COURSE GUIDE

CHM 303
INORGANIC CHEMISTRY III

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INTRODUCTION

Inorganic Chemistry III course (CHM 303) is one of the core courses for the Bachelor of Science degree programme in Chemistry. It is a three-credit unit 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 in addition to the extraction and purification of metals.

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

WHAT YOU WILL LEARN IN THIS COURSE

The course inorganic chemistry III, deals with the study of the elements of the periodic table and their compounds with the exception of the compounds formed by carbon, hydrogen and other elements, i.e., organic chemistry. The differences and similarities between the main group elements will be examined. The chemical properties of the transition and inner transition elements will be discussed, with emphasis on their coordination properties. 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 four modules. Each of these modules contains some units. You will find several **In-Text Questions** (ITQs) and **Self-Assessment Questions** (SAQs), with answers provided as well as activity exercise in each unit. This course guide introduces you to the course material, of its usage for study. It suggests how much time to be spent on each of the activity exercises.

COURSE AIM

This course aims at the understanding of the chemistry of the noble gases and the halogens. It also discusses 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 unit are some laid down 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.

By the end this unit, you should be able to:

- list the elements of the main group (groups 1, 2, 13 - 18), transition elements (groups 3-12);
- describe the chemistry of groups 1 and 2 elements;
- discuss the similarities and differences among first and the rest members of each group, especially groups 14-16.
- explain the valence bond, molecular orbital and crystal field theories;
- describe the nature of radioactivity;
- discuss the chemistry, extraction and purification of metals.

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 SAQs and ITQs. At certain points in the course you would be required to submit assignments 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. In-text questions
4. Self-Assessment Questions
5. Conclusion
6. Summary
7. References and Further Readings

STUDY UNITS

Module 1 Chemistry of the Representative Elements

Unit 1	Hydrogen, Groups 1 and 2
Unit 2	Boron
Unit 3	Carbon and Silicon
Unit 4	Nitrogen and Phosphorus
Unit 5	Oxygen and Sulphur
Unit 6	Halogens
Unit 7	Chemistry of the Noble Gases (Group 18)
Unit 8	Compounds of Noble Gases

Module 2 Transition Elements

Unit 1	Nature and Chemistry of Transition Elements
Unit 2	General Reactivity
Unit 3	Inner-Transition Elements

Module 3 Coordination Chemistry, Bonding Theories and Radioactivity

Unit 1	Introduction to Coordination Chemistry
Unit 2	Bonding Theories and Radioactivity

Module 4 Isolation and Purification of Metals and Radioactivity

Unit 1	Metallurgy
Unit 2	Purification of Metals

This course consists of four modules. Module 1 deals with the chemistry of hydrogen and those of representative elements (groups 2, 13 to 18 or IIA to VIIIA). The similarities and differences in their chemical properties were highlighted as well as their electron configurations. In modules 2, we considered the chemistry of the transition and inner transition elements, while module 3 introduces the chemistry of the coordination compounds, bonding theories and radioactivity. Module 4 deals with the isolation and purification of metals.

Each of the unit is made up of one- or two-weeks' work consisting of introduction, objectives, reading materials, self-assessment exercise, activity exercise, conclusion, summary, references and suggestion for further readings. The unit directs you to work on the exercises related to the required reading and this meant to test your basic understanding and comprehension of the course materials, which is a prerequisite for the achieving the stated aim and objectives of the course.

PRESENTATION SCHEDULE

The course materials have important dates for the timely completion and submission of your tutorial lessons. You are seriously reminded of the need to promptly submit answers to tutorials and all the assignments that you are given 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

The Tutor Marked Assignments (TMAs) 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 rejected.

FINAL EXAMINATION AND GRADING

The end of the course examination for Inorganic Chemistry III will be for about 3 hours with maximum score 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, these questions may be prototype of the self-assessment questions and the TMAs or not. The end of the course examination is intended to cover the whole 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 exercises and the assignments.

COURSE MARKING SCHEME

Assignment	**Marks**
Assignments	The best three marks of the submitted assignments count at 10% each i.e.
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 TMAs 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 keep 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 your 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 questions
- The questions in the TMAs are not clearly understood.

Accept our best wishes in the course and we do hope that you would benefit considerably from its application.

MAIN
COURSE

CONTENTS PAGE

MODULE 1 CHEMISTRY OF THE REPRESENTATIVE ELEMENTS

UNIT 1 HYDROGEN, GROUPS 1 AND 2

CONTENTS

1.0 INTRODUCTION

During the course of CHM 101 and CHM 205, you were introduced to the properties of the groups 1 and 2 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, we will focus our attention on the chemistry of hydrogen, group 1 and Group 2 elements.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- describe the electronic configuration of the elements.
- describe chemical properties of the element.
- make comparative study of the chemistry of the elements.

3.0 MAIN CONTENT

3.1 Hydrogen

3.1.1 Occurrence of Hydrogen

Lavoisier gave the name hydrogen to inflammable gas collected by reacting iron with sulphuric acid. It is the most abundant element in the universe. The element occurs in the free state and, in some volcanic gases and in the outer atmosphere of the sun. Other stars are composed almost entirely of hydrogen. The main sources 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 atom consists of one proton and one electron, with electronic configuration of $1s^1$. Most of the chemistry of hydrogen can be explained in term of its tendency to acquire the electron configuration of the noble gas helium. It does this by gaining an additional electron to form hydride ion, H^- or by sharing its electron with another atom as in the hydrogen molecule, H – H. Hydrogen also accepts a lone pair of electrons, which it does as a proton when combined with, for example water and ammonia to give the hydroxonium, $H3O^+$ and ammonium $NH4^+$ 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.

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

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) also referred to as heavy water, for example DCl, an equivalent of hydrogen chloride.

3.1.2 The Position of Hydrogen in the Periodic Table

The properties of hydrogen cannot be correlated with any of the main groups in the periodic table and so could be treated on its own. It is however, more related to groups 1 and 17 than group 14 elements.

Its similarities to group 1 elements are due to the following;

i) It has only one valence electron in its shell ($1s^1$), an electronic structure unique to group 1 elements.

ii) It can lose the valence electron to form H^+ ion. However, free H^+ ions exist only in discharge tubes because of the small and strong polarizing power. This is why the protons are always found to associate with water molecules in aqueous solution as H_3O^+.

Hydrogen cannot be considered to be a member of group 1 because of the following:

i) It is more electronegative than group 1 elements e.g., H = 2.1 as against Li = 1.0. This is why H^+ is difficult to form. It does not form ionic hydrides with non-metals.

ii) Hydrogen combines covalently with other elements, a property not exhibited by the alkali metals.

Hydrogen can also be considered to belong to group 17 because of the following

i) The atom has one electron short of the first member of noble gases (He) electron configuration. This is a common feature of the group 17 elements.

ii) Like the halogens, the hydrogen is a non-metal and occurs in the elementary state as a diatomic molecule.

iii) It can gain one electron to form a hydride ion (H^-) like group VIIA elements.

It does not also fit into the group 17 because of the following;

i) It is less electronegative than the halogens (H = 2.1 and F = 4.0)

ii) The H^- ion is formed only when it combines with the most electropositive elements of groups 1 and 2.

iii) It can be made to lose its electron to form H^+ ion, a process not achieved by the halogen members.

3.1.3 Properties of Hydrogen

It 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^oC and becomes solid at – $259^{□}$ C. Hydrogen burns in air and, under certain conditions, reacts explosively with oxygen and the halogens, e.g.,

$$2H_2(g) + O_2(g) \ □\ 2H_2O(1)$$

It reacts partially with boiling sulphur to give hydrogen sulphide.

$$\rightleftharpoons H_{2(g)} + S(s) \qquad\qquad H_2S(g)$$

It reacts 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 IIA. It forms covalent hydrides with the elements from Groups 14 to group 17 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.

3.1.4 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

$$H_2(g) \ □\ 2H_{(g)},\ □H^{\Theta}\ (298\ K) = +435.9\ kJ\ mol^{-1}$$

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 reduces 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.

3.1.5 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 following processes:

i) Manufacture of ammonia by Haber process.
ii) Manufacture of hydrogen chloride and hydrochloric acid.
iii) Manufacture of organic chemicals e.g. methanol.
iv) Manufacture of margarine.
v) Extraction of some metals from their oxide.
vi) Liquid hydrogen has been used as a rocket fuel.

3.2 Comparative Study of Group 1 and Group 2 Elements

The elements of group 1, also referred to as group IA elements includes Li, 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 move down the group, shielding effect caused by the inner field shells on the valence electrons outweighs the increase in the nuclear grip on the valence electron caused by the increase in numbers of protons in the nucleus. Cesium, 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 carbonates.

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 cut. However, they rapidly tarnish in air giving a layer of oxide, peroxide, or sometimes super oxide. They also react violently with water. For both reasons they are kept under a layer of oil.

The elements of group 2 also referred to as group IIA (Be, Mg, Ca, Sr and Ba) also exhibited properties typical of highly electropositive metals, 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 their being known as the alkaline earth metals. The exception of the common pattern is the first member, beryllium.

One reason why beryllium is different from the other heavier members of its group is due to its small size. 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 covalent nature 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.

3.3 Chemistry of Group 1 Elements

3.3.1 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,

$Na_2O_{(s)} + H_2O(1) \rightarrow NaOH(aq)$

3.3.2 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.

$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2HaOH(aq) + H_{2(g)}$

3.3.3 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.

3.3.4 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 a useful substance; it is sold as washing soda crystals $Na_2CO_3.10H_2O$. When dissolves in water, it gives a slightly alkaline solution owing to salt hydrolysis.

$Na2CO3 + H2O \square NaHCO3(aq) + NaOH(aq)$

The ease with which hydrogen carbonate releases carbon dioxide is exploited, in its being used especially in fire extinguishers and in baking powders.

3.3.5 Halides

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

3.3.6 Nitrogen and Nitrates

Sodium nitrate, $NaNO3$, and sodium nitrite, $NaNO2$ are the most important salts of nitrogen. 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.

$2KNO_{3(s)} \square 2KNO_{2(s)} + O_{2(g)}$

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, $KNO3$ 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.

3.3.7 Sulphates, Hydrogen Sulphates and Sulphites

All the members of the group gave sulphates and hydrogen sulphates which are all soluble in water. Sulphites, such as sodium sulphite, Na_2SO_3, are more reactive than either sulphates or hydrogen sulphates e.g. if you warm a sulphite with an acid, you will find sulphur dioxide been given off.

$Na_2SO_3(aq) + 2HCl$ □ $2NaCl + SO_2(g) + H_2O(1)$

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.

3.3.8 Hydrides

All the hydrides of the group are ionic, with the metal being positively and the hydrogen being negatively charged.

3.4 Chemistry of Group 2 Elements

Beryllium oxide, BeO, is more like the oxide of aluminium in Group 13 (IIIA) rather than the oxides of the other elements in Group IIA. It has a high degree of covalency, 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^{o}C), 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.,

$$MgO(s) + H_2O(1) \rightleftharpoons MgOH\ (aq)$$

3.4.1 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, better known as epsom salts are used as laxative. Crystals of $CaSO_4.2H_2O$ are found in nature as the mineral gypsum. Anhydrous calcium sulphate also occurs naturally as anhydride. When gypsum is heated to about 100^{o}C, it loses three quarters of its water of crystallisation. The powder remaining is called plaster of paris.

3.4.2 Carbonates and Hydrogen Carbonates

The Group IIA carbonates are different from those of the alkali metals of Group IA in two major respects. Firstly, 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.
$MgCO_3(s)$ □ $MgO(s) + CO_2(g)$

3.4.3 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 other halides.

SELF-ASSESSMENT EXERCISE

i. The most abundant element in the universe is

ii. Which of the following is/are the properties of H_2?
iii. Which of the following properties of hydrogen atom are similar to those of halogens?
iv. The most common way by which hydrogen atom may attain stability is by Choose the correct answer among the following options.
v. In which of the following compounds is the value of *y* maximum?
vi. Give reason(s) why group 1 and group 2 are good reducing agents.

4.0 CONCLUSION

Hydrogen is the first element in the periodic table with $1s^1$ electron configuration. The element has some unique properties. Its chemistry is similar to that of group 1 and group 17 elements of the periodic table. The structure of hydrogen also resembles that of the group 14 elements since both have a half-filled shell of electrons. However, it is best treated as a group of its own.

The elements of group 1 of the periodic table also referred to as alkali metals have a general ns^1 electron configuration an indication that they have one loosely held electron in the valence shell. Their physical and chemical properties are closely related to the sizes and electron structures. They are typically soft and highly reactive metals and are excellent conductor of electricity. Lithium shows some anomalous properties from the rest member of the group due to its very small size and high charge density.

Group 2 elements also called alkaline earth metals have two electrons in their valence shell implying they form divalent ions. The first member of the group, Be differs from the rest of the group. The elements form a well graded series of highly reactive metals. Like alkaline metals, they generally form colourless ionic compounds but are less reactive than alkali metals.

5.0 SUMMARY

- Hydrogen is a tasteless, odourless and colourless gas with a valence electron.
- The element has properties of both group 1 and group 17 of the periodic table.
- 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 and Be due to the very small size of their ions, hence have anomalous properties compared to other members of the groups.
- Group IA and IIA form ionic compounds with non-metals.
- Group IA react vigorously with water giving off hydrogen gas.
- The sulphates of Group IA are all soluble in water.
- The Group IIA metal oxides and hydroxides are less soluble in water than those of Group IA.

6.0 TUTOR-MARKED ASSIGNMENT

1. Outline some uses of alkali and alkaline earth metals. (Time allowed: 10 mins)

7.0 REFERENCES/FURTHER READING

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UNIT 2 BORON

CONTENTS

1.0 INTRODUCTION

You had already been introduced to groups 13 in CHM 101 and CHM 205. This group of elements mark the beginning of *p* blocks in the periodic table. In this unit, we will focus our attention on the chemistry of boron, the first member of the group and its compounds

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- describe the electronic configuration of the elements.
- describe chemical properties of the element.
- make comparative study of the chemistry of the elements.

3.0 MAIN CONTENT

3.1 Boron

Boron belongs to Group 13 (IIIA) elements, which marks the beginning of the *p*-block elements in period 2 of the periodic table. All these elements exhibit a group valency of three, but because of the very large amount of energy (sum of the first three ionisation energies, that is necessary for the formation of +3 ions), their compounds when anhydrous are either essentially covalent or contain an appreciable amount of covalent character. In fact, 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.

The element boron occurs principally, as borates e.g. sodium borate in which the boron atom is part of an anionic complex. Boron can be obtained as an amorphous brown powder by treating borax with hydrochloric acid, igniting the boric 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 thermal decomposition of boron trioxide on a tantalum filament.

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

3.2 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.

3.2.1 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.,

$BCl_{3(g)} + 3H_2O_{(1)} \rightarrow H_3BO_3(aq) + 3HCl_{(g)}$

$4BF3_{(g)} + 3H_2O_{(1)} \rightarrow 3BF_{4(aq)} + H_3BO_3(aq)$

Boron trifluoride is used as a Friedel-Crafts catalyst in organic chemistry, particularly for polymerisation reactions.

3.2.2 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

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

Electron diffraction studies have indicated that there are two hydrogen atoms in the molecule that are called bridging hydrogen atoms. Also, there are two boron atoms with other four hydrogen atoms that are referred to as terminal hydrogen atoms.

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. The structure of diborane is indicated in Fig 1.1

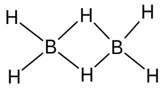

Fig. 1.1: Structure of Diborane

3.2.3 Boron trioxide

Boron trioxide, an acidic oxide can be obtained by burning boron in oxygen or by heating orthoboric acid to red heat. It is also referred to as boron *sesquioxide*. *Sesqui* means one and half, hence the formula should be $BO_{1\frac{1}{2}}$ or B_2O_3

$4B + 3O_2 \rightarrow B_2O_3$

$$H_3BO_3 \xrightarrow{373\ K} HBO_2 + H_2O$$

$$HBO_2 \xrightarrow{\text{red heat}} B_2O_3 + H_2O$$

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. Boron trioxide reacts slowly with water, forming orthoboric acid. When fused with metallic oxides it forms borate glasses which are often coloured, this is the basis of borax bead test in qualitative analysis.

3.2.4 Orthoboric Acid

Orthoboric acid, H_3BO_3 which is better written as $B(OH)_3$, is formed when the boron halides are hydrolysed or when dilute hydrochloric acid is added to a solution of borax.

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

$$B_4O_7^{2-}{}_{(aq)} + 2H^+{}_{(aq)} + 5H_2O_{(1)} \rightarrow 4H_3BO_{3(aq)}$$

It is obtained as a white solid on subsequent crystallization and is water soluble. Orthoboric acid is a weak monobasic acid and in aqueous solution, the boron atom completes its octet by removing OH^- from water molecule.

$$B(OH)_3 + 2H_2O \rightarrow H_3O^+ + [B(OH)_4]^-$$

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.

3.2.5 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 $(Mg^{2+})_3 (BO_3^{3-})_2$, 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 given in Fig. 1.2.

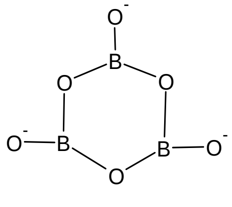

Fig. 1.2: Structure of borate ion

3.2.6 Borazine and Boron Nitride

When ammonia and diborane, in the ratio of two molecules to one, are reacted together at high temperature, 473K, a volatile compound known as borazine, $B_3N_3H_6$ is formed. The molecule has a cyclic, hexagonal structure reminiscent of benzene. Hence, it is often referred to as inorganic benzene.

$6NH_3 + 3B_2H_6 \square 2B_3N_3H_6 + 12H_2$

The structure is considered to be a resonance hybrid of the two structures as shown in Fig 1.3.

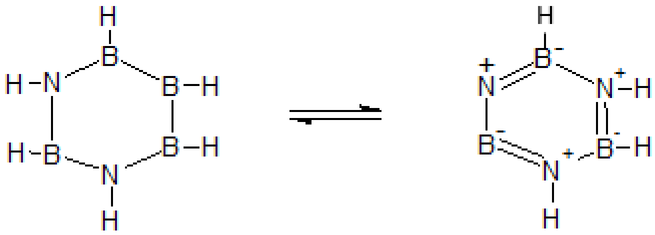

Fig. 1.3: Resonance Structure of Borazine

It is isoelectronic with benzene and resembles the latter in some of its physical and chemical properties. For example, borazine has its melting point at -58°C while that of benzene is 6°C. Also, the boiling points are 64.5 and 80.0°C for borazine and benzene respectively. However, the chemical properties of borazine are quite different from benzene. For instance, borazine 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

i. In the atoms of *p*-block elements, the differentiating electron enters
ii. Boron does not form B^{3+} ion because
iii. Which of the following does not respond to borax bead test?
iv. Borazine is isoelectronic with benzene and is commonly called inorganic benzene. Explain the differences between borazine and benzene.

4.0 CONCLUSION

The elements in the group have three valence electrons and are characterized by $ns^2 np^1$ valence electron configuration. Boron is a non-metal, and always forms covalent bonds. Due to the extremely high energy required to remove the loosely held electrons, it has no tendency to form B^{3+} ions. All BX_3 compounds are electron deficient and can accept an electron pair from another atom to form coordinate covalent or dative bond.

5.0 SUMMARY

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

- Group 13 elements form basic oxides that are insoluble in water. However, Be_2O_3 and Al_2O_3 are amphoteric in nature.

6.0 TUTOR-MARKED ASSIGNMENT

1. Boric acid can be represented with two chemical formulae. What are these formulae? Which of these formulae is the most helpful? How might you classify boric acid if this formula is used. (Time 8 mins)

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UNIT 3 CARBON AND SILICON

CONTENTS

1.0 INTRODUCTION

The elements in group 14 mark the second group of *p* block elements in the periodic table. In this unit, we will focus our attention on the chemistry of carbon as well as silicon, the second member of the group.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- describe the electronic configuration of group 14 elements;
- describe chemical properties of the elements;
- make comparative study of the chemistry of the elements.

3.0 MAIN CONTENT

3.1 Chemistry of Carbon and Silicon

Carbon and silicon belong to Group 14 (IVA) elements of the periodic table. They show many of the properties that are characteristic of non-metals, but as the group is descended, the metallic nature of the elements increases. This is because the energy required to remove the loosely held electron to form positive ions, reduces down the group. Hence, electropositive character of the elements increases down the group.

The normal valency of the elements is four, but apart from carbon, the rest elements can form more than four bonds with ligands. This is because they make use empty low-lying *d* orbitals for bond formation.

For example, e.g. the availability of the *d* orbitals is responsible for the ability of silicon to form complex ions, such as SiF_6^{2-}, with exception of carbon. Another feature of the chemistry of the Group IVA is that some carbon compounds are less reactive than the corresponding compounds of the other members of the group.

3.2 Compounds of Carbon and Silicon

3.2.1 Hydrides

Carbon and silicon give a variety number of hydrides such as CH_4, C_2H_2, SiH_4, Si_2H_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 except in the presence of flame. On the other hand, SiH_4, silicon hydrides are highly reactive. For example, Si_3H_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.

3.2.2 Halides

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 readily hydolysed by water, forming silicic acid.
$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$

3.2.3 Oxides

The oxides of carbon and silicon are predominantly covalent, but the main 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 $(SiO_2)n$. CO_2 and SiO_2 are 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.
$SiO_2(s) + Na_2CO_3 \rightarrow Na_2SiO_3(s) + CO_2(g)$

Unlike the carbonates, silica cannot be attacked by acid to liberate SiO_2, rather a gelatinous mass of silicic acid (H_2SO_3) is obtained. This acid on been heated in a platinum dish, gives a white powder of SiO_2 not reactive towards hydrogen ions as are carbonates. Rather if dilute acid is added to sodium silicate solution gives precipitate of SiO_2.

$Na_2SiO_3 + 2HCl \rightarrow H_2SiO_3 + 2NaCl$

H_2SiO_3 + heat to redness $\rightarrow SiO_2 + H_2O$

3.2.4 Organic Compounds

Carbon and silicon form many interesting organic compounds, made up of chains of representing units, e.g., organo-silicon compounds
$-(Si(CH_3)_2{-}O)_n-$

SELF -ASSESSMENT EXERCISE

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

ii. Give the reaction products of the following and balance the equation(s) where necessary.

  a. Na_2CO_3 + ~~HCl~~→ ?

  b. Na_2SiO_3 + ~~HCl~~→ ?

iii. Suggest reasons why the maximum covalency of carbon is four while that of silicon is six.

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

4.0 CONCLUSION

Carbon and silicon are *p*-block elements and belong to group 14 elements of the periodic table with $ns^2\ np^2$ electron configuration carbon is limited to forming a maximum of four covalent bonds because only *s* and *p* orbitals are available for bonding. However, the covalency of other members of the group is not limited to four due to the availability of empty low lying *d*-orbitals. The elements in the group are relatively unreactive but reactivity increases down the group.

5.0 SUMMARY

- Carbon and silicon are non-metals.
- Carbon and silicon forms compounds with oxygen and chlorides which are covalent in nature.

6.0 TUTOR-MARKED ASSIGNMENT

1. Give plausible reason why hydride of carbon is relatively unreactive compared to the hydride of silicon that is very reactive. (Time allowed: 10 mins)

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UNIT 4 NITROGEN AND PHOSPHORUS

CONTENTS

1.0 INTRODUCTION

You had already learnt about group 15 in CHM 101 and CHM 205. This group of elements constitute the third group of the p block elements in the periodic table, with a general electron configuration of ns^2np^3. Here, you will learn about the chemistry of nitrogen as well as phosphorus, the first and second member of the group respectively.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- describe the electronic configuration of group 15 elements.
- describe chemical properties of the elements.
- make comparative study of the chemistry of the elements.

3.0 MAIN CONTENT

3.1 Chemistry of Nitrogen and Phosphorus

As members 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. Nitrogen is a gas and has no allotropic form. On the other hand, other phosphorus is a solid and has three allotropes, white, black and red.

3.2 Compounds of Nitrogen and Phosphorus

3.2.1 Hydrides

Both of nitrogen and phosphorus form hydrides (MH_3) with unpleasant smell. They have pyramidal shape, but the bond angle in hydrocarbon and the hydrides of group IVA differ from that of ammonia. Like ammonia, phosphine (PH_3) contains a lone pair of electrons which can react with a proton to form phosphorium ion, PH_4^+ and it will combine to make phosphonium iodide, PH_4I. Like the analogous ammonium salts, it is ionic. However, phosphine will not accept protons as readily as ammonia.

3.2.2 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. This is due to absence of empty low-lying *d* orbitals in N.
Phosphorus pentachloride 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

$PCl_{5(s)} + 5H_2O_{(1)} \rightarrow H_3PO_{4(aq)} + 5HCl_{(g)}$

3.2.3 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.

3.2.4 Oxoacids

Phosphorous forms various oxoacids like H_3PO_4, H_3PO_3, H_3PO_2, HPO_2, etc. The structure of orthophosphoric acid (tetraphosphate(V) acid) is shown in Fig. 1.3.

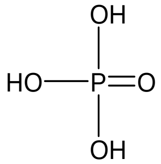

Fig. 1.3: Structure of Phosphoric Acid

3.2.5 Sulphides

The sulphide 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 head of matches, sulphide, an oxidising agent such as potassium trioxochlorate (V), $KClO_3$ and a little ground glass are mixed together. The resulting mixture is bound together with glue. The match boxes usually have a strip of sand paper along the side.

SELF-ASSESSMENT EXERCISE

i. Give two examples of the oxides formed by nitrogen.
ii. Outline three uses of nitrogen
iii. State any two uses of phsphorus
iv. Give three different sulphur compounds of phosphorus

4.0 CONCLUSION

Nitrogen and other members of the group have five valence electrons with $ns^2 np^3$ electron configuration. Nitrogen and phosphorous are non-metals. Their compounds are predominantly covalent.

5.0 SUMMARY

- All the members of group 15 elements of the periodic table have a general valence electron configuration of ns^2np^3.
- Nitrogen and phosphorus form compounds with oxygen, halides and hydrochloride.

6.0 TUTOR-MARKED ASSIGNMENT

1. Suggest reasons why PF_5 is stable but NF_5 is not. (Time allowed: 5 mins)

7.0 REFERENCES/FURTHER READING

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UNIT 5 OXYGEN AND SULPHUR

CONTENTS

1.0 INTRODUCTION

Group 16 of elements of the periodic table constitute the fourth group of the p block elements. In this unit, you will learn about the chemistry of the first two members of the group (oxygen and sulphur).

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- describe the electronic configuration of group 16 elements.
- describe chemical properties of the elements.
- make comparative study of the chemistry of the elements.

3.0 MAIN CONTENT

3.1 Chemistry of Oxygen and Sulphur

Oxygen exists as diatomic molecules, O_2. It has three isotopes, $^{16}{}_{8}O$ or the main one, and the others are $^{17}{}_{8}O$ and $^{18}{}_{8}O$, both of about 0.3%. Oxygen also exist in triatomic molecules as ozone, O_3 with a triangular shape.

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.

3.2 Compounds 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:

$H_2SO_{4(aq)} + H_2O_{(l)} \qquad HSO_4^-{}_{(aq)} \rightarrow H_3O_{(aq)}$

$HSO_4^-(aq) + H_2O \qquad SO_4^{2-}(aq) + H_3O^+(aq)$

The acid shows its oxidising nature when it is concentrated, for example

3.2.1 Hydrides

Of the hydrides of Group VIA, 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 metal sulphide, often iron(II) sulphide.

$FeS_{(s)} + 2HCl_{(aq)}$ □ $FeCl_{2(aq)} + H_2S_{(g)}$

Unlike water, but like ammonia, hydrogen sulphide can be a good reducing agent.

$H_2S_{(g)} + Cl_{2\,(g)} \qquad 2HCl_{(g)} \rightarrow S_{(s)}$

3.2.2 Halides and Oxohalides

F being more electronegative than O, its binary compounds with O are called oxygen fluorides whereas similar chlorine compounds are referred to as chorine oxides. Sulphur forms halides with all the halogens with the exception of iodine. Fluorine brings out the highest oxidation state with other elements in the group, as in SF_6. The fact that these elements can actually form six bonds is due to their use of *d* orbitals in bonding.

Only S and Se form oxohalides. 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.

$SOCl_2(1) + 2H_2O(1)$ □ $H_2SO_3(aq) + 2HCl(aq)$

3.2.3 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.

3.2.4 Sulphites, Sulphates and Other Oxoanions

Sulphites contain SO_3^{2-} ion. Many sulphites are insoluble in water or are sparingly soluble in water, e.g., $CaSO_3$. However, those of group 1 metals and ammonium are water soluble and act as reducing agents. When they are warmed with acid, SO_2 is given off.

$SO_3^{2-}(aq) + 2H^+(aq) \square SO_2(g) + H_2O(1)$

Sulphate contains SO_4^{2-} ion, and are mostly soluble in water and crystallise, forming hydrated sulphates. $CaSO_4$, $SrSO_4$, and $PbSO_4$ are sparingly water soluble while $BaSO_4$ is not soluble in water. Sulphates of alkali metals, $MgSO_4$ and $PbSO_4$ are stable to heat except at high temperatures. $CaSO_4$ decomposes at high temperature while sulphates of Sr and Ba are stable.

$Fe_2(SO_4)_3 \square Fe_2O_3(s) + 3SO_3(g)$

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.

$I_2 (aq) + 2S_2O_3^{2-} (aq) \square 2I^-(aq) + S_4O_6^{2-}(aq)$

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

$S_2O_8 + 2e^- \square 2SO_4^{2-}$

They oxidise iodide to iodine and iron(II) to iron(III).

3.2.5 Sulphides

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

3.2.6 Uses of Oxygen and Sulphur

i) Oxygen is used in oxyacetylene and in oxy-hydrogen flames for cutting metals
ii) Liquid oxygen is used in fuel in rocket

iii) Oxygen is used in steel making and in the high-pressure gasification of coal.
iv) Sulphur is used in the manufacture of H_2SO_4

SELF-ASSESSMENT EXERCISE

i. Write the full electron configuration of sulphur
ii. Although oxygen and sulphur belong to the same group of the periodic table, SF_6 is more common and stable whereas OF_6 is rare.
iii. Give two uses of sulphur
iv. Write the balanced equation for the redox reaction between iodine molecule and thiosulphate ion
v. Give the equation of SO_3 reaction with water
vi. Of what importance is sodium thiosulphate in photography and volumetric analysis?

4.0 CONCLUSION

Oxygen and Sulphur have six valence electrons with ns^2np^4 electron configuration. They are non-metallic and electronegative. Oxygen is a gas at room temperature while Sulphur is a solid. They are reactive as they combine with oxygen, halides, hydrogen etc., to form various compounds.

5.0 SUMMARY

- All the group members have a general valence electron configuration of ns^2np^4.
- Both oxygen and sulphur are non-metallic in nature.
- 3. They combine with hydrogen, halogens to give some interesting compounds.

6.0 TUTOR-MARKED ASSIGNMENT

1. Write the formula of a chemical species in which sulphur has the following oxidation states
(a) 0 (b) -2 (c) +4 (d) +6. (Time allowed: 5 mins)

7.0 REFERENCES/FURTHER READING

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UNIT 6 HALOGENS

CONTENTS

1.0 INTRODUCTION

This group of elements constitute the fifth group of the *p* block elements and are referred to as group 15 elements of the periodic table. In this unit, you will learn about the chemistry of the halogens, otherwise referred to as salt producers.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- describe the electronic configuration of group 17 elements.
- describe chemical properties of the elements.
- make comparative study of the chemistry of the elements.

3.0 MAIN CONTENT

3.1 Chemistry of the Halogens

The name *halogens* came from two Greek words, which means salt producer. These elements are members of group VIIA and can also be referred to as group 17 elements. The members of the group include fluorine, chlorine, bromine, iodine and astatine. Fluorine and chlorine are gases, bromine is a liquid, while iodine occurs as a solid at room temperature. This is because intermolecular forces between the molecules increase down the group of the periodic table. The last element of the group, At, is radioactive and is generally excluded from the comparative study of the group.

3.2 Compounds of the Halogens

F needs less energy to break the molecule due to its small size, hence it reacts more readily than other halogens. The Reactivity of the elements generally decreases down the group.

3.2.1 Halogens as Oxidising Agents

All the halogens have the highest oxidation potentials (oxidising powers) across any particular period of the periodic table, an indication that they have a high tendency to accept electrons to form only univalent anion (halide ion, X^-). This characteristic property decreases down the group of the periodic table. This shows that F has the strongest oxidising ability, followed by Cl and Br, while I is a mild oxidizing agent. They all readily form alkali halides with group IA metals. The alkali metals towards the bottom of Group I A can react violently with fluorine and chlorine. They react readily with hydrocarbon, producing carbon

$$C_{10}H_{22(s)} + 11Cl_{2(g)} \rightarrow 10C_{(s)} + 22HCl_{(g)}$$

3.2.2 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(I) acid (hypochlorous acid) is produced

$$Cl_{2(g)} + H_2O_{(1)} \rightarrow HCl_{(aq)} + HClO_{(aq)}$$

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

The halogen reacts with cold dilute alkali according to the equation

$$X_2 + 2OH^- \rightarrow X^- + XO^- + H_2O$$

and when heated with concentrated alkali as

$$3X_2(g) + 6OH^-(aq) \rightarrow 5X^-(aq) + XO_3^-(aq) + 3H_2O(1)$$

3.2.3 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, e.g., Cl is white or by their reaction with ammonia solution.

3.2.4 Uses of halogens

i) Chlorine is used in water purification as disinfectant
ii) Chlorine is used as a bleaching agent for pulp paper and in textile industries.
iii) Iodine is used as germicide in wound treatment
iv) Iodine is used in the production of dyes and in photography
v) Chlorine is used in the manufacture of important compounds such as vinyl chloride, CCl_4, $CHCl_3$ and CH_3Cl

SELF-ASSESSMENT EXERCISE

i. Explain why ICl_5 exists but FCl_5 does not
ii. Explain why the order of oxidizing strength of halogen is F > Cl > Br > I
iii. Outline any four uses of chlorine.
iv. How would you distinguish among Cl^-, Br^- and I^- in the laboratory?

4.0 CONCLUSION

Halogens, otherwise referred to as salt producers, are non-metals. They have seven valence electrons with ns^2 np^5 electron configuration. They are highly electronegative and very reactive. Halogens are good oxidizing agents and their oxidizing ability decreases down the group.

5.0 SUMMARY

- Group 17 elements have a general valence electron configuration of ns^2np^5
- All the halogens are oxidising agents, fluorine being the most vigorous.
- The halogens exist as diatomic molecules.

6.0 TUTOR-MARKED ASSIGNMENT

1. Give the formulae of the chloride of the following elements and the physical state in which the compounds exist (a) magnesium (b) hydrogen (c) carbon. (Time allowed: 5 mins)

7.0 REFERENCES/FURTHER READING

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UNIT 7 NOBLE GASES

CONTENTS

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 which were formally referred to as members of Group VIIIA, 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 this group of elements (Group VIIIA or 18) is missing. These elements were not known at that time and have been discovered only about a hundred years ago. 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 actually 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

By the end of 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.

3.0 MAIN CONTENT

3.1 Discovery of Noble Gases

The story of the discovery and investigation of noble gases is one of the most brilliant and interesting chapters in the history of science. Their discoveries can be traced back to 1784, 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 his 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 *neos*, 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 *kryptos*, meaning hidden) and *xenon* (from the Greek word *xenos*, 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.

3.2 Position of Noble Gases in the Periodic Table

Due to their 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. These 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.

Just 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.

3.3 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 2.1, 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 2.1), 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 are liquefied by cooling under pressure.

Table 2.1: 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
$C0_2$	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

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.

The 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, the 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.

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 energy loss.

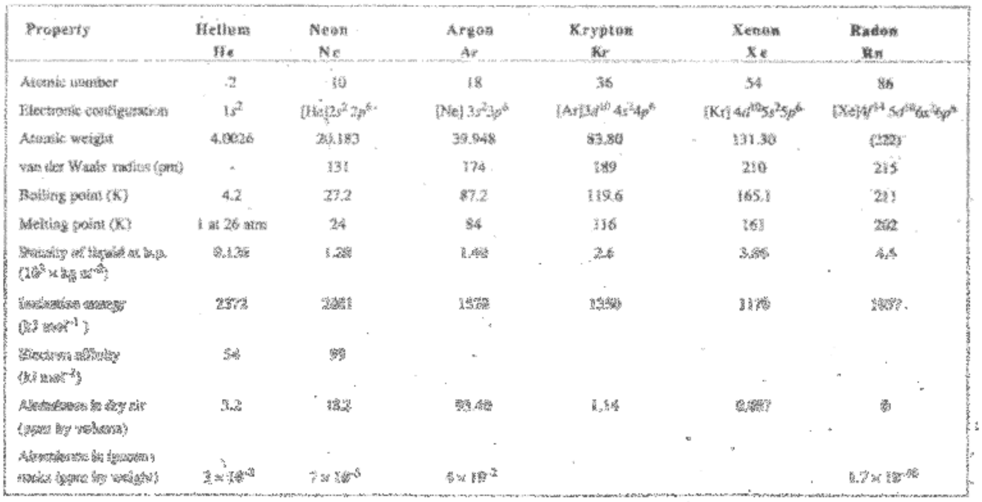
3.4 General Characteristics of Noble Gases

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 2.2

It can be observed from the Table (2.2) 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 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 $1s^2$ or ns^2np^6 configuration, they have the highest ionisation energies compared to other elements across any particular period of the periodic table. This is because, a huge amount of energy is required to disrupt this stable (fully filled shell) electron configurations. This reflects their reluctance to chemical reactivity. Analogously, the electron affinity of these elements is either zero or has a small positive value.

Table 2.2: 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	[illegible]
Abundance in igneous rocks (ppm by weight)	3×10^{-3}	7×10^{-5}	4×10^{-2}			1.7×10^{-10}

Therefore, they are unable to accept electrons to form anions. As we go down the group, the ionisation energy of the noble gases decreases. This is because their nuclear grip on the valence electron reduces down the group. 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, the melting and boiling points of helium are the lowest of any known substance.

The van der Waals forces of attraction between the atoms of the molecules increase with 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, the melting and boiling points increase with the increase in atomic number. Helium has two isotopes, ^{3}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

i. You have read above that boiling point is related to the binding forces in atoms and molecules: In noble gases, the atoms are held by van der Waals forces. Can you now explain:

   a) the relationship between the boiling points of noble gases and the van der Waals forces in their atoms?
   b) why there is a steady increase in boiling points from He to Rn in the group 18 of the periodic table?

ii. Outline the physical and chemical properties of noble gases

   a) What reasons can be advanced for the discovery of noble gases?
   b) What made Lord Raleigh to suspect that there may be an additional element in the air?

4.0 CONCLUSION

Members of this group are odourless, colourless, tasteless monoatomic gases at room temperature. They are characterized by filled valance shells and hence were initially referred to as noble, inert or non-reactive gases. The elements have highest ionization energies compared to other elements in their periods of the periodic table. The electron affinity of the elements is either zero or has a positive value, hence they do not form anion. Hence, they show extremely low reactivity. However, it was letter discovered some of them do actually react with other elements or compound to form compounds.

5.0 SUMMARY

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

- 1.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.
- 3.The characteristic stable valence electron configuration of noble gases is $1s^2$ or ns^2np^6
- They have the highest ionisation energies and the lowest electron affinity, melting and boiling
- points and heat of vapourisation in their periods.
- Noble gases have various applications, e.g., as coolants and for providing inert atmosphere.

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UNIT 8 COMPOUNDS OF NOBLE GASES

CONTENTS

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, were 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 succeed, 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 electron configuration. The first breakthrough in the noble gas compounds was achieved in l962 by an English Chemist Neil Bartlett. He was trying to make the newly discovered compound PtF_6, instead he obtained a deep red compound containing oxygen.

The X-ray diffraction of the red solid has shown 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 kJ 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

By 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 Valence Shell Electron Repulsion Theory of the compounds of noble gases.

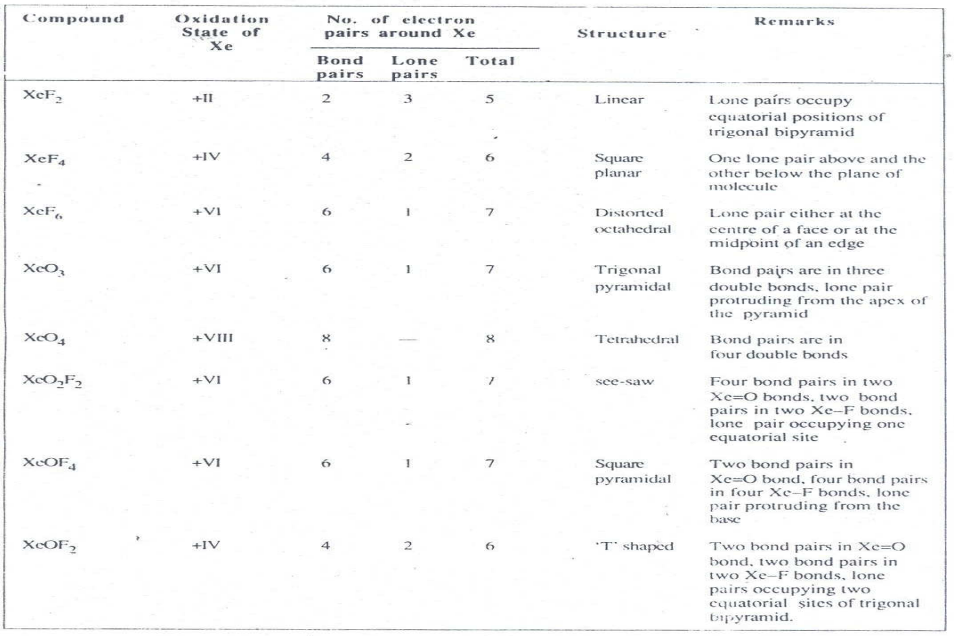
3.0 MAIN CONTENT

3.1 Compounds of Noble gases

3.1.1 Xenon Compounds

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 2.3.

Table 2.3: 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.

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:

2:1 mixture

$Xe + F_2 \longrightarrow XeF_2$

700 K, sealed vessel

1:5 mixture

$Xe + 2F_2 \longrightarrow XeF_4$

700 K, 6 atmosphere

1:20 mixture

$Xe + 3F_2 \longrightarrow XeF_6$

500-600 K, 50-60 atmosphere

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 $XeF_2 + H_2$ 4HF + Xe $XeF_2 + H_2$ 6HF + Xe

$\longrightarrow$

$\longrightarrow$

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 in water or acidic solutions, but can undergo slow hydrolysis on standing. Hydration is more rapid with alkali.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

Reaction of XeF_6, with water is violent since xenon trioxide, XeO_3, formed is highly explosive:

$$3XeF_6 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12\ HF + \frac{3}{2}O_2$$

XeF_6 also reacts violently with water and undergoes slow hydrolysis by atmospheric moisture

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

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 step-wise reaction which finally produces the dangerous XeO_3, XeF_6 cannot be handled in glass or quartz apparatus.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$
$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

$$2XeOF_6 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_6 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

XeO_3 does not ionise in aqueous solution, but in alkaline solution above pH 10.5, it forms the xenate ion, $[HXeO_4]^-$

$$XeO_3 + NaOH \longrightarrow Na^+[HXeO_4]^-$$

sodium xenate

Xenates undergoes slow disproportionation in alkaline solution to form perxenate and Xe gas

$$2[HXeO_4]^- + 2OH^- \longrightarrow [XeO_6]^{4-} + Xe + O_2 + 2H_2O$$

Perxenate ion

Alkaline hydrolysis of XeF_6 also forms perxenate

$$2XeF_6 + 16OH^- \longrightarrow XeO_6 + Xe + O_2^- + 12F^- + 8H_2O$$

Perxenates are extremely powerful oxidising agents, and can oxidise HC1 to $C1_2$

H_2O to O_2 and Mn(II) to Mn(VII). With concentrated H_2SO_4, they give xenon tetroxide XeO_4, which is volatile and explosive:

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

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 $[XeF_5]^+[PtF_6]^-$.

Before proceeding to clathrates of noble gases, try the following in-text question related to xenon compounds.

3.1.2 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 the cavities of 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 can fit into the cavities of the host lattice, to form clathrates. Thus, O_2, SO_2, H_2S and MeOH are examples of other substances which form clathrates with quinol.

When quinol (1,4-dihydroxybenzene) 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 β-quinol 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 high pressure, atoms of noble gas get trapped in the crystal lattice of ice giving clathrates corresponding to the composition, $6H_2O$:1 gas atom. 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.

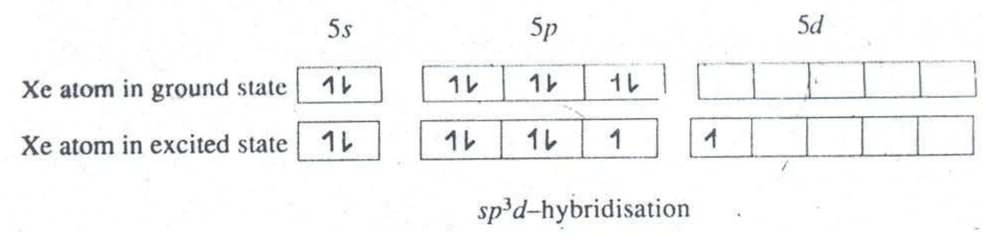
The crystal lattice with cavities is called the **host**, substance entrapped in it is known as **guest**

3.2 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 their stable electron configurations. However, the discovery that their compounds could be prepared made it necessary that some description be given of the nature of bonding in their compounds. The nature of the bonds and the orbitals used for bonding in the compounds is of great interest. It has been the subject of considerable controversy as evident from the discussion of bonding in some individual xenon compounds.

3.2.1 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 sp^3d 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. 2.1

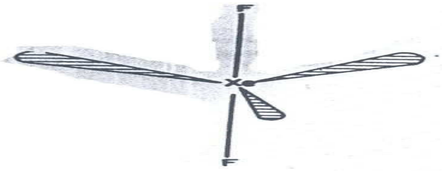
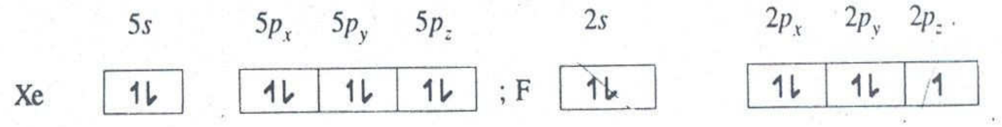


Figure 2.1: Linear structure of XeF_2

The objection to this model is that the 5*d* 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 to be more acceptable. The outer electronic configuration of the atoms involved in bonding are:



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 non-bonding and one antibonding which can be represented as shown in Fig. 2.2

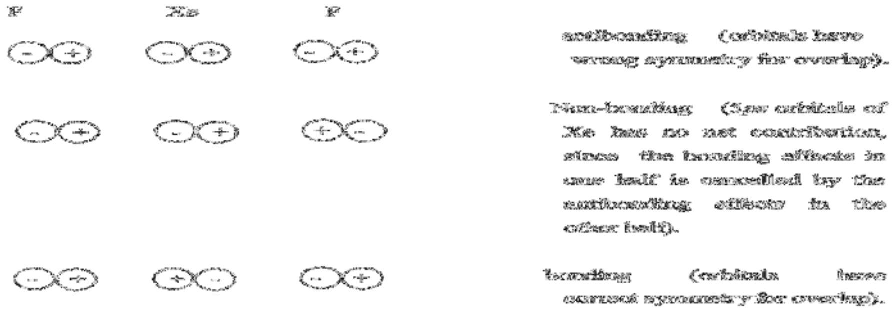


Fig. 2.2: Molecular orbital representation of the 3- centre 4-electron bond in XeF_2

The three original atomic orbitals contained four electrons. These occupy the molecular orbitals of lowest energy as shown in Fig. 2.3

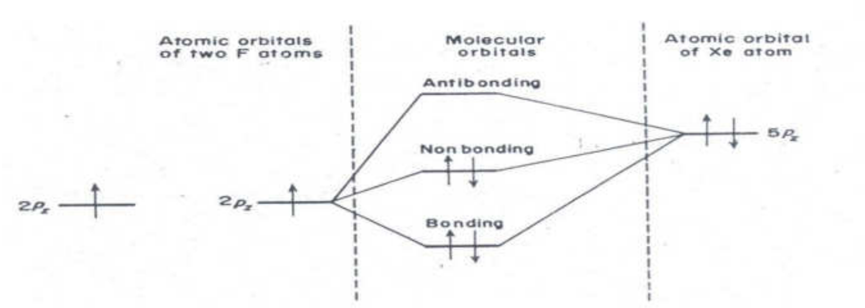


Fig. 2.3: Molecular orbital energy level diagram for XeF_2 molecule

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.

3.2.3 Xenon tetrafluoride

The structure of XeF_4 is square planar (Fig. 2.4). 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 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.

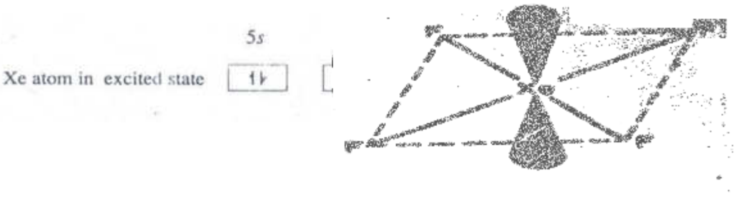
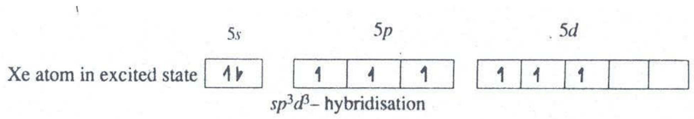


Fig. 2.4: Structure of XeF_4

3.2.4 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. 2.5.



According to molecular orbital 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, molecular orbital theory fails here to predict the correct structure. A more detailed discussion regarding this can be found in higher courses in the subject.

Fig. 2.5: Structure of XeF_6

3.3 Molecular Shapes of Noble Gas Compounds and Valence Shell Electron Pair Repulsion 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 non-bonding (lone pair) of the central atom in a compound, and that the latter exert stronger effect than the former, i.e., the repulsion between lone pair – lone pair electrons is greater than lone pair – bond pair electrons and this in turn is greater than bond pair – bond pair electrons.

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 non-bonding 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 non-bonding 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 rationalisation 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. 2.6) Similarly in xenon tetraoxide, four electron pairs from xenon can coordinate with each of the four oxygens forming a tetrahedral molecule (Fig. 2.7). 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 *pπ-dπ* 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 *pπ-dπ* bonding and considerable polar character. Structural details of some xenon compounds based on VSEPR theory are given in Table 2.3. 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 2.6: Structure of XeO_3

Fig. 2.7: Structure of XeO_4

SELF-ASSESSMENT EXERCISE

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

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

ii) $Xe + F_2 \xrightarrow[\text{Ni crucible}]{1:20\ (Xe:F_2)} ?$

i~~ii) Xe~~$F_2 + 2HCl$ Xe + ? + ?

ii. Give a brief explanation of the following:

i) There are no known compounds of He and Ne?
ii) Noble gas compounds are formed only with O_2 and F_2?

iii. On the basis of VSEPR theory, write the appropriate shapes of the compounds given in column I, in the blank spaces provided in column II.

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

iv. Of what importance are the clathrates of noble gases?

v. Explain why the tendency to form clathrate compounds in group 18 of the periodic table increases down the group.

4.0 CONCLUSION

Xenon compounds are the most numerous of the noble gas compounds. Most of them have the xenon atom in +2, (XeO_2), +4, (XeF_4), +6, (XeF_6), +8, (Na_4XeO_6) oxidation states. The shapes of Xenon compounds can be predicted using valence shell electron pair repulsion theory.

5.0 SUMMARY

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

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

6.0 TUTOR-MARKED ASSIGNMENT

1. Using valence electron pair repulsion theory, draw the structures of XeF_2 and XeF_4. (Time allowed: 10 mins)

7.0 REFERENCES/FURTHER READINGS

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MODULE 2 TRANSITION ELEMENTS

UNIT 1 NATURE AND CHEMISTRY OF TRANSITION ELEMENTS

CONTENTS

1.0 INTRODUCTION

As you already know, elements are classified on the basis of their electron 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 or representative 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 on 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 the 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 between *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 transition elements as 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 include in the discussion on transition elements in this unit.

2.0 OBJECTIVES

By the end of 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.

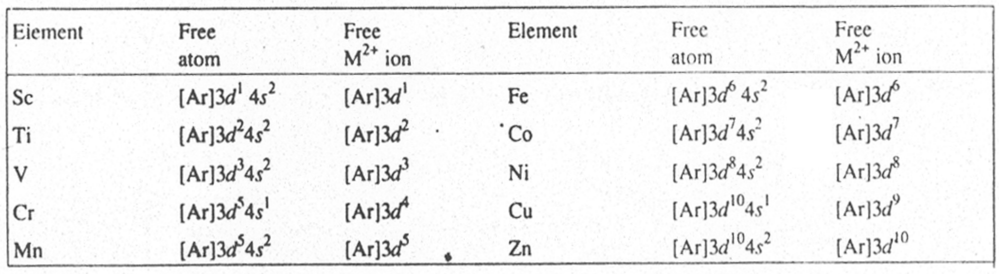
3.0 MAIN CONTENT

3.1 Electron Configuration of Transition Metals

Electron 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 electron configuration of the argon atom is $ls^2 2s^2 2p^6 3s^2 3p^6$. In atoms of the successive elements from potassium to zinc, electrons can enter either 3*d* or 4*s* orbitals. In potassium and calcium atoms the differentiating electrons enter the 4*s* orbitals, so the electron configuration of calcium can be written as $[Ar]4s^2$.

At scandium, the *3d* orbitals begins to be filled 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, Ni^{2+} has the configuration of $[Ar]3d^8$.

Table 3.1: Electron 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 than *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.

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.

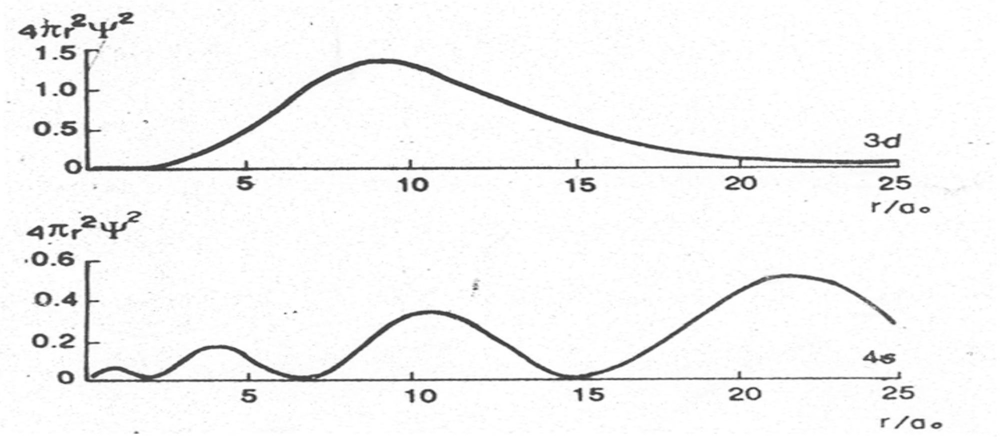


Fig. 3.1: Radial probability functions for 3*d* and 4*s* orbitals in hydrogen atom a_0, the radius of first Bohr orbit is 53.9 pm

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.

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]$4d^{10}5s^2$.

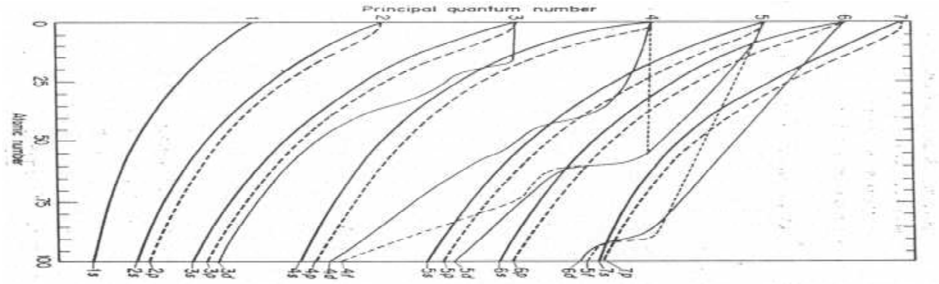


Fig. 3.2: The variation of the energy of atomic orbitals with increasing atomic number inneutral atoms

After xenon, (Kr]$4d^{10}5s^2 5p^6$, 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 Cs and Ba, respectively.

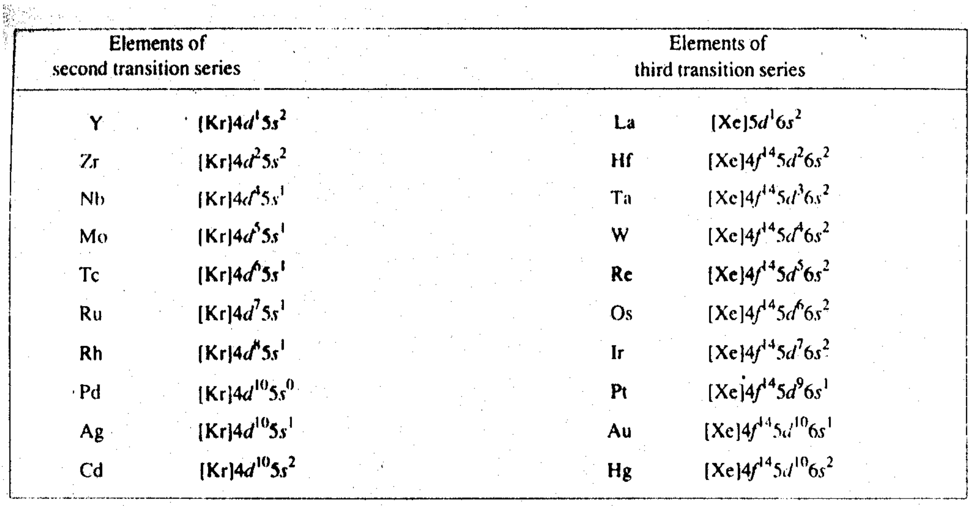
However, the 6*s* electrons do not shield the 4*f* orbitals effectively, so the latter abruptly feel an increase in effective nuclear charge and thus suffer a steep drop in energy (Fig. 3.2). At the same time, with the addition of electrons in the 6*s* orbital, the 5*d* orbitals also drop in energy in the same manner as the 3*d* ones. This creates a situation in which 5*d and* 4*f* 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 4*f* orbital till we reach ytterbium which has the configuration [Xe]$6s^2\ 4f^{14}$.

Now with the 6s and 4*f* shells being filled, the next lowest levels are the *5d* orbitals. Hence from lutetium onwards, the electrons enter the *5d* orbitals. This continues till we reach mercury which has the configuration $[Xe]6^{2}4f^{14}5d^{10}$. The electron configurations of transition elements of *4d* and *5d* transition series are given in Table 3.2.

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 and Cu (belonging to the first transition sends) and Mo and Ag (belonging to the second transition series) their electron configurations are written as $[Ar]3d^{5}4s^{1}$ and $[Ar]3d^{10}4s^{1}$ for Cr and Cu respectively while $[Kr]4d^{10}5s^{1}$ is for Ag. This is because these configurations are considered to give more stability to the elements, rather than $[Ar]\ 3d^{4}4s^{2}$ and $[Ar]\ 3d^{9}4s^{2}$ 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.

Table 3.2: Electron configuration of 4*d* and 5*d* transition elements



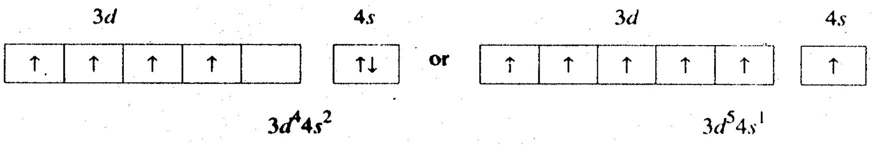
Elements of second transition series		Elements of third transition series	
Y	$[Kr]4d^{1}5s^{2}$	La	$[Xe]5d^{1}6s^{2}$
Zr	$[Kr]4d^{2}5s^{2}$	Hf	$[Xe]4f^{14}5d^{2}6s^{2}$
Nb	$[Kr]4d^{4}5s^{1}$	Ta	$[Xe]4f^{14}5d^{3}6s^{2}$
Mo	$[Kr]4d^{5}5s^{1}$	W	$[Xe]4f^{14}5d^{4}6s^{2}$
Tc	$[Kr]4d^{6}5s^{1}$	Re	$[Xe]4f^{14}5d^{5}6s^{2}$
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	$[Xe]4f^{14}5d^{10}6s^{2}$

3.2 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_{ex} = K x 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 $^{n}C_{2}$. Accordingly, values of P for different values of n are given as:

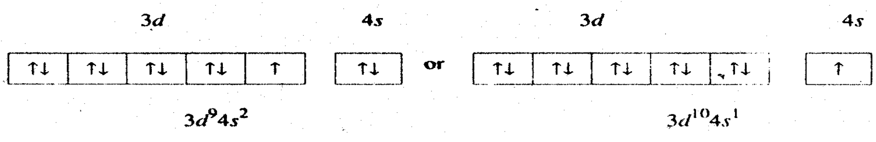
n	1	2	3	4	5	6	7
P	0	1	3	6	10	15	21

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

This gain of 4*K* in exchange energy would favour the $3d^5 4s^1$ configuration for chromium. But you should remember that in achieving this configuration, there would be loss of energy in promoting an electron from 4*s* to 3*d* 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 $3d^9 4s^2$ and $3d^{10}$ $4s^1$ for copper.



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 10*K* and 6*K* i.e. a total 16K towards exchange energy. On the other hand, the latter configuration has two sets of five electrons each with parallel spin which will contribute a total 20*K* towards exchange energy. Thus, there is a net gain of 4*K* 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 4*s* orbital to *3d* orbital, which happens to be less than *4K*, the gain in exchange energy. Hence, the $3d^{10}4s^{1}$ 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 before those of *(n-1)d*. 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.3.2). 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 see 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.

3.3 General Characteristics

In the preceding section you have learnt the electron 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:

1) All are metals and form alloys with one another and with other metallic elements.
2) They are hard, strong, ductile and malleable
3) They have high melting and high boiling points.
4) They are good conductors of heat and electricity.

5) 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.
6) They usually exhibit multiple oxidation states.
7) They form coordination compounds/ions. In fact, the chemistry of the transition elements is mainly associated with the use of *d* as well as ***s*** and *p* orbitals in forming coordination compounds.
8) The transition metal complexes are usually coloured.
9) Most of their compounds are paramagnetic.
10) Many of these elements and their compounds act as catalysts for chemical reactions.

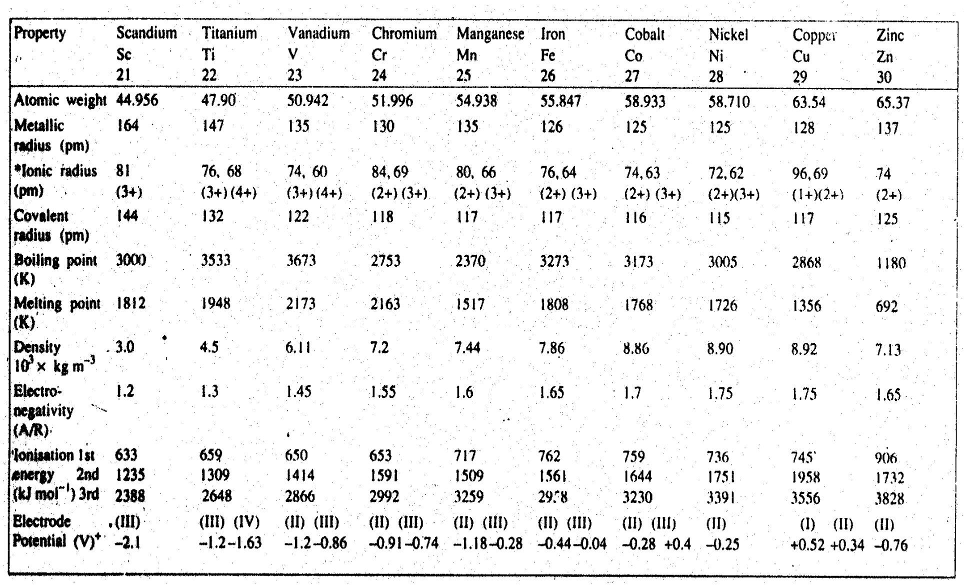
3.4 Periodic Trends in Properties

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 3*d* - series arc listed in Table 3.3. 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 are 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 3.3: 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
Electro-negativity (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	2958	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.**

3.5 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.

As a full coverage of atomic size has already been given in CHM 101 we will briefly go through this topic to recapitulate what we have already learnt earlier.

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 (Table 3.4). 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*f* 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 3.4: 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. 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.

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 the differentiating 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 *4f* orbitals in the lanthanides.

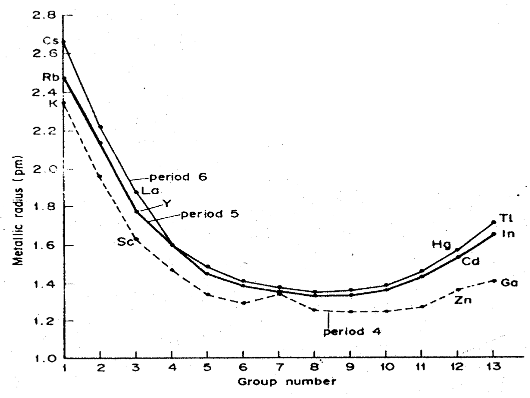


Fig. 3.3: Trend in metallic radii of alkali, alkaline earth and transition metals of fourth, fifth and sixth

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 3.4 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.

3.6 Melting and Boiling Points

The melting and the boiling points of the transition elements are usually high (Fig. 3.5). 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 up to the middle of each transition series and then it decreases with the beginning of electron pairing.

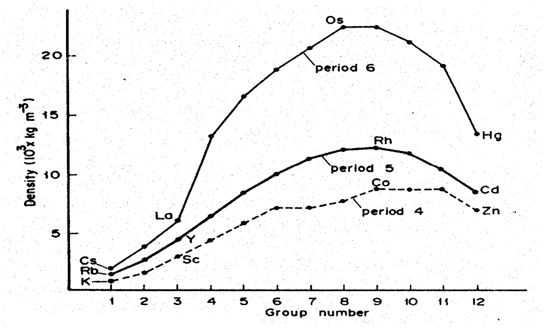


Figure 3.4: The variation of the density of alkali, alkaline earth and transition metals

For the elements of first transition series 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 Fig. 3.5.

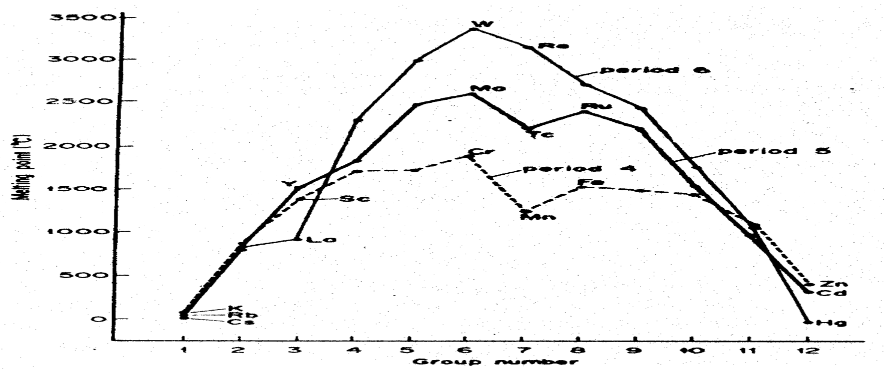


Fig. 3.5: Trend in melting points of alkali, alkaline earth and transition metals of the fourth, fifth and sixth periods

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.

3.7 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 parallel quite closely the trend in atomic size (Fig. 3.6).

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.

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.

1st I.E kJ mol^{-1}

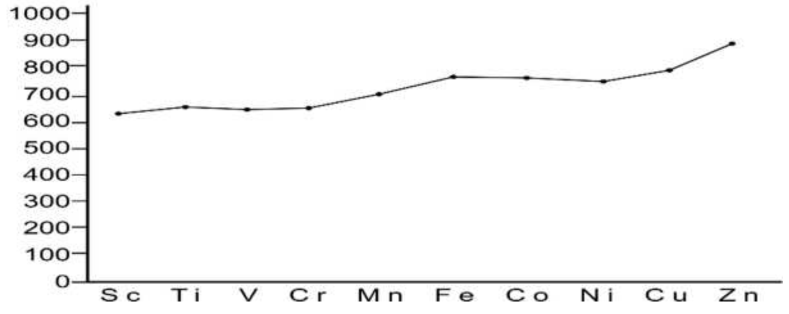


Fig 3.6: The ionisation energies of the elements of the second and the third transition series

3.8 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 lower 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).

3.9 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. Also, there is 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 1M 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 the more the negative the value of the electrode potential for the couple M^{n+}/M, the more is the reducing power of the element. Similarly, the more the positive value of electrode potential for the couple M^{n+}/M, the 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 3.3.

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 3.3, 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. 3.7

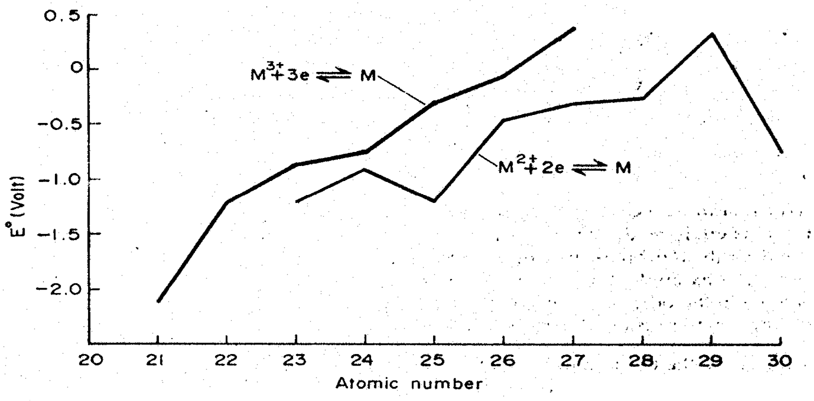


Fig. 3.7: Trends in electrode potentials of transition metals of 3*d* series

SELF -ASSESSMENT EXERCISE

i. Of the following pairs, indicate the element which is larger in size:

   (i) Calcium or scandium?
   (ii) Vanadium or titanium?
   (iii) Chromium or molybdenum?
   (iv) Iron or osmium?

ii. Briefly explain why zinc and cadmium are soft metals.
iii. Which of the two orbitals 3*d* and 4*s* has higher energy at potassium?
iv. Which of Sc^{3+} or Cu^{2+} is paramagnetic? State your reason
v. Which of Zn^{2+} and Cu^{2+} is a transition metal or ion? Justify your choice.
vi. Define standard electrode potential.

4.0 CONCLUSION

These are elements in which the differentiating electron enter (n-1)*d* orbitals. Transition metals also called *d*-block elements are elements with partially filled *d*-subshells in the free or commonly occurring oxidation states. Transition elements have metallic property, an indication that they are hard, ductile, malleable, good conductors of heat and electricity and have high melting and boiling points.

5.0 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:

- The electronic configuration of the transition elements and how the filling of the orbitals takes place with the increase in atomic number.
- 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.
- The variation of size, density, volume, melting and boiling points, ionisation energy, electronegativity, electrode potential, oxidation states and reactivity of the transition metals.

6.0 TUTOR-MARKED ASSIGNMENT

1. Suggest plausible explanation why the melting points of transition metals are generally higher than those of *s*-block elements in the same period. (Time allowed: 5mins)

7.0 REFERENCES/FURTHER READING

Inorganic Chemistry, F.A. Cotton, G. Wilkinson and C.A Murillo, 6th edition John Wiley and Sons Inc., 1999.

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

Concise Inorganic Chemistry, J.D. Lee, Fifth Edition. Wiley India Ltd., New Delhi, India, 2009

Inorganic Chemistry, C. E. Housecroft and A.G Sharpe, 2nd edition, Prentice Hall 2005

Textbook of Inorganic Chemistry. G.S. Sodhi, Viva Books Private Limited, New Delhi, India. 2013

UNIT 2 GENERAL REACTIVITY

CONTENTS

1.0 INTRODUCTION

In module 2 unit1, you learnt about the electron configuration of transition elements and their general properties. In this chapter, you will learn about their general reactivity as well as the properties that are peculiar to these elements.

2.0 OBJECTIVES

By 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 of transition metals.

3.0 MAIN CONTENT

3.1 General Reactivity

Except in 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 like 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.*

3.2 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.

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 +3 **+4**	+1 +2 +3 **+4** +5	+2 **+3** +6	+2 +3 +4 +6 +7	+2 +3 +4 +6	+2 +3 +4	+2 +3 +4	+1 +2	+2
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	**+4**	+3 **+5**	+3 +4 +5 **+6**	+4 **+6** +7	+2 +3 +4 +5 +6 +7 +8	+3 +4 +6	+2 +3 +4	+1 +2 +3	+2
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	**+4**	+4 **+5**	+2 +3 +4 +5 **+6**	+3 +4 +5 +6 +7	+2 +3 +4 +6 +8	+2 +3 +4 +6	+2 +3 +4	+1 +3	+1 +2

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).

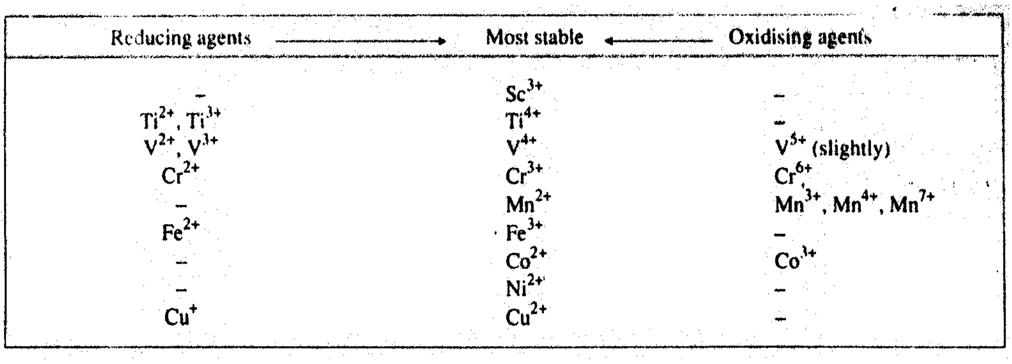
Now let us see the trend in the oxidation states as we go down the group. A full range of oxidation states of the transition elements is shown in Table 3.5. The trend in the stability of oxidation states with in the groups is different for the transition elements and the main group elements *(s* and *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_2CrO_4 is a good oxidising agent forming Cr^{3+} 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 state as in K_2MoO_4 and K_2WO_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, the 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 shows 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+}	–

3.3 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 species referred to as ligands. In the 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 π bonding with ligands.

Majority of the 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 as square planar. 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 examples of transition metal complexes are $[Fe(CN)_6]^{3-}$, $[Ni(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{2-}$, $[Cu(NH_3)4]^{2+}$, etc.

- The availability of low-lying d-orbitals enable metal ions of d-block to accept lone pair electrons from ligands.

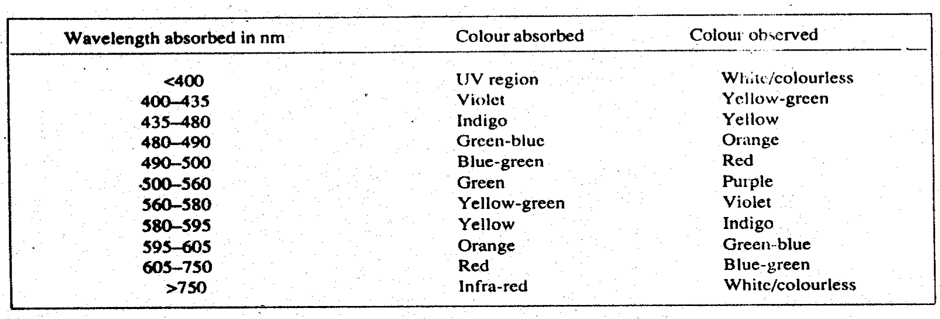
3.4 Colour of Transition Metal Compounds

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. However, on the approach of ligands to form complexes, these *d* - orbitals do no longer remain degenerate, but instead 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 $[Ti(H_2O)_6]^{3+}$, which has one electron in the 3*d* 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 colour and wavelength

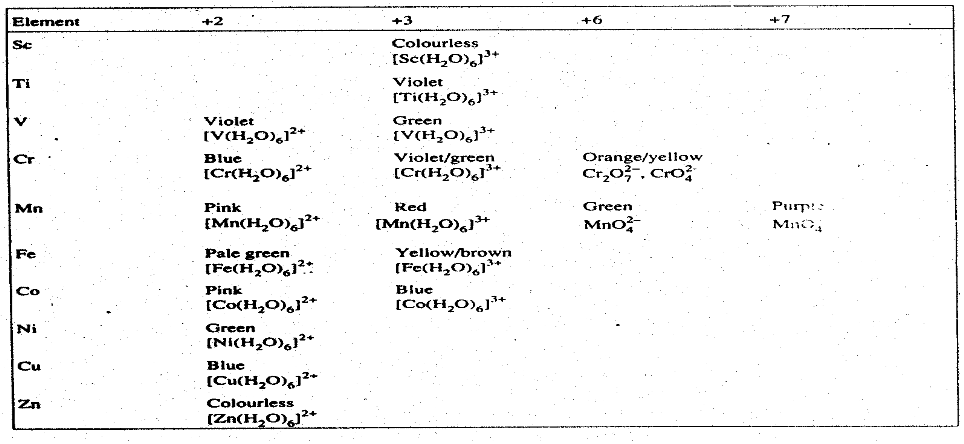


Wavelength absorbed in nm	Colour absorbed	Colour observed
<400	UV region	White/colourless
400–435	Violet	Yellow-green
435–480	Indigo	Yellow
480–490	Green-blue	Orange
490–500	Blue-green	Red
500–560	Green	Purple
560–580	Yellow-green	Violet
580–595	Yellow	Indigo
595–605	Orange	Green-blue
605–750	Red	Blue-green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

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.

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 $[Zn(H_2O)_6]^{2+}$			

3.5 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, μs.

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

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

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

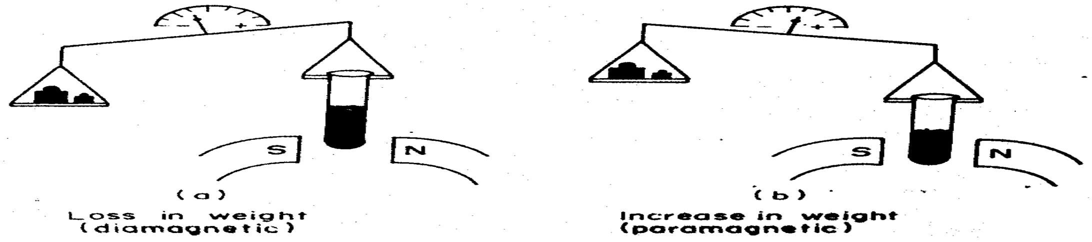
Above expression gives the value of magnetic moment in Bohr magnetons which can be converted into SI unit of Ampere square meter (Am^2) by the following relationship:

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

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)

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.

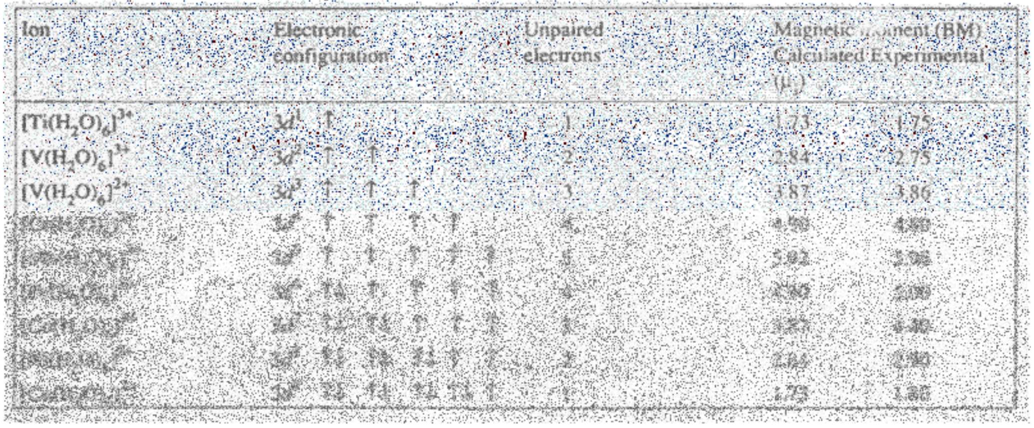
In some cases, (e.g., Mn^{2+}, or Fe^{3+}, where all the *d* orbitals are occupied singly by electrons for which m_l, = 2, 1, 0, -1 and -2, giving $L = 0$), the observed magnetic moment values agree very well with the spin only value as given in Table 3.9. But generally, experimental values differ from 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.


(a) Loss in weight (diamagnetic)

(b) Increase in weight (paramagnetic)

Fig. 3.8: Measurement of molecular paramagnetism using a Gouy balance

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



Ion	Electronic configuration	Unpaired electrons	Magnetic moment (BM) Calculated (μ_s)	Experimental
$[Ti(H_2O)_6]^{3+}$	$3d^1$ ↑	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
[illegible]	$3d^4$ ↑ ↑ ↑ ↑	4	[illegible]	[illegible]
[illegible]	$3d^5$ ↑ ↑ ↑ ↑ ↑	5	5.92	[illegible]
[illegible]	$3d^6$ ↑↓ ↑ ↑ ↑ ↑	4	[illegible]	[illegible]
[illegible]	$3d^7$ ↑↓ ↑↓ ↑ ↑ ↑	3	[illegible]	[illegible]
[illegible]	$3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑	2	2.84	[illegible]
[illegible]	$3d^9$ ↑↓ ↑↓ ↑↓ ↑↓ ↑	1	1.73	[illegible]

3.6 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. $TiCl_4$ as (Ziegler Natta Catalyst) for polymerisation of ethene;
h. Ni (Raney nickel) in reduction process.

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 for photosynthetic process. Both molybdenum and iron are contained in nitrogen fixing enzymes.

3.7 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.

SELF-ASSESSMENT EXERCISE

i. Outline four unique properties of transition metals.
ii. Calculate the magnetic moment of $[Cr(H_2O)_6]SO_4$
iii. Explain why the observed magnetic moment in $[Co(H_2O)_6]^{2+}$ is higher than the calculated value of 3.87 BM.
iv. How does transition metal forms interstitial compounds? Give two examples of such compounds?

4.0 CONCLUSIONS

Transition elements exhibit unique characteristics which include formation of complexes, coloured, paramagnetic and interstitial compounds. In addition, they also act as catalyst in some chemical reactions and exhibit multiple oxidation states.

5.0 SUMMARY

Let us now summarise what we have learnt in this unit. This unit dwells on the unique properties of transition metals. We have learnt:

- Their properties such as colour, magnetic properties, complex formation, catalytic properties and formation of interstitial compounds.
- 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.

6.0 TUTOR-MARKED ASSIGNMENT

1 Which of Sc^{3+} or Cu^{2+} is paramagnetic? State your reason. (Time: 10 mins)

7.0 REFERENCES/FURTHER READING

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UNIT 3 INNER-TRANSITION ELEMENTS

CONTENTS

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 and confusing because 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

By the end of this unit, you should be able to:

- distinguish between transition and inner transition elements;
- define the terms lanthanides and actinides;
- compute the electron 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 MAIN CONTENT

3.1 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 just 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.

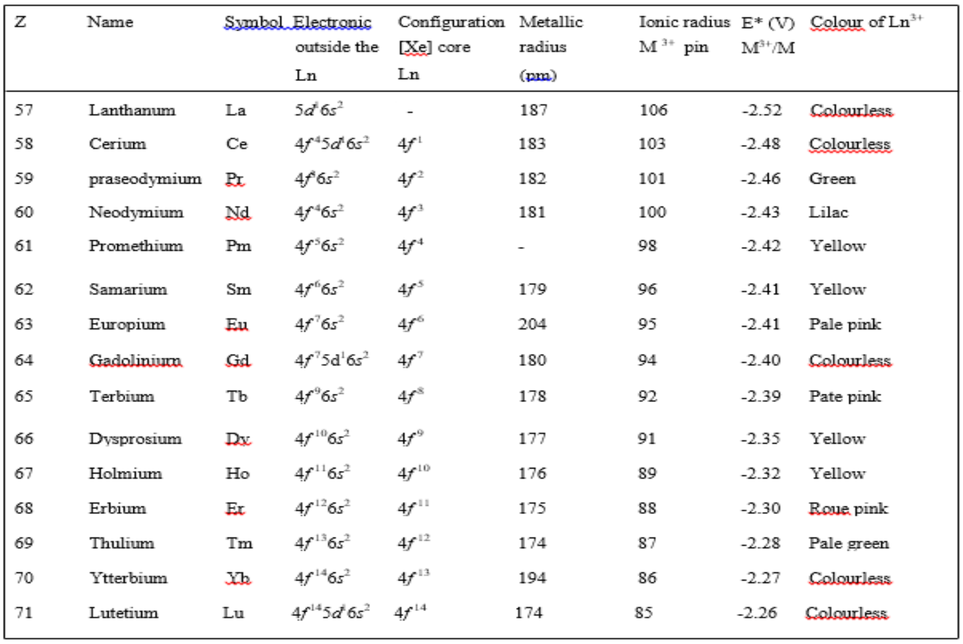
3.1.1 Electron Configuration and Position in Periodic Table

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 electron configuration.

You know that lanthanum, the element preceding the lanthanides in the periodic table, has the electron 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 4*f* orbitals, thereby the elements may have the electron configuration from [Xe] $4f^1 5d^1 6s^2$ to [Xe] $4f^{J4} 5d^1 6s^2$. The actual ground state electronic configurations of lanthanide elements have been determined by atomic spectroscopy and are given in Table 3.10.

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 4*f* orbital. This type of shuttling of electrons can be understood in terms of the comparable energies of the 4*f* 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 vary in a regular manner from [Xe]$4f^1$ for Ce $^{3+}$ to [Xe]$4f^{14}$ for Lu^{3+}(Table 3.10).

Table 3.10: Some Properties of Lanthanum and The Lanthanides

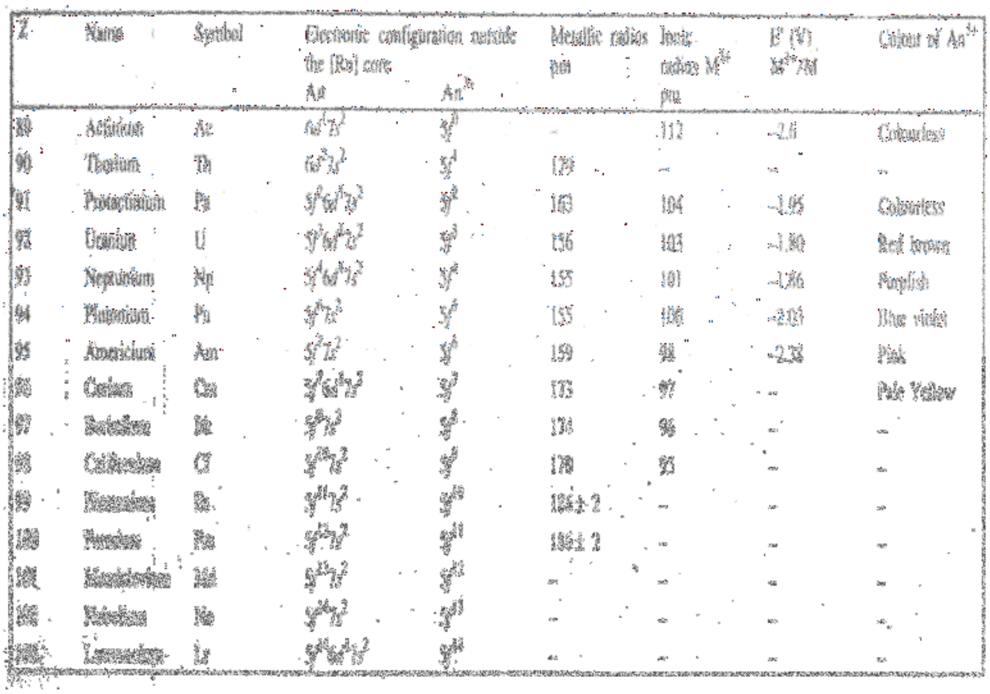


Z	Name	Symbol	Electronic outside the Ln	Configuration [Xe] core Ln	Metallic radius (pm)	Ionic radius M^{3+} pin	E* (V) M^{3+}/M	Colour of Ln^{3+}
57	Lanthanum	La	$5d^16s^2$	-	187	106	-2.52	Colourless
58	Cerium	Ce	$4f^45d^16s^2$	$4f^1$	183	103	-2.48	Colourless
59	praseodymium	Pr	$4f^36s^2$	$4f^2$	182	101	-2.46	Green
60	Neodymium	Nd	$4f^46s^2$	$4f^3$	181	100	-2.43	Lilac
61	Promethium	Pm	$4f^56s^2$	$4f^4$	-	98	-2.42	Yellow
62	Samarium	Sm	$4f^66s^2$	$4f^5$	179	96	-2.41	Yellow
63	Europium	Eu	$4f^76s^2$	$4f^6$	204	95	-2.41	Pale pink
64	Gadolinium	Gd	$4f^75d^16s^2$	$4f^7$	180	94	-2.40	Colourless
65	Terbium	Tb	$4f^96s^2$	$4f^8$	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	Lutetium	Lu	$4f^{14}5d^16s^2$	$4f^{14}$	174	85	-2.26	Colourless

The ground state electron configuration of actinium, [Rn]$6d^17s^2$ is similar to that of lanthanum and indeed the two elements possess similar chemical properties. The electron 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 5*f* and *6d* orbitals in the beginning of the actinide series is less than that between the 4*f* and *5d* orbitals for the lanthanides.

Therefore, both 5*f* and 6*d* orbitals are involved in accommodating successive electrons. Thus, the filling of 5*f* orbitals in actinides (Table 3.11) is not quite so regular as the filling of the 4*f* orbitals in the case of the lanthanides. Later, however, the 5*f* orbitals become more stable, i.e., by the time plutonium and subsequent members of the series are reached, the 5*f* orbitals seem clearly to be of lower energy than the *6d* orbitals, and so the electrons preferably fill the former.

Table 3.11: 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	$6d^1 7s^2$	$5f^0$	–	112	–2.6	Colourless
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	179	–	–	–
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	163	104	–1.95	Colourless
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	156	103	–1.80	Red brown
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	155	101	–1.86	Purplish
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	155	100	–2.03	Blue violet
95	Americium	Am	$5f^7 7s^2$	$5f^6$	159	98	–2.38	Pink
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	173	97	–	Pale Yellow
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	174	96	–	–
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	170	95	–	–
99	Einsteinium	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	$5f^{14} 6d^1 7s^2$	$5f^{14}$	–	–	–	–

3.1.2 Atomic Radius

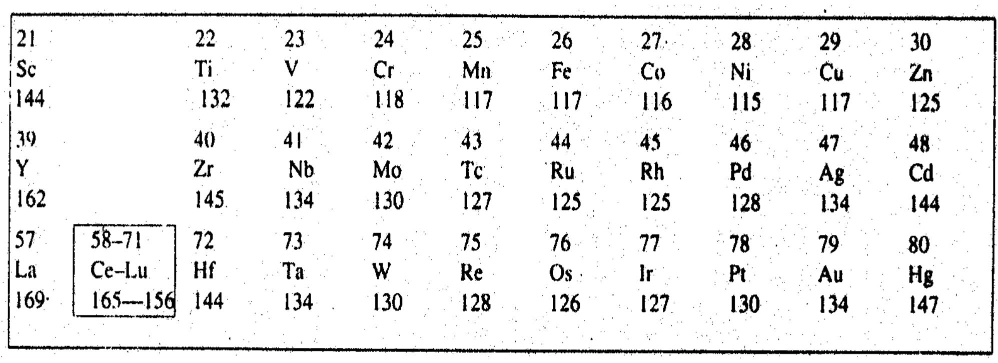
You have studied in CHM 101 that the atomic size decreases with increase in atomic number along any period in the long form of the periodic table due to increase in effective nuclear charge. However, the decrease in atomic radius is small when the difference in electronic configuration from one element 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 3.10) and also long the actinide series (Table 3.11) 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 3.12). 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 3.12: Atomic (covalent) radii (pm) of the elements preceding and following the lanthanides



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

3.1.3 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} electron 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 Table3.13 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 313: 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									

3.1.4 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.

3.1.5 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.

3.1.6 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 β-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(NO3)4(OPPh3)2] and$[Ce(NO_3)_6]^{2-}$ 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.

3.1.7 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^0 (e.g., La^{3+}, Cc^{4+}. Ac^{3+}, Th^{4+}, Pa^{5+}, U^{6+}) and f^{14} configurations (e.g., Yb^{2+}, Lu^{3+}, Lr^{3+}) are all paramagnetic. This is 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 4*f* 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 5*f* 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 5*f* and *6d* electrons as compared with 4*f* 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.

3.1.8 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:

$$2M + 6H_2O \rightarrow 2M(OH)_3 + 3H_2$$

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:

$$2Ln + 6HCl \rightarrow 2LnCl_3 + 3H_2$$

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.

$$4Ln + 3O_2 \rightarrow 2Ln_2O_3$$

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

$$Ce + 2F_2 \longrightarrow CeF_4$$

The metals react exothermically with hydrogen, though heating to 600-700 K is often 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.

3.2 Occurrence, extraction and Uses

All the lanthanide and actinide elements are highly reactive metals, therefore, none of them occurs freely in nature, but in combined form. Moreover, all the actinide elements are radioactive, so most of them do not occur naturally and have been prepared artificially since 1940. Let us now discuss the occurrence, extraction and uses of these elements.

3.2.1 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 up to 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 8.1×10^{-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 2.3×10^{-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.

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 be 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 $2Ln(NO_3)_3.3Mg(NO_3)_2.24H_2O$ and $Ln_2(SO_4)_3.Na_2SO_4.xH_2O$ 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, $-SO_3H$ 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:

$Ln(O_3SR)_3 + (NH_4)_3EDTAH \rightarrow Ln(EDTAH) + 3NH_4O_3SR$

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:

$2Ln(EDTAH) + 3(NH_4)_2C_2O_4 \rightarrow Ln_2(C_2O_4)_3 + 2(NH_4)_3EDTAH$

$Ln_2(C_2O_4)_3 \rightarrow Ln_2O_3 + 3CO + CO_2$

Samarium, europium and ytterbium are prepared by reduction of the oxides with La at high temperatures:

$2LnO_3 + 2La \rightarrow Ln_2O_3 + 2Ln$, Ln = Sm and Eu

Other lanthanides are obtained by the reaction of $LnCl_3$ or LnF_3 with Ca metal at

1300K. $LnCl_3$ or LnF_3 are prepared by heating Ln_2O_3 with appropriate ammonium halide:

$Ln_2O_3 + 6NH_4X \rightarrow 2\,LnX_3 + 6NH_3 + 3H_2O$

$2LnX_3 + 3Ca \rightarrow 2Ln + 3CaX_2$

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 or uraninite, containing mainly U_3O_8. The concentrated ore 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_8 with aluminium powder produces uranium metal. All these steps involved in extraction of uranium from pitchblende are summarized in Figure 3.9.

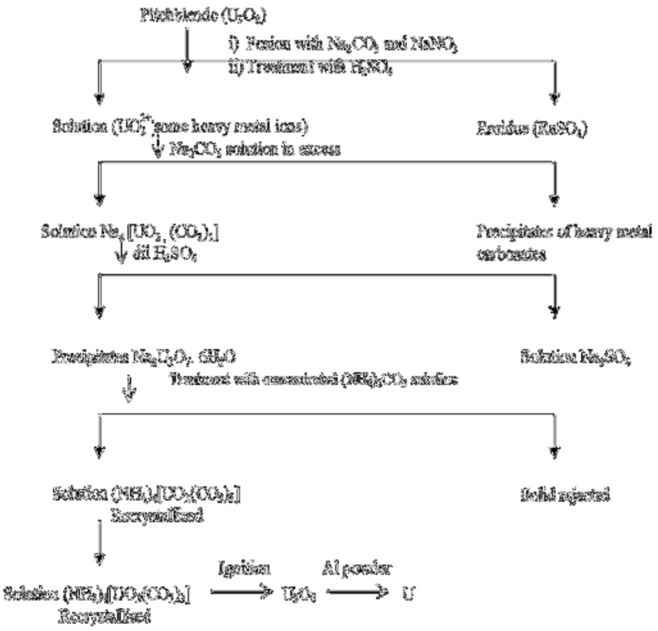


Fig. 3.9: Extraction of uranium from pitchblende

3.2.3 Uses of Inner Transition Elements

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

i. What are lanthanides and actinides? Why are they so called?
ii. Write the electron configurations of the elements of atomic numbers 61 and 95
iii. Why is the separation of the lanthanides so difficult?
iv. List three important methods that can be used for the separation of lanthanide metals.
v. Outline some similarities between lanthanides and actinides.
vi. Give two examples of double salts that can be formed by lanthanides.
vii. One of the following can be used to precipitate lanthanide element from an aqueous solution containing mixture of lanthanides. (A) NaCl (B) NaOH (C) KCl (D) $CaCl_2$
viii. Outline four uses of lanthanide elements or compounds.

4.0 CONCLUSION

These are the elements in which the differentiating electron enters (n-2)*f* orbitals. Hence, they are known as *f*-block elements. There are two series of *f*-block elements which are lanthanides or lanthanoids (4*f* series) and actinides or actinoids (5*f* series). Both lanthanides and actinides are electropositive and have strong reducing characteristics. Both series have stable oxidation state of +3 and are coloured due to *f*-*f* transition. The series also show a gradual decrease in ionic radii.

All the lanthanides occur together in nature, their separation from one another is usually a very difficult task. This is because they are typically trivalent and are identical in size and chemical properties. Ion exchange chromatography is the most important, efficient and rapid method for the separation and purification of these elements.

Most of the actinides although highly reactive are radioactive and do not occur naturally.

5.0 SUMMARY

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

- 1.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 that are 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.

6.0 TUTOR-MARKED ASSIGNMENT

1. Compare the ability of lanthanides and actinides to form complexes. (Time: 6 mins)

7.0 REFERENCES/FURTHER READING

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MODULE 3 COORDINATION CHEMISTRY, BONDING THEORIES AND RADIOACTIVITY

Unit 1 Introduction to Coordination Chemistry
Unit 2 Bonding Theories and Radioactivity

UNIT 1 INTRODUCTION TO COORDINATION CHEMISTRY

CONTENTS

1.0 INTRODUCTION

In module 2 unit 2 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.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- define the term coordination compound and coordination number;
- state the postulates of Werner theory and valence bond theory of coordination compounds.

3.0 MAIN CONTENT

A coordination compound is a compound of either neutral complex or complex ion and other ion. A complex could be an ion or a compound consisting of a central metal ion or atom surrounded by and datively bonded to other ions or molecules called ligands. A ligand is a species which can either be an ion or a molecule containing at least one atom having a lone pair of electrons which can be donated to the central cation or atom to form dative or coordinate covalent bond. Hence, in coordination compounds, the central atom acts as Lewis acids and since ligands are electron pair donors, they function as Lewis bases.

The coordination compounds are; therefore, Lewis adducts. The branch of chemistry under which properties of such compounds are studied is called Coordination Chemistry. There is no sharp dividing line between the coordinate covalent 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 cationic central species M^{n+} surrounded by ligands L_1, L_2, etc. (the ligands may be same or different). The total charge on the resulting complex, is determined by the algebraic summation of the charges 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 Werner's Complexes.

3.1 Classification of Ligands

In a coordination compound as noted earlier, 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:

- Monodentate ligands: These are ligands that donate only one lone pair to a metal atom or metal ion in a coordination compound, e.g., halide ions, ammonia, water and PR_3.
- Bidentate ligands: These are ligands having two donor atoms. As a result of the coordinate bond formation, a bidentate ligand results in the formation of a ring structure by incorporating the metal ions called the chelate ring. The bidentate ligands, may be

neutral compounds (diamines, diphosphine, disulphides) or anions like oxalate, carboxylate, nitrate, or glycinate ions.

- Polydentate ligands – These include ligands having more than two donor atoms in their molecules, and can be called the tri tetra, penta or hexadentates 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 coordination purposes. Thus, sulphide or nitrate ion may act as a mono or a bidentate ligand depending on the complexes concerned. Though OH^- or NH_2^- act as a monodentate ligand, they can also function as bidentate ligands by serving as bridging ligands between two metal ions.

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

- Ligands having no available
- 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 - 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^-, pyridine (py), acetylacetonato ion ($acac^-$), etc.
- Ligands without unshared lone pair, but having □-bonding electrons e.g., alkenes, alkynes, benzene, cyclopentadinyl anion.
- Ligands that can form two sigma bonds with two separate metal atoms and Therefore, can form bridges e.g. OH^-, Cl^-, NH_2^-, O_2^{2-}, CO, $O^{2-,}$ etc.

Many polydentates can have their donor atoms same or different and, therefore, cannot be classified as belonging to any of the above classes.

On the basis of formation of complexes with different atoms, Pearson in 1967 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 □ 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. These metal ions have nearly filled *d* orbitals electrons that can form □ bonds with the ligands and can accept *d* orbital electrons in their *d* orbitals eg. Cu(I), Hg(II), Pd(II), Pt(II), PR_3, etc.

The coordination number is the number of covalent bonds that can be formed between ligands attached directly to the central metal ion in a coordination compound. It can also be referred to as the number of atoms in a ligand that are coordinated directly to the central atom in a complex or complex ion. About 98% of the complexes belong to the coordination number 4 or 6, even though the coordination numbers from 2 to 12 are observed in the complexes. The coordination number of 3 and 7 are rare and 5 is uncommon, present mostly for stereo-chemically rigid ligand complexes.

3.2 Bonding Theories in Coordination Compounds I

3.2.1 Werner's Coordination Theory

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

- Two types of valencies exist for a coordination compound or a complex ion, and they are called
- primary (or ionisable) valency and secondary (or non-ionisable) valency.
- The number of the secondary valences for a complex ion is fixed e.g. six for Cr^{3+}, Co^{3+}, $T1^{3+}$,
- Fe^{3+}, four for Pt^{2+}, Pd^{2+}, Cu^{2+}, Ni^{2+} and two for Cu^{+}, Ag^{+}, Au^{+} and Hg^{2+}.
- The secondary valencies must be satisfied by anions or neutral molecules (e.g. halide, cyanide, ammonia, amine, water, etc.) and positive ion, in rare cases (e.g. hydrazinium ion) having at least one lone pair of electrons in each case.
- The primary valencies are satisfied by the anions if the complex formed is cationic or vice versa.
- The secondary valences are fixed in space and possess a definite geometric arrangement even in solution. Thus for four secondary valencies 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 $[Co(NH_3)_6]^{3+}3Cl^{-}$.

3.2.2 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 are that a pair of the electrons from the donor atoms are donated to empty orbital of the metal ion. 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.
- 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
- bonding.
- Hund's rule applies to the electrons in the non-bonded orbitals, presence of unpaired electrons in the complexes giving paramagnetism.

SELF-ASSESSMENT EXERCISE

i. What do you understand by the term *complex* in transition metal chemistry?
ii. Explain the terms: Ligand and metal chelate
iii. What is a chelating ligand? Give an example.
iv. Give 3 examples each of the following:
    a) anionic complexes
    b) neutral complexes
    c) cationic complexes

4.0 CONCLUSION

Coordination compounds are addition compounds formed when stoichiometric quantities of two or more species join together. The species that are linked to central metal atoms or ions are called ligands. Various bonding theories were advanced to explain some of the properties of the coordination compounds. These include valence bond theory, crystal field, ligand field theory and molecular orbital theory. None of these theories can individually explain all the properties of complexes. Hence a combination of these theories are used due to the covalent and ionic characteristics of these compounds.

The need to provide explanation to some of the properties of coordination compounds led to postulation of bonding theories

5.0 SUMMARY

In this unit, you have been introduced to the theories of coordination compounds and bonding. The main aspects are

- Classification of ligands
- the postulates of valence bond and Werner's theory of coordination compound

6.0 TUTOR-MARKED ASSIGNMENT

1. What are ligands?
2. Give four examples of ligands commonly encountered in transition metal chemistry. (Time: 3mins)

7.0 REFERENCES/FURTHER READING

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

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UNIT 2 BONDING THEORIES AND RADIOACTIVITY

CONTENTS

1.0 INTRODUCTION

In the last unit (module 4 unit 1) you were introduced to bonding theories in complex various complex formation. In this unit, we shall be dealing with other coordination theories. You would also be introduced to the phenomenon called radioactivity. This was discovered by Antoine Henri Becquerel when he observed that photographic plates developed when exposed to uranium minerals and the name radioactivity was invented sometimes later by Marie Curie.

2.0 OBJECTIVES

By the end of the unit, you should be able to:

- define bonding in coordination compound; crystal field and molecular orbital theories;
- identify the differences between valence bond and molecular orbital theories of fieldtheories;
- state characteristics of radioactivity;
- identify various types of radiations.

3.0 MAIN CONTENT

3.1 Ligand and Crystal Field Theories

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.

3.1.1 Molecular Orbital Theory

It assumes that electrons move in molecular orbitals (M.O.) which extends over all the nuclei 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.

Molecular orbitals have the following characteristics:

- Molecular orbitals like atomic orbitals have definite energy.
- Nomenclatures like *s, p, d,* etc. used for atomic orbitals are replaced by sigma, pie and delta.
- Paulis principle applies to molecular orbital, so that no single molecular orbital contains two precisely with same four quantum number.
- In filling molecular orbitals Afbau principle is applied.

3.1.2 Differences Between the Valence Bond and Molecular Orbital Theories

- The atoms in the valence bond theory, unlike in the molecular orbital still retain their individual
- identity even when they are chemically bonded.
- Valence bond theory introduces the concept of resonance but this is not significant in the molecular orbital theory.
- According to valence bond theory, an electron moves under the influence of only one nucleus of an atom but this is contrary to molecular orbital
- theory, where an electron moves under the influence of the combining atoms.
- he valence bond theory could not explain the paramagnetic behavior of B_2 and O_2. This limitation is absent molecular orbital theory approach.

- Unlike in 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.

3.1.3 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* orbitals 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.

Successes of Crystal Field Theory

The theory has been able to explain the following:

- Spectra of coordination compounds.
- The magnetic properties of such compound.
- Thermodynamic properties of metal ion such as lattice energy, ionic radii.
- The kinetics and mechanisms of coordination compounds reaction.
- The geometry of the complexes.

Limitation of Crystal Field Theory

The crystal field theory suffers the following setbacks

- inability to classify ligands in to strong and weak field;
- Nephelauxetic effect;
- anti-ferromagnetic coupling;
- intensity of d-d transitions;
- electron spin transition spectroscopy, etc.

3.2 Radioactivity

Radioactivity is the property by which some compounds emits radiation 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.

3.2.1 Characteristics of Radioactivity

Radioactive substances spontaneously and continually emit radiation. The rate at 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) fluoresce. Radioactivity is always accompanied by the evolution of a large amount energy. Radioactivity also has physiological effects, and some of them could be cumulative with time. The basic effect of radiation on any living organism is the destruction of cells.

3.2.2 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) or $^{4}_{2}\mathrm{He}$ or □ (beta) particles and □ (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 (□-rays, $^{4}_{2}\mathrm{He}$)**
They are positively charged particles being a mass four times that of the hydrogen atom and bearing two units of charge. They have very little penetrating power.

b. **Beta Rays (□-rays)**
These are fast moving streams of electrons. They may be positively or negatively charged. But usually the term □-rays refer to negatively charged particles. They have a very high penetrating power but are much less effective in ionising gases or matter.
With beta-decay the mass number is unaltered, but there is a loss of one unit of negative charge e.g.

$$^{234}_{90}\mathrm{Th} \rightarrow \quad ^{234}_{91}\mathrm{Pa}\ (\beta^{-}\ \text{decay})$$

$$^{11}_{6}\mathrm{Ca} \rightarrow \quad ^{11}_{5}\beta\ (\beta^{+}\ \text{decay})$$

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.

SELF-ASSESSMENT EXERCISE

i. The name given to a species that is bonded to a central atom in a complex is called
ii. Outline three applications of crystal field theory
iii. Outline four setbacks of crystal field theory.
iv. Give four unique properties of nuclear reactions.

4.0 CONCLUSION

Various bonding theories were advanced to explain some of the properties of the coordination compounds. None of the bonding theories could individually explain all the properties of complexes. Hence, a combination of these theories is used to explain some of the properties of coordination compounds due to their covalent and ionic characteristics.

Radioactive substances emit different types of radiations such as alpha, beta, gamma, etc.

5.0 SUMMARY

In this unit, you have been introduced to the following

- Crystal field and molecular orbital theories of coordination compounds
- Differences between the valence bond and molecular orbital theories
- Types of radioactive radiations.

6.0 TUTOR-MARKED ASSIGNMENT

1. Compare and contrast between electron and beta particles. (Time: 5 mins)

7.0 REFERENCES/FURTHER READING

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MODULE 4 ISOLATION AND PURIFICATION OF METALS

UNIT 1 METALLURGY

CONTENTS

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

By the end of 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 Abundance of Metals in the Earth Crust

3.1 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 5.1. You may note that about 75% of the earth's

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	**0.005**
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

crust is composed of non-metals, oxygen and silicon. The relative abundance of only three industrially important metals, i.e., aluminium, iron and magnesium are 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 at 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 over-burden. The thickness of over-burden 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.

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:

3.1.1 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.

3.1.2 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.

3.1.3 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 (Fe_2O_3), magnetite (Fe_3O_4), bauxite ($Al_2O_3.2H_2O$), cassiterite (SnO_2), cuprite (Cu_2O), zincite (ZnO), rutile (TiO_2), pyrolusite (MnO_2), chromite ($FeO.Cr_2O_3$), uraninite or pitchblende ($2UO_3.UO_2$), etc.

3.1.4 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.

3.1.5 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 ($KCl.MgCl_2.6H_2O$), 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 indicated 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.

3.2 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 practiced 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 floatation, which we will now discuss in brief.

3.2.1 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.

3.2.2 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 *pulley* in a magnetic field (Fig. 5.1). The non- magnetic gangue particles fall off in a *vertical* position when the belt passes over the *pulley*, 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), *wolframite* ($FeWO_4+MnWO_4$), chromite ($FeO+Cr_2O_3$) and ilmenite ($FeO.TiO_2$) are some of the minerals which are separated from non- magnetic impurities by this method.

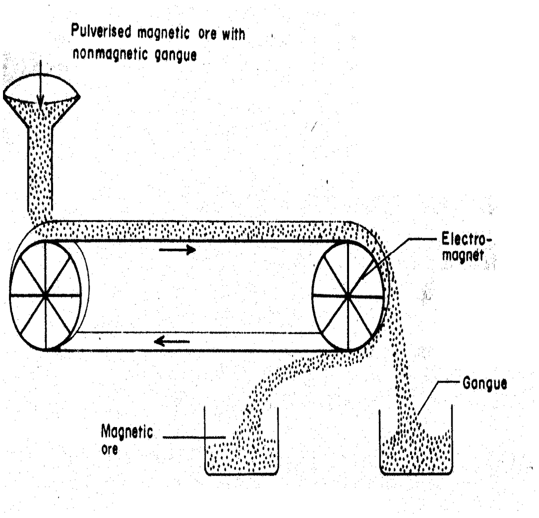

Fig. 5.1: Magnetic separation of ores

3.2.3 Froth Floatation Process

Froth floatation 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 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).

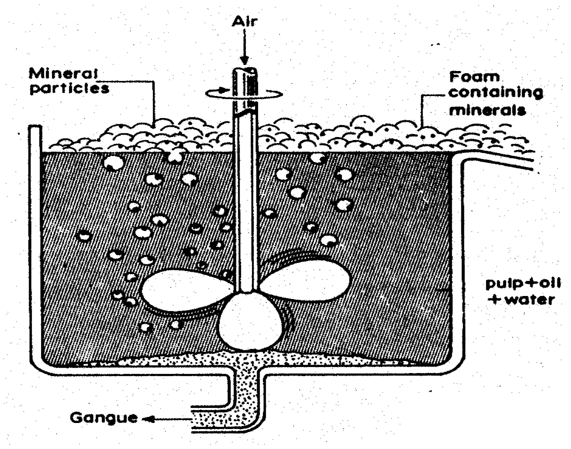

Fig. 5.2: Froth floatation process for concentration of sulphide ores

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 *depressant***,** which suppresses the *floatation* 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 floatation 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 floatation.*

3.3 Reduction to Metal

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.

3.3.1 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.

3.3.2 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.

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

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

3.3.3 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 like sulphides of arsenic and antimony also get oxidised and volatilised. For example,

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2\uparrow$$

$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

$$2ZnO + 3O_2 \longrightarrow 2ZnO + 2SO_2\uparrow$$

$$2As_2S_3 + 9O_2 \longrightarrow 2As_2O_3\uparrow + 6SO_2\uparrow$$

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:

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

$$2HgO \xrightarrow{800\ K} 2Hg + O_2 \uparrow$$

3.3.4 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.

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

$$SiO_2 + FeO \longrightarrow FeSiO_3$$

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 least 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:

$$ZnO_{(s)} + C_{(s)} \longrightarrow Zn_{(s)} + CO_{(g)}$$

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:

$$GeO_2 + 2H_2 \longrightarrow Ge + 2H_2O$$

$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

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-Thermite process (Thermite reduction).*

$$Cr_2O_{3(s)} + 2Al_{(s)} \longrightarrow 2Cr_{(l)} + Al_2O_{3(l)}$$

$$3MnO_{2(s)} + 4Al_{(s)} \longrightarrow 3Mn_{(l)} + 2Al_2O_{3(l)}$$

$$3BaO_{(s)} + 2Al_{(s)} \longrightarrow 3Ba_{(l)} + Al_2O_{3(l)}$$

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.*

$$TiCl_{4(g)} + Mg_{(l)} \xrightarrow[\text{He or Ar}]{1000\text{ K}} Ti_{(s)} + 2MgCl_{2(l)}$$

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.

3.3.5 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 the 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.

Scientist, H. J. T. Ellingham investigated the variation of standard free energy change, $\Delta G°$ for the formation of a number of oxides, sulphides and chlorides of some elements, with temperature in 1944. These plots are known as **Ellingham diagrams**. As stated earlier, $\Delta G°$ is related to $\Delta H°$, $\Delta S°$ and T according to the following equation:
$\Delta G° = \Delta H° - T\Delta S°$.

It should be reminded 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 diagram for the formation of metal oxides from free elements. By examining the diagram, the temperature at which the standard free energy change for the formation of an oxide becomes positive, can be obtained. For example, consider the $\Delta G° /T$ graph for the reaction of zinc with oxygen:

$$2\,Zn_{(s)} + O_{2(g)} \longrightarrow 2\,ZnO_{(s)}$$

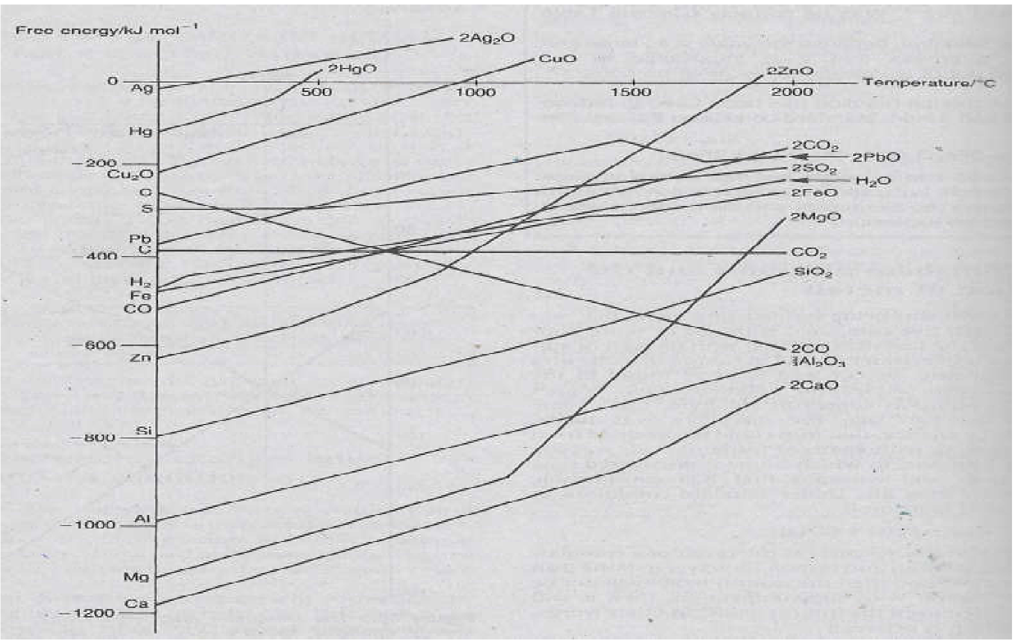

Fig. 5.3: Ellingham diagram showing the variation of the free energy of formation of metal oxides with temperature

At 0°C (273 K), the value of standard free energy change for this reaction is about -600 kJ, which becomes less negative as temperature rises and eventually at becomes zero at about 1,900°C. Above this temperature, ΔG° 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, standard free energy changes for a large number of reactions can be obtained. For example, the standard free energy change can be obtained from the plots for the following two reactions at 25°C:

$$2C_{(s)} + O2_{(g)} \rightarrow 2CO_{(g)}: \Delta G^\circ = -275\ \text{kJ} \qquad \text{(a)}$$

$$ZnO_{(s)} \rightarrow 2Zn_{(s)} + O2_{(g)}: \Delta G^\circ = +600\ \text{kJ} \qquad \text{(b)}$$

It may be noted that the standard free energy change in the above, equation (b), is positive because it represents the decomposition of zinc oxide. On adding the above two equations (a and b) and respective ΔG° values. The following overall reaction is obtained.

$$2ZnO_{(s)} + 2C_{(g)} \rightarrow 2Zn_{(s)} + 2CO_{(g)}: \Delta G^\circ = +325\ \text{kJ}$$

Because the standard free energy change for the above reaction is positive, the reaction has little tendency to occur at 25°C (298K). 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 until the point of intersection of the two plots for C/CO and Zn/ZnO systems is reached at about 900°C. Above this temperature, $\Delta G°$ will become negative. Therefore, carbon will reduce zinc oxide above this temperature - a temperature of 727°C lower than the temperature of thermal decomposition of zinc oxide. Similarly, with the help of Ellingham diagram for Zn/ZnO and H_2/H_2O systems, we can find out that H_2 will reduce ZnO at a temperature of 1,127°C. 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.

In the case of carbon or carbon(II) oxide reacting with oxygen molecule, the following reactions as illustrated by equations (c) and (d) are possible. In equation(c), there is no significant change in ΔS of the reaction, hence the plot of ΔG versus temperature is horizontal (Fig. 5.3). But in equation (d), there is a decrease in the value of ΔS, thus the slope is positive. This is also the case with all metal oxides formation.

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad (c)$$

$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)} \qquad (d)$$

Ellingham diagram is 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 in to that particular element and oxygen. In a couple of processes, one metal can be used to reduce the oxide of other metals which lie above it in the diagram. This is because the free energy will be more negative by an amount equal to the difference between the two plots at the given temperature. As it can be seen from above that carbon reduces ZnO above 900°C, but below this temperature zinc will reduce CO.

Hence, theoretically carbon will reduce all oxides. But the great difficulty in obtaining very high temperatures coupled with the formation of carbides during the process have made preparation of the more electropositive metals using this method impossible. It is also clear from the Ellingham diagram 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.

Also, all oxides can be decomposed to give metal and oxygen molecule. But in practice, some metal oxides, such as those of Ag, Au and Hg would decompose at low temperature. Therefore, these metals can be extracted by thermal decomposition of their oxides.

Figure 5.4 shows the Ellingham diagram for sulphides of various elements. When carbon and hydrogen are used to reduce sulphides, CS_2 and H_2S are obtained respectively. It can be observed from the diagram that none of the other lines are crossed by CS_2 and H_2S. Therefore, carbon and hydrogen are not effective reducing agents for metal sulphides. Instead, the sulphides are first roasted in air to convert them to oxides, which are then reduced.

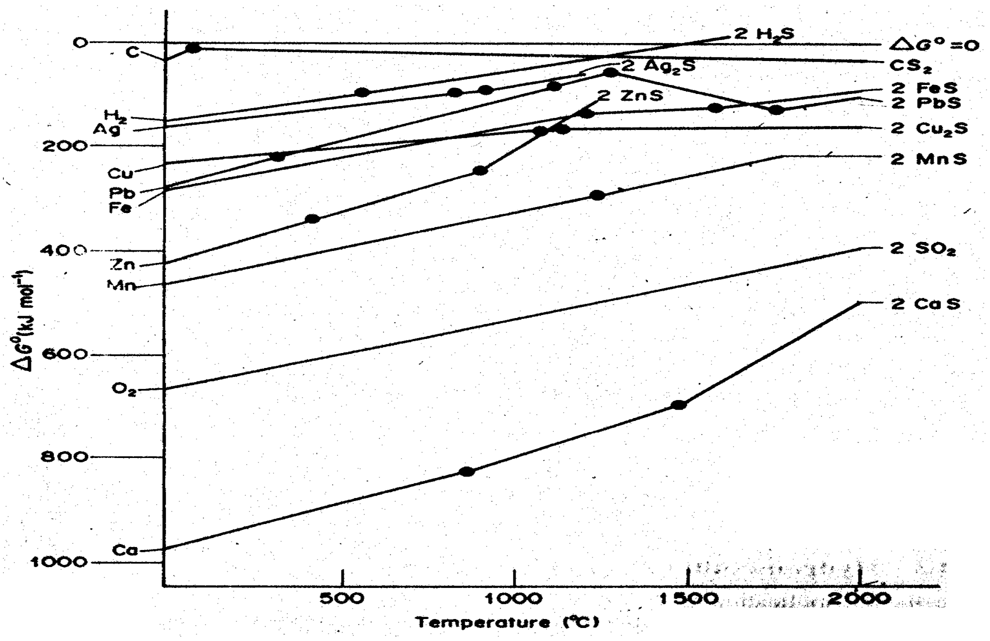

Fig. 5.4: Ellingham diagram showing the variation of the free energy of formation of metal sulphides with temperature

The Ellingham diagram for chlorides is shown in Fig 5.5. It can be considered from the diagram that carbon cannot be used as a reductant for chlorides, but hydrogen can be used for this purpose, especially at higher temperatures.

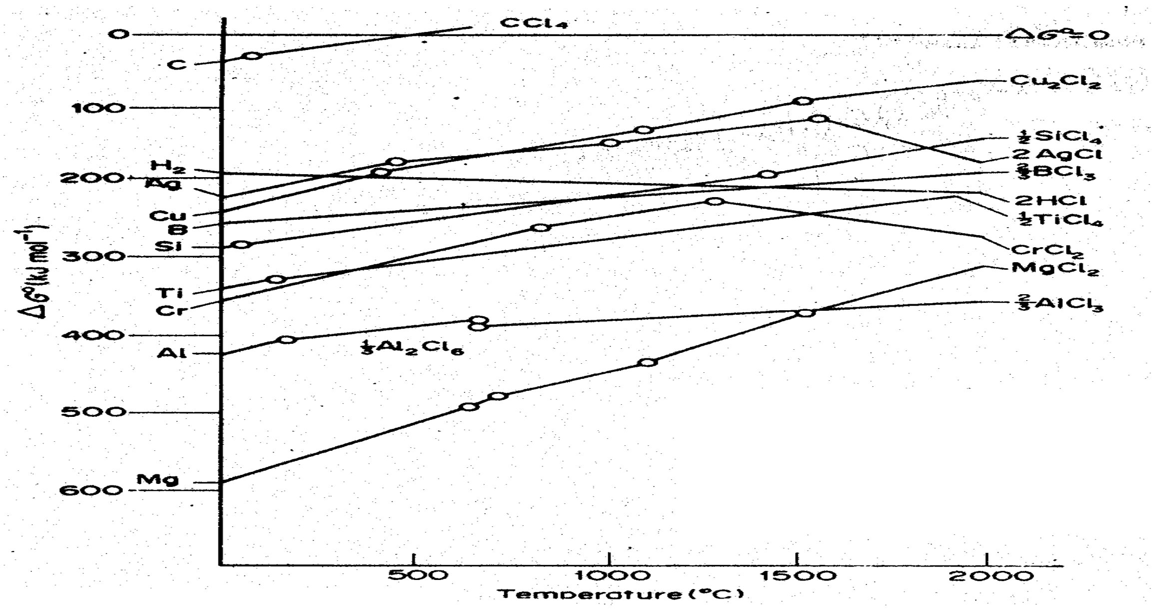

Fig 5.5: Ellingham diagram showing the variation of the free energy of formation of metal halides with temperature

3.3.6 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 particles. 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:

$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$

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

$Cu_2O + 2H_2SO_4 + 2O_2 \longrightarrow 2CuSO_4 + SO_2 + 2H_2O$

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 $Na[Ag(CN)_2]$:

$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$

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:

$CuSO_4 + Fe \longrightarrow Cu + FeSO_4$

$2Na[Ag(CN)_2] + Zn \longrightarrow 2Ag + Na_2[Zn(CN)_4]$

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:

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

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

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

3.3.6 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 no chemical-reducing agents strong enough to prepare these metals
- where the oxide gets reduced at very high temperatures where formation of carbides can take 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. 5.6). Following reactions take place during electrolysis:

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

Cathode: $2Na^+ + 2e \longrightarrow 2Na(l) \quad Mg^{2+} + 2e \quad Mg(l)$

$\longrightarrow$

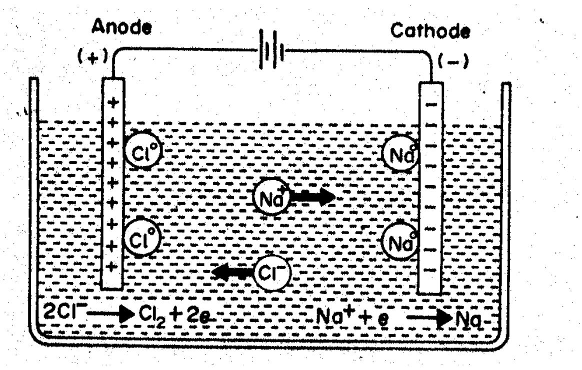

Fig. 5.6: Electrolysis of molten sodium chloride

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 1100 - 1300 K using carbon anode and iron cathode. Electrolysis yields aluminium at cathode and O_2 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: $Al^{3+} + 3e \longrightarrow Al_{(s)}$

i. Write the molecular formula of the following oxosalt minerals:
   (a) Dolomite
   (b) Malachite
   (c) Siderite
ii. What are the factors responsible for selection of a good reducing agent for extraction of metals?
iii. Why is carbon reduction not used to obtain certain metals from their ores?
iv. Explain briefly which metals are produced commercially by the electrolysis of
   (a) aqueous salt solutions
   (b) molten salts
v. Outline two disadvantages of pyrometallurgy and hydrometallurgy processes for extraction of metals.

4.0 CONCLUSION

Metallurgy deals with the science and technology applied to the extraction of metals economically on a large scale from their respective ores. Since metals do not occur freely in nature, they are found in combine state or as ores. The method for beneficiation of metals from their ores are based on differences in physical properties of ores such as colour, lustre, size, density and wettability by water or oil. Some of the beneficiation methods include gravity separation, magnetic separation and froth floatation. Of these methods, froth floatation proves to be most important.

5.0 SUMMARY

- 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.

6.0 TUTOR-MARKED ASSIGNMENT

1. Compare among the following metallurgical processes
   (a) calcination
   (b) roasting
   (c) smelting (Time allowed: 12mins)

7.0 REFERENCES AND FURTHER READING

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UNIT 2 PURIFICATION OF METALS

CONTENTS

1.0 INTRODUCTION

Generally, metals are reactive in nature, hence are not found pure form. In this unit, you are going to learn different techniques that can be used to separate these metals from their impurities. You are also going to learn about alloy, which is also an important property of transition metal, e.g., Cu and their uses.

2.0 OBJECTIVES

By 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;
- discuss the importance and uses of alloys.

3.0 MAIN CONTENT

3.1 Purification Methods

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 are 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:

3.1.1 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.

3.1.2 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.

3.1.3 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:

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

$$\text{M}^{n+}(aq) + ne \longrightarrow \text{M (pure), at the cathode}$$

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 strips the cathode and copper sulphate solution the electrolyte (Fig.5.7). The following electrode reactions take place:

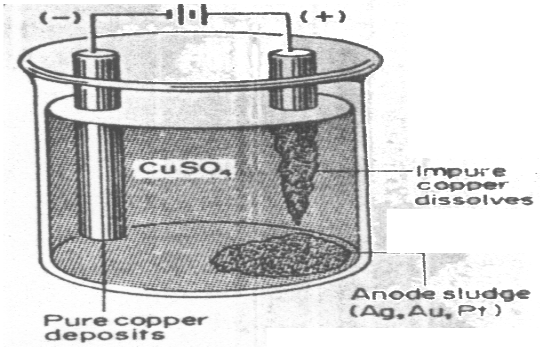


Fig. 5.7: Purification of copper by electrolysis

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

$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$, 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.

3.1.4 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. 5.8).

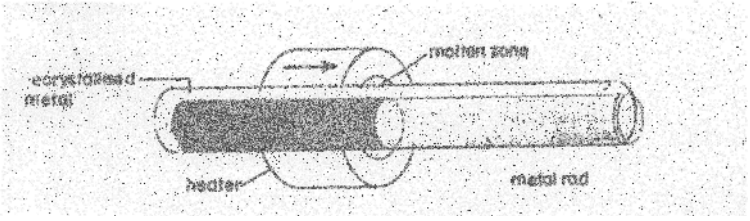


Fig. 5.8: Diagrammatic representation of zone refining process

3.1.5 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,

3.1.6 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.

$$Zr_{(s)} + 2I_{2(g)} \xrightarrow{473 - 673\ K} ZrI_{4(g)} \xrightarrow[\text{Tungsten Filament}]{1300 - 1800\ K} Zr_{(s)} + 2I_{2(g)}$$

Titanium is also purified by this method. The impure metal is heated with iodine and TiI_4 thus formed is decomposed by heating at 1700 K over tungsten filament:

$$Ti_{(s)} + 2I_{2(g)} \longrightarrow TiI_{4(g)} \xrightarrow[\text{Tungsten Filament}]{1700\ K} Ti_{(s)} + 2I_{2(g)}$$

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.

3.1.7 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:

325 K 450-475 K
$Ni_{(s)} + 4CO_{(g)} \longrightarrow Ni(CO)4_{(g)} \longrightarrow Ni_{(s)} + 4CO_{(g)}$

3.2 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.

3.2.1 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 resistant 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 are rutile (TiO_2) and ilmenite ($FeO.TiO_2$). 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:

$$TiO_2 + C + 2Cl_2 \xrightarrow{1200\ K} TiCl_4 + CO_2$$

$$2FeO.TiO_2 + 6C + 7Cl_2 \xrightarrow{1200\ K} 2TiCl_4 + 2FeCl_3 + 6CO$$

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:

$$TiCl_4 + 2Mg \xrightarrow{1225 - 1400\ K} Ti + 2MgCl_2$$

$$TiCl_4 + 4Na \xrightarrow{1225 - 1400\ K} Ti + 4NaCl$$

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 be used as a reducing agent in this process.

3.2.2 Chromium

Chromite, $FeO.Cr_2O_3$, 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:

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

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 Na_2SO_4 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:

$$Na_2Cr_2O_7 + 2C \longrightarrow Cr_2O_3 + Na_2CO_3 + CO$$

Chromium oxide is then reduced with aluminium powder by Goldschmidt-thermite 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:

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

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

3.2.3 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 from the compound.

Iron ores are of high grade. Therefore, generally the ores are not concentrated. The ore is crushed into fine particles and then washed with water to remove clay, sand, etc. This 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:

$$Fe_3O_4 \longrightarrow FeO + Fe_2O_3$$

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

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

$$2FeO + ½O_2 \longrightarrow Fe_2O_3$$

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. 5.9. A modern blast furnace is a tall vertical furnace about 30 metres 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 calcined or roasted ore mixed with coke and lime stone is fed into the furnace. The furnace is lit and a blast of hot air is passed through the tuyeres. Coke is burnt at 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:

$CO_2 + C \rightarrow 2CO$; $\Delta H = 173$kJ

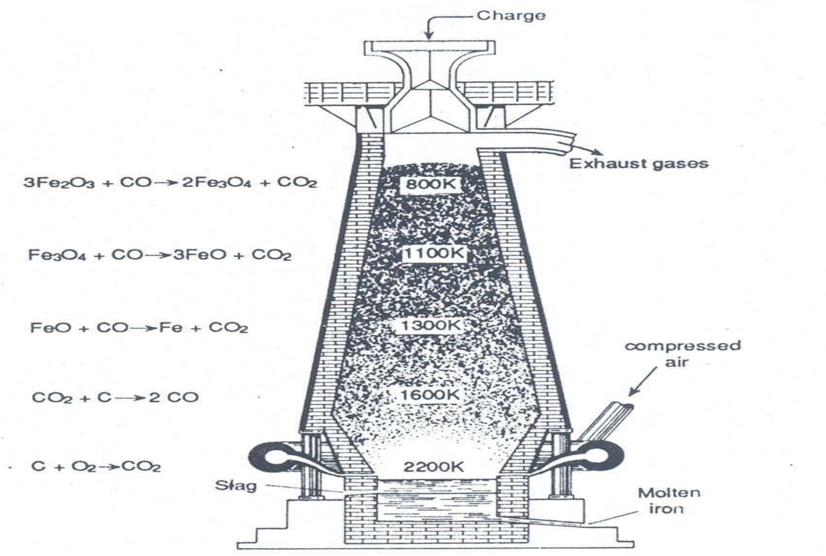


Fig. 5.9: A blast furnace

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 1100 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 the 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 $FePO_4$. 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.

3.2.4 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 up to 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 floatation process. The concentrated ore, which consists of FeS, NiS and CuS, is roasted in excess 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 called *matte*. This 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.

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

$$2CuS + 3O_2 \longrightarrow 2CuO + 2SO_2$$

The mixture of oxides is treated with sulphuric acid at 350 K, when CuO dissolves to give $CuSO_4$, 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.

3.2.5 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, $Cu(OH)_2 \cdot CuCO_3$.

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 floatation 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 Cu_2S 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 $FeSiO_3$:

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

$$2FeO + SiO_2 \longrightarrow FeSiO_3$$

The molten mixture of Cu_2S and remaining FeS (little) is known as *matte*. This is transferred to 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:

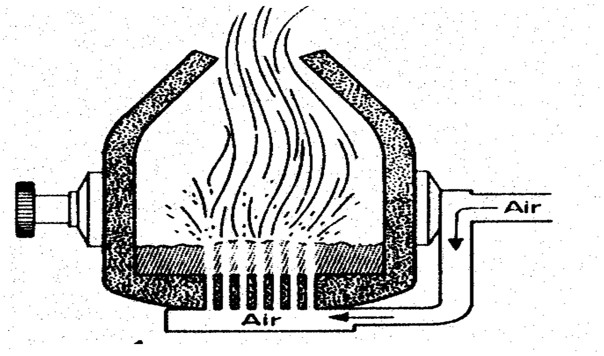


Fig. 5.10: A Bessemer converter

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

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

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.

3.3 Alloys

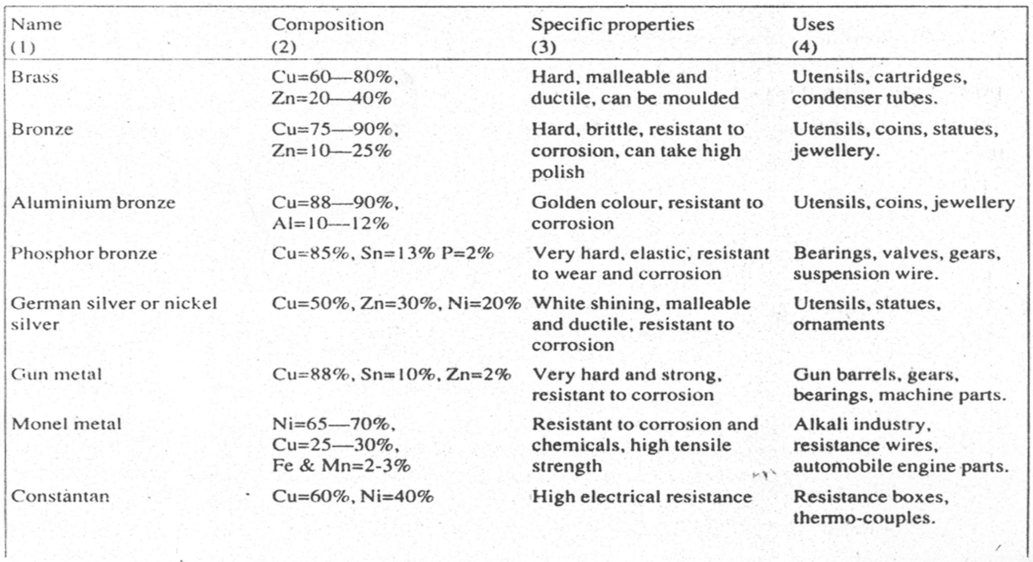
Metals have a property of combining with other metals to form alloys. An alloy may be defined as a solid which is formed by a combination of two or more metallic elements with some specific properties which are not found in the constituent elements. Most alloys are solid solutions. For example, brass 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.

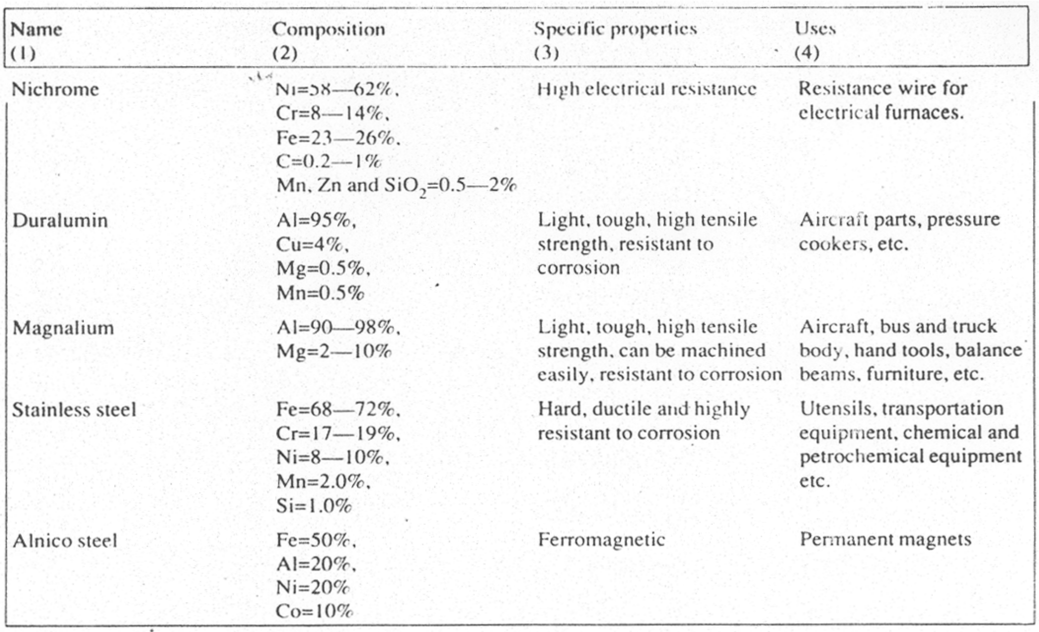
The purpose of making alloys is to impart certain desirable properties to a metal. For example, gold is too soft for making jewellery. Therefore, to make it hard, it is alloyed with copper. Solder, an alloy of tin and lead, has a melting point lower than that of both of its constituents. Pure iron is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

SELF-ASSESSMENT EXERCISE

i. Write the chemical equations for:
ii. Iron cannot be extracted commercially by thermite reduction process because
iii. Which of the following are not the byproducts of the extraction of iron?
iv. Electrorefining can be used to purify which of the following metal(s)?
v. Which of the following can be regarded as an ore of both Ca and Mg?
vi. Which of the following is the raw material for the Bessemer converter?
vii. Which of the following is correct about alloy?

4.0 CONCLUSION

After removal of the gangue from metal ores, the metals are purified by extraction process. This involves reduction of metal compounds to free metal atoms. Metallurgical processes such as pyrometallurgy, hydrometallurgy or electrometallurgy can be used for separation of metals from their ores based on the reactivity of the metal. In order to obtain very pure metals, the products obtained from the above processes can be further purified by other metallurgical processes which involves zone, refining, electrolysis, park process etc.

Alloy is a homogeneous metallic material consisting of two or have metals as a solid solution. The material can be given desired properties.

5.0 SUMMARY

Let us summarise what we have learnt in this unit.

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

6.0 TUTOR-MARKED ASSIGNMENT

1. Describe zone refining method for purification of metals. (Time allowed: 10 methods)

7.0 REFERENCES/FURTHER READING

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