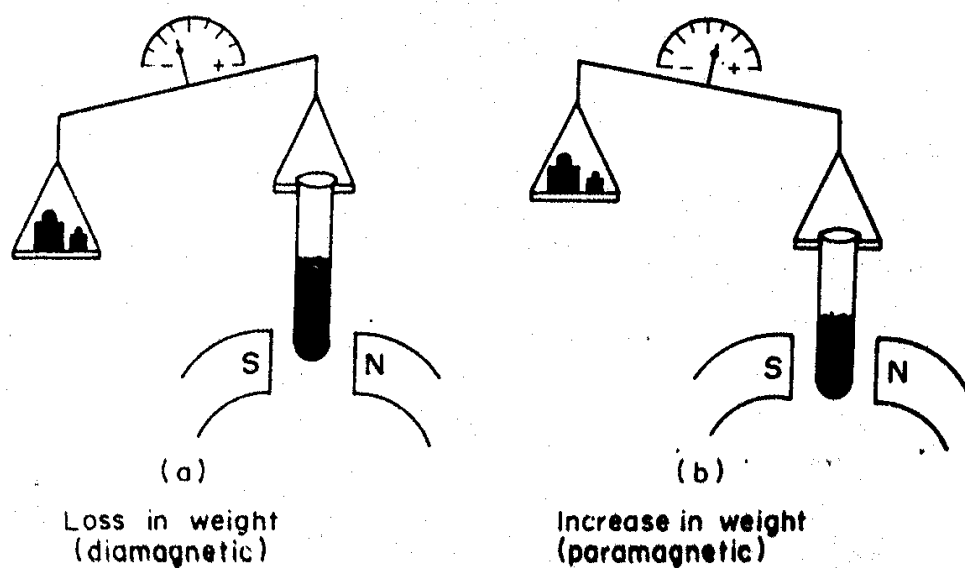
Fig. **3.8 Measurement of molecular paramagnetism using a Gouy balance**.

Diamagnetic materials have no magnetic moment and show a slight decrease in weight on weighing in the presence of magnetic field. On the other hand, paramagnetic materials show an apparent increase in weight. The magnetic moment can be calculated from the change in weight.

In some cases (e.g., $Mn^{2+}$, or $Fe^{3+}$, in which all the $d$ orbitals are occupied singly by electrons for which $m_l$, = 2, 1, 0, -1 and -2, giving $L = 0$) the observed magnetic moment values agree very well with the spin-only value as given in Table 3.9. But generally, experimental values differ from the spin-only values. This is because the orbital motion of the electron also makes some contribution to the moment. More details on the magnetic properties of the transition elements can be studied in higher courses on the subject.

**Table 3.9: Predicted and observed magnetic moment values of some transition metal hydrated ions**

| Ion | Electronic configuration | Unpaired electrons | Magnetic moment (BM) Calculated Experimental $(\mu_s)$ | |
|---|---|---|---|---|
| $[Ti(H_2O)_6]^{3+}$ | $3d^1$ ↑ | 1 | 1.73 | 1.75 |
| $[V(H_2O)_6]^{3+}$ | $3d^2$ ↑ ↑ | 2 | 2.84 | 2.75 |
| $[V(H_2O)_6]^{2+}$ | $3d^3$ ↑ ↑ ↑ | 3 | 3.87 | 3.86 |
| $[Cr(H_2O)_6]^{2+}$ | $3d^4$ ↑ ↑ ↑ ↑ | 4 | 4.90 | 4.80 |
| $[Mn(H_2O)_6]^{2+}$ | $3d^5$ ↑ ↑ ↑ ↑ ↑ | 5 | 5.92 | 5.96 |
| $[Fe(H_2O)_6]^{2+}$ | $3d^6$ ↑↓ ↑ ↑ ↑ ↑ | 4 | 4.90 | 5.00 |
| $[Co(H_2O)_6]^{2+}$ | $3d^7$ ↑↓ ↑↓ ↑ ↑ ↑ | 3 | 3.87 | 4.40 |
| $[Ni(H_2O)_6]^{2+}$ | $3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑ | 2 | 2.84 | 2.90 |
| $[Cu(H_2O)_6]^{2+}$ | $3d^9$ ↑↓ ↑↓ ↑↓ ↑↓ ↑ | 1 | 1.73 | 1.80 |

**Self Assessment Exercise 3**

In $[Co(M_2O)6]^{2+}$ the observed magnetic moment is higher than the reason for this in the space provided below.

## 5.0    CATALYTIC PROPERTIES

Many transition metals and their compounds have catalytic properties. These metals can function as catalysts because they can utilise both $d$ and $s$ electrons for the formation of bonds between reactant molecules and the surface catalyst atoms. This increases the concentration of the reactants at the catalyst surface and weakens the bonds in the reactant molecules with the result that the activation energy is lowered. Compounds of transition metals are able to act as catalysts because of the ease with which the metal can adopt different oxidation states and

also because of their ability to form complexes. Some of the common catalysts used for important reactions are :

a.    $FeSO_4$ and $H_2O_2$ as Fenton's reagent for the oxidation of alcohols to aldehydes

b.    Pd for hydrogenation, e.g., phenol to cyclohexanol

c.    Fe/Mo in manufacture of ammonia by Haber process

d.    Pt/PtO as Adians catalyst for reductions

e.    Pt/Rh in oxidation of $NH_3$ to NO in the manufacture of nitric acid

f.    $V_2O_5$ in oxidation of $SO_2$ to $SO_3$ in the manufacture of sulphuric acid by contact process

g.    Ni (Raney nickel) in reduction processes

h.    $TiCl_4$ as (Ziegler Natta Catalyst) for polymerisation of ethene.

Transition metals are important catalysts in biological systems. A number of transition elements present in very small quantities in plants and animals are essential for the enzymes to function. For example, a cobalt atom lies at the centre of the vitamin $B_{12}$ coenzyme. Iron atoms are importantly involved in hemoglobin of blood and in the ferredoxins of photosynthetic process. Both molybdenum and iron are contained in nitrogen fixing enzymes.

## 6.0    INTERSTITIAL COMPOUNDS

Transition metals can trap some small atoms like hydrogen, boron, carbon, nitrogen, etc., in vacant spaces in their crystal lattice forming interstitial

compounds. Carbon and nitrogen always occupy octahedral holes; hydrogen is smaller and always occupies tetrahedral holes. As only transition metals form such compounds, the $d$ electrons are, therefore, presumably involved in the bonding. The structure of the metal often changes during the formation of such compounds. The composition of these compounds is generally non-stoichiometric, e.g. $TiH_{1.73}$, $PdH_{0.56}$, $VH_{0.56}$, but may approach regular stoichiometry and a regular structure, e.g., TiC and VN. The later transition elements of the first series form non-stoichiometric carbides with irregular structures, such as $Cr_7C_3$, which are more reactive than the interstitial carbides of the early transition elements. These interstitial compounds are of much importance, e.g., carbon steels are interstitial iron-carbon compounds in which the interstitial carbon prevents the iron atoms from sliding over one another, making iron harder, stronger but more brittle.

**SUMMARY**

Let us now summarise what we have learnt in this unit. This unit focuses on the transition metals and their characteristics. We have learnt about the electronic configuration of the transition elements and how the filling of the orbitals takes place with the increase in atomic number. We learnt that unlike the main group elements, the differentiating electron enters the penultimate (n-1)$d$ orbital in transition metals. This reflects in the properties of the transition metals and the periodicity in their properties. In this unit we have studied the variation of size, density, volume, melting and boiling points, ionisation energy, electronegativity, electrode potential, oxidation states and reactivity of the transition metals. Besides these, a few of their properties like colour, magnetic properties, complex formation, catalytic properties and formation of interstitial compounds have also been, discussed. Thus, besides gaining the basic understanding of transition metals, we have also learnt about their applications. We now understand why silver and gold are so extensively used in jewellery, why transition metals are

used as catalysts, etc. Thus this unit outlines a broad aspect of the transition metals.

## FURTHER READING

1       *A New Concise Inorganic Chemistry*, J.D. Lee, ELBS, London, 3rd ed., 1977.

2       *Chemistry: Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

3       *Comprehensive Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3rd ed., 1986.

4       *Principles of Inorganic Chemistry*, B.R. Puri and L.R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 19th ed., 1986.

**Module 3        Transition Elements**

**UNIT 3          INNER-TRANSITION ELEMENTS**

## 1.0    INTRODUCTION

In the preceding unit, you studied the main features of the chemistry of the transition elements of the *d*-block. You learnt that in addition to the usual vertical relationship, the transition elements show a horizontal similarity in their physical and chemical properties. In this unit you will study the salient features of the chemistry of the transition elements of the *f*-block. Because of filling of electrons in the *f*-orbitals of an inner shell, these elements are also termed as inner-transition elements. The *f*-block elements comprise two series of elements — the lanthanide series and the actinide series. You will observe that in comparison to the elements of *d*-block transition series, the members of lanthanide series resemble one another much more closely. They have generally one common

stable oxidation state and occur together in the same ores in nature. Because of the similarity in their chemical properties their separation from one another is very difficult. Therefore, special techniques of solvent extraction and ion exchange are employed for their separation. On the other hand, the chemistry of the actinides is quite complicated bemuse they exhibit more than one oxidation state and their radioactivity creates problems in the study of their properties. However, the actinides do exhibit some similarities with one another and with their lanthanide congeners in a particular oxidation state. Therefore, these elements are discussed as a class in one unit. In this unit you will study the general features of the chemistry of lanthanide and actinide elements with emphasis on periodicity in their properties.

## 2.0    Objectives

After studying this unit you should be able to:

- distinguish between transition and inner-transition elements,

- define the terms lanthanides and actinides,

- compute the electronic configurations of lanthanide and actinide ions from the electronic configurations of free atoms,

- discuss the ways in which actinide elements resemble their lanthanide congeners,

- discuss the ways in which the actinides resemble more closely *d*-block transition elements,

- explain lanthanide and actinide contraction,
- describe general characteristics of lanthanide and actinide elements and bring out periodicity in their properties.

## 3.0    GENERAL CHARACTERISTICS

You know that the fourteen elements from cerium *(Z - 58)* to lutetium (Z = 71), which follow lanthanum (Z = 57) in the periodic table, are called lanthanides, lanthanoids or lanthanons. Note that some authors include lanthanum also in lanthanides, but there is no general agreement on it. These elements are characterised by successive filling of 4*f* orbitals in their atoms. These elements along with lanthanum and yttrium were originally called as rare earth elements or simply rare earths. The word 'earth' was used because they occur as oxides, which in early usage meant earth, and the word rare was used because of the great difficulty in their separation from each other. Otherwise, these are not particularly rare in earth's crust. For example, lanthanum, cerium and neodymium are more abundant than lead. Even the scarcest of them, thulium, is as abundant as bismuth and more abundant than arsenic, cadmium, mercury or selenium, none of which is generally considered rare.

The fourteen elements from thorium (Z = 90) to lawrencium (Z = 103) following actinium in the periodic table are known as actinides, actinoids or actinons. They are analogous to the lanthanides and result from the filling of the 5*f* orbitals as the lanthanides result from the filling of 4*f* orbitals. Prior to 1940, only the naturally occurring actinides, i.e., thorium, protactinium and uranium were known. The remaining actinides have been produced artificially since then and are collectively known as transuranium elements.

## 3.1    Electronic Configuration and Position in Periodic Table

The outstanding feature of the lanthanide and actinide elements is the great similarity in physical and chemical properties which they display within each series. The reason for this unique behaviour of these elements lies in their electronic configuration.

You know that lanthanum, the element preceding the lanthanides in the periodic table, has the electronic configuration [Xe] $5d^1 6s^2$. Like lanthanum, the lanthanides also exhibit the stable oxidation state of +3. It is, therefore, expected that in these elements the successive electrons will be filled in the $4f$ orbitals, thereby the elements may have the electronic configuration from [Xe] $4f^1 5d^1 6s^2$ to [Xe] $4f^{14} 5d^1 6s^2$. The actual ground state electronic configurations of lanthanide elements have been determined by atomic spectroscopy and are given in Table 4.1- You can see from the Table that there is an electron in $5d$ orbital only in Ce, Gd and Lu, in all other elements this electron is shifted to the $4f$ orbital. This type of shuttling of electrons can be understood in terms of the comparable energies of the $4f$ and $5d$ orbitals. Whether there is an electron in $5d$ orbital or not, is of little importance because the lanthanides mostly form ionic compounds in +3 oxidation state and the electronic configuration of $M^{3+}$ ions varies in a regular manner from [Xe]$4f^1$ for Ce$^{3+}$ to [Xe]$4f^{14}$ for Lu$^{3+}$, as shown in Table 4.1.

**Table 4.1: Some properties of lanthanum and the lanthanides**

| Z | Name | Symbol | Electronic configuration outside the [Xe] core Ln | configuration [Xe] core Ln | Metallic radius pm | Ionic radius $M^{3+}$ pin | E* (V) $M^{3+}/M$ | Colour of Ln$^{3+}$ |
|---|------|--------|---------------------------|-----------------|---------|--------|-------|-----------|
| 57 | Lanthanum | La | $5d^1 6s^2$ | _ | 187 | 106 | -2.52 | Colourless |
| 58 | Cerium | Ce | $4f^4 5d^1 6s^2$ | $4f^1$ | 183 | 103 | -2.48 | Colourless |
| 59 | praseodymium | Pr | $4f^3 6s^2$ | $4f^2$ | 182 | 101 | -2.46 | Green |
| 60 | Neodymium | Nd | $4f^4 6s^2$ | $4f^3$ | 181 | 100 | -2.43 | Lilac |
| 61 | Promethium | Pm | $4f^5 6s^2$ | $4f^4$ | - | 98 | -2.42 | Yellow |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 62 | Samarium | Sm | $4f^{6}6s^{2}$ | $4f^{5}$ | 179 | 96 | -2.41 | Yellow |
| 63 | Europium | Eu | $4f^{7}6s^{2}$ | $4f^{6}$ | 204 | 95 | -2.41 | Pale pink |
| 64 | Gadoliniurn | Gd | $4f^{7}5d^{1}6s^{2}$ | $4f^{7}$ | 180 | 94 | -2.40 | Colourless |
| 65 | Terbium | Tb | $4f^{9}6s^{2}$ | $4f^{8}$ | 178 | 92 | -2.39 | Pate pink |
| 66 | Dysprosium | Dy | $4f^{10}6s^{2}$ | $4f^{9}$ | 177 | 91 | -2.35 | Yellow |
| 67 | Holmium | Ho | $4f^{11}6s^{2}$ | $4f^{10}$ | 176 | 89 | -2.32 | Yellow |
| 68 | Erbium | Er | $4f^{12}6s^{2}$ | $4f^{11}$ | 175 | 88 | -2.30 | Roue pink |
| 69 | Thulium | Tm | $4f^{13}6s^{2}$ | $4f^{12}$ | 174 | 87 | -2.28 | Pale green |
| 70 | Ytterbium | Yb | $4f^{14}6s^{2}$ | $4f^{13}$ | 194 | 86 | -2.27 | Colourless |
| 71 | Lutecium | Lu | $4f^{14}5d^{1}6s^{2}$ | $4f^{14}$ | 174 | 85 | -2.26 | Colourless |

The ground state electronic configuration of actinium, $[Rn]6d^{1}7s^{2}$ is similar to that of lanthanum and indeed the two elements possess similar chemical properties. The electronic configurations of the elements that follow actinum are not known precisely; these are less certain than those of the lanthanide elements. The difference in energy between $5f$ and $6d$ orbitals in the beginning of the actinide series is less than that between the $4f$ and $5d$ orbitals for the lanthanides. Therefore, both $5f$ and $6d$ orbitals are involved in accommodating successive electrons. Thus the filling of $5f$ orbitals in actinides (Table 4.2) is not quite so regular as the filling of the $4f$ orbitals in the case of the lanthanides. Later, however, the $5f$ orbitals become more stable, i.e., by the time plutonium and subsequent members of the series are reached, the $5f$ orbitals seem clearly to be of lower energy than the $6d$ orbitals, and so the electrons preferably fill the former.

Table 4.2 : Some properties of actinium and the actinides

| Z | Name | Symbol | Electronic configuration outside the [Rn] core | | Metallic radius pm | Ionic radius $M^{3+}$ pm | $E°$ (V) $M^{3+}/M$ | Colour of $An^{3+}$ |
|---|---|---|---|---|---|---|---|---|
| | | | An | $An^{3+}$ | | | | |
| 89 | Actinium | Ac | $6d^17s^2$ | $5f^0$ | – | 112 | -2.6 | Colourless |
| 90 | Thorium | Th | $6d^27s^2$ | $5f^1$ | 179 | – | – | – |
| 91 | Protactinium | Pa | $5f^26d^17s^2$ | $5f^2$ | 163 | 104 | -1.95 | Colourless |
| 92 | Uraniun | U | $5f^36d^17s^2$ | $5f^3$ | 156 | 103 | -1.80 | Red brown |
| 93 | Neptunium | Np | $5f^46d^17s^2$ | $5f^4$ | 155 | 101 | -1.86 | Purplish |
| 94 | Plutonium | Pu | $5f^67s^2$ | $5f^5$ | 155 | 100 | -2.03 | Blue violet |
| 95 | Americium | Am | $5f^77s^2$ | $5f^6$ | 159 | 98 | -2.38 | Pink |
| 96 | Curium | Cm | $5f^76d^17s^2$ | $5f^7$ | 173 | 97 | – | Pale Yellow |
| 97 | Berkelium | Bk | $5f^97s^2$ | $5f^8$ | 174 | 96 | – | – |
| 98 | Californium | Cf | $5f^{10}7s^2$ | $5f^9$ | 170 | 95 | – | – |
| 99 | Einstenium | Es | $5f^{11}7s^2$ | $5f^{10}$ | 186± 2 | – | – | – |
| 100 | Fermium | Fm | $5f^{12}7s^2$ | $5f^{11}$ | 186± 2 | – | – | – |
| 101 | Mendelevium | Md | $5f^{13}7s^2$ | $5f^{12}$ | – | – | – | – |
| 102 | Nobelium | No | $5f^{14}7s^2$ | $5f^{13}$ | – | – | – | – |
| 103 | Lawrencium | Lr | $5f^{14}6d^17s^2$ | $5f^{14}$ | – | – | – | – |

**Self Assessment Exercise  1**

Explain briefly:

(a)     What are inner-transition elements?

(b)     What are lanthanides and actinides?  Why are they so called?

c)     Write the electronic configurations of the elements of atomic number 61 and 95.

**3.2     Atomic Radius**

You have studied in CHM 101 that the atomic size decreases with increase in atomic number along any period in the long form of the periodic table due to increase in effective nuclear charge. However, the decrease in atomic radius is small when the difference in electronic configuration from one element to the next is that of an additional inner electron. This is because the additional inner electron screens the size-determining outer electrons from the nucleus much better than an additional outer electron. For example, decrease in the covalent radius from Sc to Zn,' i.e., across ten elements of the *3d* transition series, is 19 pm. This decrease is almost one-third of the decrease in the covalent radius of the seven elements of *s* and *p* blocks of the period 3.

The rate of decrease in atomic radius along the lanthanide series (Table 4.1) and also along the actinide series (Table 4.2) is even less than that in the transition series, since the difference in the electronic configurations of these elements is in the number of electrons in the ante-penultimate (last but two) shell of electrons. But the additive effect of decrease in atomic radius across the fourteen elements of lanthanide series is quite substantial. This decrease in atomic radius across the lanthanide series is known as lanthanide contraction. Similarly, there is an actinide contraction across the actinide series. As a result of lanthanide contraction, the normal increase in size from Sc→Y→La disappears after the lanthanides, and pairs of elements such as Zr and Hf, Nb and Ta, Mo and W, etc., possess nearly similar sizes (Table 4.3). The properties of these elements, therefore, are very similar. The similarities in properties within these pairs make their separation very difficult. Thus, due to lanthanide contraction, the elements of *5d* and *4d* transition series resemble each other much more closely than do the elements of *4d* and *3d* series.

**Table 4.3: Atomic (covalent) radii of the elements preceding and following the lanthanides in pm**

| 21 | | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|---|---|---|
| Sc | | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| 144 | | 132 | 122 | 118 | 117 | 117 | 116 | 115 | 117 | 125 |
| 39 | | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 |
| Y | | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| 162 | | 145 | 134 | 130 | 127 | 125 | 125 | 128 | 134 | 144 |
| 57 | 58–71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 |
| La | Ce–Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |
| 169 | 165—156 | 144 | 134 | 130 | 128 | 126 | 127 | 130 | 134 | 147 |

**Self Assessment Exercise 2**

**3.3    Oxidation States**

The sum of the first three ionisation energies of the lanthanides is comparatively low, so the elements are highly electropositive. They readily form $M^{3+}$ for the

lanthanides, actinium and trans-americium (Cm to Lr) elements the tripositive oxidation state is the most stable in every case. It is believed that in forming tripositive lanthanide or actinide ions, the $ns^2$ $(n = 6$ or $7)$ electrons are lost along with the $(n-1)d^1$ electron. In the absence of $(n-1)d^1$ electron one of the electrons present in the $(n-2)f$ orbitals is lost.

Besides the +3 state, some of the lanthanides and actinides show other oxidation states also. In these cases there is some evidence that ions with $f^0$ (e.g., $La^{3+}$ $Ce^{4+}$, $Ac^{3+}$, $Th^{4+}$, $Pa^{5+}$, $U^{6+}$)$f^7$ (e.g., $Eu^{2+}$, $Gd^{3+}$, $Tb^{4+}$, $Cm^{3+}$, $Bk^{4+}$), and $f^{14}$ (e.g., $Yb^{2+}$, $Lu^{3+}$) configurations exhibit greater stability. However, $Pr^{4+}$ $(4f^1)$, $Nd^{4+}$ $(4f^2)$, $(Sm^{2+}$ $(4f^6)$, $Tm^{2+}$ $(4^{13})$, etc. with non-$f^0$, non-$f^2$ and non-$f^{14}$ electronic configurations also exist. This reminds us that there may be other factors also such as ionisation energies and sublimation energies of the metals and lattice energies, etc., which are responsible for the stability of these oxidation states. The known oxidation states of actinium and the actinides are given in Table 3.4 in which numbers in bold indicate the most stable oxidation state in aqueous solution. You can see from the Table that nearly all the actinides exhibit at least two stable oxidation states and oxidation states higher than +3 are easily accessible in the early actinides. For thorium, protactinium and uranium the highest accessible oxidation state is the most stable one also in aqueous solution. This may be because 5$f$ orbitals extend further from the nucleus than the 4$f$ orbitals and 5$f$ electrons are more effectively shielded from the nuclear charge than are the 4$f$ electrons of the corresponding lanthanides. Because the 5$f$ electrons are less firmly held, they are all available for bonding in the early actinides. However, as the later actinides are approached, the build-up of nuclear charge causes-contraction of the 5$f$ orbitals so that the metal-ligands overlap decreases and the +3 state becomes predominant. Interestingly, the +2 state which is achievable in case of mendelevium and nobelium, is more stable than $Eu^{2+}$

**Table 4.4: Oxidation states of actinium and the actinides. The more stable states are In bold type; unstable states are enclosed in parentheses.**

| Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|    |    |    |   |    |    | (2) |    |    | (2) | (2) | 2 | 2 | 2 | – |
| 3 | (3) | (3) | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
|    | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | (4) |    |    |    |    |    |
|    |    | 5 | 5 | 5 | 5 | 5 |    |    |    |    |    |    |    |    |
|    |    |    | 6 | 6 | 6 | 6 |    |    |    |    |    |    |    |    |
|    |    |    |   | (7) | 7 |    |    |    |    |    |    |    |    |    |

**Self Assessment Exercise 3**

Which is the most common oxidation state of the lanthanides and how is it formed? Give its configuration.

**3.4 Colour of Ions**

Ions of lanthanides and actinides are coloured in the solid state as well as in aqueous solution, as is the case with the ions of transition metals. You have studied in the preceding unit that the colours of transition metal ions arise because of absorption of light due to *d-d* electronic transitions. Because there are no electrons in the *d*-orbitals, the colours of lanthanide and actinide ions arise due to electronic transitions in the 4*f* and 5*f* orbitals. Colours of hydrated lanthanide and actinide ions are given in Table 4.1 and 4.2, respectively.

**3.5     Electrode Potentials**

The standard electrode potentials of lanthanides for the half- reaction,

$$Ln^{3+} (aq) + 3e \longrightarrow Ln (s)$$
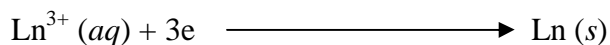
are given in Table 4.1. The electrode potentials are very low. Therefore, these elements are highly electropositive and reactive metals. The electrode potential increases from Ce to Lu, which is consistent with the slight decrease in the ionic radius due to lanthanide contraction. The electrode potentials of the actinide

elements also are quite low (Table 4.2). Therefore, the actinides also are highly electropositive and reactive metals.

## 3.6 Complexation Behaviour

Ions of lanthanide and actinide elements have a strong tendency to form complexes with a variety of oxygen and nitrogen donor ligands. Probably, because of their comparatively higher charge to size ratio, the actinide ions have a greater tendency to form complexes than the lanthanides. Also, due to the existence of a large number of oxidation states, the complexation behaviour of actinides is more varied. The lanthanide and actinide ions form the most stable complexes with chelating ligands such as oxalic acid, citric acid, tartaric acid, nitric acid, ethylenediamine tetraacetic acid (EDTA) and $\beta$-diketones. In these complexes the metal ions have very high coordination numbers. For example, the coordination number of the metal ion in $[Th(acac)_4]$, $[Ce(NO_3)_4\text{-}(OPPh_3)_2]$ and $[Ce(NO3)6]^{2-}$ is 8, 10, 12, respectively. In these complexes, the acetyl acetonate (acac) and the nitrate ligands are acting as bidentate ligands occupying two coordination sites around the metal ion. These metal ions form water soluble complexes with citric acid, tartaric acid and EDTA. The formation of water soluble complexes with these ligands facilitates separation of the metal ions by ion exchange chromatography which you will study in the next section.

## 3.7 Magnetic Properties

You have learnt in the preceding unit that paramagnetism is associated with the presence of unpaired electrons in a substance. The lanthanide and actinide ions, other than $f^O$ type (e.g., $La^{3+}$, $Cc^{4+}$. $Ac^{3+}$, $Th^{4+}$, $Pa^{5+}$, $U^{6+}$) and $f^{14}$ type (e.g., $Yb^{2+}$, $Lu^{3+}$, $Lr^{3+}$). are all paramagnetic, because each of the seven $f$ orbitals characterising inner-transition metal species (lanthanide and actinide) must contain a single electron before any pairing can take place (Hund's rule).

You have also studied that in case of transition elements, the contribution of orbital motion of electrons to paramagnetism is negligible and can be ignored. The magnetic moments of transition metal ions can be explained in terms of

unpaired electrons present in $d$-orbitals. But the magnetic moments of only those lanthanide ions, which have $f^0$, $f^7$ and $f^{14}$ configuration agree with the spin only value. In all other cases, the magnetic moment values are higher than those calculated on the basis of spin only formula. However, these can be explained by taking orbital contribution to magnetic moment also into account. In lanthanide ions, the $4f$ orbitals are comparatively better shielded from the surroundings by the overlying $5s$ and $5p$ orbitals than the $d$ orbitals in transition metal ions. Therefore, the contribution of orbital motion to paramagnetism is not quenched.

Although actinides show a variation in magnetic properties similar to that of the lanthanides, the magnetic properties of the actinide ions are more complicated than those of the lanthanide ions. This in part arises from (i) the fact that the $5f$ electrons are nearer the surface of the atom and are easily influenced by the chemical environment, although not to the same extent as do the $d$ electrons, and (ii) the less sharply defined distinctions between $5f$ and $6d$ electrons as compared with $4f$ and $5d$ electrons. From the above discussion it is clear that the magnetic moments of the $f$-block (inner transition) metal ions must be calculated taking into account both spin and orbital contributions.

## 3.8    Chemical Properties

The lanthanides are silvery-white, highly electropositive and reactive metals. They all react slowly with cold water and rapidly on heating to liberate hydrogen:

$$2M + 6H_2O \longrightarrow 2M(OH)_3 + 3H_2$$
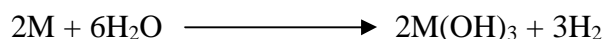
The hydroxides are ionic and basic. They are less basic than $Ca(OH)_2$ but more basic than amphoteric $Al(OH)_3$. The base strength decreases from $Ce(OH)_3$ to $Lu(OH)_3$ as the ionic radius decreases from $Ce^{3+}$ to $Lu^{3+}$

The lanthanide metals dissolve in dilute acids, even in the cold, to liberate hydrogen gas:

$$2Ln + 6HCl \longrightarrow 2LnCl_3 + 3H2$$
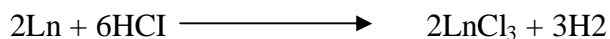
The metals tarnish readily in air forming an oxide coating. On heating in oxygen, they burn easily to give $M_2O_3$, except for cerium which forms $CeO_2$. The oxides are ionic and basic, the base strength decreases as the ionic radius decreases.

$$4Ln + 3O_2 \longrightarrow 2Ln_2O_3$$
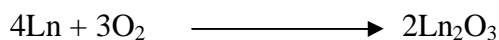
When heated in halogens, the lanthanides bum producing $LnX_3$, which can also be made by heating the oxides with the appropriate ammonium halide:

$$2Ln + 3X_2 \longrightarrow 2LnX_3$$
$$Ln_2O_3 + 6NH_4X \longrightarrow 2LnX_3 + 6NH_3 + 3H_2O$$
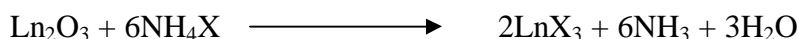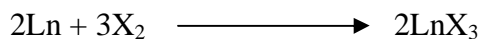
Cerium with fluorine forms $CeF_4$:
$$Ce + 2F_2 \longrightarrow CeF4$$
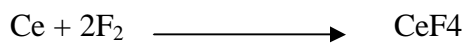
The metals react exothermically with hydrogen, though heating to 600-700 K is often ^8 required to initiate the reactions. Their hydrides are non-stoichiometric compounds having ideal formulae, $MH_2$ and $MH_3$. The hydrides are remarkably stable to heat up to 1200 K. The hydrides react with water liberating hydrogen gas:

$$MH_3 + 3H_2O \longrightarrow M(OH)_3 + 3H_2$$
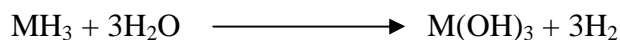
On heating, the lanthanides react with boron giving borides of the type $MB_4$ and $MB_6$, with carbon giving carbides $M_2C_3$ and $MC_2$ and with nitrogen giving nitrides MN. A wide variety of their oxosalts, like carbonates, sulphates, nitrates, phosphates, oxalate, etc., are known.

All the actinides are unstable with respect to radioactive disintegration, though the half-lives of the most abundant isotopes of thorium and uranium are so long that for many purposes their radioactivity can be neglected. Like lanthanides, actinides

are also electropositive and reactive metals. They react with water, oxygen, hydrogen, halogens and acids. Their hydrides are non-stoichiometric having ideal formulae $MH_2$ and $MH_3$. The metals also react with most non-metals especially if heated.

**Self Assessment Exercise 4**

Write down the chemical equations for the reactions of lanthanide elements with (i) water. (ii) acids, (iii) oxygen and (iv) halogens.

## 4.0    OCCURRENCE, EXTRACTION AND USES

All the lanthanide and actinide elements are highly reactive metals, therefore, none of them occurs in the free state in nature. Moreover, all the actinide elements are radioactive, so most of them do not occur naturally and have been prepared artificially since 1 940. Let us now discuss the occurrence, extraction and uses of these elements.

## 4.1    Occurrence

Apart from promethium which is unstable and is found in traces in uraniun, ores, all the lanthanides generally occur together. Although a large number of minerals are known to contain lanthanides, only three of them, viz., monazite, bastnaesite and xenotime are of commercial importance. Monazite and xenotime are a mixture of phosphates of thorium, lanthanum and lanthanides. Monazite is widely but sparsely distributed in many rocks, but because of its high density and inertness, it is concentrated by weathering into sands on beaches and river beds. Deposits of monazite occur in Southern India, South Africa and Brazil. Bastnaesite is a mixture of fluoride carbonates, $LnFCO_3$, of lanthanum and the lanthanides. Both monazite and bastnaesite are richer in the lighter lanthanides, i.e., the cerium earths, but with the difference that monazite also contains upto

30% $ThO_2$, which is absent in bastnaesite. On the other hand xenotime is a valuable source of the heavier rare earths.

Every known isotope of the actinide elements is radioactive and their half-lives are such that only $^{232}$ Th, $^{235}$ U, $^{238}$ U and possibly $^{244}$ Pu have survived during the very period of their existence. Only thorium and uranium are found in nature in amounts sufficient for practical extraction. Thorium constitutes $8.1 \times 10^{-4}$ % of the earth's crust and it is almost as abundant as boron. As described earlier, monazite is the most important source of thorium. Uranium comprises $2.3 \times 10^{-4}$ % the earth's crust and it is slightly more abundant than tin. Pitchblende or uraninite, $U_3O_8$, and carnotite, $K_2(UO_2)_2(VO_4)2 -3H_2O$, are two important ores of uranium.

## 4.2    Extraction

As all the lanthanides occur together in nature, their extraction involves two main steps: (i) separation from one another and (ii) reduction of their compounds to metals. Since the lanthanides are all typically trivalent and are almost identical in size, their chemical properties are almost similar. Therefore, the separation of lanthanides from one another is a very difficult task, almost as difficult as the separation of isotopes. Only cerium and europium can be separated from the remaining lanthanides by employing conventional chemical methods because of stabilities of Ce $^{4+}$ and Eu $^{2+}$ in aqueous solution. Cerium can be separated from a mixture of lanthanides by oxidising $Ce^{3+}$ to $Ce^{4+}$ with permanganate or bromate or hypochlorite in an alkaline medium and subsequently precipitating it as $CeO_2$. Europium can be reduced to Eu $^{2+}$ either by electrolytic reduction with a mercury cathode or by using zinc amalgam. It is then precipitated from the solution as $EuSO_4$.

Earlier the lanthanides used to he separated from each other by **selective precipitation** or by **fractional crystallisation**. With a limited amount of a precipitating agent, the substance which is least soluble is precipitated first. For example, if a base is added to a solution of lanthanide nitrates, the least soluble

Lu(OH)$_3$ is precipitated first and the most soluble La(OH)$_3$ last. As only a partial separation is effected, the precipitate is redissolved and the process is repeated several times.

The solubility of double salts of lanthanides such as 2Ln(NO$_3$)$_3$.3Mg(NO3)2.24H$_2$O and Ln2 (SO$_4$)$_3$ Na2SO$_4$.xH$_2$O increases from La to Lu. Therefore, the lanthanides could be separated from each other by **fractional crystallisation** of these salts. As these processes need to be repeated several times, these are very tedious and not very efficient. However, the individual elements can now be separated with much less difficulty on a large scale by employing more efficient techniques of **solvent extraction** and **ion exchange chromatography**.

The distribution coefficients of the salts of lanthanide elements between water and organic solvents are slightly different. Therefore, the individual elements are selectively extracted from aqueous solutions of their salts into an organic solvent. This technique of separation is known as solvent extraction. Tributyl phosphate is a very good solvent for this process. The solubility of lanthanides in +3 oxidation state in tributyl phosphate increases with atomic number. Separation is performed by using a continuous **counter-current process** in which the aqueous solution of lanthanide nitrates and the solvent are passed through a column continuously in opposite directions. This process is much less tedious than performing several crystallisations.

The process of **ion exchange chromatography** is the most important, rapid and effective method for the separation and purification of the lanthanons. In this process, a solution of lanthanide ions is run down a column of a synthetic ion exchange resin. Ion exchange resins are organic polymers consisting of functional groups such as -COOH, -SO$_3$H or -OH. In these resins, hydrogen ions are mobile and can be exchanged with other cations. Thus, the lanthanide ions replace the H$^+$ ions and get bound to the resin:

$$Ln^{3+} + 3R - SO_3H \longrightarrow Ln(SO_3R)_3 + 3H^+$$

After the $H^+$ ions have passed through the column, a solution of a complexing agent such as citric acid, α-hydroxyisobutyric acid or EDTA at the appropriate pH is passed through the column to elute, i.e., to wash off the metal ions in a selective manner:

$$Ln(O_3SR)_3 + (NH_4)_3EDTAH \longrightarrow Ln(EDTAH) + 3NH_4O_3SR$$
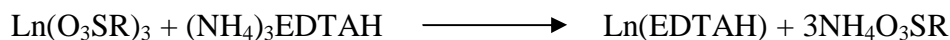
As the EDTA solution flows down the column, the lanthanide ions come off the resin and form a complex with EDTA and then go back on the resin a little lower down the column. This process is repeated many times as the metal ions gradually travel down the column. The smaller lanthanide ions like $Lu^{3+}$ form stronger complexes with EDTA than the larger ions like $La^{3+}$. Thus, the smaller and heavier ions spend more time in solution and less time on the column. Therefore, the heavier ions are eluted from the column first and the lighter ones the last. Using suitable conditions, all the individual elements can be separated. The eluates are then treated with an oxalate solution to precipitate lanthanides as oxalates which are then ignited to get the oxides :

$$2Ln(EDTAH) + 3(NH_4)_2C_2O_43 \longrightarrow Ln_2(C_2O_4)_3 + 2(NH_4)_3EDTAH$$
$$2Ln(C_2O_4)_3 \longrightarrow Ln_2O_3 + 3CO + 3CO_2$$
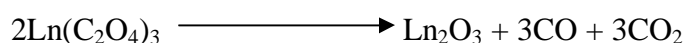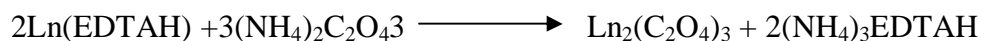
Samarium, europium and ytterbium are prepared by reduction of the oxides with La at high temperatures:

$$2LnO3 + 2La \longrightarrow Ln_2O_3 + 2Ln, Ln = Sm \text{ and } Eu$$
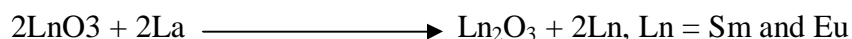
Other lanthanides are obtained by the reaction of $LnCl_3$ or $LnF_3$ with Ca metal at 1300 K. $LnCl_3$ or $LnF_3$ are prepared by heating $Ln_2O_3$ with appropriate ammonium halide:

$$Ln_2O_3 + 6NH_4X \longrightarrow LnX3 - 6NH_3 + 3H_2O$$
$$2LnX3 + 3Ca \longrightarrow 2Ln + 3CaX_2$$
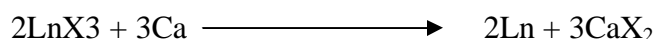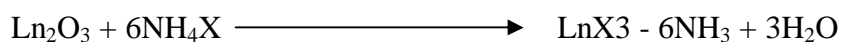
You know that actinium and all the actinides are radioactive. Of these only thorium and uranium are extracted from ores, all others are prepared artificially by nuclear reactions. The chief ores of thorium and uranium are monazite and pitchblende, respectively. For extraction of thorium, monazite is dissolved in concentrated sulphuric acid. By suitably adjusting the pH of this solution, a precipitate of $ThO_2$ is obtained. The impure $ThO_2$ is purified by dissolving it in hydrochloric acid and then extracting $ThCl_4$ by trihutylphosphate. From this solution $ThO_2$ is reprecipitated by adjusting the pH. Purified $ThO_2$ is converted into anhydrous $ThF_4$ or $ThCl_4$ by the action of HF or $CCl_4$ at 900K. Thorium metal is then prepared by reduction of $ThF_4$ or $ThCl_4$ with calcium:

$$ThX_4 + 2Ca \longrightarrow Th + 2CaX_2$$
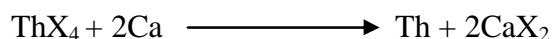
Uranium is chiefly extracted from pitchblende. The concentrated ore (pitchblende, $U_3O_8$) is washed and then fused with sodium carbonate and sodium nitrate. The fused mass is treated with sulphuric acid, which extracts uranyl sulphate, $UO_2SO_4$. Addition of sodium carbonate solution in excess to the above solution removes all the heavy metals as carbonates. Uranium goes in solution as sodium uranyl carbonate $Na_4[UO_2)(CO_3)_3]$. Addition of dilute $H_2SO_4$ to the Uranyl carbonate solution precipitates uranium as sodium diuranate, $Na_2U_2O_7$, which on treatment with concentrated solution of $(NH_4)_2CO_3$ passes into solution as ammonium uranyl carbonate, $(NH_4)_4[UO_2(CO_3)_3]$. Concentration of this solution gives pure $U_3O_8$. Reduction of $U_3O_s$ with aluminium powder produces uranium metal. All these steps involved in extraction of uranium from pitchblende are summarised in a How sheet.

Pitchblende $(U_3O_8)$

i) Fusion with $Na_2CO_3$ and $NaNO_3$
ii) Treatment with $H_2SO_4$

Solution $(UO_2^{2+},$ some heavy metal ions)          Residue $(RaSO_4)$

$\downarrow$ $Na_2CO_3$ solution in excess

Solution $Na_4[UO_2(CO_3)_3]$          Precipitates of heavy metal carbonates

$\downarrow$ dil $H_2SO_4$

Precipates $Na_2U_2O_7 \cdot 6H_2O$          Solution $Na_2SO_4$

$\downarrow$ Treatment with concentrated $(NH4)_2CO_3$ solution

Solution $(NH_4)_4[UO_2(CO_3)_3]$          Solid rejected
Recrystallised

$\downarrow$

Solution $(NH_4)_4[UO_2(CO_3)_3]$ $\xrightarrow{\text{ignition}}$ $U_3O_8$ $\xrightarrow{\text{Al powder}}$ U
Recrystallised

## 5.0 Uses

Lanthanides and many of their complexes have received wide industrial applications. For example, europium derivatives are used as phosphors in TV screen; samarium-cobalt alloys are used for making magnets, $Pr_2O_3$ and $Nd_2O_3$ are used for making welder's goggles, yttrium-aluminium garnets (YAG) are used both in electronic equipment and as synthetic gems. Various mixed oxides are used as catalysts in cracking of petroleum. Cerium in the +4 oxidation state is used as an oxidising agent in quantitative analysis. Thorium nitrate has been used for more than a century in gas mantles. Till 1940, the only industrial application of uranium was as a colouring material in the manufacture of yellow glass. At present, the principal use of thorium and uranium is as a nuclear fuel.

**Self Assessment Exercise  5**

Why is the separation of the lanthanides so difficult? List three important methods used for the separation of lanthanide metals.

### SUMMARY

In this unit, you have studied electronic structures, oxidation states, and magnetic properties. electrode potentials, chemical properties, occurrence, extraction and uses of lanthanides and actinides which can be summarised as following:

- The lanthanide and actinide elements are characterised by filling of 4*f* and 5*f* subshells, respectively.

- For the lanthanides, actinium and transamericium elements, the tripositive oxidation state is-the most stable in every case. However, the oxidation states higher than +3 are quite common for the early actinide elements.

- The lanthanides exhibit greater similarities in their properties in their most prominent oxidation state, +3. Cerium and europium are the only lanthanides to be stable as $Ce^{4+}$ and $Eu^{2+}$ in aqueous solution.

- All the lanthanide and actinide ions which have unpaired electrons are paramagnetic. Paramagnetism of lanthanide and actinide ions depends on both spin and angular momentum of the unpaired electrons.

- All the lanthanides and actinides are highly electropositive and reactive metals. They react with oxygen, halogens, hydrogen, water and acids. Their hydrides are non-stoichiometric compounds.

- Cerium is the most abundant of all the lanthanides. Its main ores are monazite and bastnaesite.

- Since the lanthanides are all typically trivalent and are almost identical in size, their chemical properties are almost similar. As all the lanthanides occur together in nature, their separation is extremely difficult. Separation of lanthanides is effected by using the techniques of solvent extraction and ion-exchange chromatography. The metals are prepared by reduction of their oxides, chlorides or fluorides with La or Ca.

- Thorium and uranium are extracted from monazite and pitchblende, respectively. All other actinides are now prepared artificially by nuclear reactions.

**FURTHER READING**

1    *A New Concise Inorganic Chemistry*, J.D. Lee, ELBS, London, 3rd ed., 1977.

2    *Chemistry: Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

3    *Comprehensive Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3rd ed., 1986.

4    *Principles of Inorganic Chemistry*, B.R. Puri and L.R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 19th ed., 1986.

**Module 4    ISOLATION AND PURIFICATION OF METALS**

**UNIT 1    Metallurgy**

1.0    Introduction

2.0    Objectives

3.0    Occurrence of Metals

   Native Minerals

   Sulphide Minerals

   Oxide Minerals

   Oxosalts

   Halide Minerals

4.0    Beneficiation of Ores

   Gravity Separation

   Magnetic Separation

   Froth Flotation Process

5.0    Reduction to Metals

   Pyrometallurgy

   Thermodynamics of Reduction Process

   Hydrometallurgy

   Electrometallurgy

## 1.0    INTRODUCTION

So far in various units of this course, you have studied the chemistry of various elements wherein an emphasis was given to periodic relationships. As you know, metals as a group of elements have acquired a unique importance in the modern world. However, nature does not generally offer us metals in the free state. Metals usually occur in nature in combined state as ores mixed with other earthy materials. The branch of science dealing with the methods of extraction of metals from their ores is called **metallurgy.**

In this unit, we will discuss the basic principles on which extraction of metals is based. We will also briefly describe various processes of extraction of metals from natural sources. In the end, extraction and purification of some important transition metals from their ores will also be discussed.

## 2.0. Objectives

After studying this unit, you should be able to:

- describe the sources of metals and the states in which they occur in nature,
- discuss the relationship between the occurrence and reactivity of metals,
- define the terms earth's crust, mineral, ore, gangue, calcination, roasting, smelting, flux, slag, etc.
- describe the methods of beneficiation of ores,

## 3.0 OCCURRENCE OF METALS

Earth's crust and sea are the two main sources of metals. In the earth's crust metals occur both in the combined state in the form of minerals as well as in the native or free state. Earth's crust is the outermost part of the earth, which has an average thickness of about 17 km. The crust is thinner under the oceans and thicker under the continents. The minerals from which the extraction of any metal is chemically feasible and economically competitive are known as ores of that metal. Metals occur in widely varying quantities in the earth's crust. The relative abundance of the most common elements in the earth's crust is given in Table 4.1. You may note that about 75% of the earth's crust is composed of nonmetals, oxygen and silicon. The relative abundance of only three industrially important metals, i.e., aluminium, iron and magnesium is more than 2%. The abundance of most other useful metals in the earth's crust is very low. Therefore, if the metals had been uniformly distributed in earth's crust, it would have not been possible to extract them. But luckily, the metals generally in the form of their minerals, are unevenly

distributed and are accumulated and some locations, making their extraction easier. These accumulations of minerals are termed as mineral deposits. Usually, the mineral is covered with a layer of soil, known as overburden. The thickness of overburden may vary from a few metres as in case of iron ore to thousands of metres as in case of deposits of gold. The mineral deposit is brought to the surface by mining.

**Table 5.1:    Relative abundance of various elements in earth's crust**

| Element | Percentage | Element | Percentage |
|---------|-----------|---------|-----------|
| Oxygen | 46.6 | Strontium | 0.015 |
| Silicon | 27.7 | Vanadium | 0.015 |
| Aluminium | 8.13 | Nickel | 0.010 |
| Iron | 5.10 | Zinc | 0.008 |
| Calcium | 3.63 | Copper | 0.007 |
| Sodium | 2.83 | Tungsten | 0.00.5 |
| Potassium | 2.60 | Cobalt | 0.004 |
| Magnesium | 2.10 | Tin | 0.004 |
| Titanium | 0.63 | Lead | 0.0016 |
| Hydrogen | 0.14 | Thorium | 0.0008 |
| Phosphorus | 0.12 | Beryllium | 0.0006 |
| Manganese | 0.10 | Arsenic | 0.0005 |
| Fluorine | 0.08 | Uranium | 0.0002 |
| Sulphur | 0.052 | Molybdenum | 0.0001 |
| Chlorine | 0.048 | Mercury | 0.00005 |
| Barium | 0.043 | Silver | 0.000008 |
| Carbon | 0.032 | Gold | 0.0000002 |
| Chromium | 0.020 | Other elements | balance |

Minerals are solid substances differing in chemical composition, colour, lustre, density, hardness and other characteristics. Depending on chemical composition, the minerals can be divided into following groups:

### 3.1  Native Minerals

These minerals contain the metal in free or elemental state, e.g., copper, silver, gold, platinum and iron. The metals are usually found mixed with clay, sand, etc. Sometimes lumps of almost pure metals are also found. These lumps are called

nuggets. Native iron is of metiorite origin and its occurrence is rare. Deposits of native iron are found in Greenland.

## 3.2 Sulphide Minerals

In these minerals metals are present as their sulphides. For example, iron pyrites ($FeS_2$), calcocite ($Cu_2S$), chalcopyrite ($CuFeS_2$), zinc blende ($ZnS$), argentite ($Ag_2S$), cinnabar ($HgS$), galena ($PbS$), millerite ($NiS$), etc.

## 3.3 Oxide Minerals

These minerals consist of oxides of metals, which are formed either by oxidation of sulphide minerals or by direct oxidation of metals. Highly electropositive metals, such as Al and Mg, occur only as oxides rather than as sulphides. Some important oxide minerals are haematite ($Fe2O_3$), magnetite ($Fe_3O_4$), bauxite ($Al_2O_3 \bullet 2H_2O$), cassiterite ($SnO_2$), cuprite ($Cu_2O$), zincite ($ZnO$), rutile ($TiO_2$), pyrolusite ($MnO2$), chromite ($FeO\ Cr_2O_3$), uraninite or pitchblende ($2UO_3 . UO_2$), etc.

## 3.4 Oxosalts

In these minerals, metals are present as their oxosalts, such as carbonates, sulphates, nitrates, phosphates, borates and silicates. Some important minerals of this group are siderite ($FeCO_3$), magnesite ($MgCO_3$). dolomite ($MgCO_3 . CaCO_3$), cerussite ($PbCO_3$), malachite ($CuCO_3.Cu(OH)2$), calamine ($ZnCO_3$), barytes ($BaSO_4$), gypsum ($CaSO_4 . 2H_2O$), epsomite ($MgSO_4 . 7H_2O$), anglesite ($PbSO_4$), soda nitre ($NaNO_3$), monazite ($LaPO_4 . CePO_4 . NdPO_4 . PrPO_4 . Th_3(PO_4)_4$), spodumene ($LiAlSi_2O_6$), zircon ($ZrSiO_4$), beryl ($Be_3Si_6O_{18}$), etc. Phosphate minerals are, in general, rare and occur in low concentrations. Silicate minerals are abundant in nature. However, the extraction of metals from silicates is difficult and the cost of extraction is very high. Therefore, only the less common metals such as lithium are extracted from silicate minerals.

## 3.5  Halide Minerals

Highly electropositive alkali and alkaline earth metals tend to form halide salts, which being soluble in water are washed away into the oceans due to leaching of the top soil. However, many deposits of halide minerals are also found under the soil. Some important halide minerals are rock salt (NaCl), sylvine (KC1), horn silver (AgCl), carnallite (KCl·MgCl$_2$-6H$_2$O), fluorspar (CaF$_2$) and cryolite (AlF$_3$·3NaF).

Ores as mined, generally contain variable amounts of unwanted minerals such as silica, clay, granite, etc. These unwanted materials are called **gangue.** The proportion of the desired metal in the ore must be sufficiently high so that the extraction of metal is chemically feasible and economically competitive. Ores of very low concentration are used only if they can be processed easily and inexpensively or if the metal produced is scarce. The lower limit of the percentage of the metal in mineral below which extraction becomes unprofitable depends on the value of the metal. Thus, ores containing 1% tin are frequently worked upon to obtain tin and ores containing 5% tin are considered rich deposits of tin. If gold is present to the extent of even 0.0015%, it is considered worth extraction. On the other hand, iron and aluminium will not be worth extracting unless they contain 30% or more of the metal.

As said earlier, in addition to the earth's crust, oceans also provide a huge storehouse of minerals in which the metals occur primarily as soluble sulphates and halides. It is estimated that one cubic kilometre of sea water contains 1 million tonnes of magnesium, 1,500 tonnes of strontium and 5 tonnes each of gold, copper, manganese, zinc and lead. Magnesium is already being extracted from sea water. In future, greater attention will be paid to sea as a source of raw materials when supplies of ore deposits on land are depleted. In addition to sea water, nodules or lumps about the size of an orange have been found on sea bed at depths of 4,000-5,000 metres. The nodules are relatively rich in manganese (25%)

and iron (15%). Recently technology for deep sea mining of these nodules has been developed.

Form the above discussion, it should be clear to you that there is a relationship between the reactivity of metals and the form in which they occur in nature. Reactive metals occur in nature in the form of their compounds such as oxides, sulphides, halides and oxosalts. On the other hand coinage and noble metals having rather low reactivity are found in nature in both combined as well as native states.

**Self Assessment Exercise  1**

How do metals occur in nature? What are some of the important sources of metals?

**4.0     BENEFICIATION OF ORES**

Most of the ores available in nature contain large amounts of impurities, i.e. gangue. Direct extraction of metals from the ores by metallurgical processes is uneconomical and technically difficult. Therefore, the ores should be processed first by some cheaper methods which remove the gangue partly or wholly. The pretreatment of ores by cheaper methods, based mainly on physical properties and without bringing out any major chemical change in the ore is known as beneficiation or concentration of the ore or ore dressing. Beneficiation of ores results in saving the cost of the transportation, fuel, fluxing agents and increased production.

The methods used for beneficiation of ores are based on differences in such properties of ores and gangue as colour, lustre, size, density, and wettability by water or oil. The simplest method of ore beneficiation consists of hand picking of ore particles, which is based on difference in colour, lustre or shape and size of

ore particles and gangue. Hand picking can be adopted in areas where labour is cheap. However, this method is outdated and is practised only in very specific cases when other methods are not possible, e.g., hand picking of diamonds from gravel and clay. Important methods of beneficiation of ores are gravity separation, magnetic separation and froth flotation, which we will now discuss in brief.

## 4.1 Gravity Separation

This is one of the simplest methods of concentration of ores. It is based on the difference in the specific gravities of the ore and gangue. In this method, the crushed ore is kept on top of a sloping table, which is made to vibrate. A stream of water is passed in the direction perpendicular to the slope. The lighter particles are thrown up by vibration and are removed by the water stream. The heavier mineral particles settle to the bottom and are collected. This method of gravity separation is known as **tabling**. Casseterite or tin-stone, chromite and pitchblende are concentrated by this method.

A modification of the above method is **sink and float** method. In this, the powdered ore is suspended in a liquid whose specific gravity is intermediate between the densities of gangue and the ore. The lighter material floats and the heavier material sinks. In this method, the difficulty is in finding a liquid of the proper specific gravity. A solution of calcium chloride in water is often used. Suspensions of sand in water giving liquids of specific gravities up to 3.2 are also used. However, due to technical problems this method is rarely used in concentration of low grade ores, but it is widely used in cleaning coal.

## 4.2 Magnetic Separation

This technique is based on the difference in magnetic properties of minerals. If the ore but not the gangue is attracted by a magnetic field, it can be concentrated to yield a sample which is rich in the metal. The pulverised mineral is passed over a

rubber belt which moves on a pully in a magnetic field (Fig. 5.1). The non-magnetic gangue particles fall off in a vertirle position when the belt passes over the pully, but the magnetic ore clings to the belt. When the belt passes out of the influence of the magnetic field the ore drops off. Magnetite ($Fe_3O_4$), haematite ($Fe_2O_3$), wulframite (FeWO4), chromite ($FeO^.Cr_2O_3$) and ilmenite ($FeO^.TiQ_2$) are some of the minerals which are separated from non- magnetic impurities by this method.
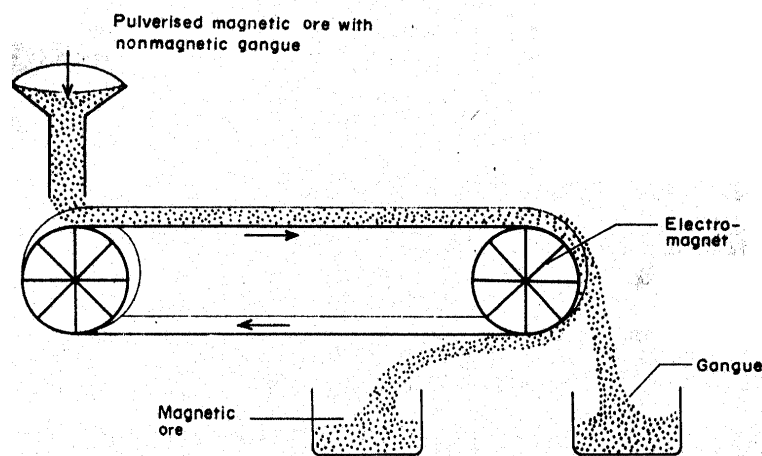


**Fig. 5.1: Magnetic separation of ores**

## 4.3     Froth Flotation Process

Froth flotation process is the most important method for beneficiation of ores. This process has made possible the beneficiation of low grade ores which could not be processed earlier. The process of froth flotation is widely employed to concentrate sulphide ores. However, many oxide ores can also be concentrated by this process. It is based on the difference in wettability of different minerals. In this process, the ore is finely ground to give a thick pulp containing 30-40% solids. A small amount of pine oil, oleic acid or cresylic acid, which cause frothing, is added to the pulp. A substance, which is capable of repelling water from the surface of mineral and thus promotes attachment of mineral particles to

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air bubbles is also added to pulp. This substance is called collector. Sodium ethyl xanthate, $C_2H_5OCS_2Na$, is commonly used as a collector in floating copper, lead and nickel sulphide ores. Another substance called **activator**, which helps in the action of collector can also be added. The entire material, i.e. the mixture of pulp, frother and collector, is taken in a container and then air is blown. Air bubbles adhere to the mineral particles and make them float in the form of a froth which is collected. The gangue is wetted by water and sinks (Fig. 5.2).
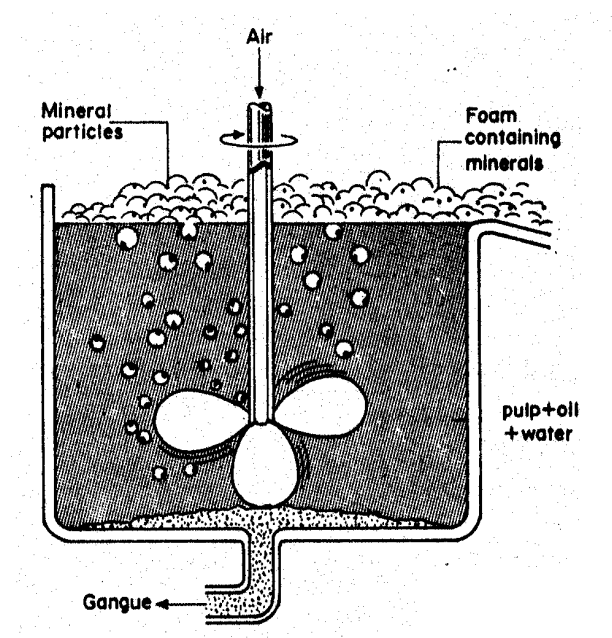


**Fig. 5.2: Froth flotation process for concentration of sulphide ores**.

Some ores contain more than one mineral, so separation of one mineral from the other in addition to separation from the gangue is necessary. To achieve this, a depressing agent or **depressor,** which suppresses the notation of one of the minerals is added. An important example is the concentration of lead-zinc ore. If the ore is concentrated without a depressor, both lead and zinc sulphides collect in the froth. If a small amount of sodium cyanide or zinc suphate is added, zinc sulphide is depressed, permitting flotation of lead sulphide. After removing lead sulphide, copper sulphate is added to activate the depressed zinc sulphide and air

is blown when zinc sulphide floats. This method is known as **differential flotation**.

**Self Assessment Exercise   2**

What method can he used for beneficiation of the following?
(i)      Haematite (ii)         Casseterite (iii)        Chromite
(iv)     Copper pyrites

## 5.0      REDUCTION TO METALS

After removal of the gangue, i.e. impurities physically mixed with the metal compounds, the concentrated ore becomes ready for the isolation of metal. In concentrated ore, the metals are present in the form of their compounds. Extraction of metals involves the reduction of metal compounds to free metals. In general, depending upon the reactivity of metals, their compounds can be reduced by one or more than one of the three types of metallurgical operations. These operations are pyrometallurgy. hydrometallurgy and electrometallurgy, which we will discuss in brief in this section.

### 5.1     Pyrometallurgy

In pyrometallurgy, the concentrated ore is heated to a high temperature and reduction is done with a suitable reducing agent. The different steps involved in pyrometallurgy are calcination, roasting and smelting. The concentrated ore is converted into the metal oxide by calcination or roasting, if it does not already exist as an oxide. This is because other metal compounds like sulphides, sulphates, carbonates, etc. are difficult to reduce. Finally, the metal oxide is reduced to metal by smelting.

### 5.2 Calcination

This is the process of heating the concentrated ore in a limited supply of air to a high temperature but below the fusion temperature. In calcination, volatile constituents of an ore are expelled. Hydroxide and hydrated ores lose their water forming metal oxides. In case of carbonate ores, carbon dioxide is lost and metal oxides are formed.

$$Al(OH)_3 \xrightarrow{1500K} Al_2O_3 + 3H_2O\uparrow$$

$$CaCO_3 \xrightarrow{1300-1500K} CaO + CO_2\uparrow$$
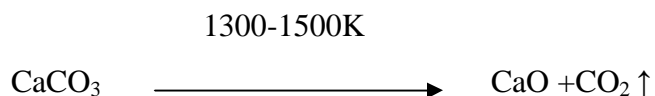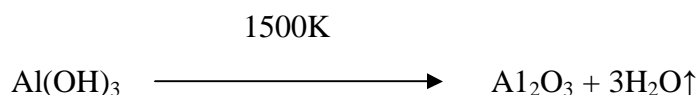
## 5.3 Roasting

Roasting is the process of heating ores in the presence of excess air and involves oxidation. It is mostly applied to sulphide ores, which are converted to oxides or sulphates. Some impurities 1ike sulphides of arsenic and antimony also get oxidised and volatilised. For example,

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2\uparrow$$
$$ZnS + 2O_2 \longrightarrow ZnSO_4$$
$$2ZnO + 3O_2 \longrightarrow 2ZnO + 2SO_2\uparrow$$
$$2As_2S_3 + 9O_2 \longrightarrow 2As2O3\uparrow + 6SO2\uparrow$$
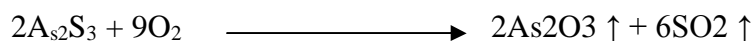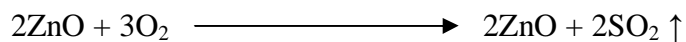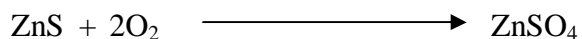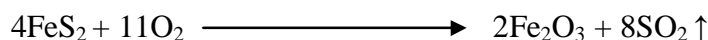
When cuprous sulphide is roasted in a limited supply of air, it is partially oxidised to $Cu_2O$, is then reduced to copper by the remaining cuprous sulphide:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$
$$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow$$
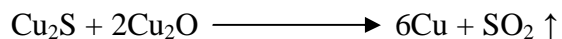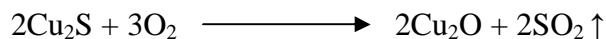
Sometimes, the oxides formed during roasting are unstable and decompose into elements at a moderately high temperature. For example, in the roasting of cinnabar, the red sulphide ore of mercury, the oxide formed decomposes to give the metal:

$$2HgS + 3O_2 \longrightarrow 2HgO + SO_2 \uparrow$$

$$2HgO \xrightarrow{800 \text{ K}} 2Hg + O_2 \uparrow$$
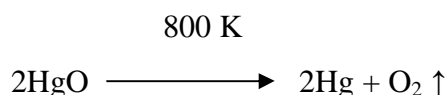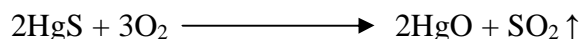
## 5.4 Smelting

The roasted ore, which is usually an oxide, is strongly heated with a suitable reducing agent as a result of which the metal is obtained in a molten state. This process is called **smelting.** In smelting, a suitable chemical substance called **flux** is also added. The flux reacts with the gangue that remains after concentration to form a low melting compound called **slag**. The liquid metal and the liquid slag are immiscible and are easily separated. Usually the slag is lighter than the liquid metal and can be easily skimmed off from the surface of the molten metal. The gangue generally contains either basic oxides like CaO, FeO, etc., or an acidic oxide like silica. When the gangue contains a basic oxide, the flux used is an acidic oxide like silica. For gangues containing an acidic oxide, a basic flux like FeO, CaO or lime stone is added.

$$SiO2 + CaO \longrightarrow CaSiO3$$
$$SiO_2 + FeO \longrightarrow FeSiO_3$$
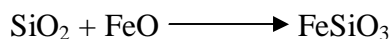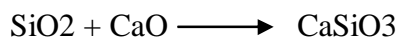
You have studied under roasting that HgO can be reduced to mercury by simply heating it to 800K — a temperature which can be conveniently managed. Most oxides can be reduced to free metals by thermal decomposition at very high temperatures, but then the process becomes very expensive. However, by using a suitable reducing agent, reduction of metal oxides can be achieved at much lower temperatures. The choice of a reducing agent is guided by two considerations. First, the reducing agent should be able to produce the desired metal at a low temperature. The second consideration is the cost of the reducing agent. It should be less expensive than the metal to be produced. Carbon in the form of coke is the (east expensive reducing agent. Iron, zinc, tin, lead, cadmium, antimony, nickel, cobalt, molybdenum and many other metals are produced by carbon reduction of their oxides at temperatures up to 1800K. For example, zinc oxide is reduced to zinc:

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$
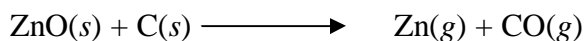
However, the reactions that occur in a high temperature carbon reduction process are not as simple as represented above. In most cases, the effective reducing agent is carbon monoxide, not carbon. This is because both the metal oxide and coke are solids, therefore, contact between them is poor and direct reaction is slow:

$$MO(s) + C(s) \longrightarrow M(l) + CO(g)$$

However, carbon monoxide, which is a gas, makes a better contact with the solid metal oxide and the reaction proceeds more readily:

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$
$$MO(s) + CO(g) \longrightarrow M(l) + CO_2(g)$$
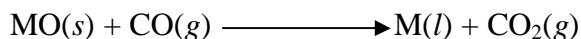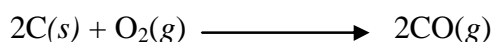
This aspect will be discussed further when we describe extraction of iron later in this unit.

Some metals such as Cr, Mo, W, Ti, Mn, Mg, Al, etc., can be produced theoretically by reduction of their oxides with carbon, but they react with carbon to produce metallic carbides. Therefore, reduction with carbon is not a satisfactory method for producing these metals in a pure form. Hydrogen, though more expensive than carbon, is used as a reductant for extraction of some of these metals, e.g., Ge, Mo and W:

$$GeO_2 + 2H_2 \longrightarrow Ge + 2H_2O$$
$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$
$$WO3 + 3H_2 \longrightarrow W + 3H_2O$$
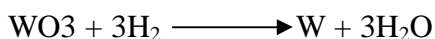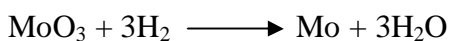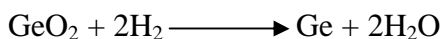
However, many metals combine with hydrogen also to form metal hydrides. Therefore, hydrogen also cannot be used for the reduction of compounds of such metals. Highly reactive metals like Na, Mg, Ca and Al are used to displace these metals from their oxides or halides. These reactive metals are comparatively more expensive reducing agents because they themselves are difficult or costly to prepare. The reduction of an oxide by aluminium is called **Goldschmidt's aluminothermic process**.

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(l) + Al_2O_3(l)$$
$$3MnO_2(s) + 4Al(s) \longrightarrow 3Mn(l) + 2Al_2O_3(l)$$
$$3BaO(s) + 2Al(s) \longrightarrow 3Ba(l) + Al_2O_3(l)$$
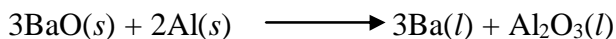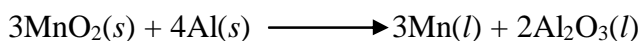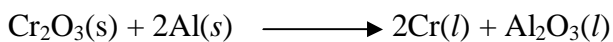
The reactions are highly exothermic producing metals in the molten state. You have already studied in Unit 6 that the reaction of $Fe_2O_3$ with Al is used in spot welding of iron pieces. Other oxides commercially reduced by metals include $UO_3$ (by Al or Ca), $V_2O_5$, $MoO_3$ and $WO_3$ (by Al), $Sc_2O_3$, $La_2O_3$, $ThO_2$ (by Ca) and $Ta_2O_5$ (by Na).

Some metals can be more conveniently produced by reduction of their halides such as $TiCl_4$, $ZrCl_4$, $HfCl_4$, $LaCl_3$, $LaCl_3$, $UF_4$, etc., by Mg, Ca or Na. This process is known as **Kroll's process.**

$$TiCl_4(g) + Mg(l) \xrightarrow[\text{He or Ar}]{1000\ K} Ti(s) + 2MgCl_2(l)$$
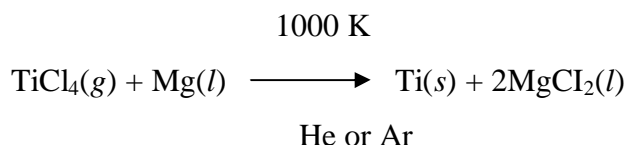
The most reactive metals, which cannot be reduced by any other reducing agent, are prepared by electrolytic reduction of their compounds in molten state. Lithium, sodium, magnesium and aluminium are produced by this method. These metals arc too reactive to be liberated by electrolysis of an aqueous solution. We will discuss electrometallurgy later in this section.

Before we discuss the thermodynamics of the reduction process, you may like to attempt the following SAQ.

**Self Assessment Exercise 3**

(a)     What are the criteria of selection of a good reading agent for extraction of metals?

(b)     Why is carbon reduction not used to obtain certain metals from their ores?

**5.5     Thermodynamics of Reduction Process**

As you have read above, metallurgy of most metals involves reduction of their oxides. The nature of the reduction process depends upon the ease with which the oxide can be reduced. Some oxides are so easily reduced that they decompose just by heating at relatively low temperatures. For example, Priestley, in his

experiments on oxygen produced metallic mercury and oxygen from mercuric oxide by simply heating it with sun light. When sun light was focused on HgO by means of a magnifying glass, it decomposed spontaneously according to the equation:

$$2HgO(s) \longrightarrow 2Hg(g) + O_2(g)$$
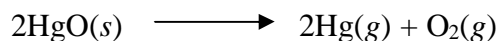
The practicality of producing a free metal by thermal decomposition depends on the extent to which the reaction proceeds to completion at a given temperature. As you know, the feasibility of the reaction is governed by the free energy change taking place during the reaction. When $\Delta G°$ for a reaction is negative, the reaction is feasible from a practical stand point because significant amounts of products will be formed. You know that the standard free energy change, $\Delta G°$, is related to the standard enthalpy change, $\Delta H°$, and the standard entropy change, $\Delta S°$, according to the following equation:

$$\Delta G' = \Delta H° - T\Delta S°$$

In other words, the sign and magnitudes of $\Delta H°$ and $\Delta S°$ control the sign and magnitude of $\Delta G°$. Let us look little deeper into this relationship.

Since in the decomposition of an oxide, oxygen is produced in the gaseous form and sometimes the metal may also be produced in vapour form, the process occurs with a sizeable increase in entropy, so $\Delta S°$ will be positive. Enthalpy of decomposition, $\Delta H°_d$ is simply the negative of the enthalpy of formation of the oxide, $\Delta H°_f$ Since $\Delta H°_f$ is generally negative for metal oxides, enthalpy of decomposition will be positive. As a result, the sign of $\Delta G°$ is determined by the difference between two positive quantities $\Delta H°$ *and* $T\Delta S°$, $T$ the absolute temperature being always positive.

From the above, we can deduce that if the enthalpy of formation of the metal oxide is small as in case of HgO, $Ag_2O$, CuO and $Au_2O_3$, then the enthalpy of

decomposition will be a small positive quantity and $\Delta G°$, which is given by the difference of $\Delta H°$ and $T\Delta S°$, will become negative at relatively low temperatures. These oxides are said to have relatively low thermal stabilities. On the other hand, if the oxide has a large negative enthalpy of formation, then the enthalpy of decomposition of the oxide will be a large positive quantity. As a result, the value of $\Delta G°$ will become negative at a very high temperature where $T\Delta S°$ becomes larger than $\Delta H°$. Thus, the metal oxide would be stable with respect to thermal decomposition. In order to decompose such a metal oxide, it would have to be heated to a. very high temperature at which cost becomes prohibitive. Thus, knowledge of how the standard free energy change, $\Delta G°$, for the reduction reaction varies with temperature is very important.

**Ellingham Diagrams**

Ellingham studied the variation of standard free energy change for the formation of a number of compounds, e.g., oxides, sulphides and chlorides, with temperature and plotted $\Delta G°$ against temperature. Such diagrams showing the variation of $\Delta G°$ with $T$ are called Ellingham diagrams after his name. As said above, $\Delta G°$ is related to $\Delta H°$, $\Delta S°$ and $T$ according to the following equation:

$$\Delta G° = \Delta H° - T\Delta S°$$

You also know that for most of the chemical reactions, $\Delta H°$ and $\Delta S°$ do not change significantly with temperature and can be regarded as constant. Thus, $\Delta G°$ plotted against $T$ gives a graph of constant slope, which is equal to $-\Delta S°$. But, due to abrupt changes in $\Delta S°$, breaks in the graph occur at temperatures at which reactants or products melt or boil, i.e., undergo phase change.

Fig. 5.3 shows the Ellingham diagrams for the formation of metal oxides from free elements. By examining the Ellingham diagram for the formation of an oxide, we can find out the temperature at which the standard free energy change for the

reaction will become positive. For example, consider the $\Delta G° / T$ graph (Fig.4.3) for the reaction of zinc with oxygen:
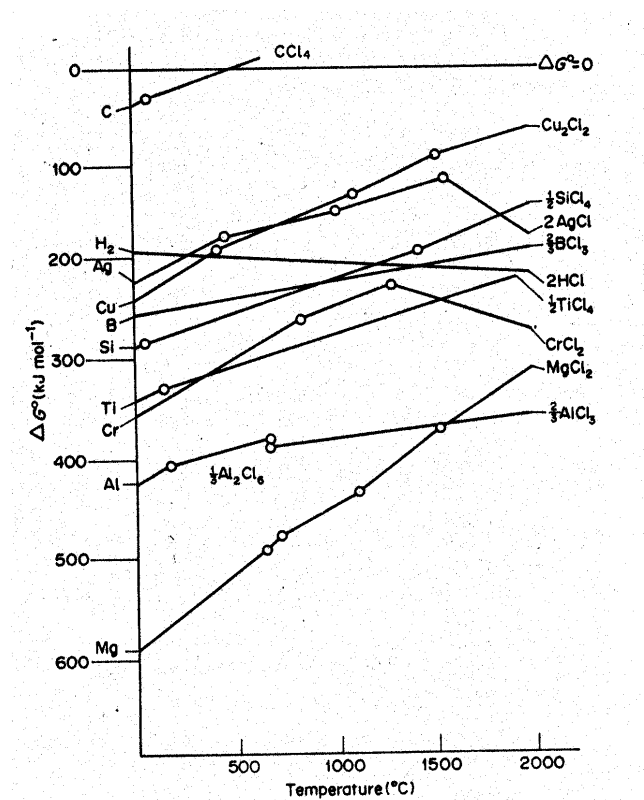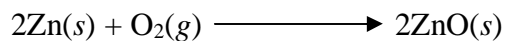
$$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$$



**Fig. 5.3: Kllingham diagram showing the variation of the free energy of formation of metal oxides with temperature**

At 273 K, the value of standard free energy change for this reaction is -600 kJ, which becomes less negative as temperature rises and eventually at 2173 K. it becomes zero. Above this temperature, $\Delta G°$ will become more positive, therefore ZnO will spontaneously decompose to zinc and oxygen. This behaviour is typical for all elements except carbon; at sufficiently high temperatures the oxides become unstable relative to their constituent elements.

With the help of Ellingham diagrams, we can find out the standard free energy changes for a large number of reactions. For example, we can read off from the diagram the standard free energy changes for the following two reactions at 298 K:

$$2C(s) + O_2(g) \longrightarrow 2CO(g): \Delta G° = -275KJ \qquad \ldots(4.1)$$

$$2ZnO(s) \longrightarrow 2Zn(s) + O_2(g): \Delta G° = +640 \text{ KJ} \qquad \ldots(4.2)$$
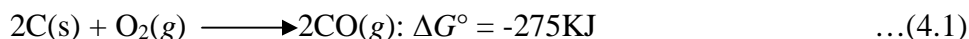
You may note that the standard free energy change in Eq. 15.2 is positive because it represents the decomposition of zinc oxide. On adding above two equations and respective $\Delta G°$ values we get.

$$2ZnO(s) + 2C(g) \longrightarrow 2Zn(s) + 2CO(g): \Delta G° = +365 \text{ KJ}$$
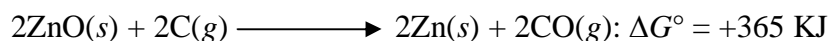
Because the standard free energy change for the above reaction is positive, the reaction has little tendency to occur at 298 K. Since, two moles of gaseous product, i.e., CO, are produced during the reaction, $\Delta S°$ is positive. Therefore, $\Delta G°$ decreases with increase in temperature and will become zero at some temperature. In this particular case, AG' becomes zero at 1173 K as can be seen from Fig.5.3. This temperature corresponds to the point of intersection of the two graphs for C/CO and Zn/ZnO systems. Above this temperature, $\Delta G°$ will become negative. Therefore, carbon will reduce zinc oxide above 1173 K - a temperature 1000 K lower than the temperature of thermal decomposition of zinc oxide. Similarly, with the help of Ellingham diagrams for Zn/ZnO and $H_2/H_2O$ systems, we can find out that $H_2$ will reduce ZnO at a temperature, of 1400 K. Since reduction of ZnO with carbon, which is also much cheaper than hydrogen, can be carried at a lower temperature, it is clear that reduction using carbon is much more economical than reduction using hydrogen.

Ellingham diagrams are very useful for finding out the temperature at which appreciable reaction occurs. The lower the $\Delta G°/T$ graph of an element is on the diagram, the more stable its oxide is relative to dissociation into element and oxygen. Such elements will reduce the oxides of other elements whose $\Delta G°/T$ graph appears above them on the diagram at a given temperature. As we have seen above, carbon reduces ZnO above 1173 K, but below 1173 K zinc will reduce CO. Since the $\Delta G°/T$ graph of C/CO system slopes downwards, it will eventually he below all oilier graphs at sufficiently high temperatures. Therefore, theoretically carbon will reduce all oxides. But difficulties in obtaining very high temperatures cheaply and the formation of carbides prevent the preparation of the more electropositive metals by this method. It is also clear from the Ellingham diagrams that hydrogen can be used as a reducing agent for the oxides of those elements whose $\Delta G°/T$ graphs are above that of hydrogen in the diagram. Thus hydrogen can reduce the oxides of tungsten, lead, antimony, copper, nickel, zinc and cadmium.

Figure 5.4 shows the Ellingham diagram for sulphides of various elements. You can see from the diagram that carbon and hydrogen are not effective reducing agents for metal sulphides. Therefore, sulphides are first roasted in air to convert them to oxides, which are then reduced.
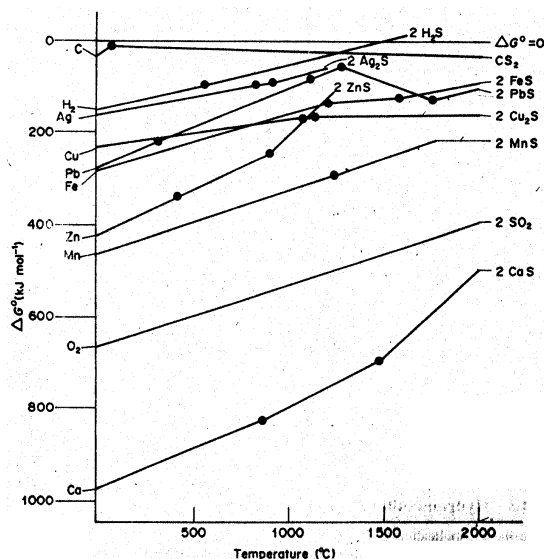
**Fig. 5.4: Ellingham diagram showing the variation of the free energy of formation of metal halides with temperature**

The Ellingham diagram for chlorides is shown in Fig 5.5. It can be considered from the diagram that carbon is useless as a reductant for chlorides, but hydrogen can be used for this purpose, specially at higher temperatures.
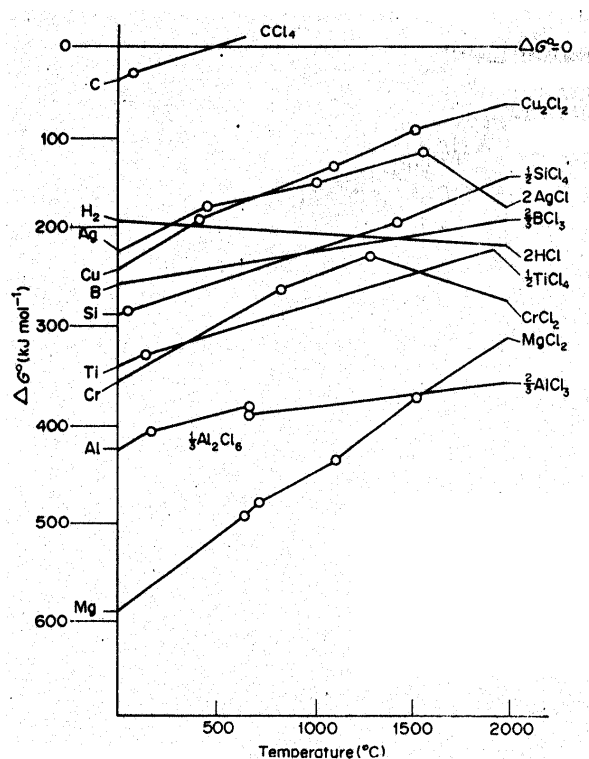


Fig 5.5: Ellingham diagram showing the variation of the free energy of formation of metal halides with temperature.

**Self Assessment Exercise 4**

Explain briefly why carbon is theoretically capable of reducing almost all metal oxides at high temperatures. From the Ellingham diagrams shown in Fig 5.3 compute the temperature of reduction of MgO, CaO, $TiO_2$ and $Al_2O_3$ by carbon.

## 5.6    Hydrometallurgy

The principal application of hydrometallurgy is in the case of low grade ores, which cannot be concentrated economically. In this process, the powdered ore is first treated with an aqueous solution of a suitable chemical whereby the metal is obtained in the form of its soluble salt leaving behind gangue panicles. This process is called leaching. Some examples of leaching are given below:

Low grade oxide, carbonate and sulphide ores of copper are treated with dilute sulphuric acid in the presence of oxygen:

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$$

$$Cu_2OS + 2H_2SO_4 + 2O_2 \longrightarrow 2CuSO_4 + SO_2 + 2H_2O$$
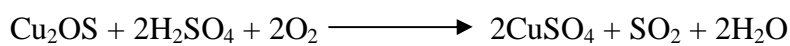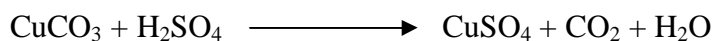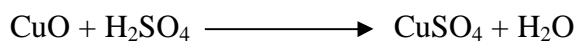
When the silver ore, AgCl, is treated with an aqueous solution of sodium cyanide, AgCl dissolves in it due to the formation of $Na[Ag(CN)_2]$:

$$AgCl + 2NaCN \longrightarrow Na[Ag(CN)_2] + NaCl$$
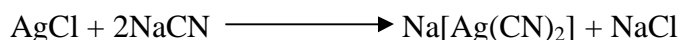
Sulphide ore, $Ag_2S$, dissolves only slowly as the reaction is reversible:

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$
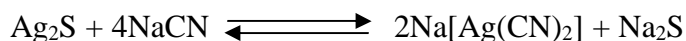
If air is passed through this solution, sodium sulphide is oxidised to sodium sulphate and the forward reaction goes to completion dissolving all the sulphide ore. In the presence of air, native silver is also leached out in the form of $Na[Ag(CN)_2]$:

$$4Ag + 8NaCN + 2H_2O + O2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$
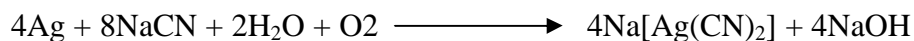
The leached out metals are recovered from the solution either by precipitation on treatment with a more electropositive metal or by electrolysis. For example, copper can be recovered from its solution by adding metals like Fe, Al, etc. Silver is obtained from its solution by treatment with Zn or Al:

$$CuSCO_4 + Fe \longrightarrow Cu + FeSO_4$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow 2Ag + Na_2[Zn(CN)4]$$
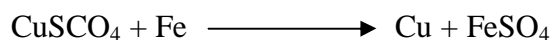
Alternatively, the dilute solution can be concentrated and then electrolysed to obtain pure metals. From leached solution of copper ores, copper is often recovered by electrolysis of the solution. In electrolysis the anode used is of lead alloy and the cathode is of a pure copper sheet. When direct current is passed through the solution, copper gets deposited on cathode. Sulphuric acid is generated during electrolysis which is recycled in leaching of ore. Following reactions take place during electrolysis:

$$\text{Anode: } 2H_2O \longrightarrow O_2(g) + 4H^+(aq) + 4e$$

$$\text{Cathode: } Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$$

$$2H^+(aq) + SO_4^{2-}(aq) \longrightarrow H_2SO_4(aq)$$
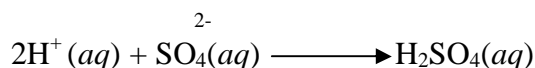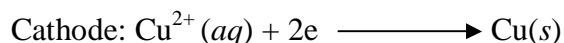
## 5.6 Electrometallurgy

The above two metallurgical processes, namely pyrometallurgy and hydrometallurgy can be used in the extraction of a fairly large number of metals. These methods, however, cannot be used in cases:

- where the metal is highly reactive, e.g., Na, Li, etc. There are not any chemical-reducing agents strong enough to prepare these metals

- where the oxide gets reduced only at very high temperatures at which formation of carbides also takes place, e.g., Al, Mg, etc.

In these cases, metals can be extracted by electrolysis of their salts in molten state. Thus, sodium and magnesium are prepared by electrolysis of fused chlorides, where the metals are liberated at the cathode and chlorine gas is evolved at the anode (Fig. 4.6). Following reactions take place during electrolysis:

Anode: $2Cl^- \longrightarrow Cl_2(g) + 2e$

Cathode: $2Na^+ + 2e \longrightarrow 2Na(l)$

$Mg^{2+} + 2e \longrightarrow Mg(l)$
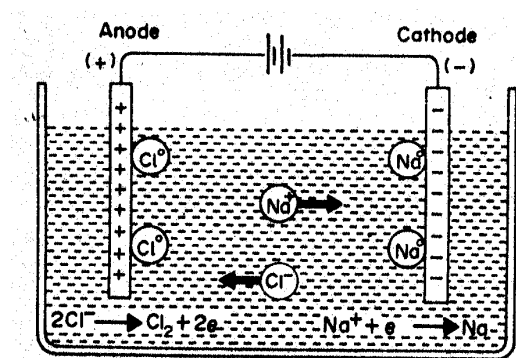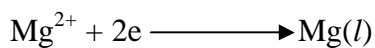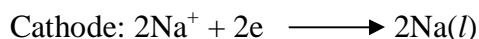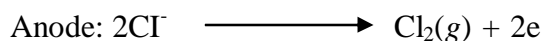


**Fig. 5.6: Electrolysis of molten sodium chloride**

In theory, aluminium metal could be made the same way. But, aluminium trichloride is covalent and it does not conduct electricity. As you will recall aluminium is obtained by electrolytic reduction of alumina in fused cryolite at 1 100-1300 K using carbon anode and iron cathode. Electrolysis yields aluminium

at cathode and 62 at anode which reacts with carbon to produce $CO_2$ The reactions at electrodes are:

Anode: $2O^{2-} \longrightarrow O_2(g) + 4e$

$C(s) + O_2(g) \longrightarrow CO_2(g)$

Cathode: $Al^{3+} + 3e \longrightarrow Al(s)$
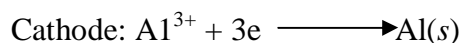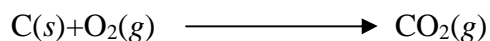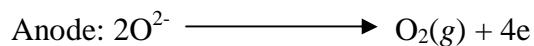
Before we discuss the various methods for purification of metals, try the following SAQ.

**Self Assessment Exercise   5**

Explain briefly which metals are produced commercially by the electrolysis of aqueous sail solutions and (b) molten salts

**FURTHER READING**

1       *A New Concise Inorganic Chemistry*, J.D. Lee, ELBS, London, 3rd ed., 1977.

2       *Chemistry: Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

3       *Comprehensive Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3rd ed., 1986.

4       *Principles of Inorganic Chemistry*, B.R. Puri and L.R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 19th ed., 1986.

**Module 4     ISOLATION AND PURIFICATION OF METALS**

**Unit 2          Purification of Metals**

**2.0 Objectives**

At the end of this unit, students should be able to;

- discuss various metallurgical processes like pyrometallurgy, hydrometallurgy and electrometallurgy,

• use Ellingham diagrams for selecting suitable reducing agents for extraction of metals;

• describe various methods of purification of metals, and

• discuss the importance and uses of alloys.

## 3.0 PURIFICATION OF METALS

The metals obtained by metallurgical processes still contain some impurities which persist from the ore or are derived from the flux or the fuel used. In order to get pure metal, further purification or refining is necessary. There arc several methods available for purification, depending upon the nature of the metal and the type of impurities present. Some refining processes are designed to recover valuable metal impurities also, such as, gold, silver and platinum. These methods of refining are as follows:

## 3.1 Liquation

Crude tin, lead and bismuth are purified by liquation. In this method, the impure metal is placed at the top of a sloping hearth maintained at a temperature slightly above the melting point of the metal. The metal melts and flows down the inclined hearth into a well leaving behind the solid impurities.

## 3.2 Distillation

Metals with low boiling points, such as zinc, cadmium and mercury can be purified by distillation. The distillation is usually carried out under reduced pressure to enable boiling of the metal at lower temperature.

## 3.3 Electrolysis

In electrorefining, the impure metal is taken as the anode and a strip of pure **metal coated** with a thin layer of graphite is made the cathode in an electrolytic cell. The electrolyte is an aqueous solution of a salt of the metal. On electrolysis, the impure metal from the anode goes into solution and metal ions are reduced and get deposited on the cathode. Only weakly electropositive metals like copper, tin

and lead which are readily oxidised at the anode and reduced at cathode can be purified in this manner. A general reaction can be written as follows:

$$M(\text{impure}) \longrightarrow M^{n+}(aq) + e, \text{ at anode}$$

$$M^{n+}(aq) + ne \longrightarrow M(\text{pure}), \text{ at anode}$$
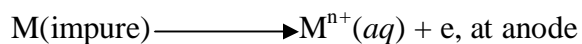
Other impurities in the metal settle down as anode mud or remain dissolved in the solution. In the case of electrolytic refining of copper, an impure copper rod is made the anode, pure copper strip the cathode and copper sulphate solution the electrolyte (Fig.5.7). The following electrode reactions take place:
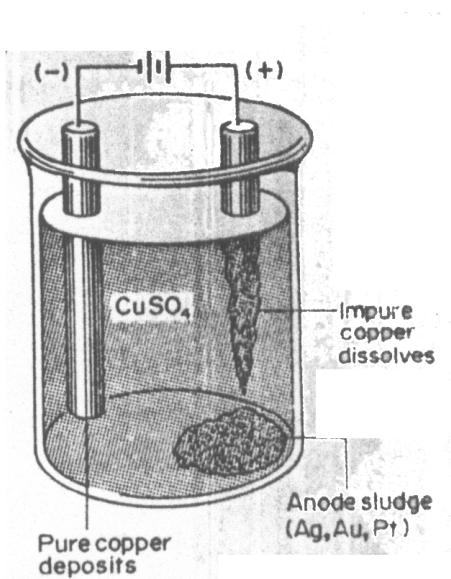


**Fig. 5.7: Purification of copper by electrolysis**

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-, \text{ at anode}$$

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s), \text{ at cathode}$$
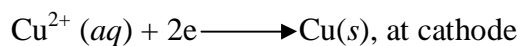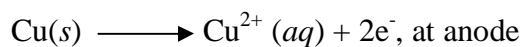
Thus, 99.95% pure copper is obtained in this process. The more reactive metals such as iron, which are present in the crude copper, are also oxidised at anode and pass into solution. The voltage is so adjusted that they are not reduced at cathode and thus remain in solution. The less reactive metals such as silver, gold and platinum if present, are not oxidised. As the copper anode dissolves, they fall to the bottom of the cell from where they are recovered as a valuable anode mud.

## 3.4    Zone Refining

This method is used to obtain metals of very high purity. The basic principle involved in this process is similar to fractional crystallisation. A small heater is used to heat a bar of the impure metal. The heater melts a small band of metal as it is slowly moved along the rod. As small bands of metal are thus melted sequentially, the pure metal crystallises out of the melt, while impurities pass into the adjacent molten zone. The impurities thus collect at the end of the bar. This end can be cut off and removed. High grade germanium and silicon are obtained by        purifying        them        by        zone        refining        (Fig.
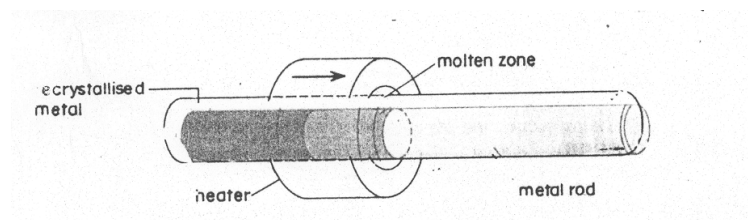


**Fig. 5.8: Diagram for some refining**

## 3.5    Parke Process

Parke process for refining lead, which is also a concentration method for silver, relies upon the selective dissolution of silver in molten zinc. A small amount of zinc, 1-2% is added to molten lead wh.ch contains silver as an impurity. Silver is much more soluble in zinc than in lead; lead and zinc are insoluble in each other. Hence, most of the silver concentrates in zinc, which comes to the top of molten

lead. The zinc layer solidifies first upon cooling; it is removed and silver is obtained by distilling off zinc, which is collected and used over and over again,

## 3.6 Van Arkel de Boer Process

This method is based on the thermal decomposition of a volatile metal compound like an iodide. In this method, first a metal iodide is formed by direct reaction of iodine and the metal to be purified at a temperature of 475-675 K in an evacuated vessel. The vapours of metal iodide, thus formed are heated strongly on a tungsten or tantalum filament at 1300-1000 K. The metal iodide decomposes to yield the pure metal, as in the case of zirconium.

$$Zr(s) + 2I_2\,(g) \xrightarrow{\text{473-673K}} ZrI_4(g) \xrightarrow[\text{Tungsten filament}]{\text{1300-1800K}} Zr(s) + 2I_2(g)$$
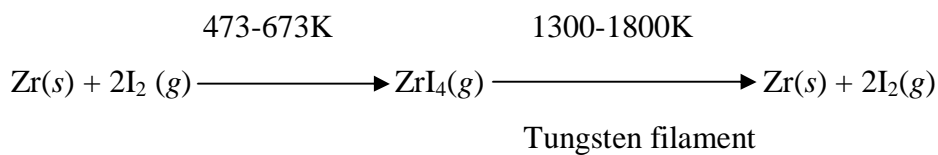
Titanium is also purified by this method. The impure metal is heated with iodine and TiLt thus formed is decomposed by heating at 1700 K over tungsten filament:

$$Ti(s) + 2I_2\,(g) \longrightarrow TiI_4(g) \xrightarrow[\text{Tungsten filament}]{\text{1700K}} Ti(s) + 2I_2(g)$$
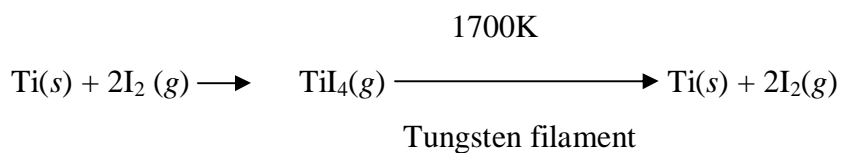
The regenerated iodine is used over and over again. This process is very expensive and is employed for the preparation of limited amounts of very pure metals for special uses.

## 3.7 Mond Process

Some metals are purified by obtaining their volatile carbonyl compounds which on heating strongly decompose to yield pure metal. Purification of nickel is done by this method. Impure nickel is reacted with carbon monoxide at 325 K to give volatile nickel carbonyl leaving solid impurities behind. Pure nickel is obtained by heating nickel carbonyl at 450-475 K:

$$Ni(s) + 4CO(g) \xrightarrow{\text{325K}} Ni(CO)_4(g) \xrightarrow{\text{450-475 K}} Ni(s) + 4CO(g)$$

**Self Assessment Exercise 1**

List the various methods employed for the refining of crude metals.

## 4.0    ISOLATION OF SOME IMPORTANT TRANSITION METALS

In the preceding section of this unit, we have discussed the basic principles and processes involved in the extraction of metals. In this section, we will now describe the extraction of some important transition metals of the first transition series.

### 4.1    Titanium

Titanium, which comprises 0.63% of the earth's crust, is the ninth most abundant element. Titanium has many useful properties. It is as strong as steel, but only about 60% as dense as steel. It is also highly resistent to corrosion. Major uses of titanium are in aircraft industry for the production of both engines and airframes. It is also widely used in chemical processing and marine equipment.

The two most important ores of titanium arc rutile, $TiO_2$ and ilmenite, $FeO \cdot TiO_2$, India possesses large reserves of ilmenite in beach sands of south and south-west

coasts while deposits of rutile are limited. Titanium is extracted from these ores by Kroll process. In this process, rutile or ilmenite ore is first heated with carbon at 1200 K in a current of chlorine gas:

$$TiO_2 + C + 2CI_2 \xrightarrow{1200K} TiCI_4 + CO_2$$

$$2FeO{\cdot}TiO_2 + 6C + 7Cl_2 \xrightarrow{1200K} 2TiCI_4 + 2FeCl_3 + 6CO$$
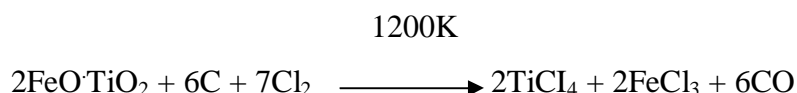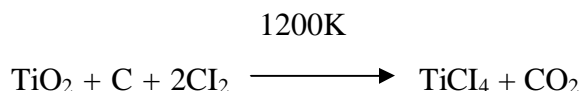
Titanium tetrachloride is separated from $FeCl_3$ and other impurities by fractional distillation. As titanium reacts with nitrogen at high temperature, $TiCl_4$ is reduced with molten magnesium in an atmosphere of argon:

$$TiCI_4 + 2Mg \xrightarrow{1225-1400K} Ti + 2MgCl_2$$

$$TiCI_4 + 4Na \xrightarrow{1225-1400K} Ti + 4NaCl$$
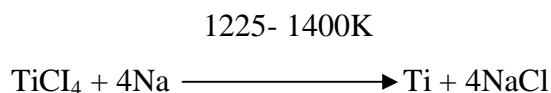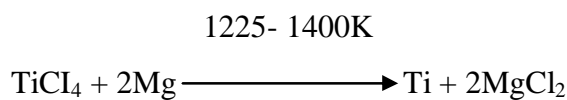
Magnesium chloride and excess of magnesium are removed by leaching with water and dilute hydrochloric acid leaving behind titanium sponge. Titanium sponge after grinding and cleaning with aqua regia is melted under argon or vacuum and cast into ingots. In place of magnesium, sodium can also used as a reducing agent in this process.

## 4.2    Chromium

Chromite, $FeO{\cdot}Cr_2O_3$, is the only commercially important ore of chromium. In order to isolate chromium, the ore is finely powdered and concentrated by gravity process. The concentrated ore is mixed with an excess of sodium carbonate and

roasted in the presence of air so that $Cr_2O_3$ present in the ore is converted into sodium chromate:

$$4FeO \cdot Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO4 + 2Fe_2O_3 + 8CO_2$$
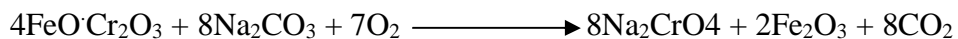
The roasted mass is then extracted with water; $Na_2CrO_4$ goes into solution leaving behind the insoluble $Fe_2O_3$. The solution is treated with sulphuric acid to convert the chromate into dichromate:

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The solution is then concentrated when the less soluble Na2SO4 crystallises out leaving more soluble $Na_2Cr_2O_7$ in solution. The solution is further concentrated to get crystals of $Na_2Cr_2O_7$, which are heated with carbon to yield chromium oxide:

$$Na_2Cr_2O_7 + 2C \longrightarrow Cr_2O_3 + Na2CO_3 + CO$$
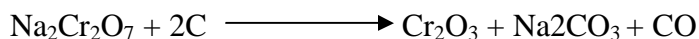
Chromium oxide is then reduced with aluminium by aluminothermic process or by heating with a calculated quantity of silicon in the presence of calcium oxide which forms a slag of calcium silicate with silica:

$$Cr_2O_3 + 2 Al \longrightarrow 2Cr + Al_2O_3$$

$$2Cr_2O_3 + 3Si + 3CaO \longrightarrow 4Cr + 3CaSiO_3$$
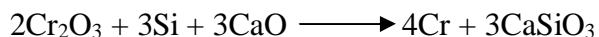
## 4.3 Iron

Iron is the second most abundant metal, aluminium being the first, constituting 5.1% of the earth's crust. Haematite, $Fe_2O_3$, containing 60-64% of iron is the most

important ore of iron. Other ores of iron are magnetite, $Fe_3O_4$, limonite, $Fe_2O_3.3H_2O$ and siderite, $FeCO_3$. Iron pyrites, $FeS_2$. which occurs abundantly is not used as a source of iron because of the difficulty in removing sulphur. A good proportion of the world's high grade iron ore reserves are located in our country in Orissa, Bihar, M.P., Karnataka and Goa.

Iron ores are of high grade. Therefore, generally the ores are not concentrated. The ore is crushed into process, about 2 to 10 cm in size and then washed with water to remove clay, sand, etc. The ore is then **calcined or roasted** in air when moisture is driven out, carbonates are decomposed and organic matter, sulphur and arsenic are burnt off. Ferrous oxide is also converted into ferric oxide during this process:

$$Fe_2O_3.3H_2O \longrightarrow Fe_2CO_3 + 3H_2O$$

$$2FeCO_3 \longrightarrow 2FeO + CO_2$$

$$4FeO_3 + O_2 \longrightarrow 2Fe_2O_3$$
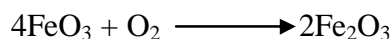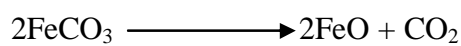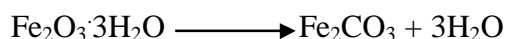
In the iron ore, the chief impurities are of silica and alumina. To remove these, lime stone is used as a flux. The calcined or roasted ore is then **smelted,** i.e., reduced with carbon, in the presence of lime stone flux. Smelting is done in a **blast furnace** shown in Fig. 4.9. A modern blast furnace is a tall vertical furnace about 30 metre high and 9-10 metres.in diameter at its widest part. It is designed to take care of volume changes, to allow sufficient time for the chemical reactions to be completed and to facilitate separation of slag from the molten metal. The outer structure of the furnace is made from thick steel plates which are lined with fireclay refractories. The furnace at its base is provided with (i) small pipes called **tuyeres** through which hot air is blown, (ii) a **tapping hole** through which molten metal can be withdrawn and (iii) a **slag hole** through which slag flows out. At the
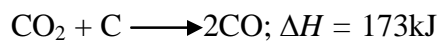
top, the furnace is provided with a cup **and** cone arrangement for introducing **charge,** i.e., starting materials in the furnace.

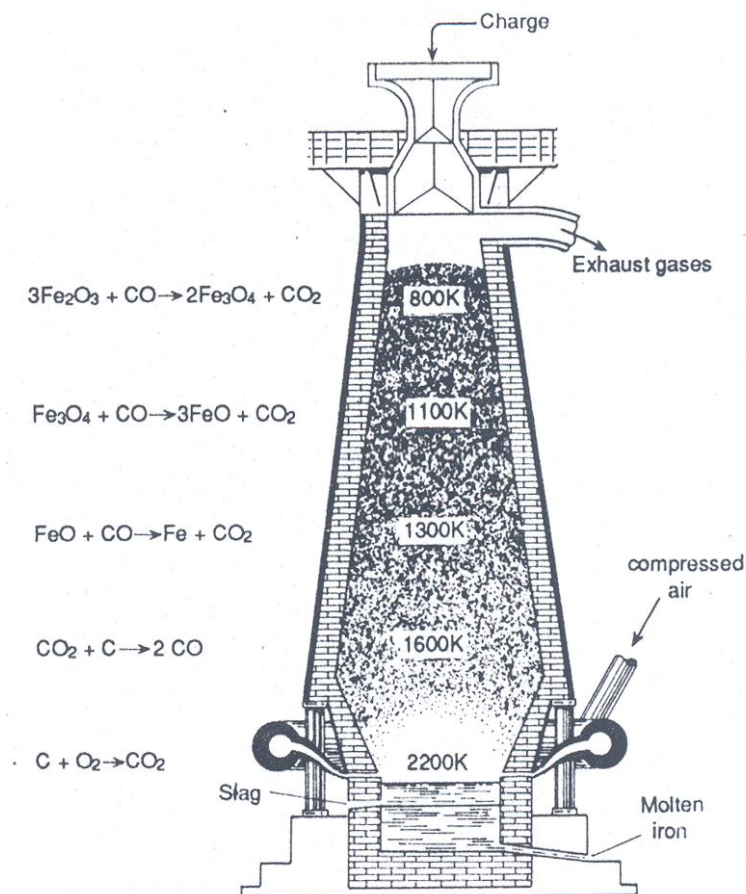The culcined or roasted ore mixed with coke and lime stone is fed into the furnace. The
furnace is lit and a blast of hoi air is passed through the tuyeres. Coke hunts in the bottom of the furnace to form $CO_2$ liberating large amount of heat, which raises the temperature to 2200 K:

$$C + O_2 \longrightarrow CO_2; \Delta H = 394 \text{ kJ}$$

As the hot gases rise, $CO_2$ reacts with additional coke to form CO which is the active reducing agent. As this reaction is endothermic, temperature drops to 1600 K:

$$CO_2 + C \longrightarrow 2CO; \Delta H = 173 \text{kJ}$$

$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$FeO + CO \rightarrow Fe + CO_2$

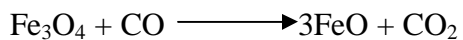$CO_2 + C \rightarrow 2\,CO$

$C + O_2 \rightarrow CO_2$

**Fig. 5.9: A blast furnace**
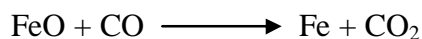
The reduction of iron oxide takes place in a series of steps. At the top of the furnace, where temperature is around 800 K, $Fe_2O_3$ is reduced to $Fe_3O_4$

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$
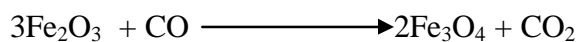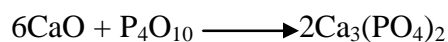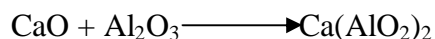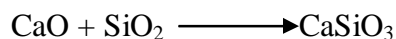
On descending below, where temperature is around 1 100 K. $Fe_3O_4$ is reduced to FeO:

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$$

Near the middle of the furnace at a temperature of around 1300 K, FeO is reduced to iron:

$$FeO + CO \longrightarrow Fe + CO_2$$

In this region, lime stone decomposes to form CaO and CO. CaO then reacts with $SiO_2$, $Al_2O_3$ and $P_4O_{10}$ to form liquid slag:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$CaO + Al_2O_3 \longrightarrow Ca(AlO_2)_2$$

$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$

Iron produced is in the solid state up to this temperature. It is porous and is known as spongy iron .But as the spongy iron drops down further through the hotter portions of the finance, where temperature is around 1600 K, it melts, absorbs some carbon, phosphorus, sulphur, silicon and manganese, and collects at the bottom of the furnace. Slag being lighter floats on top of the molten iron. The molten iron withdrawn from the furnace is known as **pig iron.** The molten pig iron can be poured into moulds to produce **cast iron.**

Composition of pig iron or cast iron varies widely, but on an average it contains 92-95% Fe, 3-4.5% C, 1-4% Si, 0.1-2% P, 0.2-1.5% Mn and 0.05-0.1% S. Cast iron melts at 1473 K. Due to the presence of impurities, cast iron is hard and brittle. It is so hard that it cannot be welded and it is so brittle that it cannot be shaped into articles by hammering, pressing or rolling. Cast iron is quite cheap and is used for making drain pipes, fire-grates, railway sleepers, radiators, lamp posts etc., where economy is more important than strength.

Wrought iron is the purest form of iron containing 0.10-0.25% carbon and impurities of Si, P, S and Mn not more than 0.3%. It is prepared by heating pig iron in a reverberatory furnace lined with haematite. Haematite oxidises C, Si, P, S and Mn to CO, $SiO_2$, $P_2O_5$, $SO_2$ and MnO, respectively. Thus MnO combines with $SiO_2$ to form a slag of $MnSiO_3$ and so does $Fe_2O_3$ with $P_2O_5$ to give a slag of FePO4. Wrought iron is soft and malleable but very tough. It can be easily welded and forged. Its melting point is 1773 K and is resistant to corrosion. It is used to make anchors, wires, bolls, chains and agricultural implements. Owing to its high cost it has been replaced by steel.

## 4.4    Nickel

Nickel is the twenty-second most abundant element in the earth's crust. Nickel occurs in combination with sulphur arsenic and antimony. Important ores of nickel are:

- Pentlandite — a nickel and iron sulphide, $(Ni, Fe)_9S_8$, containing about 1.5% nickel. It is found mainly in Sudbury, Canada. This is also called Sudbury ore.

- Garnierite — a double silicate of nickel and magnesium, $(Ni,Mg)_6S_{14}O_{10}(OH)_8$ containing upto 8% nickel.

- Pyrrhotite — an iron mineral, $Fe_nS_{n+1}$, also contains 3-5% nickel.

- Kupfer nickel, NiAs.

- Nickel glance, NiAsS.

Pentlandite is the principal ore of nickel. The metallurgy of nickel involves several complicated steps but the basic principle is to change nickel suphide to nickel oxide and then reduce it with water gas to get the metal.

Pentlandite ore is crushed and subjected to froth flotation process. The concentrated ore, which consists of FeS, NiS and CuS, is roasted in excess of air. The FeS is converted into FeO, whereas NiS and CuS remain unchanged. The uncombined sulphur, if present, is also oxidised to $SO_2$:

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$S + O_2 \longrightarrow SO_2$$
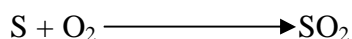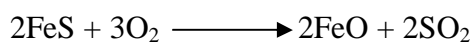
The roasted mass; is mixed with silica, lime stone and coke and is smelted in a blast furnace. Thus FeO combines with $SiO_2$ to give $FeSiO_3$ and CaO formed by decomposition of lime stone reacts with excess of $SiO_2$ to form $CaSiO_3$. $CaSiO_3$ and $FeSiO_3$ both form slag, which being lighter floats on the molten mass:

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$
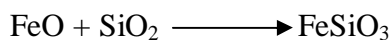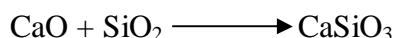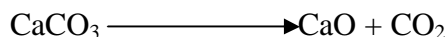
The slag is continuously removed. Molten mass now contains impure sulphides of nickel and copper and some iron sulphide. It is called matte. The matte is heated in a Bessemer converter, which is fitted with tuyeres for passing hot air in controlled manner. The remaining iron sulphide is converted to iron oxide which is slagged off as $FeSiO_3$. The bessemerised matte consisting of NiS and CuS is roasted again to convert sulphides into oxides:

$$2Nis + 3O_2 \longrightarrow 2NiO + 2SO_2$$

$$2CuS + 3O2 \longrightarrow 2CuO + 2SO_2$$
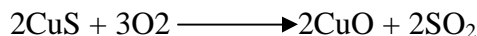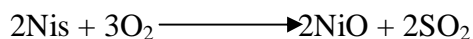
The mixture of oxides is treated with sulphuric acid at 350 K, when CuO dissolves to give CuSO4, while NiO remains unaffected. Residue of NiO is dried and reduced with water gas to give crude nickel:

$$2NiO + H_2 + CO \longrightarrow 2Ni + H_2O + CO_2$$
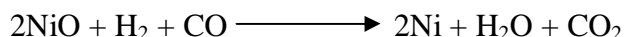
Crude nickel containing iron and copper as impurities is purified by Mond process.

## 4.5 Copper

Copper is found in both the native as well as the combined slate. Native copper is found in USA, Mexico, USSR and China. Native copper is 99.9% pure, but it is only a minor source of the metal. In the combined state, copper is found mainly as the suphide, oxide or carbonate ore. Copper occurs as sulphide in chalcopyrites or copper pyrites, $CuFeS_2$ and in chalcocite or copper glance, $Cu_2S$. The oxide ores of copper are cuprite or Ruby copper, $Cu_2O$ and malachite, $Cu(OH)_2 CuC0_3$. Copper pyrites is the main ore of copper. Workable deposits of copper ore occur in Khetri copper belt in Rajasthan and Mosabani and Rakha mines in Bihaf.
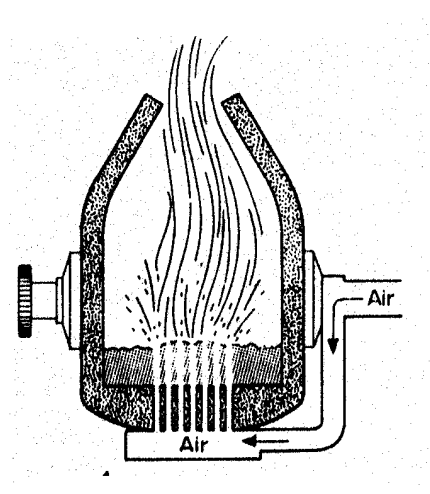
For extraction of copper, the sulphide ore is concentrated by froth flotation process and is then roasted in air when some sulphur is removed as $SO_2$:

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$
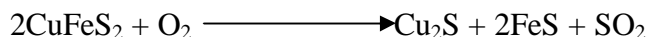
The mixture of Cu2S and FeS thus obtained is subjected to smelting with coke and silica in a blast furnace. FeS is changed into FeO, which reacts with $SiO_2$ and is slagged off as $FeSiC_3$:

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$2FeO + SiO_2 \longrightarrow FeSiO_3$$
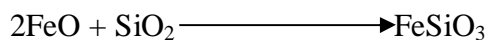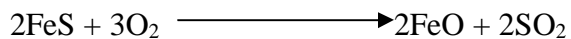
The molten mixture of $Cu_2S$ and remaining FeS is known as **matte**. It is transferred to a Bessemer converter (Fig. 5.10) and a blast of hot air mixed with silica is blown through the molten mass. As a result, residual FeS is converted into a slag of $FeSiO_3$ and $Cu_2S$ is reduced to copper. The supply of air is so adjusted that about two thirds of $Cu_2S$ is converted into $Cu_2O$. The two then react together to give copper metal. The extra step involving reduction with carbon is thus avoided:



**Fig. 5.10: A Bessemer converter**

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$FeO + SiO_2 \longrightarrow FeSiO_3$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$
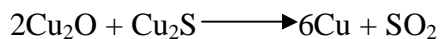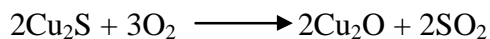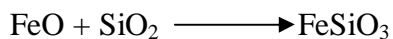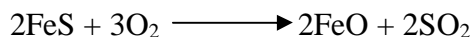
The copper thus obtained is called blister copper as bubbles of escaping $SO_2$ during cooling give it a blister like appearance. Blister copper is about 99.0% pure and is used as such for many purposes. If required, it can be further purified electrolytically as described in the preceding section.

**Self Assessment Exercise 2**

Write the chemical equations for:

a)      reduction of $Fe_2O_3$ in blast furnace

b)      reduction of $TiCl_4$ to Ti by Kroll process

c)      reduction of $Cr_2O_3$ by aluminothermic process

d)      reduction of NiO by watergas

## 5.0    ALLOYS

Metals have a property of combining with other metals to form alloys. An alloy may be defined as a solid which is formed by a combination of two or more metallic elements, but it itself has metallic properties. Most alloys are solid solutions. For example, brass an alloy of copper and zinc is a solid solution of zinc in copper. In brass some of the copper atoms of face-centred cubic lattice are randomly replaced by zinc atoms. Similarly, bronze an alloy of copper and tin. is a solid solution of tin in copper. But not all alloys are solid solutions. Some alloys, such as bismuth-cadmium alloys are heterogeneous mixtures containing tiny crystals of the constituent metals. Others such as $MgCu_2$, are intermetallic compounds which contain metals combined in definite proportions.

The purpose of making alloys is to impart certain desirable properties to a metal. For example, gold is too soft for making jewellery. Therefore, to make it hard, it is alloyed with copper. Solder, an alloy of tin and lead, has a melting point lower than that of both of its constituents. Pure iron is soft, ductile and it is easily corroded. Stainless steel, an alloy of iron, chromium, nickel and carbon is tough,

hard and highly resistant to corrosion. Compositions and uses of some important alloys are given in Table 5.2

A solid solution is a solution in which a solid, liquid or gas is dissolved in a solid.

**Table 5.2: Composition, specific properties and uses of some important alloys**

| Name (1) | Composition (2) | Specific properties (3) | Uses (4) |
|---|---|---|---|
| Brass | Cu=60—80%, Zn=20—40% | Hard, malleable and ductile, can be moulded | Utensils, cartridges, condenser tubes. |
| Bronze | Cu=75—90%, Zn=10—25% | Hard, brittle, resistant to corrosion, can take high polish | Utensils, coins, statues, jewellery. |
| Aluminium bronze | Cu=88—90%, Al=10—12% | Golden colour, resistant to corrosion | Utensils, coins, jewellery |
| Phosphor bronze | Cu=85%, Sn=13% P=2% | Very hard, elastic, resistant to wear and corrosion | Bearings, valves, gears, suspension wire. |
| German silver or nickel silver | Cu=50%, Zn=30%, Ni=20% | White shining, malleable and ductile, resistant to corrosion | Utensils, statues, ornaments |
| Gun metal | Cu=88%, Sn=10%, Zn=2% | Very hard and strong, resistant to corrosion | Gun barrels, gears, bearings, machine parts. |
| Monel metal | Ni=65—70%, Cu=25—30%, Fe & Mn=2-3% | Resistant to corrosion and chemicals, high tensile strength | Alkali industry, resistance wires, automobile engine parts. |
| Constantan | Cu=60%, Ni=40% | High electrical resistance | Resistance boxes, thermo-couples. |

| Name (1) | Composition (2) | Specific properties (3) | Uses (4) |
|---|---|---|---|
| Nichrome | Ni=58—62%, Cr=8—14%, Fe=23—26%, C=0.2—1% Mn, Zn and $SiO_2$=0.5—2% | High electrical resistance | Resistance wire for electrical furnaces. |
| Duralumin | Al=95%, Cu=4%, Mg=0.5%, Mn=0.5% | Light, tough, high tensile strength, resistant to corrosion | Aircraft parts, pressure cookers, etc. |
| Magnalium | Al=90—98%, Mg=2—10% | Light, tough, high tensile strength, can be machined easily, resistant to corrosion | Aircraft, bus and truck body, hand tools, balance beams, furniture, etc. |
| Stainless steel | Fe=68—72%, Cr=17—19%, Ni=8—10%, Mn=2.0%, Si=1.0% | Hard, ductile and highly resistant to corrosion | Utensils, transportation equipment, chemical and petrochemical equipment etc. |
| Alnico steel | Fe=50%, Al=20%, Ni=20% Co=10% | Ferromagnetic | Permanent magnets |

**SUMMARY**

Let us summarise what we have learnt in this unit.

• The earth's crust is the biggest source of metals. Only those metals which are relatively inactive occur in the free or native state. Metals which are reactive are found in the form of their compounds like oxides, chlorides, sulphides, carbonates, etc. mixed with impurities.

• Before the extraction of a metal, the ore is concentrated by mechanical washing, magnetic or froth flotation process depending upon nature of the ore and impurities.

- Different ores of metals require different treatment based on the reactivity of the metal, i.e., pyrometallurgy, hydrometallurgy or electrometallurgy.

- In pyrometallurgy, the concentrated ore is converted into the metal oxide, by calcination or roasting, which can be easily reduced to metal by smelting.

- In hydrometallurgy, the ore is heated with aqueous solvents containing a chemical reagent with a view to extracting the metal in the form of a suitable compound by leaching action.

- Metals, oxides of which cannot be reduced by carbon, hydrogen or even other metals .can be obtained by electrolysis. The metal is liberated at the cathode.

- The metals obtained by the above metallurgical processes can be further purified by liquation, electrolysis, distillation, zone refining, Parke process, Van Arkel de Boer process and Mond process.

- Titanium, chromium, iron, nickel and copper can be isolated from ilmenite, chromite, haematite, pentlandite and copper pyrites, respectively.

- Metals have the special property of combining with other metals to form alloys. Alloys can be given desired properties.

## FURTHER READING

A *New Concise Inorganic Chemistry,* J.D. Lee, ELBS, London, 3rd ed., 1977.
*Chemistry: Facts, Patterns and Principles,* W.R. Kneen, M J.W. Rogers and P. Simpson,
    ELBS, London, 4th ed., 1984.

*Comprehensive Inorganic Chemistry,* F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 9th reprint, 1986.

**Module 5    COORDINATION CHEMISTRY AND IELD THEORY**
**UNIT 1: INTRODUCTION TO COORDINATION CHEMISTRY**


1.0    Introduction

2.0        Objectives

3.0    Coordination Compounds

    Werner's Coordination Theory

    Classification of Coordination Compounds

4.0    Radioactivity

    Characteristics of Radioactivity

    Types of Radiation


## 1.0    INTRODUCTION

In unit 3 of this course you were introduced to complex formation, as one of the properties exhibited by d block transition elements. In this unit, we shall be dealing with this class of compound, usually referred to as complexes. In view of a special mode of bonding called coordination being involved in their formation, they are also termed as coordination compounds. They are name in a systematic way different from simple inorganic compounds, this will be dealt with in another course CHM 423.

Radioactivity was discovered in a strange way by Becquerel due to the blackening of a plate expose to chromium compounds and the name radioactivity was invented sometimes later by Marie Curie.

## 2.0    Objectives

− Define the term coordination compound and coordination number

− Classification of coordination compound.

− Properties of radioactivity.

− Types of radioactivity


## 3.0    COORDINATION COMPOUND

The compounds in which the central atom or group of atoms (e.g. VO), is surrounded by anions or neutral molecules called ligands, are known as coordination compounds. In the coordination compounds, the central group acts as lewis acids. The ligands are electron pair donors and function as the lewis bases. The coordination compounds are, therefore, lewis adducts. The branch of chemistry under which properties of such compounds are studied is called the coordination chemistry. There is no sharp dividing line between the covalent, coordination and ionic compounds. The only justification of classifying a compound as a coordination compound is that its behaviour can be predicted conveniently by considering a catonic central species $M^{n+}$ surrounded by ligands $L_1$, $L_2$, etc. (the ligands may be same or different) the charge on the resulting complex, is determined by the algebraic summation of the changes on the central ion and the ligands attached to it.

The basic features of the coordination compounds were elucidated by the Danish Chemist S. M. Jorgensen (1887-1914) and the Swiss Chemist Alfred Werner (1866-1919). They synthesised thousands of coordination compounds to find out the manner in which the metal salts and the ligands united to form coordination compounds. As Werner was able to give theory for these compounds which explained and correlated a large number of observations, these compounds, are called the Werners Complexes.

## 3.1    Werner's Coordination Theory

Werner's coordination theory is basically very simples. It can be expressed in the form of the following postulations:

−    Two types of valencies exist for an ion, and they are called the primary (or ionisable) valences and secondary (or nonionisable) valences.

−    The number of the secondary valences for an ion is fixed e.g. six for $Rt^{42}$, $Co^{32}$, $Tl^{32}$, $Fe^{32}$, four for $nd^{27}$, $Rt^{27}$, $Cu^{27}$, $Ni^{27}$ and two for $Cu^+$, $Ag^+$, $Au^+$ and $Hg^{21}$.

−    The secondary valences must be satisfied by the anions or neutrals molecules having lone electron pair (e.g. halide, cyanide, ammonia, amine, water, etc.).

- In a compound, the secondary valences must be satisfied complexly. After which the primary valences are satisfied by the anions if the complex formed is cationic or vice versa.

- The secondary valences are fixed in space and posses a definite geometric arrangement even in solution. Thus for four secondary valences of nickel are tetrahedral, of $Cu^{2+}$ are planar, and the six secondary valences of $Co^{3+}$ or $Cr^{3+}$ are octahedral, for example, the Werner's formula, for complex $CoCl_3.6NH_3$ or $[Co(NH_3)_6]^{3+}{}_3Cl^-$.


## 3.2    Classification of Coordination Compounds

In a coordination compound, the ligands act as the lewis bases, whereas the central metal ion acts as a lewis acid. The ligands that coordinate with the metal ion may be classified as follows:

- Monodenate ligands, ligands donating only one pair of electrons to only one metal ion in a coordination compound are called the mono dental ligands e.g. halide ions, ammonia, water and $PR_3$.

- Bidentate ligands, ligands having two donor atoms. As a result of the coordinate bond formation, a bidentale ligand results in the formation of a ring structure incorporating the metal ions called the chelate ring. The bidentate ligands, may be neutral compounds (deamines, diphosphine, disulphides) or anions like exalate, carboxylate, nitrate, or glycinate ions.

- Polydentate ligands – These include ligands having more than two donor atoms attached in the molecule, and can be called the tri tetra, penta or hexadentales depending upon the number of the donor atoms present.

It is not necessary that a polydentate ligand should always use all its donor atoms for the coordination purposes. Thus sulphide or nitrate ion may act as a mono or a bidentale ligand depending on the complexes concerned. Through $OH^-$ or $NH_2^-$ act as a monodentales, they can also function as bidentales for the bridging purposes.

On the basis of the nature of the coordinates bond formed, a ligand can be classified as:

- Ligands having no available $\pi$ electrons and no vacant orbitals so that they can coordinate only through the bond, e.g. $H^-$, $NH_3$, $SO_3^{2-}$ or $RNH_2$.

- Ligands with two or three lone pair of electrons which may split into one pair of lower energy and form a sigma bond, and others may become higher energy bonding electron pairs, e.g. $N^{3-}$, $O^{2-}$, $F^-$, $Cl^-$, $Br^-$, $I^-$, OH-, $S^{2-}$, $NH^{2-}$, $H_2O$, RS, RQ, $NH_2^-$, etc.

- Ligands having a sigma-bonding pair of electrons and low energy empty $\pi$-antibonding orbital, that can accept suitably oriented d orbital electrons from the metals (back bonding), e.g. CO, $R_3P$, $R_3As$, $Br^-$, $I^-$, $CN^-$, Py, acac.

- Ligands without unshared lone pair, but having $\pi$-bonding electrons e.g. alkenes, alkynes, benzene, cyolopentadinyl anion.

- Ligands that can form two sigma bonds with two separate metal atoms and therefore can form bridges e.g. $OH^-$, $cl^-$, $F^-$, $NH_2^-$, $O_2^{2-}$, CO, $SO_4^{2-}$ and $O^2$.

Many polydentates can have their donor atoms same or different and, therefore, cannot be classified as any one of the types mentioned above.

On the basis of formation of complexes with different atoms, person has classified the ligands as well the metals into hard acid that is metal ions with almost empty or completely filled d sub-shell that cannot be used for the formation of $\pi$ bond such as Group IA, IIA, Al, Ga, In, Sn, Pb, etc. and soft bases, which are metals and ligands that form stronger complexes with this class of metals. This metal ions have nearly filled d orbitals electrons that can form $\pi$ bonds with the ligands and can accept d orbital electrons in their d orbitals eg. Cu(I), Hg(II), nd(II), Rt(II), PR3, etc.

The coordination number, is the number of ligands attached directly to the central metal ion in a coordination compound. About 98% of the complexes belong to the coordination number (CN) 4 or 6, even though the coordination number from 2 to 12 are seen in the complexes. The coordination number of 3 and 7 are rare and 5 is uncommon, present mostly for stereo-chemically rigid ligand complexes.

Self Assessment Exercise 1

Explain the terms, Ligand and chelate

## 4.0    RADIOACTIVITY

Radioactivity is the property by which compounds emits radio action which could penetrate objects opaque to light. From scientific investigations, it is now known that there are elements, although some of them are weakly active.

## 4.1    Characteristics of Radioactivity

Radioactive substances spontaneously and continually emit radiation. The rate of which they emit radiation is not affected by variation of ordinary experimental conditions, such as temperature, chemical change, pressure, and gravitational, magnetic or electric fields. This radiation affects photographic plates, causes gases to ionise, initiates chemical reaction (polymerisation) and makes certain substances (e.g. crystalline ZnS) fluoreses. Radioactivity is always accompanied by the evolution of a large amount energy. Radioactivity also has physiological effects, some of them cumulative with time. The basic effect of radiation on any living organism is the destruction of cells.

## 4.2    Types of Radiation

The essential nature of radioactivity is the unstable state of the nucleus of the atoms of the radioactive substance. Thus instability leads to a rearrangement of the nucleus with the release of energy in the form of $\alpha$ (alpha) or $_4$He or $\beta$ (beta) particles and $\gamma$ (gamma) radiation. The nucleus which is formed after this rearrangement will be that of a different element and may be stable or unstable. The whole process is called disintegration or radioactive decay.

a.    **Alpha Rays ($\alpha$-rays, $_2^4$He)**

They are positively charged particles being a mass four times that of the hydrogen atom and baring two units of charge. They have very little penetrating power.

b.    **Beta Rays ($\beta$-rays)**

These are fast moving streams of electrons. They may be positively or negatively charged. But usually the term β-rays refers to negatively charged particles. They have a very high penetrating power but are much less effective in ionsing gases or matter.

With beta-decay the mass number is unaltered, but there is a loss of one unit of negative charge e.g.

$$^{234}_{90}Th \rightarrow\ ^{234}_{91}P_a\ (\beta^{-}decay)$$
$$^{11}_{6}C \rightarrow\ ^{11}_{5}\beta\ (\beta^{+}\ decay)$$
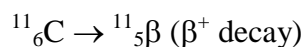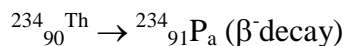
c.    **Gamma Rays**

Gamma rays have no charge and are not affected by electric or magnetic fields. They are electromagnetic rays of the same kind as light or x-rays but have very short wavelengths and energies which vary from 0.01 to 3 Mev.

**SUMMARY**

In this unit, you have been introduced to the theories of coordination compounds and radio chemistry. The main aspect are

-    The definition and Weiner's theory of coordination compound
-    Classification of coordination compound

**FURTHER READING**

1      *A New Concise Inorganic Chemistry*, J.D. Lee, ELBS, London, 3rd ed., 1977.

2      *Chemistry: Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

3      *Comprehensive Inorganic Chemistry*, F.A. Cotton and G. Wilkinson, Wiley Eastern Ltd., New Delhi, 3rd ed., 1986.

**Module 5    COORDINATION CHEMISTRY AND IELD THEORY**

**UNIT 1:    FIELD THEORY**

1.0    Introduction

2.0    Objectives

3.0    Ligand and Crystal field Theory

4.0    Valence Bond Theory

5.0    Molecular Orbital Theory

6.0    Crystal Field Theory

2.0 **Objectives**

At the end of the init, you should be able to:

− Define Bonding in coordination compound; ligand and crystal solid theories.

− Identify the nature of field theories

**3.0    LIGAND AND CRYSTAL FIELD THEORY**

Linus Pauling considered the formation of a complex as a result of coordinate bond formation between the metal ion (Lewis acid) and the ligand (lewis base). The metal ion accommodates the electron pairs (from hybridised ligand orbitals) in suitably hybridised orbitals. The hybridisation of orbitals on the metal decides the geometric arrangement of the complex.

**4.0    Valence Bond Theory**

The theory is based on the idea that the formation of complexes involves the donor-acceptor reaction. The most important postulates for the theory is that a pair of the electrons from the donor atoms are donated to empty orbital of the metal ion and in order to receive the donated electron the atomic orbitals on the metal must be hybridised to give a set of equivalent orbitals with the necessary symmetry required. The following assumptions are made in the theory:

– The metal ion must make available a number of orbitals, equal to its coordination number, for accommodating the electrons from the ligands.

The metal ion uses hybrid orbitals involving s, p and d orbitals for accepting the electrons from the ligand, which also must have the electron pairs in hybrid orbitals, so that a maximum and fruitful overlap of orbitals is possible with the strongly directional metal hybrid orbitals.

– $\pi$ bonding formation by the electron donation filled dxy, dyz and dzx, orbitals of the metal, was incorporated to reduce the accumulated negative charge on metal ions by back donation of electrons to the ligands through $\pi$ bonding.

– Hunds rule applies to the electrons in the non bonded orbitals, presence of unpaired electrons in the complexes giving paramagnetism.

## 5.0    Molecular Orbital Theory

It assumes that electrons move in molecular orbitals (M.O.) which extends over all the nuclear on the system. Mathematically the molecular orbitals are constituted by a linear combination of atomic orbitals (L.C.A.O.). Thus if two atomic orbitals overlap they form a molecular orbital which holds a maximum of two electrons and this electron are under the influence of the two nuclear.

A molecular orbital can be represented by 4 and they have the following characteristics:

– They like atomic orbitals have definite energy.

– Nomenclatures s, p. d, etc. used for atomic orbitals are replaced by sigma , pie ($\pi$) and delta ($\delta$).

– Paulis principle applies to molecular orbital, so that no single molecular orbital can contain two precisely similar electrons.

– In filling molecular orbitals Atbau principle is applied.

## 5.1  Differences between the valence bond and molecular orbital theories

– Unlike the molecular orbital theory, the Atom still retain to some extent these distinct character even when chemically bonded.

– It introduces the concept of resonance into bonding theory.

- Instead of considering the electrons as been associated all the time with both nuclear value bond theory, in the case of molecular orbital theory, an electron is considered to be associated first with one nucleus and then with the other nucleus, so that the complete wave function of the electron can be written as the linear combination of both.

- The valence bond theory is much easier to follow when treating polyatomic molecules.

- Unlike the molecular theory where spin pairing arises from the application of pauli exclusion principle, in valence bond theory, spin pairing is a necessary condition for energy minimum and hence for bonding.

## 6.0    CRYSTAL FIELD THEORY

The crystal field theory (CFT) developed by Bethe (1929) and Van Black (1935) considers the electrostatic interactions of the ligands (taken as charges) with the d orbials of the metal ions.

In an isolated gaseous metal ion, the five d orbital are degenerate, as dxz, dyz, dxy, $dx^2- y^2$ and $dz^2$

The electronic configuration of the metal ions, and hence the magnetic properties of the complexes can easily be understood from the d orbital splitting in the ligand fields. The electronic configuration of the ion will be given the following considerations:

- The electrons occupy the orbitals of lowest energy in the ground state.

- Due to reduced interelectronic repulsions in different orbitals, in a degenerate level, Hund's rule is obeyed.

- The quantum mechanical exchange energy for parallel spins is higher than that for the opposite spin.

- If pairing of electrons take place, the energy of the system will be raised by P, the pairing energy for the system.

The consequences of the splitting of the inner orbital which the CFT can explain are:

- Spectra of coordinate compound.

- The manganese properties of such compound.

- Thermodynamic properties of metal ion such as lattice energy, ionic radii.

- The kinetic and mechanism of their reaction.

- The geometry of the complexes.

**Further reading**

*Advanced Chemistry (physical and industrial)* Philip Mathews Cambridge university press 2003

*Theoretical principles of inorganic chemistry* GS Manku Tata McGraw-Hill 1981

*Modern Inorganic Chemistry*: GF Liptrot ELBS 1971