स्वाध्याय स्वमन्थन स्वावलम्बन

UTTAR PRADESH RAJARSHI TANDON OPEN UNIVERSITY

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Indira Gandhi National Open University

UP Rajarshi Tandon Open University

UGCHE-03
Inorganic Chemistry

FIRST BLOCK : Periodicity and s-Block Elements

SECOND BLOCK : *p*-Block Elements-I

THIRD BLOCK : *p*-Block Elements-II

FOURTH BLOCK : *d*-and *f*-Block Elements

Shantipuram (Sector-F), Phaphamau, Allahabad - 211013

Uttar Pradesh
Rajarshi Tandon Open University

UGCHE-03

Inorganic Chemistry

Block

1

PERIODICITY AND *s*-BLOCK ELEMENTS

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INORGANIC CHEMISTRY

This course in Inorganic Chemistry is one of the elective courses for the students of Bachelor's Degree Programme in Science. The course entitled 'Atoms and Molecules' is a co-requisite for this course. This is because the basic theories of atomic and molecular structure discussed in that course are essential for a clear understanding of the concepts described in this course.

According to Moeller. **Inorganic Chemistry is the experimental investigation and theoretical interpretation of the properties and reactions of all the elements and of all their compounds except the hydrocarbons and most of their derivatives.** This definition considers all chemistry either to be inorganic or organic. But no clear-cut line of demarcation can be drawn between the two, as there are overlapping areas like bio-inorganic chemistry and organometallic chemistry. Specific aspects or inorganic chemistry are useful in the study of geochemistry, industrial chemistry, environmental chemistry, biochemistry, mining and metallurgy, glass and ceramic technology, energy sources and waste disposal. The emerging field of material science and solid state chemistry draws heavily on the knowledge of inorganic chemistry. The super-conducting materials, for instance, are basically ceramic materials. Inorganic compounds are found all the way from earth's core to the farthest corners of the universe. Inorganic materials find applications in diverse fields of human activity starting from agriculture, transport, communication, industry, education, entertainment, to providing shelter. Thus, the scope of inorganic chemistry is very vast.

However, it is impossible to describe all the aspects of inorganic chemistry in one course in a comprehensive manner. Therefore, we have adopted the approach of relating the characteristics of elements and their compounds to their electronic structure, highlighting periodic relationships. As such, this course will give you a brief overview of inorganic chemistry. If you want to know more about the subject, you can take our advanced courses in inorganic chemistry later.

In Block 1 we start with a discussion on the periodic table and periodicity. We go on to describe the main features of the chemistry of *s*-block elements. Blocks 2 & 3 deal with the main features of the chemistry of p-block elements. In Block 4 we discuss the general methods of isolation and purification of metals. In this block you will also study the chemistry of transition and inner-transition elements and coordination compounds. All through these four blocks our main emphasis will be on describing the periodic trends observed in the properties of elements and their compounds.

Broad Objectives

What has been said above, may be summarised in terms of the broad objectives of this course, which are as follows:

- explain the importance of inorganic chemistry,
- describe the relationship of inorganic chemistry with other branches of chemistry,
- explain the role of the periodic table in systematising the study of inorganic chemistry,
- discuss the periodic trends in the properties of elements and their compounds in terms of their electronic structure,
- explain the properties of elements and their compounds in terms of structure and bonding,
- describe the general methods of isolation and purification of metals, and
- appreciate the importance of different elements and their compounds in living systems.

BLOCK 1 PERIODICITY AND *s*-BLOCK ELEMENTS

A systematic approach to inorganic chemistry is today almost synonymous with studying the periodic table and the periodic relationships in the properties of elements and their compounds. Therefore, it is quite logical to begin your study of this course with the development of the periodic table in Unit 1. In Unit 2, you will study the periodic trends in atomic properties, use of which will be made in explaining the periodicity in properties of elements and their compounds in the subsequent units.

Hydrogen is a unique element. Therefore, Unit 3 has been devoted to the chemistry of hydrogen and its relationship with the alkali metals on one hand and with the halogens on the other. Alkali metals constitute Group 1 and alkaline earth metals Group 2 of the periodic table. These are the most reactive of all the metallic elements. You will study these elements in Units 4 and 5.

We expect that after reading this block, you should be able to:

- describe various attempts at classification of elements,
- state the Periodic Law and explain the basis of periodicity in the properties of elements,
- describe the periodic trends in the properties of elements,
- describe the periodic trends in the properties of *s*-block elements; and main features of their chemistry.

Study Guide

Before you begin the study of this block, we would like to give you some advice about how best to study it. The total time allotted for the study of this block is 30 hours, out of which you have to reserve 3 hours for doing assignments related to this block. So, you have to complete the study of this block in about 27 hours. Unit 1 deals with the development of the periodic table which is mostly recapitulation of what you have studied upto Class XII. You can finish this unit in 5 hours. In Unit 2, you will study the concept of periodicity in atomic properties. You may require 7-8 hours to finish this unit. Learn these concepts thoroughly as you will need them to explain the periodic trends in properties described in the following units of the course. Unit 3 and 4 deal with hydrogen and the alkali metals, respectively. You may need 5 hours each to finish their study. Unit 5 is on alkaline earth metals. It is a comparatively smaller unit and can be studied in 4 hours. But don't worry too much about the time suggested, as you may take slightly more or less time to complete your study depending on your pace of learning. We have given you a rough idea so that you may plan your study properly.

To facilitate learning, many figures, diagrams and marginal remarks have been given in all these units. We advise you to study these carefully. Chemistry, you know, needs a lot of practice. So, you better keep paper and a pencil or pen along, when you sit to study the units. We advise you to practice writing the reactions and formulae after reading the text.

We have given many self assessment questions (SAQs) and terminal questions in each unit. SAQs have been placed within the text after each major concept and space has been provided after each SAQ for writing the answer. The terminal questions are given at the end of each unit. Model answers to these SAQs and terminal questions are also given at the end of each unit. But we advise you to resist the temptation of looking up the answers first. Work out these questions first and then compare your answers with the model answers to assess that you have learnt the concepts correctly. Our intention is not to make you memorise each fact, but to make you understand the ideas and concepts related to these facts. In keeping with the SI convention, we are using the following units to represent the quantities specified against them as given below:

Atomic radius and bond length	——	picometre (pm)
Energy	——	kilojoule per mole (kJ mol^{-1})
Temperature	——	kelvin (K)
Density	——	kilogram per cubicmetre (kg m^{-3})

We have explained the difficult chemical terms as marginal remarks. For ordinary English words which you may find difficult, you may need to look up a dictionary. Finally, if you wish to go deeper into some aspects, you may refer to the books listed as further reading at the end of this block. These books will be available in the library at your Study Centre.

UNIT 1 THE PERIODIC TABLE

Structure

1.1 Introduction
  Objectives
1.2 Earlier Attempts at Classification
1.3 Modern Periodic Law
1.4 Nomenclature of Elements having Z >100
1.5 Electronic Configuration of Atoms
1.6 Electronic Configuration and Types of Elements
1.7 Summary
1.8 Terminal Questions
1.9 Answers

1.1 INTRODUCTION

Scientists from the very beginning have attempted to systematise the knowledge they gain through their observations and experiments. Development of the periodic law and the periodic table of the elements is one such attempt. This has brought order in the study of the vast chemistry of more than a hundred elements known now. Therefore, it is quite natural to begin your study of inorganic chemistry with the study of the periodic table in this unit.

By the mid-nineteenth century, more than 60 elements were known and many more were being discovered. The rate of discovery of the new elements was so fast that the chemists started wondering "where would it all lead to"? "Has nature provided a limit to the number of elements and if so, how would one know about it"? During this period, it was also realised that certain groups of elements exhibited similar physical and chemical properties. Was it a mere coincidence or did a relationship exist among the properties of the elements? Attempts to reply such probing questions ultimately resulted in the development of the periodic law.

Objectives

After studying this unit, you should be able to:

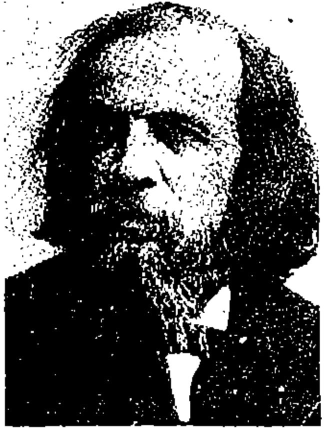
- explain the origin of various forms of the periodic table,
- state and explain the periodic law,
- define periodicity,
- explain the cause of periodicity in properties,
- classify the elements into four categories according to their electronic configuration, and
- write the IUPAC symbols of the elements of atomic number greater than 100.

1.2 EARLIER ATTEMPTS AT CLASSIFICATION

One of the earliest attempts to classify elements was to divide them into metals and non-metals. As you know metallic elements have a certain lustrous appearance, are malleable (can be beaten into thin sheets) and ductile (can be drawn into wires), conduct heat and electricity, and form basic oxides. Non-metallic elements, on the other hand, do not have any one characteristic appearance, but they are brittle, do not generally conduct heat and electricity, and form acidic oxides. As more elements were discovered and knowledge of physical and chemical properties was refined, it became clear that within these two divisions of elements, there existed families of elements whose properties varied systematically from each other. Furthermore, certain elements, the metalloids, possessed properties intermediate between the two divisions. Therefore, attempts were made to search for other classifications.

In 1829, **J. W. Dobereiner** observed that there existed certain groups of three elements which he called **triads**. He also observed that elements in a triad not only had similar properties but also the atomic weight of the middle element was approximately an average of the atomic weights of the other two elements of the triad. A few examples cited by him were: Li, Na, K; Ca, Sr, Ba; S, Se, Te and Cl, Br, I. Although, Dobereiner's relationship seemed to work only for a few elements, he has the first to point out a systematic relationship among the elements.

The next reported attempt to classify elements was made by a French geologist, **A. de Chancourtois** in 1862. He arranged the then known elements in order of increasing atomic weight on a line which spiralled around a cylinder from bottom to top. He divided the circumference of the cylinder into 16 sub-divisions and pointed out that the elements with similar properties ended up above each other on adjacent turns of the spiral. He called his representation as a '**Telluric Screw**'. This also did not attract much attention.



Dmitri Ivanovich Mendeleev, 1834-1907. A Russian Chemist and a Professor of Chemistry at the Technological Institute of St. Petersburg (now Leningrad). He developed the periodic table of the elements and wrote an outstanding Chemistry textbook. In 1906, he failed by one vote to receive the Nobel Prize in Chemistry.

In 1864, the English chemist **John Newlands** reported his "**Law of Octaves**". He suggested that if the elements be arranged in the order of increasing atomic weight, every eighth element had properties similar to the first element just like every eighth note resembles the first in octaves of music. For example, he arranged the elements in the following manner:

Element	Li	Be	B	C	N	O	F
At. Wt.	7	9	11	12	14	16	19
Element	Na	Mg	Al	Si	P	S	Cl
At. Wt.	23	24	27	29	31	32	35.5
Element	K	Ca	Ti	Cr			
At. Wt.	39	40	48	52			

Thus we see, K resembles Na and Li; Ca resembles Mg and Be; Al resembles B; Si resembles C, etc. Newlands' law of octaves was rejected due to two reasons. Firstly, it did not hold good for elements heavier than Ca. Secondly, he believed that there existed some mystical connection between music and chemistry.

The periodic law, as we know it today owes its development to two chemists, **Lothar Meyer** and **Dmitri Mendeleev**, each one working independently propounded it simultaneously in 1869. Lothar Meyer reported that when physical properties like atomic volume, boiling point, etc., were plotted against atomic weight, a periodically repeating curve was obtained in each case. Fig. 1.1 is a graph showing the variation in atomic volume with the atomic number (similar curve was obtained by Lothar Meyer by plotting atomic volume versus atomic weight). The atomic volume behaviour is periodic. It goes through cycles, dropping from a sharp maximum to a minimum and then sharply rising again. Each of the cycles is called a **period.** The location of elements on the peaks or in the troughs has an important correlation with their chemical reactivity. The elements at the peaks (e.g., alkali metals) are the most reactive, those in the troughs (e.g., noble metals) are characteristically less reactive.

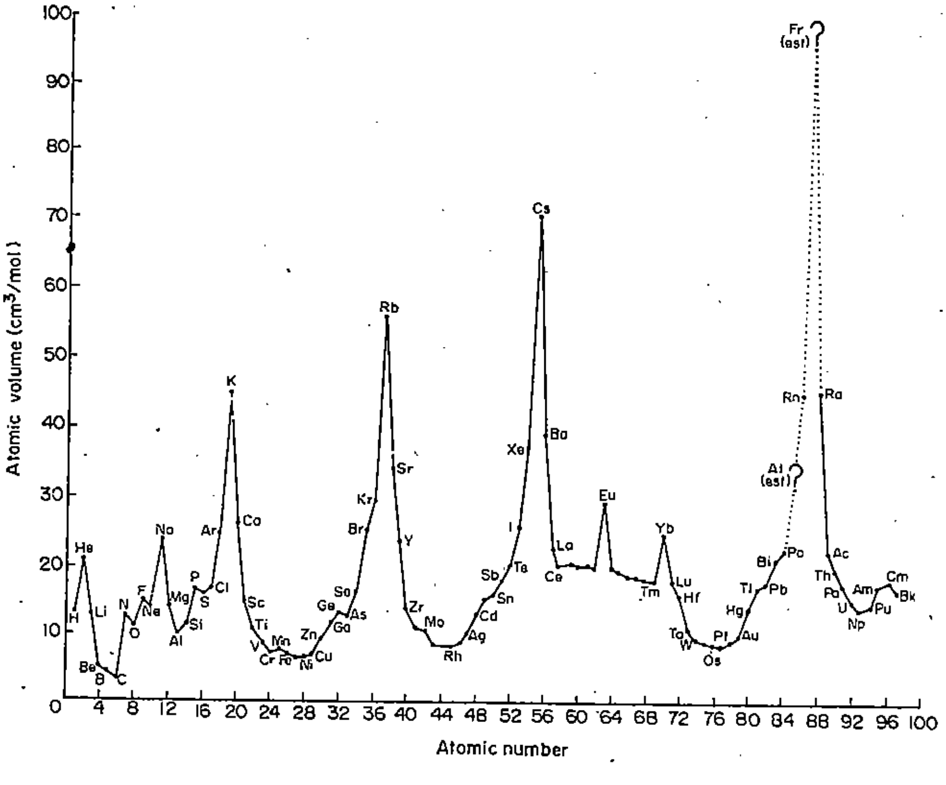


Fig. 1.1: Periodic dependence of atomic volume on atomic number.

Mendeleev's Periodic Law

Mendeleev, on the other hand, used chemical properties like valence and formulae of hydrides, chlorides and oxides of the elements to illustrate his periodic law. According to Mendeleev's periodic law, "**if the elements are arranged sequentially in the order of increasing atomic weight, a periodic repetition, i.e., periodicity in properties is observed.**" Mendeleev arranged elements in horizontal rows and vertical columns in order of increasing atomic weight so that the elements having similar properties were kept in the same vertical column. Fig. 1.2 shows the periodic table devised by Mendeleev in 1871.

Series	Group I — R_2O	Group II — RO	Group III — R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII — RO_4
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59 Ni=59, Cu=63
5	(Cu=63)	Zn=65	=68	=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	=100	Ru=104, Rh=104 Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— —
9	—	—	—	—	—	—	—	— —
10	—	—	?Er=178	?La=180	Ta=182	W=184		Os=195, Ir=195 Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208			
12	—	—		Th=231	—	U=240	—	— —

Fig. 1.2: Mendeleev's periodic table of 1871; against each element is the 1871 value of atomic weight

Although Newlands and Lothar Meyer also contributed in developing the periodic law, the main credit goes to Mendeleev because of the following reasons:

- He included, along with his table, a detailed analysis of the properties of all the known elements and correlated a broad range of physical and chemical properties with atomic weights.
- He kept his primary goal of arranging similar elements in the same group, quite clearly. Therefore, he was bold enough in reversing the order of certain elements. For example, iodine with lower atomic weight than that of tellurium (Group VI) was placed in Group VII along with fluorine, chlorine and bromine because of similarities in properties.
- He also corrected the atomic weights of certain elements to include them in proper groups. For example, he corrected the atomic weights of beryllium (from 13.5 to 9), and indium (from 76 to 114) without doing any actual measurements; his conjecture was proved correct as Be and In with equivalent weights of 4.5 and 38, respectively are actually bivalent and trivalent.
- Keeping to his primary goal of arranging similar elements in the same vertical column (group), he realised that some of the elements were still undiscovered and therefore, left their places vacant in the table and predicted their properties. He predicted the existence in nature of over ten new elements and predicted properties of three of them, e.g., eka-boron (scandium), eka-aluminium (gallium) and eka-silicon (germanium) from the properties of known elements surrounding them. When these elements were discovered, Mendeleev's predictions proved to be amazingly accurate. This you can see by comparing the predicted and observed properties of eka-aluminium (gallium) and eka-silicon (germanium) given in Table 1.1.

It is very interesting to know that out of more than ten elements predicted by Mendeleev, eka-aluminium was discovered first of all and named gallium by **Lecoq de Boisbaudran** in 1875. He determined the density and melting point of gallium and also studied its compounds. He first reported the density of gallium as 4.7 × 10^3 kg m^{-3}. But when he received a letter from Mendeleev saying that everything was quite correct in his description of gallium except for the density which should be 6.0 × 10^3 kg m^{-3}, Boisbaudran was highly

Table 1.1 Comparison of predicted and observed properties of eka-aluminium (gallium) and eka-silicon (germanium)

Property	Predicted by Mendeleev for eka-aluminium	Observed for gallium	Predicted by Mendeleev for eka-silicon	Observed for germanium
At. weight	68	69.72	72	72.59
Density (kg m^{-3})	6.0×10^3	5.9×10^3	5.5×10^3	5.3×10^3
Melting point (K)	low	302.8	High	1220 K
Reaction with acids and alkalies	slow	sl	slow	Reacts with conc. acids and alkalies
Formula of oxide	E_2O_3	Ga_2O_3	—	—
Density of oxide (kg m^{-3})	5.5×10^3	5.88×10^3	—	—
Formula of chloride	ECl_3	$GaCl_3$	$EsCl_4$	$GeCl_4$
Boiling point of chloride (K)	Volatile	474	373	357

surprised. He thought could it be possible that someone else also had discovered gallium before him? He determined the density of gallium again after purifying the metal more carefully. You will be equally surprised to know that Mendeleev was right; the density of gallium is 5.9×10^3 kg m^{-3}.

Another four years later in 1879, the Swedish chemist **Lars Fredrick Nilson** discovered a new element which he named scandium (for Scandinavia). When its properties were investigated, it became absolutely obvious that it was nothing but eka-boron predicted by Mendeleev. In 1886, the German chemist **Winkler** discovered eka-silicon which he renamed as germanium (for Germany). Winkler found that germanium completely corresponds to Mendeleev's eka-silicon. You can yourself see by comparing the properties of eka-silicon and germanium given in Table 1.1.

In this way, the discovery of these three elements provided a striking proof for the validity of the periodic law. The development of periodic law is an excellent example where careful observation, critical analysis of available data without any preconceived notions and scientific foresight led to the discovery of a fundamental law of nature. Thus, when Mendeleev arranged elements in order of increasing atomic weight and critically analysed the properties of then known elements, he discovered that the properties of any element are an average of the properties of its neighbours in the periodic table. On this basis he predicted the properties of undiscovered elements representing the gaps in his table.

SAQ 1

a) What property did Mendeleev use to classify the elements in his periodic table?

b) Enumerate four defects in the Mendeleev's periodic table.

c) For appreciating the excellent achievement of Mendeleev and for assessing your own understanding of the Periodic Law, imagine for a while that one of the elements, say calcium, is still undiscovered. Predict its properties from the properties of the known surrounding elements and then, compare your predictions with those already known.

1.3 MODERN PERIODIC LAW

You must have studied in previous classes that there were some anomalies in Mendeleev's original periodic table. Between 1869 - 1907 he, therefore, tried to improve it further. However, the most significant improvement of his periodic table came through the discovery of the concept of atomic number in 1913 by **Henry Moseley**, who suggested that the atomic number of an element is a more fundamental property than its atomic weight. Mendeleev's Periodic Law was, therefore, accordingly modified. This is now known as **the Modern Periodic Law** and can be stated as **"the properties of elements are periodic functions of their atomic numbers"**. Mendeleev could not arrive at this conclusion because atomic numbers were not known at that time. However, the table given by him (Fig. 1.2) broadly resembles the modern table (Fig. 1.3) because the atomic weight and atomic number vary almost in a parallel manner.

In the modern plan of classification (Fig. 1.3), elements are arranged in the table in order of their increasing atomic numbers, and this removes most of the anomalies of Mendeleev's

Henry G.J.Moseley-1887-1915. A brilliant English physicist discovered the concept of atomic number in 1913. He had to go to battlefield during World War I and got killed in 1915.

Periods	A I B	A II B	A III B	A IV B	A V B	A VI B	A VII B	A VIII B
1	1 H 1.008						1 H 1.008	2 He 4.003
2	3 Li 6.941	4 Be 9.012	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.80	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 27 28 Fe Co Ni 55.85 58.93 58.71
	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 45 46 Ru Rh Pd 101.07 102.91 106.4
	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
6	55 Cs 132.91	56 Ba 137.54	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 77 78 Os Ir Pt 190.2 192.2 195.09
	79 Au 197.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po 210	85 At 210	86 Rn 222
7	87 Fr 223	88 Ra 226.03	89 Ac** 227.03	104 Unq	105 Unp	106 Unh	107 Uns	108 109 Uno Une

* LANTHANIDES

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 146.92	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97

** ACTINIDES

90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 239.05	95 Am 241.06	96 Cm 247.07	97 Bk 249.08	98 Cf 251.08	99 Es 254.09	100 Fm 257.10	101 Md 258.10	102 No 255.0	103 Lr 257.0

Fig. 1.3: Modern periodic table in the form devised by Mendeleev

original periodic table. The positions of K and Ar, Co and Ni, Te and I do not remain anomalous any longer. There was no place for isotopes of an element in Mendeleev's original periodic table. As isotopes of an element have the same atomic number, they can all be placed at one and the same place in the periodic table. You also know the atomic number cannot be fractional and it increases by one integer from one element to the next; it has thus placed a limit on the number of elements. Thus today, 109 elements (from 1 to 109) have been discovered and any more elements that may be discovered in future will be beyond 109.

Long Form of the Periodic Table

You have now learnt that in the modern form of Mendeleev's periodic table, elements are arranged in seven horizontal rows and eight vertical columns. Normal and transition elements belonging to A and B subgroups of a group were placed in one and the same column of the table. In the long form of the periodic table (Fig. 1.4), elements are arranged in eighteen vertical columns by keeping the elements belonging to A and B subgroups in separate columns. You have also studied that the Group VIII B of Mendeleev's periodic table contains three triads — Fe, Co, Ni (4th period); Ru, Rh, Pd (5th period) and Os, Ir, Pt (6th period). But in the long form of the table, each element of the triad is kept in a separate column. So, the group VIII B occupies three columns of the table. Thus, you can see that the long form of periodic table is an extension of the modern periodic table. It is also related to the electronic configuration of elements and displays the order in which the electrons are filled in *s*, *p*, *d* and *f* orbitals about which you will study in Section 1.5.

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
<-sBlock->												← *p*-block elements →					
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	← *d*-block elements →										13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.90	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.71	29 **Cu** 63.54	30 **Zn** 65.37	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.6	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	57 **La*** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.09	79 **Au** 197.97	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	89 **Ac**** 227.03	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Uno**	109 **Une**									

← *f*-block elements →

*** Lanthanides**	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.93	71 **Lu** 174.97
**** Actinides**	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 247.07	97 **Bk** 249.08	98 **Cf** 251.08	99 **Es** 254.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 255	103 **Lr** 257

Fig. 1.4 : Long form of the periodic table

Originally Mendeleev gave A and B designations to the groups containing normal and transition elements, respectively. However, in his periodic table, this division into A and B groups is often done arbitrarily. In different books, for the elements of III to VIII groups, this designation of A and B groups is often reversed. To avoid this controversy, **International Union of Pure and Applied Chemistry (IUPAC)** has adopted Arabic Numerals 1, 2, 3, ... 18 as the newest group designations in the long form of periodic table. In this system, therefore, the alkali and alkaline earth metals constitute Group 1 and 2; transition elements of Sc to Zn families become Groups 3, 4, 5, ... 12 and finally the *p* block elements become Groups 13, 14, ... 18 of the table. In this unit and throughout the rest of this course we will use this IUPAC representation for the elements of different groups in the periodic table.

SAQ 2

a) Which group of elements appears in the modern periodic table, but did not appear in Mendeleev's original table? Why?

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....

....

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

....

....

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1.4 NOMENCLATURE OF ELEMENTS HAVING Z>100

It has been a historical practice to allow the discoverer of an element to assign the element's name. In recent times, this had led to some controversy, because elements with very high atomic numbers are so unstable that only minute quantities of them, sometimes only one or two atoms, are prepared before scientists claim credit for their discovery. This has led to questions of the reliability of the data and whether the said new element has in fact been discovered. For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it rutherfordium and the Soviets named it kurchatovium. To avoid this problem, the **IUPAC** has made an official recommendation that until a new element's discovery has been proved, a systematic nomenclature be applied according to the following **IUPAC nomenclature rules:**

1. The name be derived directly from the atomic number of element using the following numerical roots:

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

2. The roots be put together in the order of the digits which make up the atomic number and be terminated by 'ium', an ending occurring in the names of all the metallic elements, as these are. The final 'n' of enn be dropped when it occurs before 'nil' and the final 'i' of 'bi' and 'tri' be dropped when it occurs before 'ium'.
3. The symbol of the element be composed of the initial letters of the numerical roots which make up the name.

In Table 1.2 systematic names and symbols of elements having Z=101 to 106 derived by IUPAC norms are listed.

Table 1.2: Systematic names for elements having Z>100.

Atomic Number	Systematic Name	Symbol	Trivial Name
101	unnilunium	Unu	Mendelevium
102	unnilbium	Unb	Nobelium
103	unniltrium	Unt	Lawrencium
104	unnilquadium	Unq	—
105	unnilpentium	Unp	—
106	unnilhexium	Unh	—

SAQ 3

Write the IUPAC names and symbols for elements having $Z = 107$ to 114.

1.5 ELECTRONIC CONFIGURATION OF ATOMS

In the preceding section you have studied the arrangement of elements in the long form of the periodic table. In this section you will study the electronic configurations of atoms to understand the cause of periodicity in the properties of the elements. The electronic configurations of isolated atoms of elements are verified experimentally by a detailed analysis of atomic spectra which are too complex for discussion here. However, the electronic configurations of the atoms can be predicted with the help of *aufbau* or the building up process.

In the *aufbau* process, it is assumed that there exists a set of empty hydrogen like orbitals around the nucleus of an atom. The electronic configuration of the atom in the ground state is then derived by adding electrons one at a time to the orbitals of lowest energy in the sequence shown by arrows in Fig. 1.5 given below.

Order of orbitals in the above filling diagram you can remember in the form of $n+l$ rule. According to this rule, in the building up of electronic configuration of the elements, the subshell with the lowest value of $n+l$ fills first; when two subshells have the same value of $n+l$, the orbital with lower value of n fills first. This useful rule reminds us that the energy of subshells of multi-electron atoms, depends upon the value of both the quantum numbers n and l, but mainly on the value of n. For example, which fills first, the $5s$ or the $4p$ subshell? For the $5s$ subshell the value of $n+l = 5 + 0 = 5$; for $4p$ subshell also, the value of $n+l = 4 + 1 = 5$, but the $4p$ subshell has the lower value of the principal quantum number n and therefore, it fills first.

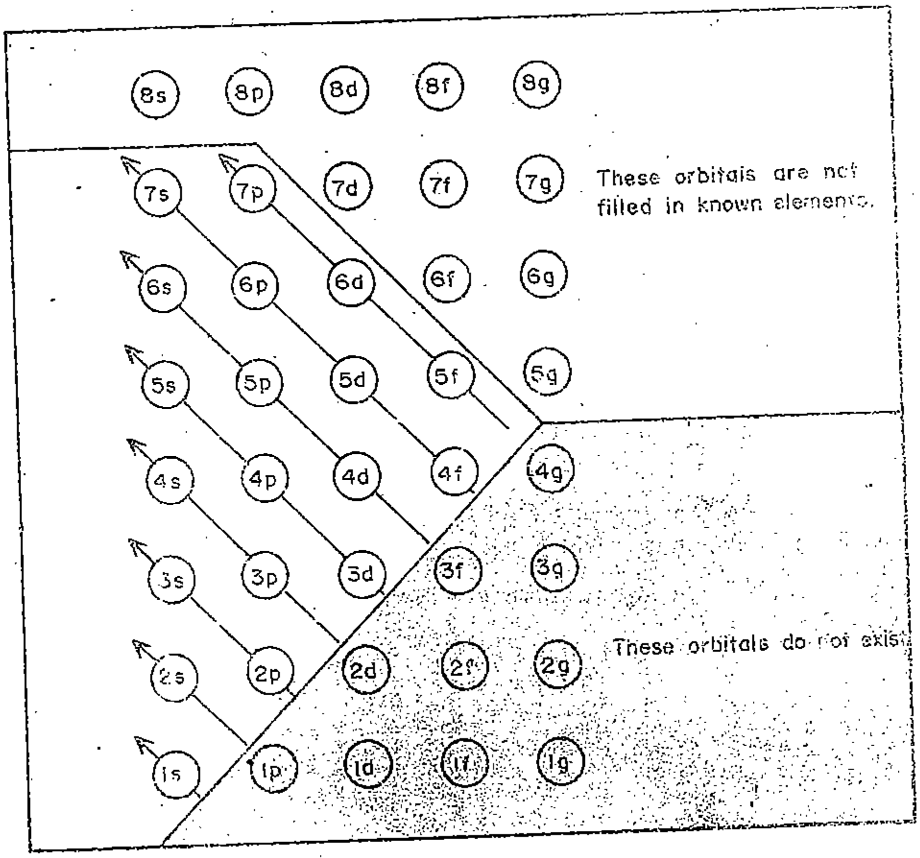

Fig. 1.5: Order of filling of atomic orbitals in polyelectronic atoms

Filling of electrons in orbitals is governed by **Pauli's Exclusion Principle** and **Hund's Rule.** According to the **Exclusion Principle** no two electrons in the same atom can have the same values of all the four quantum numbers. Even if two electrons have the same values of n, l and m_l, they will differ in their m_s values. In other words, an orbital can have at the most two electrons of opposite spin. Since there is only one s-orbital for any given value of n, it can contain only two electrons. However, the three p orbitals, for any given value of n, can contain six electrons, the five d orbitals can hold a total of ten electrons and the seven f orbitals can have fourteen electrons. Permitted combinations of all the four quantum numbers for the electrons in different orbitals are given in Table 1.3.

Table 1.3: Permitted combinations of quantum numbers for s, p, d and f orbitals.

n	l	m_l	m_s	Common name	Number of electrons
1	0	0	±1/2	1s	2
2	0	0	±1/2	2s	2
2	1	−1 0 +1	±1/2 ±1/2 ±1/2	2p	6
3	0	0	±1/2	3s	2
3	1	−1 0 +1	±1/2 ±1/2 ±1/2	3p	6
3	2	−2 −1 0 +1 +2	±1/2 ±1/2 ±1/2 ±1/2 ±1/2	3d	10
4	0	0	±1/2	4s	2
4	1	−1 0 +1	±1/2 ±1/2 ±1/2	4p	6
4	2	−2 −1 0 +1 +2	±½ ±½ ±½ ±½ ±½	4d	10
4	3	−3 −2 −1 0 +1 +2 +3	±1/2 ±1/2 ±1/2 ±1/2 ±1/2 ±1/2 ±1/2	4f	14
5	0		etc.		

Hund's rule of maximum multiplicity states that as far as possible in a given atom in the ground state, electrons in the same subshell will occupy different orbitals and will have parallel spins. That is when electrons are added to orbitals of the same energy such as three p orbitals or five d orbitals, one electron will enter each of the available orbitals before a second electron enters any one orbital. This behaviour, can be explained in terms of electron-electron repulsion. Two electrons in separate orbitals feel less repulsion than two electrons paired in the same orbital. For example, carbon in the ground state, has the configuration $1s^2 2s^2 2p_x^1 2p_y^1$ rather than $1s^2 2s^2 2p_x^2$.

So far you have studied the rules governing the filling of electrons in the orbitals of atoms. We shall now consider the electronic configurations of all the elements in the periodic table. These are given in Table 1.4.

Period 1: This is the smallest of all the periods of the table. Hydrogen ($Z=1$) and helium ($Z=2$) are the two elements belonging to this period. The electronic configurations of hydrogen and helium are $1s^1$ and $1s^2$, respectively. Thus, the 1s orbital which is the only orbital corresponding to $n=1$ is completely filled. The $1s^2$ configuration of helium is also represented by [He].

Period 2 : This period contains elements from lithium ($Z=3$) to neon ($Z=10$). In lithium and beryllium, the filling of 2s orbital takes place. Then in the next six elements from boron to neon, the 2p orbitals are filled. Neon thus has the electronic configuration [He]$2s^2 2p^6$ which is also represented by [Ne]. At this stage the shell having $n=2$ is complete.

Table 1.4: Ground-state electronic configuration of gaseous atoms

Z	Symbol	Configuration as [Core] plus "Outermost" Orbitals
1	H	$1s^1$
2	He	$1s^2$, or [He]
3	Li	$[He]2s^1$
4	Be	$[He]2s^2$
5	B	$[He]2s^22p^1$
6	C	$[He]2s^22p^2$
7	N	$[He]2s^22p^3$
8	O	$[He]2s^22p^4$
9	F	$[He]2s^22p^5$
10	Ne	$[He]2s^22p^6$, or [Ne]
11	Na	$[Ne]3s^1$
12	Mg	$[Ne]3s^2$
13	Al	$[Ne]3s^23p^1$
14	Si	$[Ne]3s^23p^2$
15	P	$[Ne]3s^23p^3$
16	S	$[Ne]3s^23p^4$
17	Cl	$[Ne]3s^23p^5$
18	Ar	$[Ne]3s^23p^6$, or [Ar]
19	K	$[Ar]4s^1$
20	Ca	$[Ar]4s^2$
21	Sc	$[Ar]3d^14s^2$
22	Ti	$[Ar]3d^24s^2$
23	V	$[Ar]3d^34s^2$
24	Cr	$[Ar]3d^54s^1$
25	Mn	$[Ar]3d^54s^2$
26	Fe	$[Ar]3d^64s^2$
27	Co	$[Ar]3d^74s^2$
28	Ni	$[Ar]3d^84s^2$
29	Cu	$[Ar]3d^{10}4s^1$
30	Zn	$[Ar]3d^{10}4s^2$
31	Ga	$[Ar]3d^{10}4s^24p^1$
32	Ge	$[Ar]3d^{10}4s^24p^2$
33	As	$[Ar]3d^{10}4s^24p^3$
34	Se	$[Ar]3d^{10}4s^24p^4$
35	Br	$[Ar]3d^{10}4s^24p^5$
36	Kr	$[Ar]3d^{10}4s^24p^6$, or [Kr]
37	Rb	$[Kr]5s^1$
38	Sr	$[Kr]5s^2$
39	Y	$[Kr]4d^15s^2$
40	Zr	$[Kr]4d^25s^2$
41	Nb	$[Kr]4d^45s^1$
42	Mo	$[Kr]4d^55s^1$
43	Tc	$[Kr]4d^55s^2$
44	Ru	$[Kr]4d^75s^1$
45	Rh	$[Kr]4d^85s^1$
46	Pd	$[Kr]4d^{10}$
47	Ag	$[Kr]4d^{10}5s^1$
48	Cd	$[Kr]4d^{10}5s^2$
49	In	$[Kr]4d^{10}5s^25p^1$
50	Sn	$[Kr]4d^{10}5s^25p^2$
51	Sb	$[Kr]4d^{10}5s^25p^3$
52	Te	$[Kr]4d^{10}5s^25p^4$
53	I	$[Kr]4d^{10}5s^25p^5$
54	Xe	$[Kr]4d^{10}5s^25p^6$, or [Xe]
55	Cs	$[Xe]6s^1$
56	Ba	$[Xe]6s^2$
57	La	$[Xe]5d^16s^2$
58	Ce	$[Xe]4f^15d^16s^2$
59	Pr	$[Xe]4f^36s^2$
60	Nd	$[Xe]4f^46s^2$
61	Pm	$[Xe]4f^56s^2$
62	Sm	$[Xe]4f^66s^2$
63	Eu	$[Xe]4f^76s^2$
64	Gd	$[Xe]4f^75d^16s^2$

Z	Symbol	Configuration as [Core] plus "Outermost" Orbitals
65	Tb	$[Xe]4f^96s^2$
66	Dy	$[Xe]4f^{10}6s^2$
67	Ho	$[Xe]4f^{11}6s^2$
68	Er	$[Xe]4f^{12}6s^2$
69	Tm	$[Xe]4f^{13}6s^2$
70	Yb	$[Xe]4f^{14}6s^2$
71	Lu	$[Xe]4f^{14}5d^16s^2$
72	Hf	$[Xe]4f^{14}5d^26s^2$
73	Ta	$[Xe]4f^{14}5d^36s^2$
74	W	$[Xe]4f^{14}5d^46s^2$
75	Re	$[Xe]4f^{14}5d^56s^2$
76	Os	$[Xe]4f^{14}5d^66s^2$
77	Ir	$[Xe]4f^{14}5d^76s^2$
78	Pt	$[Xe]4f^{14}5d^96s^1$
79	Au	$[Xe]4f^{14}5d^{10}6s^1$
80	Hg	$[Xe]4f^{14}5d^{10}6s^2$
81	Tl	$[Xe]4f^{14}5d^{10}6s^26p^1$
82	Pb	$[Xe]4f^{14}5d^{10}6s^26p^2$
83	Bi	$[Xe]4f^{14}5d^{10}6s^26p^3$
84	Po	$[Xe]4f^{14}5d^{10}6s^26p^1$
85	At	$[Xe]4f^{14}5d^{10}6s^26p^5$
86	Rn	$[Xe]4f^{14}5d^{10}6s^26p^6$, or [Rn]
87	Fr	$[Rn]7s^1$
88	Ra	$[Rn]7s^2$
89	Ac	$[Rn]6d^17s^2$
90	Th	$[Rn]6d^27s^2$
91	Pa	$[Rn]5f^26d^17s^2$
92	U	$[Rn]5f^36d^17s^2$
93	Np	$[Rn]5f^46d^17s^2$
94	Pu	$[Rn]5f^67s^2$
95	Am	$[Rn]5f^77s^2$
96	Cm	$[Rn]5f^76d^17s^2$
97	Bk	$[Rn]5f^97s^2$
98	Cf	$[Rn]5f^{10}7s^2$
99	Es	$[Rn]5f^{11}7s^2$
100	Fm	$[Rn]5f^{12}7s^2$
101	Md	$[Rn]5f^{13}7s^2$
102	No	$[Rn]5f^{14}7s^2$
103	Lr	$[Rn]5f^{14}6d^17s^2$
104	Unq	$[Rn]5f^{14}6d^27s^2$
105	Unp	$[Rn]5f^{14}6d^37s^2$
106	Unh	$[Rn]5f^{14}6d^57s^1$
107	Uns	$[Rn]5f^{14}6d^57s^2$
108	Uno	$[Rn]5f^{14}6d^67s^2$
109	Une	$[Rn]5f^{14}6d^77s^2$

Period 3: Similar to period 2, this period also consists of 8 elements from sodium (Z=11) to argon (Z=18). In these elements, 3*s* and 3*p* orbitals are successively filled in the sequence analogous to that in period 2. Thus, argon has the electronic configuration $[Ne]2s^22p^6$ represented as [Ar]. Although, the third principal shell (n=3) can accommodate 10 more electrons in 3*d* orbitals but filling of 4*s* orbital takes place first because of its lower energy.

Period 4: This period contains 18 elements from potassium (Z=19) to krypton (Z=36). In K and Ca, the first two elements of this period, the successive electrons go into the 4*s* orbital giving them the configuration $[Ar]4s^1$ and $[Ar]4s^2$, respectively. Then in the following 10 elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn), filling of hitherto unoccupied 3*d* orbitals takes place. Thus, the electronic configuration of zinc becomes $[Ar]3d^{10}4s^2$. Occasionally an electron from 4*s* orbital is shifted out of turn to the 3*d* orbital due to the higher stability of half filled and completely filled orbitals. For example, Cr($Z = 24$) and Cu (Z=29) have the configurations $[Ar]3d^54s^1$, and $[Ar]3d^{10}4s^1$ instead of expected $[Ar]3d^44s^2$ and $[Ar]3d^94s^2$, respectively. After the 3*d* level is filled, in the next six elements of this period, i.e., Ga, Ge, As, Se, Br and Kr, the 4*p* orbitals are gradually filled and Kr has the electronic configuration $[Ar]3d^{10}4s^24p^6$ represented as [Kr].

Period 5: The next 18 elements from rubidium (Z=37) to xenon (Z=54) belong to this period. In the building up of the atoms of these elements 5*s*, 4*d* and 5*p* orbitals are successively filled just as the 4*s*, 3*d* and 4*p* orbitals are filled in the elements of **period 4.** In Rb (Z=37) and Sr (Z=38), the 5*s* orbital is filled. After that, in elements from Y (Z=39) to Cd (Z=48) filling of 4*d* orbitals takes place. You can see from the Table 1.4 that once again there are minor irregularities in the distribution of electrons between 4*d* and 5*s* orbitals. For example, Mo (Z=42) and Ag (Z=47) have respectively $[Kr]4d^5 5s^1$ and $[Kr]4d^{10}5s^1$ configurations similar to those of Cr and Cu, respectively. Anomalous electronic configurations of Nb, Ru, Rh and Pd cannot be explained in simple terms. You have to, therefore, remember them as exceptions. Now in the next six elements, i.e., In, Sn, Sb, Te, I and Xe filling of 5*p* orbitals takes place and thus Xe (Z=54) attains $[Kr]\ 4d^{10}5s^2 5p^6$ configuration.

Period 6: This period contains 32 elements from caesium (Z = 55) to radon (Z=86) in which the 6*s*, 4*f*, 5*d* and 6*p* orbitals are filled. The first two elements of this period have configurations analogous to those of the corresponding members of the lower periods. Thus caesium (Z=55) and barium (Z=56) have $[Xe]6s^1$ and $[Xe]6s^2$ configurations, respectively. According to the *aufbau* principle, in the next element La (Z=57), the additional electron should enter 4*f* orbital. Instead, it goes to the 5*d* orbital and La has the configuration $[Xe]5d^1 6s^2$. But why? The extra electron in the building up of La atom goes to 5*d* orbital instead of 4*f* orbital because in La atom, the 5*d* and 4*f* orbitals have almost the same energy and, hence, the electron is free to enter any of these two orbitals.

In the next 14 elements from cerium (Z=58) to lutecium (Z=71), the 4*f* orbital is successively filled pertaining to $[Xe]4f^1 5d^1 6s^2$ and $[Xe]4f^{14}5d^1 6s^2$ configurations, respectively. But you should remember, it is only Ce (Z=58), Gd (Z=64) and Lu (Z=71) that 5*d* orbitals have one electron while in all the remaining lanthanides the 5*d* orbitals remain vacant.

After lutecium, successive electrons occupy 5*d* orbitals and the electronic configuration builds up from $[Xe]\ 4f^{14}5d^2 6s^2$ for hafnium to $[Xe]\ 4f^{14}5d^{10}6s^2$ for mercury, the homologue of zinc and cadmium. Again, a minor departure from a steady increase in the number of *d* electrons occurs. For example, gold has $[Xe]4f^{14}5d^{10}6s^1$ configuration instead of $[Xe]4f^{14}5d^9 6s^2$. This, as you can see, has to do with the greater stability of half-filled/fully-filled orbitals. Finally the period is completed with successive occupation of the 6*p* orbitals from thallium, $[Xe]4f^{14}5d^{10}6s^2 6p^1$ to radon, $[Xe]4f^{14}5d^{10}6s^2 6p^6$.

Period 7: This period is still incomplete and contains 23 elements from francium (Z=87) to unnilennium (Z=109). In these elements, electrons are filled in 7*s*, 5*f* and 6*d* orbitals. Francium ($[Rn]7s^1$), radium ($[Rn]7s^2$) and actinium ($[Rn]6d^1 7s^2$) have electronic configurations analogous to those of caesium, barium and lanthanum, respectively. Thorium has the configuration $[Rn]6d^2 7s^2$. Thereafter, in next 13 elements from protactinium (Z=91) to lawrencium (Z=103) filling of 5*f* orbitals takes place successively. However, out of these, only Pa (Z=91), U = (Z=92), Np (Z=93), Cm (Z=96) and Lr (Z=103) have an electron in 6*d* orbitals. In the rest of the elements, the 6d orbitals remain vacant. Thus, the electronic configuration of Lr (Z=103) is $[Rn]5f^{14}6d^1 7s^2$. The next six known elements of this period are members of 6*d* transition series which have the configurations $[Rn]5f^{14}6d^2 7s^2$ to $[Rn]5f^{14}6d^7 7s^2$.

Thus, we have examined the electronic configurations of elements in the periodic table. You can see from Table 1.4 that the elements occupying the same group of the periodic table have the same valence-shell electronic configuration. In other words, the elements having the same valence-shell electronic configuration recur periodically, that is after intervals of 2, 8, 8, 18, 18 and 32 in their atomic numbers. Therefore, periodicity in the properties of elements can be easily understood.

SAQ 4

a) What principles or rules are violated in the following electronic configurations? Write the name of the principle or rule in the space provided alongside each configuration.

i) $1s^2 2s^3$ ....

ii) $1s^2 2s^2 2p_x^2 2p_y^1$ ....

iii) $1s^2 2p_x^2$ ....

b) In the space provided write the electronic configuration of the atoms whose atomic numbers are

i) 21 ....

ii) 24 ....

iii) 29 ....

(iv) 35 ....

(v) 57 ....

Electronic Configuration of Ions

So far you have studied the electronic configuration of neutral atoms of elements. At this stage you will be naturally interested in knowing the electronic configuration of ions that are obtained by removal of electrons from the elements. When a gaseous iron atom having $[Ar]3d^64s^2$ ground state electronic configuration loses an electron, the Fe^+ ion is formed. This ion has its minimum energy in the configuration $[Ar]3d^7$, although the isoelectronic manganese atom has the configuration $[Ar]3d^54s^2$ in the ground state. Similarly, the ground states of the Fe^{2+} and Fe^{3+} ions are $[Ar]3d^6$ and $[Ar]3d^5$, respectively rather than $[Ar]3d^54s^1$ and $[Ar]3d^34s^2$ which are the ground states of isoelectronic atoms of chromium and vanadium, respectively. Evidently the differences in nuclear charge between Fe^+ and Mn, Fe^{2+} and Cr, and Fe^{3+} and V are important in determining the orbitals to be occupied by the electrons. However, along a series of ions carrying the same charge, the electronic configuration often changes much more regularly than the electronic configuration of the corresponding atoms. Thus, for dipositive ions from Sc^{2+} to Zn^{2+}, the ground state electronic configuration changes regularly from $[Ar]3d^1$ to $[Ar]3d^{10}$. For tripositive ions, there is a similar regular change from [Ar] for Sc^{3+} to $[Ar]3d^9$ for Zn^{3+}. For tripositive ions of lanthanide elements, there is a regular change from $[Xe]4f^1$ for Ce^{3+} to $[Xe]4f^{14}$ for Lu^{3+} Since the chemistry of elements is essentially that of their ions, the regularities in configuration of ions are much more important than the irregularities in the electronic configuration of the neutral atoms.

1.6 ELECTRONIC CONFIGURATION AND TYPES OF ELEMENTS

In the previous section you have studied the electronic configuration of the elements. Now we shall discuss the division of elements into various types depending upon their electronic configuration. Elements are thus, divided into four types, viz., *s*, *p*, *d* and *f* block elements depending upon the nature of the atomic orbitals into which the differentiating or the last electron enters.

***s*-Block elements:** In these elements, the differentiating electron enters the '*ns*' orbital. Alkali and alkaline earth metals of Groups 1 (IA) and 2 (IIA) belong to this block. You have already seen that their valence shell electronic configurations are ns^1 and ns^2, respectively. You have also studied that each period of the periodic table begins with an alkali metal. All the elements of this block are metals.

***p*-Block elements:** In the elements belonging to this block, the *p*-orbitals are successively filled. Thus, the elements of the Groups 13 (IIIA), 14 (IVA), 15 (VA), 16 (VIA), 17 (VIIA) and 18 (Zero) are members of this block, since in the atoms of these elements, the differentiating electron enters the *np* orbitals. The *ns* orbitals in the atoms of these elements are already completely filled so they have the valence shell electronic configuration ns^2np^{1-6}.

The elements of *s*- and *p*-blocks are also known as normal, representative or main group elements.

***d*-Block elements:** The elements in which the differentiating electron enters the $(n-1)d$ orbitals are called *d*-block elements. These elements are placed in the middle of the periodic table between the *s*- and *p*- block elements. You can represent the configuration of the atoms of the elements of this block by $(n-1)d^{1-10}ns^{0,1,2}$. These elements which are also called transition elements are divided into four series corresponding to the filling of 3*d*-, 4*d*-, 5*d*-, or 6*d*- orbitals. While the 3*d*, 4*d* and 5*d* series consist of 10 elements each, the 6*d* series is incomplete and has only seven elements, viz., Ac (Z=89) and from Unq (Z=104) to Une (Z =109). The elements from Sc (Z=21) to Zn (Z=30), Y (Z=39) to Cd (Z=48), La (Z=57) and from Hf (Z=72) to Hg (Z=80) are the members of 3*d*, 4*d*, and 5*d* series, respectively.

d-Block elements are also known as transition elements.

***f*-Block elements:** The elements in which the extra electron enters $(n-2)f$ orbitals are called the *f*-block elements. The atoms of these elements have the general configuration $(n-2)f^{1-14}(n-1)d^{0,1}ns^2$. These elements belong to two series depending upon the filling of 4*f* and 5*f* orbitals. Elements from Ce(Z = 58) to Lu (Z = 71) are the members of the 4*f* series while those from Th(Z = 90) to Lr (Z = 103) belong to the 5*f* series. Elements of 4*f* series which follow lanthanum in the periodic table are known as **lanthanides** whereas those of 5*f* series following actinium are called **actinides.** All these elements are collectively referred to as **inner-transition** elements because of filling of electrons in an inner $(n-2)f$ subshell.

f-Block elements are also known as inner-transition elements.

SAQ5

a) Name the blocks into which the elements in the periodic table have been divided.

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b) Differentiate between transition and inner-transition elements in terms of their electronic configuration.

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1.7 SUMMARY

In this unit you studied the development of the periodic table and the periodic law. We have followed the development of modern periodic law from the earliest classification of elements into metals and non-metals, to Dobereiner's Triads, Newlands' Law of Octaves, Chancourtois' Telluric Screw, Lothar Meyer's curves and Mendeleev's Periodic Law.

The periodic table organises the elements into periods and groups in order of increasing atomic number so as to display the periodic law. The periodic law can be stated as "the properties of elements are the periodic function of their atomic number". This periodicity in properties arises due to the periodicity in the electronic configuration of the elements. Thus, the elements occurring in the same group of periodic table have similar electronic configurations and depict similar physical and chemical properties.

Electronic configurations of atoms can be determined with the help of *aufbau* principle, Pauli's exclusion principle and Hund's rule of maximum multiplicity.

On the basis of their electronic configurations, elements are divided into four categories. Those having $ns^{1,2}$ configuration are called *s*-block elements. Elements of Groups 1 and 2 are the members of this block. Elements having ns^2np^{1-6} configuration are known as *p*-block elements. Elements of Groups 13 to 18 belong to this class. *d*-Block elements have $(n-1)d^{1-10}ns^{0,1,2}$ configuration and thus, elements of Groups 3 to 12 belong to this block. *f*-Block elements have $(n-2)f^{1-14}(n-1)d^{0,1}ns^2$ configuration. Lanthanide and actinide elements are members of this block.

1.8 TERMINAL QUESTIONS

1. Newlands attempted to show that there was a periodic similarity in the properties of every eighth element. Yet today, we see that for the elements of period 2 and 3, it occurs at every ninth element. Explain.
2. What are the advantages of classifying elements into groups?
3. State the modern periodic law. What is the cause of periodicity in the properties of the elements?
4. Explain how elements are arranged in the long form of the periodic table.
5. Explain what is meant by a group and a period.
6. Explain why there are only two elements in the first period, eight elements each in the second and third periods, eighteen elements each in the fourth and fifth periods, thirty-two elements in the sixth period of the periodic table.
7. Explain *aufbau* principle and *n+l* rule.

8. Explain Pauli's exclusion principle.
9. State Hund's rule of maximum multiplicity.
10. Explain how the elements are classified into *s*, *p*, *d* and *f*-blocks.

1.9 ANSWERS

Self Assessment Questions

1 a) Mendeleev used atomic weight to classify elements. He arranged the elements in order of increasing atomic weight in his periodic table.

b) Some of the defects of Mendeleev's periodic table are:

i) Anomalous position of hydrogen.

ii) No place for isotopes of elements.

iii) No proper place for lanthanides and actinides.

iv) In some cases, elements of higher atomic weights were placed before those having lower atomic weights, e.g., Co before Ni and Te before I.

v) He could not predict the existence of noble gases.

c)

Property	K	Sc	Prediction for Ca	Observed for Ca
At. weight	39.1	41.6	40.3	40
Density $(10^3\ \text{kg m}^{-3})$	0.86	3.0	~1.9	1.55
Melting Point (K)	336.7	1812	1074	1111
Formula of oxide	K_2O	Sc_2O_3	CaO	CaO
Formula of chloride	KCl	$ScCl_3$	$CaCl_2$	$CaCl_2$
Nature of chloride	Ionic	Ionic	Ionic	Ionic
Reactivity towards water and acids	Reacts vigorously evolving H_2	Reacts when finely divided or heated evolving H_2	Should be moderately reactive and should liberate H_2	As predicted

2 a) Group 18 containing noble gases appears in the modern periodic table, but it did not appear in Mendeleev's original table because noble gases were not discovered at that time.

b) In periodic table, elements are arranged in the order of increasing atomic number.

3

Atomic Number	IUPAC name	Symbol
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu
112	Ununbium	Unb
113	Ununtrium	Unt
114	Ununquadium	Unq

4 a) i) Exclusion principle ii) Hund's rule iii) *aufbau* principle

b) i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ or $[Ar]3d^1 4s^2$

ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ or $[Ar]\ 3d^5 4s^1$

iii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ or $[Ar]\ 3d^{10} 4s^1$

iv) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$ or $[Ar]\ 3d^{10} 4s^2 4p^5$

v) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^1 6s^2$ or $[Xe]\ 5d^1 6s^2$

5 a) In the periodic table, elements are divided into four blocks, namely, *s*-, *p*-, *d*- and *f*-block elements. Elements of *s*- and *p*-blocks are representative elements whereas those of *d*- and *f*- blocks are known as transition and inner-transition elements.

b) Transition elements are called *d*-block elements. In these elements, the differentiating electron is added to the *d*- orbitals of the penultimate shell. Their electronic configuration can be represented by $(n-1)d^{1-10}ns^{0-2}$. Inner-transition elements are known as *f*-block elements. In these elements the differentiating electron enters the *f*-orbitals of the shell which is second from the outermost shell. They have the general electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.

Terminal Questions

1 In Newlands' time, the noble gas elements were not known. He, therefore, reported a periodic similarity in properties of every eighth element. Obviously with the inclusion of noble gases in the periodic table, for the elements of period 2 and 3 this similarity will occur at every ninth element.

2 The necessity of classifying elements into groups was to facilitate the study of the vast chemistry of a large number of elements and their compounds.

3 Modern periodic law can be stated as "the properties of the elements are the periodic function of their atomic numbers". Cause of periodicity in the properties of elements lies in the electronic configuration of the elements. Elements having similar valence-shell electronic configuration recur at regular intervals in their atomic number, therefore, they exhibit similarities in properties.

4 In the long form of the periodic table elements are arranged in seven horizontal rows and eighteen vertical columns in the order of increasing atomic number in such a manner that elements having similar properties occur in the same vertical column.

5 Vertical columns and horizontal rows in the periodic table are known as groups and periods, respectively. Elements of a particular group in the table have similar properties and differ from the elements of other groups in the table. Properties of elements in a period vary gradually from one element to another.

6 Answer to this lies in the electronic configurations of the atoms of the elements. Each period of the table begins with an element in the atoms of which filling of *s*-orbitals of a new principal shell starts. Except for the first period which ends with the completion of 1*s* orbital in noble gas helium, all others end with noble gas elements in whose atoms the *p*-orbitals of the same principal shell get completely filled. Thus, the first period contains only two elements, hydrogen and helium pertaining to $1s^1$ and $1s^2$ configuration. The second period contains eight elements in the atoms of which 2*s* and 2*p* orbitals are filled. The third period also contains eight elements due to filling of 3*s* and 3*p* orbitals. The fourth period begins with filling of 4*s* orbital and ends with the completion of 4*p* orbitals. But in between 4*s* and 4*p* orbitals, 3*d* orbitals are also filled. Thus, the fourth period contains eighteen elements. Similarly, in the elements of fifth period the 5*s*, 4*d*, and 5*p* orbitals are filled, so it also contains eighteen elements. The sixth period contains thirty-two elements pertaining to the filling of 6*s*, 4*f*, 5*d* and 6*p* orbitals. Period 7 can also accommodate an equal number of elements, but it is incomplete and contains only twenty-three elements pertaining to the complete filling of 7*s* and 5*f* orbitals and partial (7) filling of 6*d* orbitals.

7 Electronic configuration of atoms can be derived with the help of *aufbau* principle. According to this principle, electrons are filled in orbitals one at a time in order of increasing energy. Order of filling of orbitals is $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow 5d \rightarrow 6p \rightarrow 7s \rightarrow 5f \rightarrow 6d$. Order of filling of electrons in orbitals can be remembered in the form of $n+l$ rule according to which the subshell with the lowest value of $n+l$ fills first. When two subshells have the same value of $n+l$, the subshell with lower value of n fills first.

8. Pauli's exclusion principle states that no two electrons in an atom can have the same values of all the four quantum numbers. In other words, an orbital can accommodate at the most two electrons.

9 Hund's rule of maximum multiplicity states that as far as possible in a given atom in the ground state, electrons in the same subshell will occupy different orbitals and will have the parallel spins.

10 Depending upon the filling of electrons in *s*, *p*, *d* or *f* orbitals, elements are classified into *s*, *p*, *d* or *f*-blocks in the periodic table.

UNIT 2 PERIODICITY

Structure

2.1 Introduction
    Objectives
2.2 Atomic Radii
    Covalent Radius
    Van der Waals Radius
    Metallic or Crystal Radius
    Ionic Radius
    Factors Affecting Atomic Radii
    Periodicity in Atomic Radii
2.3 Ionisation Energy
    Factors Affecting Ionisation Energy
    Periodicity in Ionisation Energy Across Periods
    Trends in Ionisation Energy Down the Groups
    Trends in Second and Higher Ionisation Energies
2.4 Electron Affinity
    Factors Affecting Electron Affinity
    Periodicity in Electron Affinity
2.5 Electronegativity
    Pauling Electronegativity Scale
    Mulliken-Jaffe Electronegativity Scale
    Allred-Rochow Electronegativity Scale
    Periodicity in Electronegativity
2.6 Summary
2.7 Terminal Questions
2.8 Answers

2.1 INTRODUCTION

In the preceding unit, you have studied that the properties of elements are a periodic function of their atomic numbers. As a result of their similar valence-shell electronic configuration, elements belonging to the same group of periodic table exhibit similarities in properties like valence and formulae of their highest oxides, hydrides and chlorides. Further, they also exhibit a gradation in properties with their position in the group because of the valence electrons occupying different electronic levels. For example, in Group 14 (IVA) of the periodic table, C is a non-metal, Si and Ge are semi-metals, whereas Sn and Pb are metallic elements. All these elements exhibit the highest oxidation state of 4, as the valence shells in all of these belong to $s^2 p^2$ type. However, the stability of tetravalent species decreases down the group and bivalent species become more stable.

In Group 1 (IA) having highly electropositive alkali metals, the reactivity of elements towards water increases down the group. At 298 K, Li reacts slowly, Na reacts vigorously, K inflames whereas Rb and Cs react explosively with water. These differences in the properties arise due to differences in the atomic properties like the atomic size, ionisation energy, electron affinity and electronegativity. These atomic properties are directly related to the total electronic configurations of the elements and form an important link between the properties of elements and their electronic configuration. In this unit you will study the periodicity in these atomic properties in general and in the following units, you will learn to make use of these in explaining the trends in the properties of elements in a particular group.

Objectives

After studying this unit, you should be able to:

- define atomic radii, ionisation energy, electron affinity and electronegativity,
- discuss the factors affecting atomic radii,
- describe the relationship of atomic radii with ionisation energy and electron affinity,
- describe the periodicity in atomic radii, ionisation energy, electron affinity and electronegativity.

2.2 ATOMIC RADII

Atomic radii are a measure of the size of the atoms. Atomic radii are important, because other atomic properties like ionisation energy, electron affinity and electronegativity can be related to them. You have studied the wave mechanical picture of an atom, according to which an atom is composed of a compact nucleus surrounded by an electron cloud. This electron cloud does not have a definite boundary surface similar to that of a ball. There is a definite but very small probability of finding an electron at an infinite distance from the nucleus of the atom. Does this mean that atom is infinitely large? This just does not make any sense. Thus, we have to find a way to define the size of an atom. **The radius of an atom can be defined as the distance from the centre of the nucleus to the point where the electron density is virtually zero.**

After we have defined the size of an atom, the problem arises as to how we are going to measure it? Thus, if we are measuring the size of an atom when it is occupying a lattice site in the crystal, the value will be different from the one when it is colliding with another atom in the gaseous state. Furthermore, the size of the neutral atom will be different from the one when it is present as a cation or anion. Consequently, we cannot have one set of atomic radii applicable under all conditions. It, therefore, becomes necessary to specify the bonding conditions under which the size is being measured. Pertaining to four major types of bonding, atomic radii are of following four types:

i) Covalent radius

ii) Crystal or Metallic radius

iii) van der Waals radius

iv) Ionic radius.

2.2.1 Covalent Radius

Covalent radius is defined as one half of the distance between the nuclei of two like atoms bonded together by a single covalent bond. If in a homonuclear diatomic molecule of A_2 type (e.g., F_2, Cl_2, Br_2, I_2), $r_{A\text{-}A}$ is bond length or internuclear distance and r_A is the covalent radius of atom A, then $r_A = \frac{1}{2} r_{A\text{-}A}$.

The internuclear distance $r_{C\text{-}C}$ between two carbon atoms in diamond is 154 pm, so the covalent radius of carbon, r_C, is equal to 77 pm. Similarly, the $r_{Cl\text{-}Cl}$ for solid Cl_2 is 198 pm, r_{Cl} is, therefore, 99 pm. In a heteronuclear diatomic molecule of AB type, if the bonding is purely covalent, then the bond length $r_{A\text{-}B}$ is equal to the sum of covalent radii of A and B, i.e.,

$$r_{A\text{-}B} = r_A + r_B$$

Thus covalent radii are additive. It is possible to calculate the radius of one of the atoms in a heteronuclear diatomic molecule of AB type if we know the internuclear distance $r_{A\text{-}B}$ and radius of the other atom. For example, the Si-C bond length in carborundum is 193 pm and covalent radius of C is 77 pm; so you can calculate the covalent radius of Si as follows:

$$r_{Si\text{-}C} = r_{Si} + r_C \text{ or } r_{Si} = r_{Si\text{-}C} - r_C$$

$$\text{or } r_{Si} = 193 - 77 = 116 \text{ pm}$$

As stated earlier, the above relation holds good only if the bond between the atoms A and B is purely covalent. If there is a difference in the electronegativities of the bonded atoms, it causes shortening of the bonds. Schomaker and Stevenson have proposed the following relationship between the shortening of the bond and the electronegativity difference of the atoms:

$$r_{A\text{-}B} = r_A + r_B - 0.07\,(X_A - X_B)^2$$

Here X_A and X_B are the electronegativities of A and B, respectively, about which you will study in Section 2.5 of this unit.

Multiplicity of the bond also causes a shortening of the bond. Usually a double bond is about 0.86 times and a triple bond about 0.78 times the single bond length for the second period elements. Covalent radii of the elements are listed in Table 2.1.

Table 2.1: Covalent and van der Waals radii of elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 37 120	<——— Covalent radius in pm <——— van der Waals radius in pm																**He** 120
Li 123	**Be** 89											**B** 82	**C** 77	**N** 70 150	**O** 66 140	**F** 64 135	**Ne** 131
Na 156	**Mg** 136											**Al** 125	**Si** 117	**P** 110 180	**S** 104 190	**Cl** 99 185	**Ar** 174
K 203	**Ca** 174	**Sc** 144	**Ti** 132	**V** 122	**Cr** 118	**Mn** 117	**Fe** 117	**Co** 116	**Ni** 115	**Cu** 117	**Zn** 125	**Ga** 125	**Ge** 122	**As** 121 200	**Se** 117 200	**Br** 114 195	**Kr** 189
Rb 216	**Sr** 191	**Y** 162	**Zr** 145	**Nb** 134	**Mo** 130	**Tc** 127	**Ru** 125	**Rh** 125	**Pd** 128	**Ag** 134	**Cd** 144	**In** 144	**Sn** 140	**Sb** 141 220	**Te** 137 220	**I** 133 215	**Xe** 210
Cs 235	**Ba** 198	**La** 169	**Hf** 144	**Ta** 134	**W** 130	**Re** 128	**Os** 126	**Ir** 127	**Pt** 130	**Au** 134	**Hg** 147	**Tl** 155	**Pb** 154	**Bi** 148	**Po** 146	**At** —	**Rn** 215
			Ce 165	**Pr** 165	**Nd** 164	**Pm** —	**Sm** 166	**Eu** 185	**Gd** 161	**Tb** 159	**Dy** 159	**Ho** 158	**Er** 157	**Tm** 156	**Yb** 170	**Lu** 156	

SAQ 1

Assuming that the atoms are touching each other, what would be the internuclear distance between two fluorine atoms in F_2?

....

....

2.2.2 van der Waals Radius

In the solid state, the non-metallic elements usually exist as aggregates of molecules. The bonding within a non-metal molecule is largely covalent, yet individual molecules are held to each other by what is called van der Waals force. **Half of the distance between the nuclei of two atoms belonging to two adjacent molecules in the crystal lattice is called van der Waals radius.** Table 2.1 also lists the values of van der Waals radii of some elements.

Figure 2.1 illustrates the difference between the covalent and van der Waals radii of chlorine. It is evident from the figure that half of the distance between the nuclei X and X' of the two non-bonded neighbouring chlorine atoms of adjacent molecules A and B is the van der Waals radius of chlorine atom, whereas half of the distance between the two nuclei X and Y in the same molecule is the covalent radius of chlorine atom. Thus van der Waals radii represent the distance of the closest approach of an atom to another atom it is in contact with, but not covalently bound to it. Values of van der Waals radii are larger than those of covalent radii because the van der Waals forces are much weaker than the forces operating between atoms in a covalently bonded molecule.

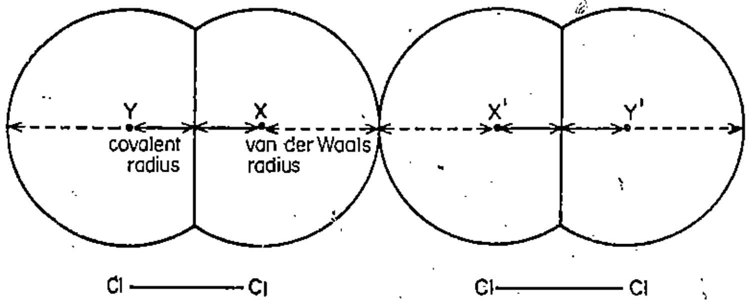

Fig. 2.1: Covalent and van der Waals radii of solid chlorine

2.2.3 Metallic or Crystal Radius

Metallic or crystal radius is used to describe the size of metal atoms which are assumed to be closely packed spheres in the metallic crystal. The metal atoms are supposed to touch one another in the crystal. **Metallic radius is defined as one-half of the distance between the nuclei of two adjacent metal atoms in the close packed crystal lattice.** For example, the internuclear distance between two adjacent Na atoms in a crystal of sodium metal is 382 pm, so the metallic radius of Na metal is 382/2, i.e., 191 pm.

The metallic radius depends to some extent on the crystal structure of the metal. Most metals adopt a close packed lattice, either hexagonal close packed (hcp) or cubic close packed (ccp) lattice (Fig. 2.2).

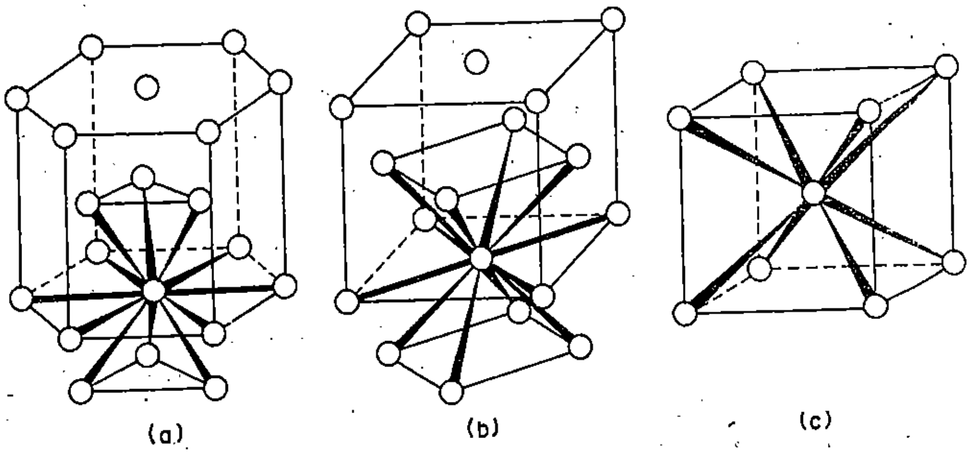

Fig. 2.2: Types of metal lattices: (a) hexagonal; (b) cubic close packed (c) body-centred cubic

In both these structures, a given metal atom has twelve nearest neighbours. However, a significant number of metals adopt a body centred cubic lattice (bcc) in which the number of nearest neighbours is eight. The number of nearest neighbours of a metal atom in a lattice is known as the **coordination number** of the metal. Experimental studies on a number of metals having more than one crystal lattice have shown that the radius of a metal in a eight coordinate lattice is about 0.97 of the radius of the same metal in a twelve coordinate environment. Table 2.2 gives a set of twelve coordinate radii for metal atoms which can be compared with the covalent radii or van der Waals radii in Table 2.1.

The metallic radii are generally larger than the corresponding covalent radii, although both involve a sharing of electrons. This is because the average **bond order** of an individual metal-metal bond is considerably less than one and therefore, the individual bond is weaker and longer than a covalent bond. This does not mean that the overall bonding is weak, as there is a large number of these bonds, eight or twelve per metal atom. On the other hand, the metallic radii are smaller than the van der Waals radii, since the bonding forces in the metallic crystal lattice are much stronger than the van der Waals forces.

2.2.4 Ionic Radius

Ionic radius is defined as the distance between the nucleus of an ion and the point upto which the nucleus has influence on the electron cloud. In other words, it may also be defined as the distance of the closest approach from the centre of ion by anther ion. Ionic radius is usually evaluated from the distance determined experimentally between the centres of nearest neighbours. Thus, if we wish to estimate the ionic radius of Na^+, we may measure the internuclear distance between Na^+ and Cl^- ions in the NaCl crystal lattice. This distance is the sum of radii of Na^+ and Cl^- ions. From the electron density maps obtained by X-ray analysis, it has become possible, in some cases, to apportion the internuclear distance into the radius of cation and anion. A small number of ionic crystals have thus been studied and the ionic radii of some of the elements have been determined. These radii have become the basis for assigning the ionic radii of most of the other elements.

Ionic radii are of two types: cation radii and anion radii. All common cations are smaller than all common anions except for the rubidium and caesium cations (largest single atom cations) which are larger than oxide and fluoride anions (smallest single atom anions). This is not too surprising, since not only there is a loss of electron(s) from a partially filled outer shell on cation formation, but there is also an increase in the overall positive charge on the ion. Conversely, in anion formation, the addition of an electron to an atom increases the size due to increase in inter-electronic repulsion in the valence-shell and decrease in effective nuclear charge. In general, there is a decrease in size from anions, to covalent radii of corresponding atoms to cations. Thus in a series of isoelectronic species (e.g., N^{3-}, O^{2-}, Ne, Na^+, Mg^{2+}, Al^{3+}), the greater the effective nuclear charge, the smaller is the radius of the species. In Table 2.2 radii of some of the common ions have been listed.

Table 2.2: Metallic and ionic radii of elements.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 208(-1)																	**He**
Li 155 60(+1)	**Be** 112 ← Metallic radius (CN = 12) in pm 31(+2) ← Ionic radius in pm with oxidation state in parenthesis											**B** 98 20(+3)	**C** 91 15(+4) 260(-4)	**N** 11(+5) 171(-3)	**O** 9(+6) 140(-2)	**F** 7(+7) 136(-1)	**Ne**
Na 190 95(+1)	**Mg** 160 65(+2)											**Al** 143 50(+3)	**Si** 132 41(+4) 271(-4)	**P** 128 34(+5) 212(-3)	**S** 29(+6) 184(-2)	**Cl** 26(+7) 181(-1)	**Ar**
K 235 133(+1)	**Ca** 197 99(+2)	**Sc** 164 81(+3)	**Ti** 147 76(+3) 68(+4)	**V** 135 74(+3) 60(+4)	**Cr** 130 84(+2) 69(+3)	**Mn** 135 80(+2) 66(+3)	**Fe** 126 76(+2) 64(+3)	**Co** 125 74(+2) 63(+3)	**Ni** 125 72(+2) 62(+3)	**Cu** 128 96(+1) 69(+2)	**Zn** 137 74(+2)	**Ga** 141 113(+1) 62(+3)	**Ge** 137 93(+2) 53(+4)	**As** 129 47(+5) 222(-3)	**Se** 140 42(+6) 198(-2)	**Br** 39(+7) 195(-1)	**Kr**
Rb 248 148(+1)	**Sr** 215 113(+2)	**Y** 178 93(+3)	**Zr** 160 80(+4)	**Nb** 146 70(+5)	**Mo** 139 68(+4) 62(+6)	**Tc** 136	**Ru** 134 69(+3) 67(+4)	**Rh** 134 86(+2)	**Pd** 137 86(+2)	**Ag** 144 126(+1)	**Cd** 154 97(+2)	**In** 166 132(+1) 81(+3)	**Sn** 162 112(+2) 71(+4)	**Sb** 159 62(+5) 245(-3)	**Te** 160 56(+6) 221(-2)	**I** 50(+7) 216(-1)	**Xe**
Cs 267 169(+1)	**Ba** 222 135(+2)	**La** 188 115(+3)	**Hf** 160 81(+4)	**Ta** 149 73(+5)	**W** 141 68(+4) 64(+6)	**Re** 137	**Os** 135 69(+4)	**Ir** 136 66(+4)	**Pt** 139 96(+2)	**Au** 146 137(+1)	**Hg** 157 110(+2)	**Tl** 171 140(+1) 95(+3)	**Pb** 175 120(+3) 84(+4)	**Bi** 170 120(+3) 74(+5)	**Po** 176	**At**	**Rn**

AQ 2

ill in the blanks in the following statements about atomic radii:

Atomic radii are of four types:

i) ....

ii) ....

iii) ....

iv) ....

) van der Waals radii are always .... than the covalent radii of the same atoms.

) Covalent radius of an atom is larger than the .... radius and .... than the anion radius of the same atom.

) In isoelectronic species, anion radius is always .... than the cation radius.

2.2.5 Factors Affecting the Atomic Radii

So far we have defined different types of atomic radii. Before describing periodicity in atomic radii, we shall first discuss two of the factors which affect them.

a) **Principal Quantum Number (*n*):** As the principal quantum number (*n*) increases, the outer electrons get farther and farther away from the nucleus and hence the atomic radius generally increases.

b) **Effective Nuclear Charge (Z^*):** You know that the magnitude of effective nuclear charge determines the magnitude of the force of attraction exerted by the nucleus on the outermost electrons. Greater the magnitude of effective nuclear charge, greater is the force exerted by the nucleus on the outermost electrons. Hence, the electron cloud of the outermost shell is pulled inward nearer to the nucleus and consequently its distance from the nucleus, i.e., atomic radius decreases.

Effective nuclear charge, Z^*, is the amount of positive charge felt by the outer electrons in an atom. It is always less than the actual charge, Z, of the nucleus of the atom. This is because electrons in inner shells partially shield the electrons in the outer shell from nuclear attraction. The effective nuclear charge felt by an outer electron depends upon the actual nuclear charge and the number and type of inner screening electrons. It can be calculated by subtracting the screening or shielding constant, S, from the atomic number, Z. Thus,

$$Z^* = Z - S$$

You can estimate the value of screening constant, S, with the help of Slater's rules in the following manner:

i) Write out the electronic configuration of the element in the following order and groupings: (1*s*) (2*s*, 2*p*) (3*s*, 3*p*) (3*d*) (4*s*, 4*p*) (4*d*) (4*f*) (5*s*, 5*p*) (5*d*) (5*f*) (6*s*, 6*p*), etc.

ii) Electrons in any group higher in this sequence than the electron under consideration contribute nothing to S. For example, in Ti atom (electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$), the two electrons in 4*s* orbital will contribute nothing towards the screening constant for an electron in 3*d* orbital.

iii) Then for an electron in an *ns* or *np* orbital

   a) All other electrons in the (*ns*, *np*) group contribute $S = 0.35$ each except for the electron in 1*s* which contributes $S = 0.30$.

   b) All electrons in the (*n*-1) shell contribute $S = 0.85$ each.

   c) All electrons in (*n*-2) or lower shells contribute $S = 1.00$ each.

iv) For an electron in an *nd* or *nf* orbital,

   a) All electrons in the same group, i.e., *nd* or *nf* contribute $S = 0.35$ each;

   b) Those in the groups lying lower in the sequence than the *nd* or *nf* group contribute $S = 1.00$ each.

To demonstrate the application of Slater's rules we shall now calculate the Z^* for an electron in N, K and Zn atoms.

i) Electronic configuration of N = $1s^2\ 2s^2\ 2p^3$. Grouping of the orbitals gives $(1s^2)$ $(2s^2\ 2p^3)$.

   Value of screening constant for an electron in 2*p* orbital will be

   $S = (4 \times 0.35) + (2 \times 0.85) = 3.10$. Hence,

   $Z^* = Z - S = 7 - 3.10 = 3.90$

ii) Electronic configuration of K = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. Grouping of orbitals will be $(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (4s^1)$. Value of screening constant for an electron in 4*s* orbital will be $S = (0.85 \times 8) + (1 \times 10) = 16.80$

   Hence, the effective nuclear charge

   $Z^* = Z - S = 19 - 16.80 = 2.20$

iii) Electronic configuration of Zn = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$. Grouping of the orbitals gives

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

   Value of screening constant S for an electron in 4*s* orbital will be

   $S = (0.35 \times 1) + (0.85 \times 18) + (1 \times 10)$
   $= 25.65$

Hence, the effective nuclear charge felt by 4*s* electron will be

$Z^* = Z - S = 30 - 25.65 = 4.35$

If we consider a 3*d* electron in Zn, the grouping is as above, but the effective nuclear charge felt by a 3*d* electron will be

$Z^* = Z - S = 30 - [(9 \times 0.35) + (18 \times 1.00)] = 8.85$

Thus, you can see that an electron in 3*d* orbitals in Zn is more strongly held by the nucleus than that in 4*s* orbital.

In Table 2.3 values of effective nuclear charge for electrons in valence shell for the first thirty elements calculated by Slater's rules have been listed. You can see from Table that there is a steady increase in Slater's Z^* across rows of the periodic table.

Effective nuclear charge felt by electrons also depends on the oxidation state of an atom in a compound. The higher the oxidation state of the atom, the higher will be the effective nuclear charge felt by the electrons and therefore, smaller will be the atomic radius. Thus, the ionic radius of Fe^{3+} ion will be smaller than that of the Fe^{2+} ion. Similarly the covalent radius of bromine in $BrCl_3$ will be smaller than that in BrCl.

Table 2.3: Effective nuclear charge for first 30 elements

Period	Element	Z	S	Z^*
1	H	1	0	1.0
	He	2	0.30	1.70
2	Li	3	1.70	1.30
	Be	4	2.05	1.95
	B	5	2.40	2.60
	C	6	2.75	3.25
	N	7	3.10	3.90
	O	8	3.45	4.55
	F	9	3.80	5.20
	Ne	10	4.15	5.85
3	Na	11	8.80	2.20
	Mg	12	9.15	2.85
	Al	13	9.50	3.50
	Si	14	9.85	4.15
	P	15	10.20	4.80
	S	16	10.55	5.45
	Cl	17	10.90	6.10
	Ar	18	11.25	6.75
4	K	19	16.80	2.20
	Ca	20	17.15	2.85
	Sc	21	18.0	3.0
	Ti	22	18.85	3.15
	V	23	19.70	3.30
	Cr	24	20.55	3.45
	Mn		21.40	3.60
	Fe	26	22.25	3.75
	Co	27	23.10	3.90
	Ni	28	23.95	4.05
	Cu	29	24.80	4.20
	Zn	30	25.65	4.35

SAQ 3

Compare the variation in the values of Slater's effective nuclear charge for the valence electrons in the elements of period 2 with that in the elements of 3d series.

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2.2.6 Periodicity in the Atomic Radii

After having an overview of the various types of atomic radii and the factors affecting them, we will now consider the periodicity in them. But before doing that, we would like to emphasise that trends observed in one type of radii (e.g., covalent radii) are generally found in the other types of radii also (e.g., ionic and metallic radii). Two general periodic trends are found for all four types of atomic radii. These are: the atomic radii decrease along a period and generally increase down a group in the long form of the periodic table (Fig. 2.3). These changes in the atomic radii can be related to the changes in effective nuclear charge and the principal quantum number in the periodic table.

In Table 2.3, we have listed Slater's values of effective nuclear charge for the first thirty elements. As shown in this Table, there is a steady increase (by 0.65 units) in the value of Z^* from alkali metals to halogens for the elements of period 2 and 3. But there is no change in the value of n because the electrons fill the same principal shell. As a result of this, there is a steady decrease in the covalent radius from 123 and 156 pm, for Li and Na to 64 and 99 pm for F and Cl, respectively.

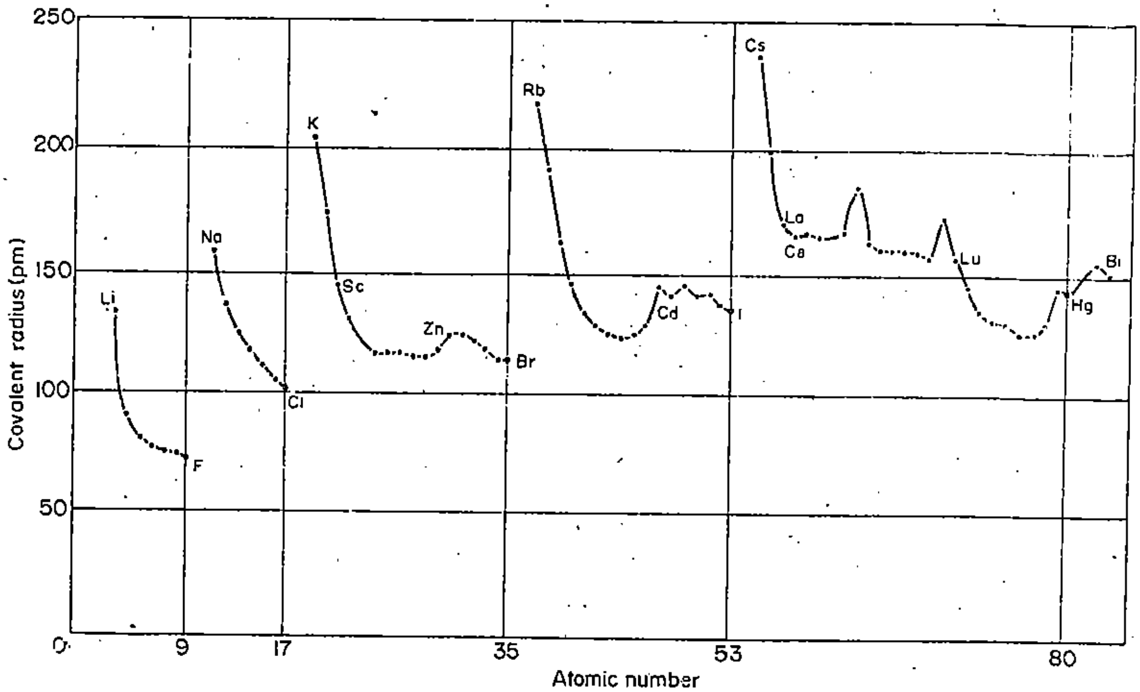

Fig. 2.3: Variation of covalent radius with atomic number

In comparison to the above, the decrease in covalent radii across a transition series is much smaller. As you know, electrons are successively filled in the $(n\text{-}1)d$ orbitals across a transition series and hence screen the size determining ns electrons from the nuclear charge more effectively. Therefore, across a transition series, there is only a small increase in effective nuclear charge (by 0.15 units), therefore, only a small decrease in atomic radius from one element to another takes place. Thus, in $3d$ series, covalent radius decreases from 144 pm for Sc to 115 pm for Ni. Then, in copper and zinc due to completion of $3d$ subshell, the electronic charge density in this subshell becomes very high which increases the interelectronic repulsion. As a result, covalent radii of Cu and Zn increase slightly to 117 and 125 pm, respectively. Thus, across ten elements of the first transition series, there is an overall decrease in covalent radius by 19 pm which is much less than that across seven normal elements of period 2 (59 pm) and period 3(57 pm). But due to this, the covalent radii of elements from Ga to Kr, following Zn, become much smaller than that expected by simple extrapolation of the values for elements of period 2 and 3. For example, the covalent radii of Al and Ga are equal whereas the covalent radii of elements Ge, As, Se, Br are only slightly larger than those of corresponding elements (Si, P, S and Cl) of period 3.

The rate of decrease in the size across the lanthanide series is even less than that across the first transition series. In the lanthanide elements, filling of $(n\text{-}2)f$ orbitals takes place, while simultaneously the nuclear charge increases. The electrons in the $(n\text{-}2)f$ orbitals shield the ns electrons, which largely determine the size, from the increase in nuclear charge almost completely ($S = 1.00$). As a result of this, there is only a small decrease in the atomic radius from one element to another. But there are 14 elements in the series, there is a total contraction of 13 pm across the series from La ($Z = 57$) to Lu ($Z = 71$). This is known as lanthanide contraction, because of which the atoms of elements (Hf to Hg) following Lu are unusually smaller than they would be if the lanthanides had not been built up before them. Lanthanide contraction almost exactly cancels out the effect of the last shell added in the sixth period and therefore, the transition elements of $4d$ and $5d$ series have almost the same atomic radii.

On descending any group of the periodic table, the number of electrons in the valence shell remains constant but the number of shells around nucleus increases monotonically. The effective nuclear charge felt by valence electrons stays nearly the same. So, with the increase in principal quantum number (n) of the valence shell, an increase in atomic radii is generally observed down any group of the periodic table. For example, as shown in Fig. 2.4, there is an increase in the atomic radii of alkali and alkaline earth metals as we proceed downwards in the group. But as discussed earlier, with the inclusion of 3*d* transition elements in period 4, increase in the radii of elements from Ga to Br is smaller than expected. Similarly, because of inclusion of lanthanide elements in period 6, atoms of the transition elements of this period (Hf to Hg) are almost of the same size as the atoms above them in period 5(Zr to Cd). After that only a small increase in size of the remaining elements of period 6 (Tl to At) as compared to the size of elements above them in period 5 (In to I) is observed.

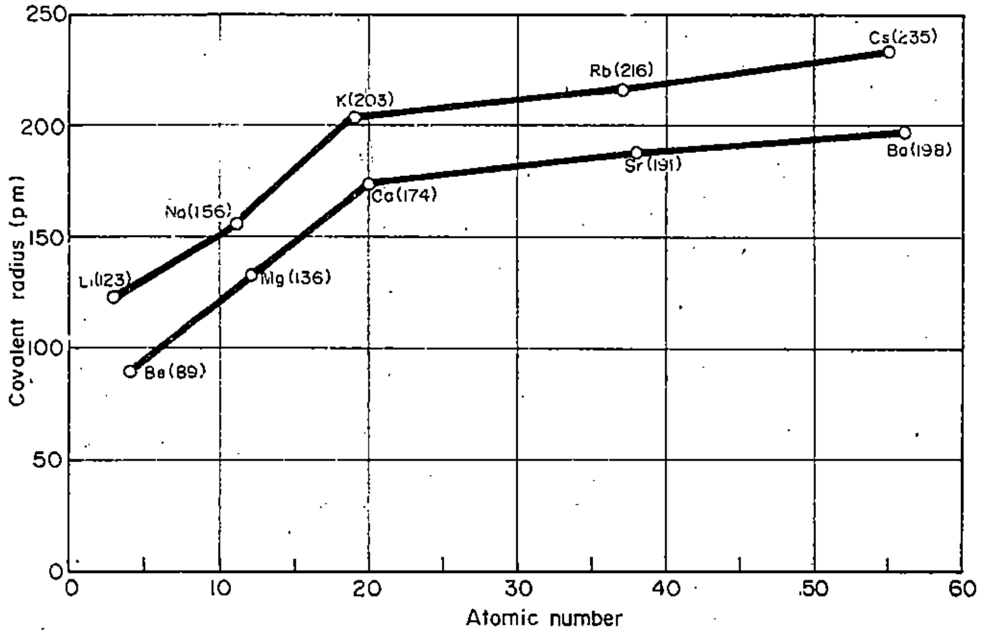

Fig. 2.4: Variation of covalent radius with atomic number down the group.

SAQ 4

a) For each of the following pairs, tick (√) the one which is larger in size?

i) Na, Na^+ ii) Br, Br^- iii) Br, I iv) O, S v) K^+,Cl^- vi) Li, F

b) Arrange the following isoelectronic species in order of decreasing atomic radius:

Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, N^{3-}, O^{2-}, F^-, Ne.

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2.3 IONISATION ENERGY

Chemical reactivity of an element has a direct relation with its tendency to gain, lose or share its valence electrons with those of other elements. This process of gain, loss or sharing of electrons is accompanied by energy changes. You know that electrons are bound to the nucleus of an atom by an electrostatic force of attraction. To remove an electron from an atom, this force of attraction would have to be overcome. This can be done by supplying energy. **Energy required to remove the least strongly bound electron from an isolated gaseous atom in its ground state is known as the ionisation energy.** You can represent this process by the following equation:

$$M(g) \longrightarrow M^+(g) + e$$

Since more than one electron may be removed from an atom, the energy required for the above process is called the first ionisation energy. Second ionisation energy is the energy required to remove an electron from a univalent cation, that is, to cause the following reaction to occur:

$$M^+(g) \longrightarrow M^{2+}(g) + e$$

Second ionisation energy is much larger than the first ionisation energy, as in this case an electron is being removed from a positively charged cation. Similarly you can define third, fourth and higher ionisation energies. **S I unit of ionisation energy** which we will use throughout this course is **kilojoule per mole.**

2.3.1 Factors Affecting Ionisation Energy

The ionisation energy, *I*, of an outer valence electron is related to the effective nuclear charge felt by the electron and its average distance from the nucleus as given below:

$$I = \frac{Z^{*} \cdot e^{2}}{2} \cdot (1/r)\text{av}$$

where Z^{*} is the effective nuclear charge, e is the charge on electron and $(1/r)$av is the average value of $1/r$, r being the distance of the electron from the nucleus. Thus, the higher is the effective nuclear charge felt by the electron, the higher will be the ionisation energy; also the farther the electron is from the nucleus, the lower will be the ionisation energy and *vice versa.*

In addition to the above, ionisation energy also depends upon the relative stabilities of the subshells from which the electron is removed. As we have stated before, completely filled and half filled subshells are comparatively more stable. So, removal of an electron from them requires more energy. The valence shell electronic configurations of noble gases are exceptionally stable and, therefore, their ionisation energies are the highest in the respective periods. Try the following SAQ to see whether you understand the effect of various factors on ionisation energy.

SAQ 5
Explain briefly why is the second ionisation energy of an element [illegible] first ionisation energy.

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2.3.2 Periodicity in Ionisation Energy Across Periods

In the above sub-section, we have defined ionisation energy and have identified the factors which affect it. Now, we shall examine the variation in ionisation energy across the periods and down the groups in the periodic table. Values of ionisation energies of elements are given in Table 2.4.

Table 2.4: Ionisation energies of elements in kJ mol^{-1}

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 1312																	**He** 2372
Li 520	**Be** 900											**B** 800	**C** 1086	**N** 1403	**O** 1314	**F** 1681	**Ne** 2081
Na 495	**Mg** 738											**Al** 577	**Si** 787	**P** 1060	**S** 1000	**Cl** 1255	**Ar** 1520
K 418	**Ca** 590	**Sc** 633	**Ti** 659	**V** 650	**Cr** 653	**Mn** 717	**Fe** 762	**Co** 759	**Ni** 736	**Cu** 745	**Zn** 906	**Ga** 579	**Ge** 760	**As** 946	**Se** 941	**Br** 1142	**Kr** 1350
Rb 403	**Sr** 549	**Y** 615	**Zr** 659	**Nb** 664	**Mo** 688	**Tc** 697	**Ru** 711	**Rh** 720	**Pd** 804	**Ag** 731	**Cd** 867	**In** 558	**Sn** 707	**Sb** 833	**Te** 869	**I** 1007	**Xe** 1170
Cs 374	**Ba** 502	**La** 541	**Hf** 674	**Ta** 745	**W** 770	**Re** 761	**Os** 837	**Ir** 879	**Pt** 870	**Au** 890	**Hg** 1006	**Tl** 589	**Pb** 715	**Bi** 703	**Po** 813	**At** 912	**Rn** 1037

Ce 540	**Pr** 527	**Nd** 527	**Pm** 540	**Sm** 540	**Eu** 547	**Gd** 594	**Tb** 577	**Dy** 573	**Ho** 582	**Er** 586	**Tm** 561	**Yb** 598	**Lu** 594

However, the variation of ionisation energy in a particular group or period, is best shown by plotting ionisation energies against atomic number. Fig. 2.5 shows the plot of first ionisation energies of the elements of first six periods against their atomic numbers. As is evident from the figure, the first ionisation energy generally increases from alkali metals to noble gases across any row of the periodic table. But the increase is not perfectly regular. We will consider this aspect a little later.

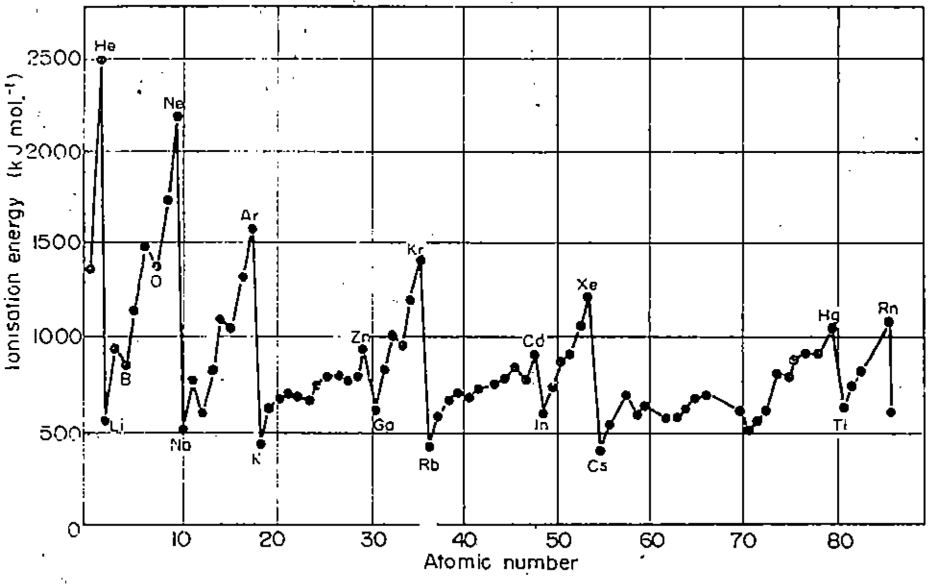

Fig. 2.5: Variation of ionisation energy with atomic number

You have studied in Sub-section 2.2.6 that across any row of the periodic table, the effective nuclear charge steadily increases and the atomic radii decrease. These two effects reinforce each other to increase the ionisation energy across a period. Thus, the ionisation energies of the alkali metals are the lowest and those of the noble gases are the highest in their respective periods. But as pointed out earlier, the increase is not smooth and some anomalies are observed. For example, in the elements of period 2, inspite of increase in Z^* and decrease in r, the first ionisation energies of B and O are lower than those of Be and N, respectively. However, these anomalies in the trend in ionisation energy can be explained by electronic structures of these elements.

In case of beryllium, the electron is removed from the filled $2s$ subshell, whereas in boron, the electron is removed from the singly occupied $2p$ subshell. The $2p$ subshell is higher in energy than the $2s$. So, the $2p$ electron of boron is more easily removed than a $2s$ electron of beryllium. When we come to nitrogen, we find that we have a half filled $2p$ subshell (electronic configuration $1s^2\,2s^2\,2p^3$), while in oxygen the $2p$ subshell is occupied by four electrons. The fourth electron in this $2p$ subshell is in an orbital already occupied by another electron. So, it experiences considerable repulsion. As a result, this electron is more easily removed than one of the electrons from a singly occupied orbital in nitrogen atom. Thus, the ionisation energy of oxygen becomes less than that of nitrogen. Similar anomalies are observed in elements of period 3, where the first ionisation energies of magnesium and phosphorus are higher than those of aluminium and sulphur, respectively.

You have studied in Sub-section 2.2.6, that across a transition series, the increase in effective nuclear charge and consequent decrease in atomic radius is small. Therefore, increase in their first ionisation energies is also small. But following the transition elements, the first ionisation energy drops abruptly in gallium, indium and thallium. This again is due to the removal of an electron from the singly occupied np orbitals which are of relatively higher energy than the ns orbitals of Zn, Cd and Hg.

2.3.3 Trends in Ionisation Energy Down the Groups

In Sub-section 2.2.6, you have already studied that on moving down a group of s-and p-block elements in the periodic table, effective nuclear charge remains almost steady. But there is a general increase in the atomic radius due to increase in the value of the principal quantum number, n. Thus, the dominant factor in determining the ionisation energies of the elements on moving down the groups, is their atomic radius rather than the effective nuclear charge. Therefore, as expected, the first ionisation energies decrease down the groups in case of the main group elements in the periodic table. But in the case of transition elements opposite trends are observed. Thus, the first ionisation energies of the corresponding elements of $3d$ and $4d$ series are almost similar but these are smaller than the first ionisation energies of the elements of 5*d* series. Certainly, the higher values of ionisation energies of the 5*d* transition elements are consistent with the relatively smaller size of their atoms.

2.3.4 Trends in Successive Ionisation Energies

We have already defined successive ionisation energies, i.e., second, third, etc. Values of eight successive ionisation energies of first twenty elements are listed in Table 2.5.

Table 2.5: Successive ionisation energies (kJ mol^{-1}) of first 20 elements

	First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eighth
H	1 312							
He	2 372	5 250						
Li	520	7 297	11 810					
Be	900	1 757	14 850	21 000				
B	800	2 427	3 658	25 024	32 824			
C	1 086	2 352	4 619	6 220	37 820	47 280		
N	1 403	2 858	4 578	7 473	9 443	53 270	64 360	
O	1 314	3 391	5 300	7 469	10 983	13 326	71 330	84 050
F	1 681	3 381	6 046	8 418	11 017	15 163	17 870	92 000
Ne	2 081	3 964	6 150	9 376	12 200	15 230	—	—
Na	495	4 563	6 912	9 540	13 350	16 732	20 110	25 490
Mg	738	1 450	7 730	10 550	13 625	18 035	21 735	25 660
Al	577	1 816	2 745	11 575	14 850	18 370	23 350	27 460
Si	787	1 577	3 230	4 355	16 090	19 795	23 770	29 250
P	1 060	1 869	2 908	4 954	6 272	21 270	25 413	29 840
S	1 000	2 258	3 381	4 565	6 995	8 494	27 112	31 720
Cl	1 255	2 297	3 849	5 163	6 540	9 330	11 029	33 600
Ar	1 520	2 665	3 947	5 770	7 238	8 810	11 965	13 840
K	418	3 069	4 439	5 875	7 950	9 619	11 384	14 950
Ca	590	1 146	4 941	6 464	8 142	10 500	12 350	13 830

It is evident from the values in the Table that the successive ionisation energies of an element inevitably become larger because the removal of successive electrons leaves a higher charge on the nucleus to hold the remaining electrons. It is also clear from the Table that the difference between successive ionisation energies of the same element is not constant. Big jumps occur whenever an electron from a subshell of lower principal quantum number is removed for the first time. For example, for alkali metals the second ionisation energies are much higher than the first; for alkaline earth metals the third ionisation energies are much larger than the second and for the halogens the eighth ionisation energies are much greater than the seventh. These cannot be explained on the basis of increase in nuclear charge alone. The stabilities of closed shell configurations similar to those of noble gases are more important in these cases.

In this section so far you have studied that the ionisation energy generally increases across a period and decreases down the group in the periodic table. Accordingly, the tendency to form cation, i.e., metallic character decreases across a period and increases down the group. For example, in period 3 metallic character decreases from Na to Cl whereas in the elements of Group 14, C is a nonmetal, Si and Ge are semimetals or metalloids whereas Sn and Pb are metals.

SAQ 6

a) Which of the atoms having following electronic configurations will have the highest first ionisation energy and why?

i) [Ne] $3s^2\ 3p^2$ ii) [Ne] $3s^2\ 3p^3$ iii) [Ne] $3s^2\ 3p^4$ iv) [He] $2s^2\ 2p^3$

v) [Ar] $3d^{10}\ 4s^2\ 4p^3$.

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b) The order of increasing ionisation energy for the atoms N, Ne, Na and P is

i) Na<P<N<Ne ii) N<Ne<Na<P

iii) N<Na<Ne<P iv) Na<N<P<Ne

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2.4 ELECTRON AFFINITY

Electron affinity of an atom is a measure of its ability to accept an electron to form an anion. It is defined as **the energy released or absorbed, when an electron is added to a gaseous atom in its ground state**. It can be represented by the following equation in which E_A represents the electron affinity of X:

$X(g) + e \longrightarrow X^-(g) + E_A$

When one mole of chlorine atoms pick up one mole of electrons, 348 kJ energy is released. So, the electron affinity of chlorine is – 348 kJ mol^{-1}:

$Cl\,(g) + e \longrightarrow Cl^-\,(g),\ E_A = -348\ \text{kJ mol}^{-1}$

But in the reverse process of removal of an electron from the chloride ion to form a chlorine atom, obviously an equal amount of energy has to be supplied. So, the electron affinity can also be expressed as the ionisation energy of the anion. Thus, the electron affinity of chlorine atom is clearly the ionisation energy of the chloride ion. Electron affinities are difficult to measure and accurate values are not known for all elements. Values for the representative elements are given in Table 2.6.

In the preceding section, you have studied that for removing an electron from isolated neutral atoms in the gaseous state, energy is required to overcome the attractive force of the nucleus. Therefore, the reverse process of the addition of an electron to the neutral atom should release energy. Thus, the electron affinities of most elements are negative, but a few elements are known to have positive values for electron affinity which means that the electron must be forced on to the neutral atom to form an anion. For example, nitrogen, alkaline earth metals and noble gases have positive values. All second and higher electron affinities also have large positive values. This is not surprising, since the second and the subsequent electrons must be forced on against the negative charge of the anion. For example:

$O^-(g) + e \longrightarrow O^{2-}(g)\ ;\ E_A = +701\ \text{kJ mol}^{-1}$

$S^-(g) + e \longrightarrow S^{2-}(g)\ ;\ E_A = +565\ \text{kJ mol}^{-1}$

Here, we will like to point out that a little confusion regarding the sign convention of the electron affinity generally prevails. But we are following the standard thermodynamic convention, according to which the negative value means an exothermic process, i.e., the reaction

$X(g) + e \longrightarrow X^-(g)$

is exothermic. Also by high electron affinity we mean to say that the value of electron affinity is large and negative.

Table 2.6: Electron affinities of some elements in kJ mol^{-1}

1	2	13	14	15	16	17	18
H –73							
Li –60	Be ≈ +100	B –27	C –122	N +9	O –141	F –328	He +54
Na –53	Mg ≈ +30	Al –44	Si –134	P –72	S –200	Cl –348	Ne +99
K –48	Ca –	Ga –30	Ge –120	As –77	Se –195	Br –325	
Rb –47	Sr -	In –30	Sn –121	Sb –101	Te –190	I –295	
Cs –45	Ba –	Tl –30	Pb –110	Bi –110	Po –183	At –270	

2.4.1 Factors Affecting Electron Affinity

Factors affecting electron affinities are generally the same which affect the ionisation energies. These factors are:

Atomic radius: When an electron adds on to any atom, the nucleus of the atom holds it by an electrostatic force of attraction, which depends upon the effective nuclear charge and size of the atom. The smaller is the size of the atom, the greater will be the force of attraction of the nucleus for the extra electron and, therefore, higher will be the electron affinity of the atom, that is more energy will be released in picking up an electron.

Effective nuclear charge: The higher the effective nuclear charge, greater the force of attraction exerted by the nucleus on the added electron and hence, higher will be the electron affinity of the atom.

Electronic configuration: Electronic configuration of the atom also plays an important role in determining the magnitude and sign of electron affinity. Halogens can achieve a stable noble gas configuration by accepting just one electron. Therefore, they have large negative (exothermic) electron affinities. On the other hand, the noble gases with closed shell ns^2np^6 configuration, beryllium and magnesium with ns^2 (stable due to filled subshell) and nitrogen having ns^2np^3 (stable due to half filled p subshell) configuration strongly resist the addition of any electron. Therefore, the electron affinities of these elements are either zero or have small positive values.

2.4.2 Periodicity in Electron Affinity

In this section you have so far studied the definition of electron affinity and have considered the factors that affect it. In this sub-section you will now learn how the electron affinity varies in the periodic table.

Trends across periods: On moving from left to right in a period, size of the atoms decreases and effective nuclear charge increases. Both these factors favour an increase in the force of attraction exerted by the nucleus on the extra electron. Consequently, the electron affinity generally increases across a period, though irregularly. Thus, electron affinities of alkali metals have small negative values indicating their reluctance to form an anion. On the other hand, electron affinities of halogens in a period are the highest negative values which is reflected in their ability to form anions most readily. As explained earlier, the electron affinities of noble gases, beryllium, magnesium and nitrogen have small positive values.

Trends across groups: You have learnt in Sub-section 2.2.6 that on moving down a group of s–and p-block elements in the periodic table, the effective nuclear charge remains almost steady, but there is a general increase in atomic radius due to increase in the value of the principal quantum number, n. As a result, the electron affinity generally decreases down any group in the periodic table, as is evident from the values listed in Table 2.6. Values of electron affinities of second row nonmetals, i.e., B, C, N, O, F are, however, against the general trend, being smaller than those of corresponding elements, i.e., Al, Si, P, S, Cl of period 3. This is apparently an indirect result of the small size of the atoms of these elements, i.e., B, C, N, O, F. Thus, the crowding of electrons in the smaller outer shell of an atom of an element of period 2 makes mutual repulsion of electrons substantially greater than that in the relatively larger outer shell of an atom of an element of period 3. Therefore, even though, an electron added to an atom of an element of period 2 is closer to the nucleus than the one added to an atom of an element of period 3, greater inter-electronic repulsion in a smaller shell leads to a lower electron affinity.

SAQ 7

State which of the following statements are true or false. Write 'T' if true and 'F' if false.

a) Values of second electron affinities are always positive.

b) Electron affinity of nitrogen is much lower than that of its neighbouring elements, carbon and oxygen.

c) Electron affinity of fluorine is higher than that of chlorine.

d) Electron affinities of noble gases are zero.

e) Electron affinities of elements of period 3 are lower than those of the corresponding elements of period 2.

2.5 ELECTRONEGATIVITY

In the Sections 2.3 and 2.4 you have studied ionisation energies and electron affinities of isolated gaseous atoms. These quantities are a measure of the tendency of isolated atoms to lose or gain electrons. In the present section, you will learn about electronegativity of an element, which is a measure of the power of an atom in a molecule to attract shared electrons to itself. Unlike ionisation energy and electron affinity, it is not a directly measurable physical quantity, but rather a theoretical concept for which several numerical scales have been developed. In this section we shall discuss three of them, namely Pauling's, Allred-Rochow's and Mulliken's scales which are comparatively more important.

2.5.1 Pauling Electronegativity Scale

As you know, in homonuclear diatomic molecules like A_2 and B_2, the electron pair is equally shared between the bonded atoms. But in a heteronuclear diatomic molecule of the AB type, the situation is quite different. In the process of formation of bond between A and B, atom A slowly starts stripping off its electron and thereby it is becoming a partially cationic species. As the positive charge develops on A, its tendency to attract electrons increases. An analogous process also takes place on B. Thus, both the atoms A and B start attracting the electron pair towards themselves. They continue doing so until the tendencies of both the atoms in the bonded state to attract the electron pair towards themselves balance. If one of the atoms, say B, has higher tendency to attract the electron pair towards itself compared to that of the other atom, say A, the electron pair will spend more time on B than on A. Partial charges will thus be generated on A and B. **This tendency of attracting the electron pair towards itself by an atom in a molecule has been termed as electronegativity of the element.**

This concept was first developed by Pauling. He defined it on the basis of the patterns discernible in the single bond energies of elements, which were derived from the thermochemical data. He realised that bond energy, E_{A-B}, between two unlike atoms A and B is greater than $\sqrt{E_{A-A}}\cdot\sqrt{E_{B-B}}$ where E_{A-A} and E_{B-B} are bond energies of A–A and B–B homonuclear bonds. He assigned the cause of this excess bond energy, $E_{A-B} - \sqrt{E_{A-A}}\cdot\sqrt{E_{B-B}}$, to the electrostatic attraction between partially charged atoms $(A^{\delta+} - B^{\delta-})$ in the molecule. Partial charges on the atoms are separated due to difference in electron attracting tendencies of A and B. i.e., the difference in the electronegativities of A and B. He was able to correlate the difference in electronegativities of two atoms, with the excess bond energy and derived a relationship

$$E_{A-B} - \sqrt{E_{A-A}}\cdot\sqrt{E_{B-B}} = 96.49\,(X_A - X_B)^2$$

where X_A and X_B designate electronegativities of the elements A and B, respectively and are assumed to be the same for all molecules containing A and B. You can write this relationship as

$$\Delta X^2_{AB} = (X_A - X_B)^2 = \frac{E_{A-B} - \sqrt{E}_{A-A}\cdot\sqrt{E}_{B-B}}{96.49}$$

$$\text{or } \Delta X_{AB} = \sqrt{\frac{E_{A-B} - \sqrt{E}_{A-A}\cdot\sqrt{E}_{B-B}}{96.49}}$$

Knowing bond energies, it is thus possible to calculate the difference between the electronegativities of the two elements. This formula, however, gives the difference in the electronegativities and not the absolute value assigned to a particular element. As the largest electronegativity difference on this scale between the most electronegative element fluorine and the most electropositive element caesium came out to be 3.3, Pauling assigned arbitrarily a whole number value 4.0 for fluorine so that values of electronegativity of all elements remain positive. In Table 2.7, the values of electronegativity of different elements are represented in bold face as calculated by Pauling using the above formula for differences in electronegativity.

2.5.2 Mulliken - Jaffe Electronegativity Scale

Mulliken defined electronegativity as the mean value of first ionisation energy and first electron affinity. Both quantities are given a positive value if loss of electron involves absorption of energy and gain of electron involves release of energy. Thus, electronegativity X_A of atom A is given by the following relationship:

$$X_A = \frac{(I)_A + (E_A)_A}{2}$$

According to this relationship, a very electronegative element has a very high ionisation energy. So, it will be difficult to remove its electrons. It also has a very high electron affinity. Hence, a very stable species results when electrons are added. On the other hand, an element of low electronegativity will have a low ionisation energy and low electron affinity. So, it loses electrons readily, and has little tendency to pick them up. Unfortunately, it is

Table 2.7: Electronegativity values of elements.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H 2.1 2.1	<——Pauling Scale <——Allred - Rochow Scale																**He**
Li 1.0 1.15	**Be** 1.5 1.50											**B** 2.0 2.0	**C** 2.5 2.5	**N** 3.0 3.05	**O** 3.5 3.5	**F** 4.0 4.1	**Ne**
Na 0.9 1.0	**Mg** 1.2 1.25											**Al** 1.5 1.45	**Si** 1.8 1.74	**P** 2.1 2.05	**S** 2.5 2.45	**Cl** 3.0 2.85	**Ar**
K 0.8 0.9	**Ca** 1.0 1.05	**Sc** 1.3 1.2	**Ti** 1.5 1.3	**V** 1.6 1.45	**Cr** 1.6 1.55	**Mn** 1.5 1.6	**Fe** 1.8 1.65	**Co** 1.8 1.7	**Ni** 1.8 1.75	**Cu** 1.9 1.75	**Zn** 1.6 1.65	**Ga** 1.6 1.8	**Ge** 1.8 2.0	**As** 2.0 2.2	**Se** 2.4 2.5	**Br** 2.8 2.75	**Kr**
Rb 0.8 0.9	**Sr** 1.0 1.0	**Y** 1.2 1.1	**Zr** 1.4 1.2	**Nb** 1.6 1.25	**Mo** 1.8 1.3	**Tc** 1.9 1.35	**Ru** 2.2 1.4	**Rh** 2.2 1.45	**Pd** 2.2 1.35	**Ag** 1.9 1.4	**Cd** 1.7 1.46	**In** 1.7 1.5	**Sn** 1.8 1.7	**Sb** 1.9 1.8	**Te** 2.1 2.0	**I** 2.5 2.2	**Xe**
Cs 0.7 0.85	**Ba** 0.9 0.95	**La** 1.1 1.1	**Hf** 1.3 1.25	**Ta** 1.5 1.35	**W** 1.7 1.4	**Re** 1.9 1.45	**Os** 2.2 1.5	**Ir** 2.2 1.55	**Pt** 2.2 1.45	**Au** 2.4 1.4	**Hg** 1.9 1.45	**Tl** 1.8 1.45	**Pb** 1.8 1.55	**Bi** 1.9 1.65	**Po** 2.0 1.75	**At** 2.2 1.90	**Rn**
Fr 0.7	**Ra** 0.9	**Ac** 1.1	**Unq**	**Unp**	**Unh**	**Uns**	**Uno**	**Une**									

Ce 1.1 1.82	**Pr** 1.1 1.82	**Nd** 1.2 1.82	**Pm** — —	**Sm** 1.2 —	**Eu** — 2.04	**Gd** 1.1 1.79	**Tb** 1.2 1.77	**Dy** — 1.77	**Ho** 1.2 1.76	**Er** 1.2 1.75	**Tm** 1.2 1.74	**Yb** 1.1 1.93	**Lu** 1.2 1.74
Th 1.3 1.80	**Pa** 1.5 —	**U** 1.7 1.4	**Np** 1.3 —	**Pu** 1.3 —	**Am** 1.3 —	**Cm** 1.3 —	**Bk** 1.3 —	**Cf** 1.3 —	**Es** 1.3 —	**Fm** 1.3 —	**Md** 1.3 —	**No** 1.3 —	**Lr** — —

very difficult to measure electron affinity for all elements. Therefore, this method also is not universally applicable. The electronegativity values on Mulliken's scale are about 2.8 times those of Pauling's values. The trends in the variation of electronegativities are, however, the same.

2.5.3 Allred-Rochow Electronegativity Scale

According to Allred and Rochow, electronegativity is equated to the force of attraction between an atom and an electron separated by a distance equal to the covalent radius of the atom. The force of attraction is expressed according to Coulomb's law as,

$$F = \frac{Z^* e^2}{r^2}$$

where Z^* is the Slater's effective nuclear charge, e the electronic charge and r the covalent radius. A plot of Pauling electronegativities against Z^*/r^2 gives an approximately straight line. Values of the slope and intercept indicate that on the Pauling scale, Allred-Rochow electronegativities are given by the numerical relationship,

$$X_A = 3590 \frac{Z^*}{r^2} + 0.744, \text{ where value of } r \text{ is in pm.}$$

This method has an advantage in that it can be applied to a comparatively larger number of elements. Electronegativities of elements on Allred-Rochow scale have been listed in Table 2.7.

Electronegativity is a measure of the attraction that an atom has for electrons in a bond it has formed with another atom. The ability of an atom to attract electrons depends upon the charge on the atom and the hybridisation of the atom. An atom which has acquired a positive charge will tend to attract electrons to it more readily than will a neutral atom. In turn, a negatively charged atom will attract electrons less than a neutral atom. Hybridisation also affects electronegativity because of the lower energy and hence, greater electron attracting power of *s*-orbitals. Thus, hybrid orbitals having greater *s*-character possess higher electronegativity. An atom in *sp* hybridised state will be more electronegative than the same atom in sp^2 hybridised state which in turn will be more electronegative than the same atom in sp^3 hybridised state. Thus, the carbon atom in CH_4, C_2H_4 and C_2H_2 has different values of electronegativity. So, you can say that electronegativity is not a constant quantity. All the electronegativity scales give average values of electronegativities of elements in different bonding environments.

So far, you have studied different definitions of electronegativity for which three numerical scales have been proposed. All these scales, give relative values of electronegativity which are useful in making quantitative comparisons between elements. Electronegativities can be used to predict the nature of the bonding that a compound will have. The larger the difference between the electronegativities of two elements, the more polar will be the bond between these elements. An electronegativity difference of about 1.7 corresponds to a partial ionic character of about 50%. So, a bond can be considered predominantly ionic, if the difference in the electronegativities of the bonded atoms is more than 1.7. On the contrary, a difference in the range of 0.4 to 1.7 results in a covalent bond with partial ionic character or polar covalent bond.

2.5.4 Periodicity in Electronegativity

Electronegativity values of elements show a fairly discernible periodic trend throughout the periodic table. The trend is similar to that of ionisation energies. Thus, as expected electronegativity of elements increases sharply across a row of *s*-and *p*-block elements, since the effective nuclear charge of these elements is increasing sharply for example, from lithium to fluorine . However, across a series of transition elements, the increase in electronegativity is much smaller. This is because the additional electron is being added to an inner shell which provides relatively good shielding for the outer electron from the nucleus.

On moving down a group of representative elements, for example, in the lithium group, there is a general decrease in electronegativity. The decrease is relatively small except between the first two elements. The much greater electronegativity of lithium row elements correlates well with their small size. As expected, the elements of period 4 from gallium onwards, i.e., Ga, Ge, As, Se and Br have greater electronegativities than would be expected by extrapolation from values for the first two elements in the respective groups. This is due to the insertion of transition elements, because of which, the effective nuclear charge of these elements is greater than that if the transition elements were not there. Similarly, the presence of the lanthanide elements is responsible for greater electronegativities of the elements of 5*d* series than would be expected by extrapolation from values of the elements of 3*d* and 4*d* series.

SAQ 8

a) Explain the difference between electron affinity and electronegativity.

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b) Arrange the following elements in the order of increasing electronegativity:

Be, Li, C, B, O, F, N

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c) Name the least and most electronegative elements in the periodic table.

....

2.6 SUMMARY

In this unit you have studied that properties like atomic radii, ionisation energy, electron affinity and electronegativity are called atomic properties because they depend on the nature of individual atoms of the elements. These atomic properties are related to the electronic configuration of the atoms of elements. These vary in a more or less regular way that is to say exhibit periodicity as we go across a period of the periodic table. Therefore, these atomic properties are also called periodic properties.

Atomic radius is a measure of the size of an atom. Atomic radius depends on two factors: i) principal quantum number, n and ii) effective nuclear charge, Z^*. Atomic radius increases with increase in principal quantum when we go down a group. It decreases with increase in effective nuclear charge when we move across a period in the periodic table.

Ionisation energy is the energy required to remove an electron form a neutral gaseous atom producing a gaseous unipositive ion. Ionisation energy increases as we go across a period. There are some notable irregularities in this trend which can be explained in the light of the electronic configuration of the elements. Ionisation energy also decreases regularly as we go down a group of normal elements.

Electron affinity is a measure of the tendency of an atom or ion to acquire an electron. Most electron affinities are negative, but some are positive. A negative electron affinity means that energy is released when an atom or ion picks up an electron. As a general trend, electron affinity increases (i.e., becomes more negative) as we go across a period from left to right upto the halogens, and decrease as we go down a group of normal elements. Second and higher electron affinities are always positive because addition of an electron to an anion is difficult due to repulsion between anion and the electron being added.

Electronegativity is defined as the power of an atom in a molecule to attract electrons to itself. The most electronegative of all the elements is F; on Pauling scale its electronegativity is set at 4.0. Metals have electronegativities less than 2. The least electronegative elements are Cs and Fr, with their electronegativity of 0.7. Electronegativity increases as we go across a period from left to right, and decreases as we go down a group of normal elements in the periodic table. However, in a series of transition or inner-transition elements, value of electronegativity changes only gradually.

2.7 TERMINAL QUESTIONS

1 a) How does atomic size vary in a group and in a period? Give reasons for the variation.

  b) Arrange H, H^+ and H^- in order of increasing atomic radius.

2 What are isoelectronic ions? How does their size vary with the change of atomic number?

3 Which is the larger member of each of the following pairs of ions?

  i) Tl^+ or Tl^{3+} ii) N^{3-} or F^- iii) O^{2-} or S^{2-} iv) Na^+ or K^+ v) Ca^{2+} or Zn^{2+}

4 Why is the second ionisation energy of sodium higher than that of magnesium?

5 Among the elements Li, K, Ca, S and Ne, which ones have the lowest and highest first ionisation energy?

6 Among the elements of the second period, i.e., Li, Be, B, C, N, O, F, pick out:

  i) the element with the highest first ionisation energy

  ii) the element with the highest electronegativity

  iii) the element with the largest atomic radius

  iv) the most reactive nonmetal

  v) the most reactive metal

7. Alkali metals and coinage metals have the same outer electronic configuration. Then, why are the alkali metals more reactive than coinage metals?

8 Explain why the second electron affinity values are always positive.

9 Explain why is the electron affinity of nitrogen much lower than that of its neighbouring elements oxygen and carbon.

10 Explain why the electronegativity values of noble gases are zero while those of halogens are the highest in each period.

11 Predict which element has the higher electronegativity in the following pairs:

i) Na or Mg

ii) O or S

iii) C or N

iv) F or Cl

12 Which one of the following elements has the highest electronegativity?

a) Cl, Br, F, I

b) O, S, C, Mg

2.8 ANSWERS

Self Assessment Questions

1 Distance between two fluorine atoms in F_2 molecule will be twice the covalent radius of fluorine atom.

2 a) i) covalent ii) van der Waals iii) metallic iv) Ionic

b) larger

c) cation, anion

d) larger

3 In the elements of period 2, i.e., from Li to Ne the value of effective nuclear charge increases by 0.65 units whereas in the elements of 3*d* series it increases by 0.15 units from one element to another. In other words in the elements of period 2, it increases more steeply.

4 a) i) Na ii) Br^- iii) I iv) S v) Cl^- vi) Li

b) $N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$

5 Second ionisation energy of an element is always higher than the first because the second electron is to be removed from a cation having a comparatively higher effective nuclear charge than a neutral atom.

6 a) Atom having $[He]2s^2\,2p^3$ configuration will have the highest first ionisation energy because this is the smallest atom having exactly half filled *p* subshell.

b) i) $Na < P < N < Ne$

7 a) True b) True c) False d) False) False

8 a) Electron affinity is the energy change in acquiring an electron by an isolated atom or ion, whereas electronegativity is a measure of power of an atom to attract the electron pair in a bond to itself.

b) $Li < Be < B < C < N < O < F$

c) Caesium and francium are the least electronegative elements, whereas fluorine is the most electronegative element in the periodic table.

Terminal Questions

1 a) Atomic size generally decreases across a period and increases down a group in the periodic table. Across a period as the atomic number increases, effective nuclear charge also increases, whereas the number of shells remains the same. As a result of this, the electrons are pulled in and the size of the atom decreases. On the other hand, when we move down a group, the effective nuclear charge remains almost the same, but the number of shells increases from one element to the next in the group. Therefore, the electrons become farther from the nucleus and the size generally increases.

b) $H^+ < H < H^-$

2 Ions having equal number of electrons are called isoelectronic ions. In a series of isoelectronic ions, size decreases from anion to cation. The higher is the charge on the anion, the larger is its size. For a cation, the higher the charge, the smaller is its size.

3 i) Tl^+ ii) N^{3-} iii) S^{2-} iv) K^+ v) Ca^{2+}

4 The second ionisation energy of sodium is higher than that of magnesium because for removal of a second electron from the former, the stable core of 8 electrons is to be disrupted. Therefore, more energy has to be supplied. In the latter case, removal of second electron leaves behind a stable core.

5 Among the elements, Li, K, Ca, S and Ne, K and Ne have the lowest and the highest first ionisation energies.

6 i) F ii) F iii) Li iv) F v) Li

7 Alkali metals and coinage metals have the same outer electronic configuration, but the coinage metals have higher effective nuclear charge and smaller atomic radius than those of the corresponding alkali metals. Due to this, the ionisation energies of coinage metals are much higher than those of the alkali metals. Therefore, the alkali metals are more reactive than the coinage metals.

8 When an electron is added to an anion, electron is repelled by the anion. Therefore, to overcome this repulsion, energy has to be supplied. So, the second electron affinities are always positive values.

9 Electronic configuration of nitrogen is $1s^2 2s^2 2p^3$ which is stable due to half filled p subshell. It therefore, resists the addition of electron, thereby its electron affinity is around zero. On the other hand, addition of an electron to carbon, changes its configuration to $1s^2 2s^2 2p^3$, which is more stable than that of the neutral carbon atom; $1s^2 2s^2 2p^2$. Similarly, addition of an electron to oxygen changes its configuration to $1s^2 2s^2 2p^5$ bringing it nearer to the configuration $1s^2 2s^2 2p^6$ of the next higher inert gas Ne. Therefore, the electron affinities of carbon and oxygen are higher (more negative values) than that of nitrogen.

10 Since noble gases have a stable electronic configuration, they have no tendency to attract the bond pair to themselves. Therefore, their electronegativity is zero. On the other hand, halogens are only one electron short of noble gas configuration. So, they have a very high tendency of attracting the bond pair to themselves. Therefore, their electronegativity values are the highest in the respective periods.

11 i) Mg ii) O iii) N iv) F

12 a) F b) O

UNIT 3 HYDROGEN

Structure

3.1 Introduction
    Objectives
3.2 Position of Hydrogen in the Periodic Table
3.3 Isotopes of Hydrogen
    Deuterium Compounds
    Tritium
3.4 *Ortho* and *Para* Hydrogen
3.5 Manufacture of Hydrogen
3.6 Properties of Hydrogen
3.7 Uses of Hydrogen
3.8 Hydrides
    Ionic or Salt-like Hydrides
    Covalent Hydrides
    Metallic Hydrides
3.9 Hydrogen Bonding
    Intermolecular Hydrogen Bonding
    Intramolecular Hydrogen Bonding
    Effect of Hydrogen Bonding
3.10 Polarising Power of H^+
3.11 Summary
3.12 Terminal Questions
3.13 Answers

3.1 INTRODUCTION

In Units 1 and 2, you studied the periodic table and periodicity in the properties of elements. You must have noticed that the very first element in the periodic table is hydrogen. Hydrogen atom consists of only one proton and one electron. Hydrogen forms more compounds than any other element. Besides this, you should know that hydrogen is the most abundant of all the elements in the universe (73.9% by weight) and is the principal element in the solar atmosphere. However, it is much less abundant (0.14% by weight) on earth, where it exists only in the combined state. Keeping in view the importance of hydrogen, we will discuss some important aspects of the chemistry of hydrogen in this unit. Here, we will discuss its position in the periodic table, isotopes, manufacture, uses and hydrides in general. The specific hydrides, e.g., boranes, ammonia will be dealt with in their corresponding groups in the following units.

Objectives

After studying this unit you should be able to:

- justify the position of hydrogen in the periodic table,
- describe isotopes of hydrogen,
- differentiate between *ortho* and *para* forms of hydrogen molecule,
- describe the various methods for the manufacture of hydrogen,
- discuss the importance of hydrogen as a fuel,
- classify the binary hydrides according to their structure, and
- describe the conditions that are necessary for hydrogen bonding to occur and the characteristic properties of hydrogen bonded systems.

3.2 POSITION OF HYDROGEN IN THE PERIODIC TABLE

Position of hydrogen in the periodic table is of particular interest. Hydrogen is the first element of the periodic table having electronic configuration $1s^1$. On one hand this configuration is similar to the outer electronic configuration (ns^1) of the alkali metals. On the other hand, like halogens, it is one electron short of the corresponding inert gas helium. Hydrogen, therefore, shows some properties similar to alkali metals, while some others are similar to those of the halogens.

Like alkali metals, hydrogen forms halides, oxides and sulphides. You know, the alkali metals have a high tendency of losing their outermost electron to form M^+ ions. Hydrogen also forms H^+ ion, but it does not do so, under normal conditions, because the ionisation energy of hydrogen (1312 kJ mol^{-1}) is much higher than that of the alkali metals, e.g., Li, 520; Na, 495; K, 418 kJ mol^{-1}.

In its high ionisation energy, hydrogen resembles more with halogens. The first ionisation energies of fluorine, chlorine, bromine and iodine are 1618, 1255, 1142 and 1007 kJ mol^{-1}, respectively. Due to its high ionisation energy, hydrogen forms a large number of covalent compounds by sharing a pair of electrons. Hydrogen like halogens forms a diatomic molecule by sharing a pair of electrons between the two atoms. By picking up an electron, hydrogen forms the hydride ion (H^-), just like the halogens form the halide ion (X^-).

From the above discussion, it is clear that hydrogen resembles both the alkali metals as well as the halogens. So, hydrogen can be placed with either of them in the periodic table. However, conventionally, it is kept along with the alkali metals in group 1 in the periodic table.

SAQ 2

a) Why does hydrogen resemble the alkali metals?

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b) Explain the formation of hydride ion.

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3.3 ISOTOPES OF HYDROGEN

You have studied that atoms of an element which have the same atomic number but different mass numbers are called **isotopes**. Hydrogen has three different isotopes having mass numbers, 1, 2 and 3, called ordinary hydrogen or protium ^1H, **deuterium** (D) or ^2H and **tritium** (T) or ^3_1H respectively. These isotopes differ from one another in respect of the presence of neutrons. Ordinary hydrogen has no neutrons, deuterium has one and tritium has two neutrons in the nucleus (Fig. 3.1).

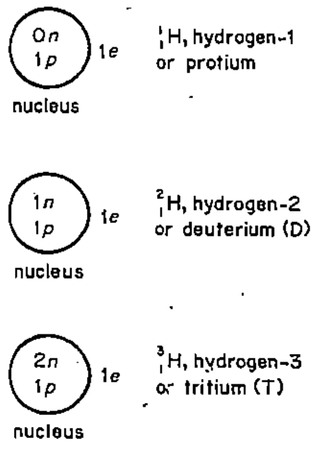

Fig. 3.1: Isotopes of hydrogen.

Deuterium is also called heavy hydrogen. These isotopes have same electronic configuration and therefore their chemical properties are almost the same. The only difference is in the rate of reactions. For example, hydrogen has a lower energy of activation than deuterium in its reaction with halogens and therefore, reacts faster.

However, the physical properties of hydrogen, deuterium and tritium differ considerably due to their large mass differences. Some of the important physical properties of hydrogen, deuterium and tritium are tabulated in Table 3.1.

3.3.1 Deuterium Compounds

Naturally occurring hydrogen contains 0.0156% deuterium. Like water, H_2O, which is the oxide of hydrogen, deuterium also forms an oxide, D_2O, which is known as **heavy water**. It can be obtained from ordinary water which contains 0.016% of deuterium oxide, either by fractional distillation or by electrolysis. Hydrogen is liberated more quickly than deuterium at the cathode and the residual liquid continuously gets richer in deuterium content on prolonged electrolysis. We can obtain virtually pure deuterium oxide, D_2O, by continuous electrolysis of water. Deuterium oxide is used as a moderator in nuclear reactors since it slows down neutrons quickly. Physical properties of H_2O and D_2O also differ from each other as in the case of H_2 and D_2. These are given in Table 3.2.

Table 3.1: Properties of atomic and molecular hydrogen

Properties	Hydrogen	Deuterium	Tritium
Natural abundance (%)	99.985	0.0156	10^{-15}
Atomic weight (C = 12)	1.008	2.014	3.016
Boiling point (K)	20.4	23.6	25.0
Melting point (K)	13.8	18.5	20.62
Density of liquid at b.p., H_2 ($10^3 \times$ kg m^{-3})	0.071		
*Ionisation energy, (kJ mol^{-1})	1312		
*Electron affinity, (kJ mol^{-1})	–73		
*Electronegativity (Pauling Scale)	2.1		
*Bond length, H_2(g) (pm)	74.9		
*Bond energy (ΔH_{atom}), H_2 (kJ mol^{-1})	436		
*Ionic radius, H^- (pm)	208		
*Covalent radius (pm)	37		
*van der Waals radius (pm)	120		

* As expected hydrogen, deuterium and tritium will have similar values.

Table 3.2: Properties of water and heavy water

	H_2O	D_2O
Density at 293K (10^3 x kg m^{-3})	0.9982	1.1059
Melting point (K)	273.16	276.97
Boiling point (K)	373.16	374.58
Temperature of maximum density (K)	277.04	284.39
Dielectric constant at 298 K	78.39	78.06

Hydrogen and deuterium are obtained by similar methods.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2Na + 2D_2O \longrightarrow 2NaOD + D_2$$

Many deuterium compounds, similar to those of hydrogen, are obtained from D_2O.

$$PCl_3 + 3D_2O \longrightarrow D_3PO_3 + 3DCl$$

$$Mg_3N_2 + 6D_2O \longrightarrow 3Mg(OD)_2 + 2ND_3$$

$$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$

We can also employ exchange reactions like those given below for the preparation of deuterium compounds:

$$NaOH + D_2O \longrightarrow NaOD + HDO$$

$$\begin{tikzcd} NH_4Cl + D_2O \arrow[r] & HDO + NH_3DCl \arrow[d, "D_2O"] \\ & NH_2D_2Cl \arrow[d, "D_2O"] \\ ND_4Cl & NHD_3Cl \arrow[l, "D_2O"'] \end{tikzcd}$$

3.3.2 Tritium

Tritium differs from the other two isotopes of hydrogen in being radioactive. Naturally occurring hydrogen contains nearly 10^{-15} % tritium. The concentration of tritium increased by over a hundredfold when thermonuclear weapon testing began in 1954 but is now subsiding again as a result of the ban on atmospheric weapon testing.

Tritium was first obtained synthetically by the bombardment of deuterium compounds such as $(ND_4)SO_4$ with fast deuterons.

$${}^{2}_{1}D + {}^{2}_{1}D \longrightarrow {}^{3}_{1}T + {}^{1}_{1}H$$

It is now prepared on a large scale by irradiation of lithium-6 in the form of Li/Mg alloy of LiF with slow neutrons in a reactor.

$^{6}_{3}Li + ^{1}_{0}n \longrightarrow ^{3}_{1}T + ^{4}_{2}He$

The following reaction occurs in nature:

$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{3}_{1}T + ^{12}_{6}C$

Tritium is radioactive and decays by emission of a beta-particle. Its half life period is 12.3 years.

$^{3}_{1}T \longrightarrow ^{3}_{2}He + \beta-$particle

Tritium can be easily incorporated into biological molecules because it behaves chemically, just like ordinary hydrogen. The radiation that tritium gives off within an organism, as a result of its decay, can cause many diseases, including cancer.

SAQ 2

Explain why chemical properties of isotopes of hydrogen are similar.

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3.4 *ORTHO* AND *PARA* HYDROGEN

Ortho and *para* are the two **different forms of hydrogen molecule**. We can explain this on the basis of the direction of the nuclear spin. When two hydrogen atoms combine to form a molecule, there are two possibilities. The two nuclei will either spin in the same direction (parallel spins) to give the form called ***ortho* hydrogen**, or they would spin in the opposite directions to give ***para* hydrogen** (Fig. 3.2). This phenomenon is known as **spin isomerism**.

Fig. 3.2: *Ortho* and *para* forms of hydrogen.

Internal energy is the sum total of translational, rotational, vibrational, and electronic energy of the molecule.

Due to spin isomerism, difference in their internal energy arises causing differences in physical properties like boiling point, specific heat and thermal conductivity of the *ortho* and *para* forms of hydrogen. *Para* hydrogen has a lower **internal energy** than that of *ortho* hydrogen. Hydrogen gas is an equilibrium mixture of *ortho* and *para* hydrogen. The ratio of *ortho* to *para* hydrogen varies with temperature as shown in Fig.3.3.

Evidently, this ratio increases with the rise in temperature upto a temperature of about 300 K (27°C) and remains constant thereafter. The percentage of *ortho* hydrogen at 300 K and above is 75%. This means that it is not possible to get 100% *ortho* hydrogen at any

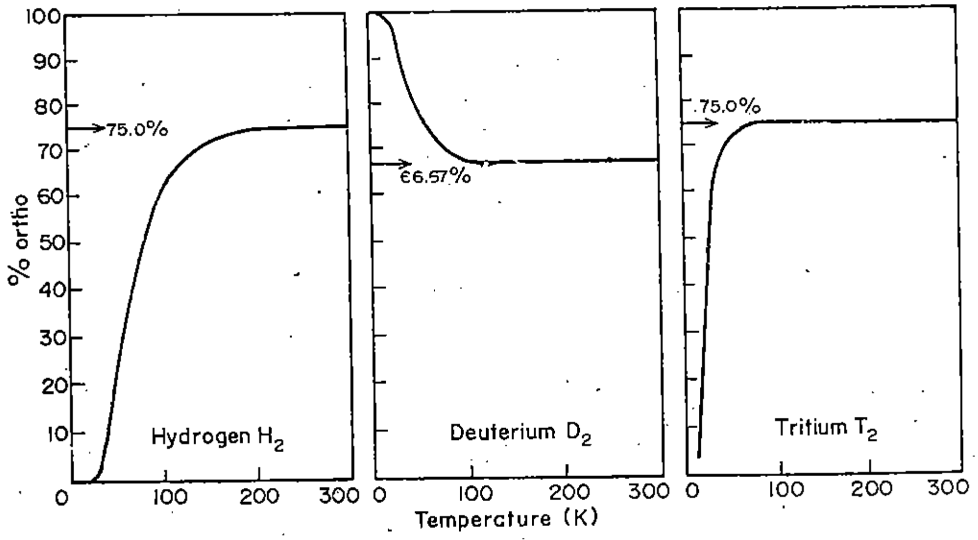


Fig. 3.3: *Ortho-para* equilibria for H_2, D_2 and T_2.

temperature. The equilibrium mixture of *para* and *ortho* hydrogen changes to almost 100% *para* hydrogen when cooled nearly to absolute zero. *Para* hydrogen is stable for weeks in the absence of catalysts like activated charcoal, Fe, Ni, Pt, O_2, NO_2, etc., which catalyse the conversion of *para* to *ortho* hydrogen. Similarly, deuterium and tritium also exhibit spin isomerism and exist in *ortho* and *para* forms. However, the ratio of *ortho* and *para* forms in deuterium and tritium is different from that in hydrogen. The variation of *ortho/para* ratio at different temperatures is also different. If you look carefully in Fig. 3.3, you will see that tritium resembles hydrogen more closely than deuterium in this respect.

SAQ 3

Write 'T' for true and 'F' for false in the given boxes for the following statements about *ortho* and *para* forms of hydrogen:

i) *Ortho* and *para* hydrogen are different due to difference in their nuclear spins. ☐

ii) *Ortho* and *para* hydrogen are different due to difference in their electron spins ☐

iii) Physical properties of *ortho* and *para* hydrogen are similar. ☐

iv) *Para* hydrogen is more stable at lower temperatures. ☐

v) At 100 K percentage of *ortho* hydrogen in the mixture is 70%. ☐

3.5 MANUFACTURE OF HYDROGEN

So far we studied the various isotopes of hydrogen and also the two forms of the hydrogen molecule. Hydrogen is an important industrial chemical about which you will study more in the following section. Let us start with its manufacture.

Water is the natural abundant source for the manufacture of hydrogen. Reduction of water to hydrogen can be carried out chemically as well as electrolytically. The common reducing agents are coke, carbon monoxide or hydrocarbons which reduce water to hydrogen at high temperatures.

Residue left from distillation of coal in the absence of air is known as coke.

Hydrogen is manufactured by allowing steam to react with red hot coke at about 1250K.

$$C + H_2O \xrightarrow{\sim 1250K} CO + H_2$$

This mixture of CO and H_2 is also known as **water gas** and the reaction is referred to as water gas reaction. As this mixture ($CO + H_2$) is used for the synthesis of methanol and a number of hydrocarbons, this is also called **synthesis gas**.

Hydrogen is now produced by the reaction of natural gas (chiefly methane) with steam in presence of a nickel catalyst.

$$CH_4 + H_2O \xrightarrow[920-1170K]{\text{Ni catalyst}} CO + 3H_2$$

Similar reaction can occur with other hydrocarbons also. In both the above processes CO is converted to CO_2 and more hydrogen generated by passing the gases ($CO + H_2$) and steam over iron oxide or cobalt oxide catalyst.

$$CO + H_2O \xrightarrow[450-650K]{\text{catalyst}} CO_2 + H_2$$

Hydrogen and carbon dioxide can be easily separated from each other by bubbling the gas mixture through water in which CO_2 is fairly soluble and H_2 virtually insoluble.

At higher temperatures, in the presence of catalysts (silica, alumina) hydrocarbons decompose and rearrange in what are called cracking reactions. These reactions, which are used in refining of petroleum, produce hydrogen as a by-product. One example of simple cracking reaction is the cracking of propane:

$$2\,CH_3 - CH_2 - CH_3 \xrightarrow[\text{catalyst}]{875K} CH_4 + CH_2 = CH_2 + CH_3 - CH = CH_2 + H_2 \uparrow$$

Electrolysis of acidified water using platinum electrodes is a convenient source of hydrogen (and oxygen). On a large scale, very pure hydrogen (>99.95%) can be obtained from the electrolysis of aqueous solutions of barium hydroxide between nickel electrodes.

But hydrogen obtained by electrolysis of water is relatively expensive because of the cost of the electrical energy. However, hydrogen is economically obtained as a by-product in the electrolysis of brine solution in the manufacture of sodium hydroxide.

During electrolysis there is a competition at the anode between the oxidation of chloride ion and the oxidation of water.

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

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

When a concentrated salt solution (brine) is used, the first reaction is the one that is observed. At the cathode, the reaction is the reduction of water because it is more easily reduced than Na^+.

$$2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-(aq)$$

When we combine the anode and cathode reactions and include the Na^+ ion (which is actually a spectator ion), the overall reaction becomes

$$2Na^+ + 2Cl^- + 2H_2O \longrightarrow Cl_2(g) + H_2(g) + 2Na^+ + 2OH^-$$

Mercury dissolves many metals including sodium, zinc, tin, silver and gold to form amalgam.

In the laboratory hydrogen can be prepared by the reaction of water or dilute acids on electropositive metals such as alkali metals, alkaline earth metals, the metals of Group 12 (e.g., Zn) and the lanthanides. The reaction can be explosively violent with alkali metals (e.g., K, Rb). Convenient laboratory methods employ sodium amalgam or calcium with water, or zinc and tin with hydrochloric acid.

SAQ 4

Complete the following chemical reactions which take place during the formation of hydrogen:

i) $C + H_2O \longrightarrow$ .... + ...

ii) $CH_4 + H_2O \longrightarrow$ .... + ...

iii) $CO + H_2O \longrightarrow$ .... + ...

iv) $2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}}$ .... + ... + ...

v) $Ca + 2H_2O \longrightarrow$ .... + ...

3.6 PROPERTIES OF HYDROGEN

Hydrogen is the lightest element known. It is a colourless, odourless and tasteless gas. Hydrogen molecule is thermally stable and has little tendency to dissociate at normal temperatures, since the reaction

$$H_2(g) \longrightarrow 2H(g), \quad \Delta H = 436\,kJ\,mol^{-1}$$

is highly endothermic. However, at high temperatures in an electric arc or under ultraviolet light, it does dissociate. The **atomic hydrogen** produced, exists for less than half a second after which it recombines to give molecular hydrogen and liberates a large amount of energy (436 kJ mol^{-1}) in the form of heat. Most of the transition metals catalyse the recombination reaction of atomic hydrogen.

Atomic hydrogen is a powerful reducing agent and reduces copper, silver and mercury salts to the metallic state. It combines with alkali metals to form hydrides, which we shall discuss in Section 3.8, reduces sulphur to hydrogen sulphide and carbon monoxide to formaldehyde. It also reacts with oxygen at room temperature to form hydrogen peroxide. The reactions can be written as:

$$AgNO_3 + H \longrightarrow Ag + HNO_3$$

$$Na + H \longrightarrow NaH$$

$$CO + 2H \longrightarrow HCHO$$

$$O_2 + 2H \longrightarrow H_2O_2$$

Atomic hydrogen is generally produced by passing ordinary hydrogen through an electric arc maintained between two tungsten electrodes. The atoms set free are carried away by a stream of incoming hydrogen gas. These free atoms recombine at once on coming in contact with a metallic surface liberating a large amount of heat and thus raising the temperature of the metal very high, say to 4000-5000K. This principle is utilised in making of the 'atomic hydrogen welding torch' (Fig. 3.4). It provides an opportunity of welding at a very high temperature but in a reducing atmosphere.

Despite fairly high bond dissociation energy of hydrogen molecule, it is moderately reactive because hydrogen forms strong bonds with many other elements. It reacts with almost all elements except the noble gases. Hydrogen reacts with alkali and alkaline earth metals by accepting an electron to form ionic hydrides, e.g., KH and CaH_2. With non-metals, it forms covalent hydrides, e.g., NH_3, H_2O and HF. In Section 3.8, you will study more about the hydrides.

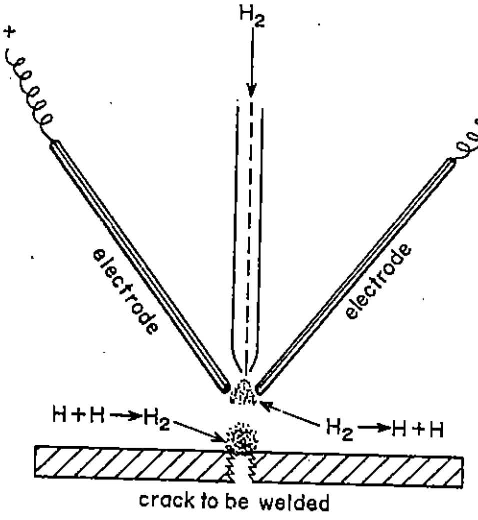


Fig.3.4: Atomic hydrogen welding torch.

Hydrogen is easily oxidised to water and; therefore, it acts as a very good reducing agent in a variety of situations. Hydrogen is used in metallurgy to reduce metal oxides to metals in cases where carbon cannot be used because the metal, e.g., Mo and W can form a carbide:

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

$$(NH_4)_2MoO_4 + 3H_2 \longrightarrow Mo + 2NH_3 + 4H_2O$$

Hydrogen adds on the multiple bonds in organic compounds. In the presence of catalysts such as finely divided nickel, palladium or mixtures of metal oxides, unsaturated organic compounds are thus reduced to saturated compounds. For example,

$$\underset{\text{2 – butene}}{CH_3CH = CHCH_3} + H_2 \xrightarrow[\text{Pd, 1 atm}]{278K} \underset{\text{n – butane}}{CH_3CH_2CH_2CH_3}$$

$$\underset{\text{methyl cyanide}}{CH_3C \equiv N} + 2H_2 \xrightarrow[ZnO/Cr_2O_3]{673K} \underset{\text{ethyl amine}}{CH_3CH_2NH_2}$$

Catalytic hydrogenation of unsaturated liquid vegetable oils to solid edible fats illustrates the industrial application of the reduction reaction; as the reduction of an oleate (ester of oleic acid) to the corresponding stearate (ester of stearic acid) would show:

$$\underset{\text{Oleate}}{CH_3(CH_2)_7CH = CH(CH_2)_7COOR} + H_2 \longrightarrow \underset{\text{Stearate}}{CH_3(CH_2)_{16}COOR}$$

Hydrogen reacts with carbon monoxide in the presence of catalysts to form methanol:

$$CO + 2H_2 \xrightarrow{\text{cobalt}} CH_3OH$$

This reaction is known as hydroformylation reaction and is used in industrial preparation of methanol.

SAQ 5

Write chemical equations for the following reactions:

i) Formation of methanol from coal

....

....

ii) Reduction of methyl cyanide

....

iii) Conversion of oleic acid into stearic acid

....

iv) Reduction of ammonium molybdate to molybdenum

....

3.7 USES OF HYDROGEN

Hydrogen is a very important industrial chemical. The largest single use of hydrogen is in the synthesis of ammonia which is used in the manufacture of nitric acid and nitrogenous fertilizers. As described in Section 3.6, hydrogen is used in the hydrogenation of vegetable oils, and manufacture of methanol. It is also used in metallurgy to reduce metal oxides to metals in special cases, e.g., Mo and W.

In spacecrafts, hydrogen gas is used in fuel cells (Fig. 3.5) for generating electrical energy and for providing clean drinking water to the astronauts. In a fuel cell, electrical energy is generated by the reaction of hydrogen and oxygen without evolution of any heat. This is sometimes called "**cold combustion**". A hydrogen-oxygen fuel cell may have an alkaline or acidic electrolyte. Figure 3.5 shows a hydrogen-oxygen fuel cell with porous carbon electrodes and KOH as electrolyte.

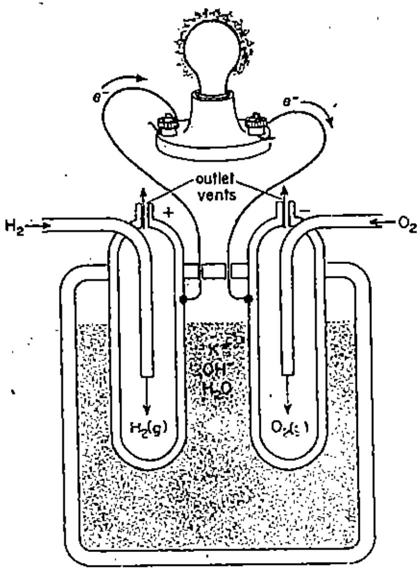


Fig. 3.5: A hydrogen-oxygen fuel cell with KOH electrolyte and porous carbon electrodes.

The half cell reactions are as given below:

$$H_2(g) + 2OH^- \longrightarrow 2H_2O(l) + 2e,\ E^\circ = -0.828V,\ \text{Anode}$$

$$\tfrac{1}{2}O_2(g) + H_2O(l) + 2e \longrightarrow 2OH^-,\ E^\circ = 0.401V,\ \text{Cathode}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l),\ E^\circ = 1.229V$$

With acidic electrolyte, the half-cell reactions are as under:

$$H_2(g) \longrightarrow 2H^+ + 2e,\ E^\circ = 0,\ \text{Anode}$$

$$\tfrac{1}{2}O_2(g) + 2H^+ + 2e \longrightarrow H_2O(l),\ E^\circ = 1.229V,\ \text{Cathode}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l),\ E^\circ = 1.229V$$

Thus, you can see from the above, that the electromotive force (e.m.f.) of the cell remains the same whether we use alkaline or acidic electrolyte. This is because we are using the same reactants at the electrodes in both the cases. Fuel cells have several advantages over other sources of energy. Firstly, in a fuel cell unlike in the dry cell or storage battery (which requires recharging also), the cathode and anode reactants are continuously supplied so that energy can be indefinitely withdrawn from it. Secondly, in a fuel cell energy is extracted from the reactants under more nearly ideal conditions. Therefore, the thermodynamic efficiency of the fuel cells is higher than that of the most of the ordinary combustion processes. Fuel cells have efficiencies approaching 75%, whereas power plants that burn fuels have efficiencies of only about 40%.

Combustion of hydrogen is a highly exothermic reaction and produces no pollutants:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l), \ \Delta H = -572 \text{ kJ}$$

Liquid hydrogen is, therefore, used as a rocket fuel.

It has been recognised during the past two decades that the world reserves of fossil fuels like coal, oil and gas are finite, so they cannot last for ever. Similarly, the nuclear and hydroelectric power also cannot meet all our energy requirements. Moreover, these sources pose a danger of environmental degradation. This has prompted an active search for alternative sources of energy. In addition to solar power, hydrogen is being considered a potential fuel for the future.

Hydrogen as a fuel has many advantages over the conventional fossil fuels and electric power. It is available in unlimited quantities in sea water. It is pollution free because the major product of its combustion is water with only traces of nitrogen oxides. It releases greater energy per unit weight of fuel in comparison to gasoline and other fuels. Hydrogen can be transported as a gas in high pressure pipelines, as a liquid in tankers and even as a solid in the form of metal hydrides. Unlike electricity, hydrogen can be stored and used when needed. You may then naturally think, why hydrogen has not replaced other fuels. There is a reason for this of course. At present, its manufacture from water is expensive. But that may change in future.

Hydrogen like electricity is a secondary source of energy because it is produced using energy from a primary source such as coal, nuclear fission or the sun. Water is very stable to thermal decomposition, it does not decompose to hydrogen and oxygen to any appreciable extent at practically viable temperatures. However, hydrogen can be conveniently prepared by electrolysis of water. But this method is not economical at present. In fact more energy has to be spent in electrolysis of water than that can be liberated by burning hydrogen as a fuel. Great efforts are being made to make electrolysis of water more energy-efficient so that the use of hydrogen as a fuel can become economically viable.

Non-electrolytic methods of preparation of hydrogen, e.g., thermochemical and photochemical hydrogen generation are also being studied. In thermochemical hydrogen generation, water is heated with certain chemicals to liberate hydrogen at much lower temperatures. In the past few years, several water splitting cycles have been identified, out of which two potentially useful cycles are given below:

Cycle 1

i) $3FeCl_2 + 4H_2O \xrightarrow{775K} Fe_3O_4 + 6HCl + H_2$

ii) $Fe_3O_4 + \frac{3}{2}Cl_2 + 6HCl \xrightarrow{375K} 3FeCl_3 + 3H_2O + \frac{1}{2}O_2$

iii) $3FeCl_3 \xrightarrow{575K} 3FeCl_2 + \frac{3}{2}Cl_2$

Cylce 2

i) $CaBr_2 + H_2O \xrightarrow{1025K} CaO + 2HBr$

ii) $Hg + 2HBr \xrightarrow{375K} HgBr_2 + H_2$

iii) $HgBr_2 + CaO \xrightarrow{280K} HgO + CaBr_2$

iv) $HgO \xrightarrow{775K} Hg + \frac{1}{2}O_2$

Thus by repeating reactions (i) — (iii) in Cycle 1 or reactions (i) — (iv) in Cycle 2, water can be splitted to H_2 and O_2.

Decomposition of water by solar energy in presence of catalysts is known as photochemical decomposition of water. Using special catalysts, scientists in France have been able to achieve the efficient decomposition of water under visible and ultraviolet light. If this process can be made industrial, a convenient method of converting solar energy directly to a useful form of stored chemical energy will be available.

SAQ 6

Write five important industrial uses of hydrogen.

....

....

....

....

3.8 HYDRIDES

Hydrogen combines with a number of elements to form compounds called hydrides. As electronegativity of the element increases, the stability of hydrides also increases. Three types of hydride compounds are formed depending upon the electronegativity of the elements. These are classified into:

i) Ionic or saltlike or saline hydrides.

ii) Covalent or molecular hydrides.

iii) Metallic or non-stoichiometric hydrides.

Now we shall discuss each type of hydrides in detail.

3.8.1 Ionic or Saltlike Hydrides

These are formed by metals which have low electronegativity values and are more electropositive with respect to hydrogen. These hydrides are formed by transfer of an electron from the metal to the hydrogen atom. Hydride ion is a peculiar chemical species and in contrast to proton which has vanishingly small size, it is unusually large. It is larger than any of the halide ions except iodide. The source of this apparent paradox lies in the lack of control by a single nuclear proton over two mutually repelling electrons.

Alkali and alkaline earth metals of groups 1 and 2 are sufficiently electropositive and force the hydrogen atom to accept an electron to form the hydride ion, H^-, e.g., lithium hydride Li^+H^- and calcium hydride $Ca^{2+}(H^-)_2$. When the metals are heated in hydrogen at 973 K, ionic hydrides are obtained. Ionic hydrides are white crystalline solids. They have high melting points and conduct electricity in fused state liberating hydrogen at the anode. Their density is higher than that of the metal.

They are powerful reducing agents specially at higher temperature, e.g.,

$$2CO + NaH \longrightarrow HCOONa + C$$

$$SiCl_4 + 4NaH \longrightarrow SiH_4 + 4NaCl$$

$$PbSO_4 + 2CaH_2 \longrightarrow PbS + 2Ca(OH)_2$$

Li^+H^- and Na^+H^- are used in making valuable reducing agents like lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). These complex hydrides are frequently used in the reduction of aldehydes, ketones, acids and their derivatives to give alcohols.

$$\underset{\text{Organic acid}}{R-COOH} \xrightarrow{LiAlH_4/NaBH_4} \underset{\text{Primary Alcohol}}{R-CH_2OH}$$

$$\underset{\text{ketone / aldehyde}}{>C=O} \xrightarrow{LiAlH_4/NaBH_4} \underset{\text{Secondary alcohol}}{>CH-OH}$$

3.8.2 Covalent Hydrides

These hydrides are formed by elements of comparatively higher electronegativity, generally *p*-block elements and Be and Mg. The bonds formed in this class of hydrides are mostly covalent in character but in some cases, for example, in HF, the bond may be partially ionic.

The covalent hydrides can be prepared either by direct reaction of non-metals with hydrogen under suitable conditions or by the reaction of H_2O or acids on nitrides, carbides, borides, silicides, stannides of alkali and alkaline earth metals or by the reduction of halides. These are illustrated by the following reactions:

$$N_2 + 3H_2 \xrightarrow{\text{catalyst, 750K}} 2NH_3$$

$$Mg_3N_2 + 6H_2O \xrightarrow{\text{600–1000 atm.}} 3Mg(OH)_2 + 2NH_3$$

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

$$AsCl_3 + 6H \xrightarrow{Zn+HCl} 4AsH_3 + 3HCl$$

$$4PCl_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 4PH_3 + 3LiCl + 3AlCl_3$$

These hydrides have a molecular lattice made up of individual saturated covalent molecules with only weak van der Waals forces and in some cases hydrogen bonds holding the molecules together. This accounts for their softness, low melting and boiling points, their volatility and lack of conductivity. Some covalent hydrides are unstable in the presence of air, e.g., stannane, SnH_4.

Some covalent hydrides of Groups 2 and 13 are electron deficient. These have structures between ionic and covalent hydrides. These are either dimeric, e.g., boron hydride (B_2H_6), or polymeric, e.g., beryllium hydride $(BeH_2)_n$, magnesium hydride $(MgH_2)_n$ and aluminium hydride $(AlH_3)_n$. You will study the detailed structure of these hydrides in Units 5 and 6 of this course.

3.8.3 Metallic Hydrides

On heating, hydrogen reacts with many transition metals, lanthanides and actinides to form metallic hydrides. Most of these have metallic appearance and are less dense than the parent metal. They all conduct heat and electricity though not as well as the parent metal (cf. ionic hydrides). Unlike the saline hydrides, they are almost always non-stoichiometric, being deficient in hydrogen. For example, $TiH_{1.5-1.8}$, $VH_{0.56}$, $CrH_{1.7}$, $NiH_{0.6-0.7}$, $PdH_{0.6-0.8}$, $TaH_{2.76}$, $LaH_{2.87}$, $YbH_{2.55}$, etc., approach the stoichiometric formulae given in Table 3.3. Most of these hydrides are stable to water upto 375 K but are quantitatively decomposed by acids and show reducing properties.

Table 3.3: Stoichiometric formulae of some metallic hydrides.

MH	(M = V, Cr, Ni, Cu, Ta, Pd)
MH_2	(M = Ti, Zr, Hf, V, Nb, Cr, Zn, Y; La-Lu except Pm; Th, Np, Pu, Am, Cm)
MH_3	(M = Y, La-Lu except Pm and Eu; Pa, U, Np, Pu, Am)

Formerly, these hydrides were termed as interstitial compounds in which hydrogen was thought to be accommodated in the interstices in the metal lattice producing distortion but no change in its type. But recent studies have shown that except for the hydrides of nickel, palladium, cerium and actinium, other hydrides of this class have lattice of a type different from that of the parent metal. For example, the hexagonal close packed lattice of some lanthanides is transformed to a face-centred cubic lattice in their dihydrides. As pointed out earlier, these interstitial hydrides are poorer conductors of electricity, exhibit less paramagnetism and are more brittle than the parent metal. These characteristics suggest that hydrogen is present in the metal lattice as hydrogen atoms rather than as hydrogen molecules. The single electron of hydrogen is paired with an electron of the metal, thereby reducing the extent of metallic bonding. Breaking of the H-H bond is in agreement with the fact that these metals catalyse reactions of hydrogen.

SAQ 7

What types of bonding do you expect in sodium hydride, methane and ammonia?

....

....

....

3.9 HYDROGEN BONDING

One very important aspect of the chemistry of hydrogen is **hydrogen bonding**. When hydrogen is covalently bonded to a highly electronegative element like F, O, N, the electronegative element attracts the electron pair towards itself giving rise to an induced positive charge (δ^+) on the hydrogen atom and negative charge (δ^-) on the electronegative atom. For example,

$H^{\delta+}\ X^{\delta-}$, where X = electronegative atom.

Due to this positive character, hydrogen attracts another electronegative atom of the neighbouring molecule forming a bond. This bond is known as the hydrogen bond. This is illustrated below:

$$\text{--------}H^{\delta+} — X^{\delta-}\text{ --------- }H^{\delta+} — X^{\delta-}\text{ --------- }H^{\delta+} — X^{\delta-}\text{ ---------}$$

'———' denotes covalent bond.

'---------' denotes hydrogen bond.

Thus hydrogen bond can be defined as "the attractive force which binds hydrogen atom of one molecule with electronegative atom of another molecule, generally of the same compound."

The hydrogen bond energy is only about 7-59 kJ mol^{-1} compared to the normal covalent bond energy of 389-665 kJ mol^{-1} for H-N, H-O and H-F bonds. Thus, hydrogen bond is much weaker than a covalent bond. Obviously, its length is also much longer than the covalent bond.

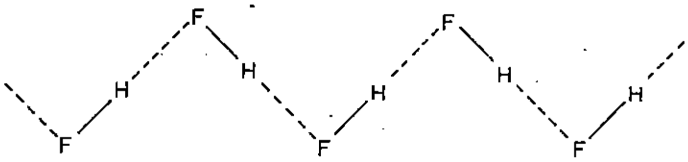
There are two types of hydrogen bonding:

i) Intermolecular hydrogen bonding

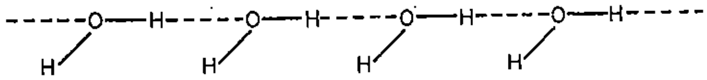
ii) Intramolecular hydrogen bonding

3.9.1 Intermolecular Hydrogen Bonding

In this case, two or more molecules of the same compound or of different compounds are involved in hydrogen bonding. Some common examples of the intermolecular hydrogen bonding occurring between the molecules of same compound are HF, H_2O, alcohols, etc.

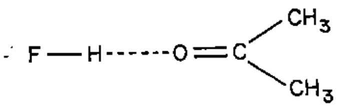


Hydrogen fluoride, $(HF)_n$

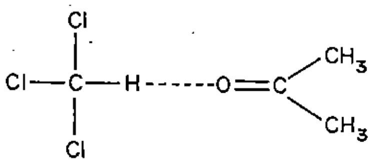


Cluster of water molecules, $(H_2O)_n$

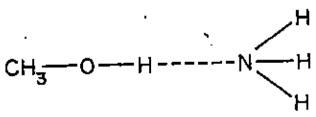
Examples of the intermolecular hydrogen bonding occurring between two different kinds of molecules are as following:



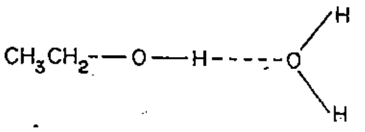
Hydrogen fluoride **Acetone**



Chloroform **Acetone**



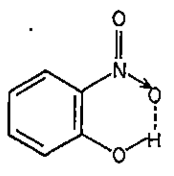
Methanol **Ammonia**



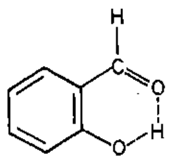
Ethanol **Water**

3.9.2 Intramolecular Hydrogen Bonding

Intramolecular hydrogen bond is formed between two atoms of the same molecule. As a consequence of this, generally a five or six membered ring called chelate ring is formed, e.g.,

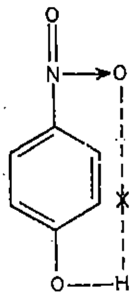


o-Nitrophenol

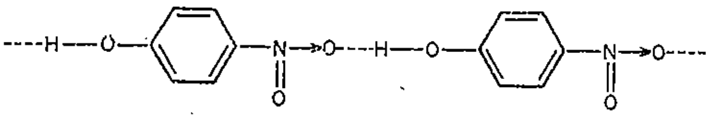


Salicylaldehyde

You have seen above, that intramolecular hydrogen bonding takes place in molecules like *o*-nitrophenol and salicylaldehyde. Now, you may ask why intramolecular hydrogen bonding does not take place in *p*-nitrophenol? This is due to the large distance between the two groups (NO_2 and OH) in *p*-nitrophenol.



This type of hydrogen bonding is not possible.
However, it does show the usual intermolecular hydrogen bonding.



p-Nitrophenol

It is significant to note that the vast majority of intramolecular hydrogen bonding occurs where a five or six membered ring can be formed because of the stability associated with such rings.

3.9.3 Effect of Hydrogen Bonding

Hydrogen bonding plays a very significant role in determining the properties of compounds. It is also very important in most of the biological processes about which you may study in the **Biochemistry** course. We shall confine our discussion to a few important physical properties only, e.g., boiling point, melting point and solubility in water.

Boiling Point and Melting Point

If you look at the melting and boiling points of the hydrides of Group 14 elements, i.e., CH_4, SiH_4, GeH_4 and SnH_4 in Fig. 3.6, you will observe that melting and boiling points of the hydrides generally increase with the increase in molecular weight of the hydrides. But NH_3 in Group 15, H_2O in Group 16 and HF in Group 17 have abnormally high melting and boiling points as compared to other hydrides in their respective groups in the periodic table. This anomaly is explained on the basis of hydrogen bond formation.

In compounds where the molecules are linked by hydrogen bonds, some extra energy is required to break the intermolecular hydrogen bond and this is responsible for their higher boiling and melting points.

However, intramolecular hydrogen bonding has the opposite effect. For example, in *ortho* nitrophenol the groups present in *ortho* position are involved in intramolecular hydrogen bonding thus preventing the intermolecular hydrogen bond formation, i.e. association of the molecule. Due to the intramolecular chelated structure, *o*-nitrophenol is steam-volatile, whereas *p*-nitrophenol is not.

Water Solubility

Solubility of a substance increases markedly when hydrogen bonding is possible between the solvent and the solute molecules. For example, lower alcohols like methanol, ethanol etc., are highly miscible with water due to the hydrogen bonding with water molecules.

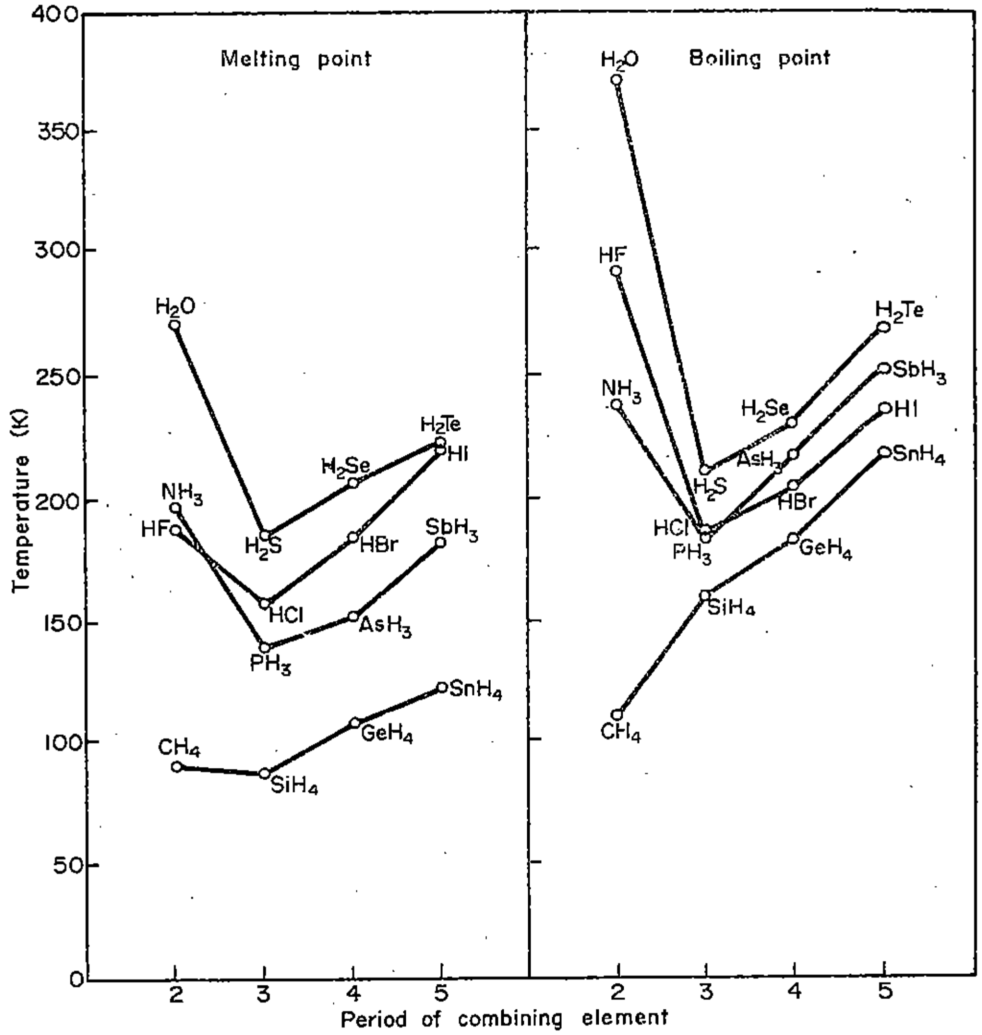


Fig.3.6: (a) Melting point curves and (b) Boiling point curves of the molecular hydrides.

[illegible] effect of hydrogen bonding [illegible] properties [illegible] HF and HCl

[illegible]

3.10 POLARISING POWER OF H⁺

You know that the polarising power of a cation, i.e., its ability to distort or polarise an anion is directly proportional to its positive charge and inversely proportional to its size. You can also say that the polarising power of a cation is proportional to the ratio of its charge to its size. This ratio is called the ionic potential of the cation. As the hydrogen cation, i.e., proton, is vanishingly small, it has a very high ionic potential and a vast polarising power. Due to this, free protons exist only in discharge tubes. Generally, these are found associated with other molecules. For example, with ammonia and water, these form species like NH_4^+ and H_3O^+, $H_5O_2^+$, $H_9O_4^+$, etc. The aquated proton species are represented as $H^+(aq)$. Enthalpy of formation of these aquated proton species is very large (−1075 kJ mol^{-1}). It is mainly because of this reason that many covalent hydrides (H-X) are acidic in aqueous solution, i.e., they release $H^+(aq)$ ions even though the H-X bonds are often very strong, e.g.,

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

3.11 SUMMARY

Let us now summarise what we discussed in this unit:

- Hydrogen is the most abundant element in the universe.
- Hydrogen atom has only one electron and the cation is an elementary particle, the proton.
- It is difficult to assign one particular position to hydrogen in the periodic table due to its resemblance to alkali metals as well as to halogens.
- Hydrogen has three isotopes namely hydrogen (^1H), deuterium (D or ^2H) and tritium (T or ^3H).
- Hydrogen molecule exists in two forms, *ortho* and *para*.
- Hydrogen reacts with other elements to form three types of hydrides, i.e., ionic, covalent and metallic hydrides.
- Hydrogen can bridge electronegative elements (hydrogen bonding) and electropositive elements (hydride bridging).
- The largest single use of hydrogen is in the manufacture of ammonia. Its other uses are in the hydrogenation of vegetable oils, manufacture of methanol from coal, extraction of metals and in fuel cells.

3.12 TERMINAL QUESTIONS

1 Which of the following is correct? Tick (√) the correct one.

i) Hydrogen acts as

(a) reducing agent

(b) oxidising agent

(c) both oxidising and reducing agent

(d) None of the above

ii) The electronic configuration of deuterium atom is

(a) $1s^1$ (b) $2s^1$ (c) $1s^2$ (d) $2s^2$

iii) Hydrogen molecule ion, H_2^+ contains

(a) 1 electron (b) 2 electrons

(c) 3 electrons (d) No electrons

iv) SiH_4 is an example of which of the following type of hydrides:

(a) ionic (b) interstitial

(c) metallic (d) covalent

v) Heavy water is

(a) DOD (b) HDO (c) H_2O_2 (d) DTO

vi) Polarising power of an ion increases

(a) when charge of cation increases

(b) when size of cation increases

(c) when size of anion decreases

(d) none of the above

2 Do *ortho* and *para* forms of hydrogen exist in deuterium and tritium?

3 Which hydrogen bond do you expect to be stronger and why?

(a) S – H ----- O or (b) O–H ---- S

4 Explain why the boiling points of hydrogen halides follow the trend

$HF(293K) > HCl(188K) < HBr(206K) < HI(237K)$

5 When a hydrogen bond is symbolized by X–H - - - - Y, what do the solid and the dotted lines represent? Which distance is shorter?

3.13 ANSWERS

Self Assessment Questions

1. a) Hydrogen resembles alkali metals because like alkali metals it also has one electron in '*s*' orbital, i.e., $1s^1$ configuration (see the similar properties from the text).

   b) Hydrogen needs one electron to reach the noble gas configuration, therefore, it has a tendency to take one electron and form hydride ion, H^-.

2 Most of the chemical properties are governed by the electronic configuration of the element. As the isotopes of hydrogen have the same electronic configuration, their chemical properties are closely similar.

3 i) T ii) F iii) F iv) T v) F

4 i) $C + H_2O \longrightarrow CO + H_2$

ii) $CH_4 + H_2O \longrightarrow CO + 3H_2$

iii) $CO + H_2O \longrightarrow CO_2 + H_2$

iv) $2NaCl + 2H_2O \xrightarrow{electrolysis} 2NaOH + H_2 + Cl_2$

v) $Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$

5. i) $C + H_2O \longrightarrow CO + H_2$

$CO + 2H_2 \longrightarrow CH_3OH$

ii) $CH_3CN + 2H_2 \longrightarrow CH_3CH_2NH_2$

iii) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + H_2 \longrightarrow CH_3(CH_2)_{16}COOH$

iv) $(NH_4)_2MoO_4 + 3H_2 \longrightarrow Mo + 2NH_3 + 4H_2O$

6. i) manufacture of ammonia

ii) manufacture of methanol

iii) hydrogenation of vegetable oils

iv) extraction of molybdenum and tungsten

v) in fuel cells

7 Sodium hydride — ionic

Methane — covalent

Ammonia — covalent.

8 a) Because of strong intermolecular hydrogen bonding, H_2O, HF and NH_3 exist as associated molecules. Therefore, their melting and boiling points are much higher than those of the corresponding hydrides in their respective groups.

b) Water is a liquid because of hydrogen bonding, whereas in H_2S even if hydrogen bonding is present it is very weak.

Terminal Questions

1 i) a ii) a iii) a iv) d v) a vi) a

2 Yes, but the percentage ratio of *ortho*/*para* in D_2 and T_2 is different from the ratio in H_2.

3 Hydrogen bond in, S–H -----O is stronger than O–H ----- S as O is more electronegative than S.

4 As we move down the group the boiling point of HCl, HBr, HI increases due to increased van der Waals forces. However, in HF the boiling point is anomalously high due to the hydrogen bonding.

5 Solid line represents the covalent bond and the dotted line represents the hydrogen bond. As hydrogen bond is much weaker than the covalent bond, the bond length of the former is more than that of the latter.

UNIT 4 ALKALI METALS

Structure

4.1 Introduction
    Objectives
4.2 Occurrence, Extraction and Uses
4.3 General Characteristics
    Physical Properties
    Chemical Properties
4.4 Solvation of Alkali Metal Ions
4.5 Solution of Alkali Metals in Liquid Ammonia
4.6 Complexation Behaviour of Alkali Metals
4.7 Anomalous Behaviour of Lithium
4.8 Summary
4.9 Terminal Questions
4.10 Answers

4.1 INTRODUCTION

You have studied the classification of the elements and the periodicity in their various atomic properties in Units 1 and 2. You must be well acquainted now with the concept of periodicity observed in the properties of elements. Presuming this, let us start proper group study from the *s*-block elements. In the previous unit, we discussed hydrogen separately as its properties resemble the Group 1 elements in some respects and the Group 17 elements in others.

3 A

The elements of Group 1 and Group 2 are called the *s*-block elements because the outermost electron(s) in these elements occupy the *s*-orbital. In this unit, we will take up Group 1 elements, which are some of the most reactive elements. Group 1 consists of the elements Li, Na, K, Rb, Cs and Fr. They are called **alkali metals** because they form hydroxides which are strong alkalies. We will discuss in this unit, the general trends in properties and the comparative behaviour of the Group 1 elements. One important fact which you will notice here, and later in subsequent groups also, is that the first member in all the groups behaves 'abnormally' which means that the first member of each group is rather different in its properties from the rest of the members of the same group. All the Group 1 elements are metals. Of these, francium is in the form of a short lived radioactive isotope and will not be discussed in detail here.

Objectives

After studying this unit, you should be able to:

- outline the occurrence of Group 1 elements and their isolation,
- list their uses,
- describe the general characteristics of Group 1 elements,
- explain the stability of alkali metal salts,
- explain the solvation phenomenon of the metals,
- describe the complexation tendency of the alkali metals, and
- explain the anomalous nature of lithium.

4.2 OCCURRENCE, EXTRACTION AND USES

Alkali metals are useful as metals as well as in the form of their compounds. Let us see how they occur in nature and also how they are extracted from their compounds. We will also discuss some of their important uses.

Occurrence

Before describing the chemistry of the elements of Group 1, let us first see how they are present in nature. The alkali metals are highly reactive, so they do not occur in the free state in nature. They occur in the combined form in the earth's crust in the following relative abundance: sodium 2.27%, potassium 1.84% and lithium, rubidium and caesium in trace amounts $1.8 \times 10^{-3}\%$, $7.8 \times 10^{-3}\%$ and $0.26 \times 10^{-3}\%$, respectively. Sodium as sodium

Sea water is actually a 3% solution of various salts, out of which 98% is sodium chloride.

chloride is the most abundant metal in sea water (~1.08%). Lithium occurs in alumino-silicate rocks, e.g., spodumene, LiAl $(SiO_3)_2$ and lepidolite, (Li, Na, K)$_2$Al$_2$ $(SiO_3)_3$ (F, OH)$_2$, sodium in rock salt, NaCl, Chile saltpetre, $NaNO_3$ and cryolite, Na_3AlF_6; potassium in carnallite, $KCl.MgCl_2.6H_2O$, saltpetre KNO_3, and kainite, $KCl.MgSO_4.3H_2O$. Rubidium and caesium are rare elements and generally occur in small quantities along with other alkali metals. For example, carnallite contains upto 0.04 per cent rubidium chloride and lepidolite, a lithium ore contains about 0.2 to 0.7 per cent of caesium expressed as caesium oxide. Francium being a radioactive element with a very short half-life period (21.8 minutes) occurs in very minute traces in nature.

Compositions of silicate ores are often expressed in terms of percentage of oxides of constituents.

Extraction

Lithium and sodium are extracted by electrolysis of their fused (molten) chlorides. Potassium is obtained by the reduction of its chloride with sodium vapour. This reduction by Na appears to be contrary to the normal order of reactivity, K>Na. However, at about 1150 K the following equilibrium is set up:

$$Na\,(g) + K^+\,(l) \rightleftharpoons Na^+\,(l) + K(g).$$

Since potassium is more volatile, it distils off more readily displacing the equilibrium to the right and allowing the forward reaction to proceed. Rubidium and caesium, can be prepared by the reduction of their chlorides with calcium metal at 1000 K under reduced pressure. Rubidium and caesium salts are obtained during the recrystallisation of other naturally occurring alkali metal salts. Francium is produced as a result of α–emission (1%) during the radioactive decay of actinium, as shown in Fig. 4.1.

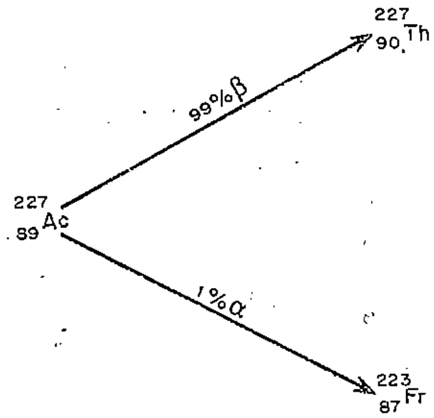


Fig. 4.1 : Production of francium from actinium as a result of α-decay.

Uses

The alkali metals are very good conductors of heat and electricity. But due to their highly reactive nature, they cannot be used for this purpose. Sodium in polyethylene enclosed cables is used in some underground high voltage transmission applications. Because of the high specific heat and thermal conductivity, liquid sodium is used as coolant in nuclear reactors. You must have seen bright yellow lights on the streets and particularly on the highways. These are sodium vapour lamps and the light from them can penetrate the fog well.

Caesium has the distinction of being the metal from which electrons are ejected most easily on exposure to light. This phenomenon is called photoelectric effect. Photocells, which are a device for converting light into electricity are based on this phenomenon.

Besides the above uses as metals, alkali metal compounds have a variety of applications. Lithium in the form of lithium stearate is used for the production of lubricating greases. The hydrides of lithium and sodium, viz., $LiAlH_4$ and $NaBH_4$ are used as reducing agents in synthetic organic chemistry. Lithium and potassium compounds are used in picture tubes of colour televisions.

Can you imagine food without common salt! Apart from being an essential constituent of food, sodium chloride has many other important industrial uses like in the manufacture of NaOH, Na_2CO_3, Cl_2 and H_2 gases. Other compounds of sodium also have many uses. Caustic soda or sodium hydroxide is used in making soaps, sodium carbonate also known as washing soda, in laundering and in manufacture of glass, sodium bicarbonate as baking soda in baking powder, in medicine and in fire extinguishers.

Baking soda (sodium bicarbonate) puts out fires.

Potassium compounds also have many uses, like potassium hydroxide is used in liquid detergents, potassium superoxide in breathing apparatus, potassium chlorate in matches and explosives, and potassium bromide (KBr) in photography. Potassium nitrate is used along with charcoal and sulphur in gun powder. Potassium is a major component of plant fertilisers also where it is used in the form of chloride and nitrate salts.

4.3 GENERAL CHARACTERISTICS

Now let us study some of the physical and chemical properties of Group 1 elements. All the elements of Group 1 have one electron in their outermost orbital. Because of the similar outer electronic configuration of these elements, many similarities in their chemical behaviour are to be expected. However, lithium shows considerable differences from the rest of the elements of Group 1 about which we will discuss later in Section 4.7.

4.3.1 Physical Properties

Most of the physical properties are directly related to atomic properties of elements. Variation of the physical properties from one element to the other in a group is governed by the trends of the various atomic properties which we have already discussed in Unit 2. Let us apply them to understand the group trends in the various physical properties of the Group 1 elements given in Table 4.1.

Table 4.1: Properties of the Group 1 metals

Property	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Caesium Cs
Atomic number	3	11	19	37	55
Electronic configuration	[He]$2s^1$	[Ne]$3s^1$	[Ar]$4s^1$	[Kr]$5s^1$	[Xe]$6s^1$
Atomic weight	6.939	22.898	39.102	85.47	132.905
Covalent radius (pm)	123	156	203	216	235
Ionic radius (pm)	60	95	133	148	169
Boiling point (K)	1620	1154	1038	961	978
Melting point (K)	453	371	337	312	301.5
Density (10^3 x kg m^{-3})	0.53	0.97	0.86	1.53	1.87
Electronegativity (Pauling)	1.0	0.9	0.8	0.8	0.7
Electronegativity (A/R)	1.15	1.0	0.9	0.9	0.85
Ionisation energy (kJ mol^{-1})	520	495	418	403	374

Atomic Size

If you recall Unit 2, you will see that alkali metals are the largest in their corresponding periods in the periodic table. The size of the atom or its ion increases on descending the group (Table 4.1). This is due to the addition of an extra shell of electrons as we move down the group from one element to the next. The addition of the extra shell of electrons outweighs the effect of increased nuclear charge and thus there is an increase in size from Li to Cs. This trend is shown in Fig. 4.2.

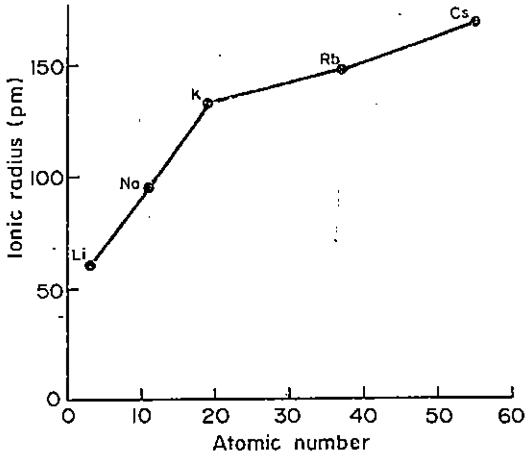


Fig. 4.2: Trend in ionic radii of Group 1 elements.

Density

Related to atomic size is the density of the elements. Density can be defined as mass per unit volume. For solids, the density is a function of atomic weight, size of the atom and the structure of the solid which determines the closeness of the packing of the atoms. There are two general trends observed in the densities of the elements in the periodic table. Along a period there is a general increase in density because of the increase in atomic mass and decrease in the size of the atom. Thus, in a particular period the alkali metals have the lowest density, considering the solid elements only. In a group also, density increases on going down the group. Since the elemental structures are often the same within any group, the factors which determine the density are atomic mass and volume. As you can see from Table 4.1, density increases as we move from Li to Cs. This means that the increase in atomic weight from one element to the next in passing down the group overweighs the effect of increase in the size of the atom. There are, however, some exceptions to this general trend and in this particular group of alkali metals, you can see from Table 4.1 that the density of potassium is less than that of sodium. Thus, potassium is an exception in this trend.

Melting Points and Boiling Points

These metals are soft and can be cut with a knife. As a result of increase in size and repulsion of the non-bonded electrons, their cohesive energy and tendency for metallic bonding decrease down the group and thus softness increases as we go down from Li to Cs. These metals have low melting and boiling points which also reflect the low values of cohesive energy between the atoms. Their melting and boiling points decrease as we go down the group. This trend in their melting points is shown in Fig. 4.3.

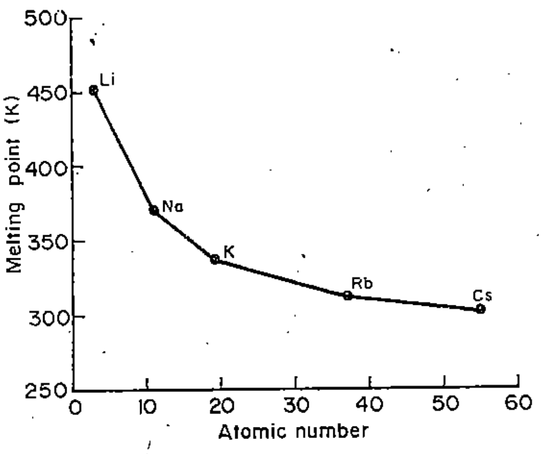


Fig. 4.3: Trend in the melting point of Group 1 elements.

Thermal and Electrical Conductivity

In alkali metals, electrons of the noble gas core efficiently shield the lone valence shell electron from the nuclear charge. Therefore, the effective nuclear charge felt by the electron in the valence shell of an atom of an alkali metal is the least and their atoms are the largest in respective periods. As a consequence, the sole valence electron is very loosely held by the nucleus. It can move freely from one metal ion to the other in the lattice, thereby the alkali metals are good conductors of heat and electricity. This loosely bound electron is also responsible for the silvery lustre of the alkali metals when freshly cut.

Ionisation Energy

By losing the loosely bound solitary outermost electron, these elements can acquire the electronic configuration of the preceding noble gas elements. They have, therefore, a high tendency of giving up this electron to form univalent cations. Their first ionisation energies are the lowest in the respective periods and so, they are the most reactive of all the metals. As we go down the group, their atomic size increases, their ionisation energies decrease, resulting in an increase in their reactivity. The effective nuclear charge felt by the electrons increases after the removal of one electron from the atom of any element and hence, their second ionisation energies are always higher than the first. However, in the case of alkali metals, the unipositively charged ions (Li^+, Na^+, K^+, etc.) have the stable electronic configuration of the preceding noble gases. Removal of an electron from a stable noble gas configuration is extremely difficult. These metals, therefore, form univalent cations only. Fig. 4.4 shows the trend in the first ionisation energies of the alkali metals down the group.

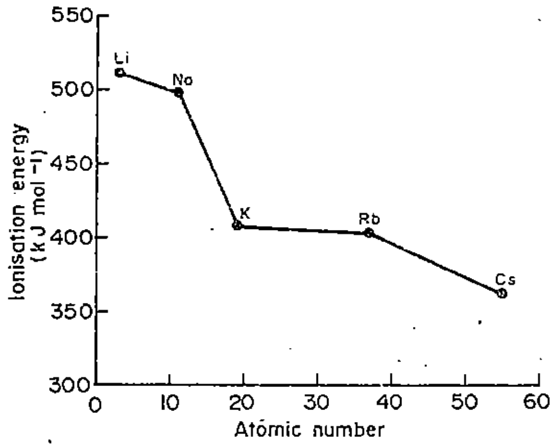


Fig. 4.4: Trend in first ionisation energies of alkali metals.

On account of their low ionisation energies, these elements have a high tendency to form cations. In other words, they have high electropositive or metallic character which increases as we move down in the group from Li to Cs. In fact, Rb and Cs are so highly electropositive that they emit electrons even when exposed to light; that is, they exhibit photoelectric effect.

Electronegativity

Because alkali metals have a tendency to lose electron easily rather than to gain, values of electronegativity of these elements are very small. In fact, alkali metals are the least electronegative elements in the periodic table. As expected the electronegativity decreases on moving down the group.

Ionic Character of Compounds

Compounds formed by alkali metals with highly electronegative elements like halogens and oxygen are largely ionic in nature because of a large electronegativity difference. The trends in ionic character of alkali metal halides are shown in Fig. 4.5. You can see that the trends are as expected; the ionic character increases with increase in cation size and decreases with increase in anion size. Because of the small size of Li^+, it has more polarising power and, therefore, favours covalent bonding.

Solubility, Lattice Energy and Hydration Energy

Alkali metal salts like halides, oxides, hydroxides, carbonates, sulphates, etc. exhibit some interesting trends in their solubility in water. To understand these trends, let us first recapitulate lattice energy and hydration energy which you have studied in **Unit 3** of the **'Atoms and Molecules'** course. Lattice energy is the driving force for the formation of an ionic compound and its stability. Lattice energy is directly proportional to the charge on the

Lattice energy is the **enthalpy** change when one mole of crystal lattice is formed from the isolated gaseous ions.

Hydration energy is the enthalpy change when one mole of solute is dissolved in water.

ions and inversely proportional to the distance between the cation and anion. This distance is taken as the sum of radii of cation and anion ($r_c + r_a$). In a group, the charge on cations remains constant. Thus, lattice energy depends mainly on the size of the cation. Similarly, hydration energy also varies with the charge and size of the cation. The higher the charge and the smaller the size of the ion, the more is the hydration energy. In a group, lattice energy and hydration energy decrease as we move down. While the decrease in lattice energy favours the solubility, the decrease in hydration energy makes the compound insoluble.

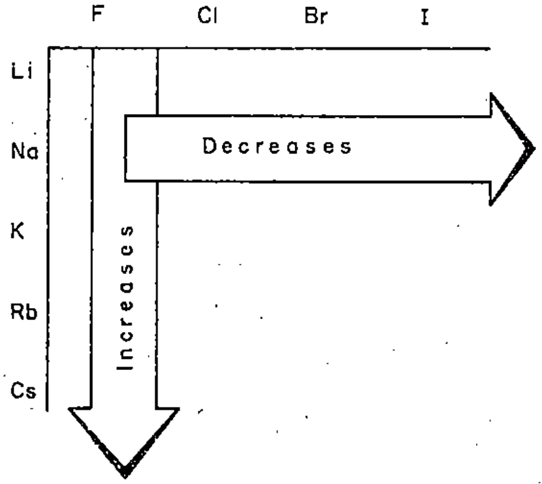


Fig. 4.5: Trend in the ionic character of alkali metal halides.

For the salts of small anions (like F^-, O^{2-}, OH^-, etc.), the lattice energy which is inversely proportional to $r_c + r_a$, is very sensitive to the change in the size of the cation, anion being very small in size has little contribution in the total ($r_c + r_a$) and decreases sharply as we move down the group. Thus, in these salts, the decrease in lattice energy is greater than the decrease in hydration energy and, therefore, the solubility of these salts increases as we go down the group. For example, in the case of alkali metal fluorides, the solubility increases in the order LiF<NaF<KF<RbF<CsF.

For the salts having large anions (SO_4^{2-}, I^-, NO_3^-, HCO_3^-, CO_3^{2-}, etc.), as $r_a >> r_c$, the radii of the cation has little effect on $r_a + r_c$ and thus on lattice energy. The main factor for solubility is , therefore, hydration energy which decreases as the size of the cation increases. Thus, in this case, the decrease in hydration energy is more than the decrease in lattice energy and the solubility decreases as we move down the group. For example, in the case of alkali metal carbonates, lithium carbonate is highly soluble while the solubility of caesium carbonate is very little.

Another important factor contributing to the solubility of the compound is the match in the size of the cation and anion. Whenever there is a mismatch, e.g., cation is small, anion is large or *vice-versa*, this will result in the increased solubility of the compound. Let us keep the cation constant say caesium. If we, then, change the anion from fluoride to iodide, then the solubility of the compounds will vary as CsF > CsCl > CsBr > CsI. Thus, caesium fluoride will be most soluble and caesium iodide will be the least. Similarly, from lithium

Table 4.2: The main trends in the properties of alkali metals.

increasing:	decreasing:	
electropositivity	m.p. and b.p.	Li
density*	hardness	Na
atomic radii	ionisation energy	K
atomic volume	conductivity	Rb
reactivity	electronegativity	Cs
reducing power	solubility of salts having large anions	
anion stabilisation		
solubility of salts having small anions		

* The density of K is less than that of Na.

fluoride to lithium iodide, the solubility will increase in the order: LiF < LiCl < LiBr < LiI. There can be many more examples which can be explained on the basis of above reasonings. So far we have discussed the periodic trends observed in the physical properties of the alkali metals and their compounds. These trends are summarised in Table 4.2.

SAQ 1

Given below are some of the statements about the alkali metals. Write 'T' if true and 'F' if false against them.

i) Sodium is the most abundant alkali metal in the earth's crust.

ii) Sodium is the most abundant metallic element in sea water.

iii) Alkali metals occur in the free state in nature.

iv) Lepidolite is an ore of lithium.

v) Atomic radii of the alkali metals increase down the group.

vi) Ionisation energy increases from lithium to francium.

vii) Melting and boiling points of alkali metals decrease down the group.

viii) Lithium is the lightest of all the metallic elements.

ix) Solubility of alkali metal fluorides in water increases down the group.

x) Ionic character of alkali metal halides decreases down the group.

4.3.2 Chemical Properties

In the previous subsection you have studied the important physical properties of the alkali metals. In accordance with their highly electropositive character, these metals are very reactive and are powerful reducing agents reacting with water and most non-metals. They form crystalline ionic salts with high melting and boiling points. These salts are usually soluble in water giving conducting solutions. Now we shall discuss some of the important classes of these salts.

Oxides and Hydroxides

As alkali metals are very reactive, their lustre is lost in air due to the formation of oxide with atmospheric oxygen. Three types of oxides are formed by the alkali metals, viz., normal oxides having O^{2-} ion and the peroxides having O_2^{2-} [$^-O-O^-$] ion, both of which are **diamagnetic** and colourless. The third one which is coloured and **paramagnetic** is superoxide containing O_2^- ion. Controlled oxidations of these metals are shown below:

Materials that are **diamagnetic** experience no attraction for another magnet. **Paramagnetic** substances, on the other hand, are weakly attracted to a magnetic field.

$$2Li \xrightarrow{\frac{1}{2}O_2} \mathbf{Li_2O} \xrightarrow{\frac{1}{2}O_2} Li_2O_2$$

$$2Na \xrightarrow{\frac{1}{2}O_2} Na_2O \xrightarrow{\frac{1}{2}O_2} \mathbf{Na_2O_2}$$

$$2K \xrightarrow{\frac{1}{2}O_2} K_2O \xrightarrow{\frac{1}{2}O_2} K_2O_2 \xrightarrow{O_2} \mathbf{2KO_2}$$

$$2Rb \xrightarrow{\frac{1}{2}O_2} Rb_2O \xrightarrow{\frac{1}{2}O_2} Rb_2O_2 \xrightarrow{O_2} \mathbf{2RbO_2}$$

$$2Cs \xrightarrow{\frac{1}{2}O_2} Cs_2O \xrightarrow{\frac{1}{2}O_2} Cs_2O_2 \xrightarrow{O_2} 2CsO_2$$

In the above scheme the products in bold letters are the main products when the metals are burnt in a free supply of air. You may notice in the above scheme that **lithium forms normal oxide, sodium forms peroxide while potassium, rubidium and caesium form superoxide as the main product.** All the Group 1 metal oxides are strongly basic and react vigorously giving hydroxides,

$Li_2O + H_2O \longrightarrow 2LiOH$ (less violent)

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

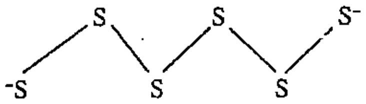
$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

As we see, the peroxides and the superoxides on reaction with water give H_2O_2 which in turn is a powerful oxidising agent. Thus, the peroxides and the superoxides are also oxidising in nature.

The basic strength of the hydroxides increases down the group. As the charge density (charge/size ratio) of the cation decreases from Li^+ to Cs^+, attraction between M^+ and OH^- also decreases. So, OH^- can be liberated readily into the solution, as we go down the group.

Sulphides

Alkali metals react with sulphur to form two types of sulphides: simple sulphides Na_2S and polysulphides like Na_2S_n where n = 2, 3, 4, 5 or 6. These polysulphides have a zig-zag chain structure of sulphur atoms as shown below:



Hydrides

The alkali metals react with hydrogen and form ionic hydrides, M^+H^-. These hydrides on reaction with water liberate hydrogen. Thus, they are a useful source of hydrogen:

$$MH + H_2O \longrightarrow MOH + H_2$$

Lithium hydride on reaction with $AlCl_3$ in ether solution forms lithium aluminium hydride which is a useful reducing agent in organic chemistry.

$$4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$$

Similarly, sodium hydride forms sodium borohydride which is also used as a reducing agent.

Carbides

Lithium reacts with carbon to form ionic carbide whereas similar carbides of other metals are not formed on reacting them with carbon. They can, however, be formed on heating the metal with acetylene or when acetylene is passed through a solution of the metal in liquid ammonia:

$$Na + C_2H_2 \xrightarrow{Liq{\cdot}NH_3} NaHC_2 \longrightarrow Na_2C_2$$

These carbides contain the carbide ion $(C{\equiv}C)^{2-}$. On hydrolysis they give acetylene. Hence, they are termed as **acetylides**:

$$Na_2C_2 + 2H_2O \longrightarrow 2NaOH + C_2H_2$$

Alkali metals also form covalent compounds such as methyllithium, $LiCH_3$ and ethylsodium, NaC_2H_5. These come under the separate class of organometallic compounds.

The main reactions of Group !elements are summarised in Table 4.3.

Table 4.3: The reactions of theGroup 1 elements.

$2Li + O_2 \xrightarrow{excess} Li_2O$	The higher metals from Na_2O_2, K_2O_2, KO_2, RbO_2, CsO_2.
$2M + S \longrightarrow M_2S$	Very vigorous reaction. Polysulphides are also formed.
$M + H_2O \longrightarrow MOH + \frac{1}{2}H_2$	With Li fairly slow, whereas K explodes.
$M + ROH \longrightarrow MOR + \frac{1}{2}H_2$	Vigorous (R = alkyl, aryl). With Li fairly slow.
$M + \frac{1}{2}H_2 \longrightarrow MH$	At high temperatures, ionic hydrides. LiH is the most stable.
$M + \frac{1}{2}X_2 \longrightarrow MX$	X = halogen. The higher members can form polyhalides, e.g., KI_3.
$3Li + \frac{1}{2}N_2 \longrightarrow Li_3N$	Slow at room temperature; rapid at elevated temperatures.
$M + NH_3\,(l) \longrightarrow [M(NH_3)_n]^+ + e^-(NH_3) \xrightarrow{catalyst} M^+NH_2^- + \frac{1}{2}H_2$	
$2M + C(\text{or } C_2H_2) \longrightarrow M_2C_2$ (acetylides) $\xrightarrow{H_2O} C_2H_2$	
$M + Hg \longrightarrow$ amalgams	

SAQ 2

Explain briefly in the space given below why do alkali [illegible]

....

....

....

The standard **enthalpy of formation** of a compound is the enthalpy change when one mole of the compound in the standard state is formed from the elements in the standard state.

Thermal Stability of Salts

The ease of thermal decomposition of a salt is related to the **enthalpy of formation** of the salt. The **enthalpy of formation**, ΔH_f° of a salt MA (M is the metal, A is anion) is given by

$$\Delta H_f^\circ = (\Delta H_{atom} + I)_{metal} + (\Delta H_{atom} - E_A)_{anion} - \Delta H_{latt}$$

where ΔH_{atom} is the **enthalpy of atomisation**, I is the ionisation energy and E_A is the electron affinity. Since for any salt in a particular group the terms involving the anion alone remain constant, the value of ΔH_f^o for such compounds is dependent upon the sum of the enthalpy terms of the particular metal, $(\Delta H_{atom} + I)_{metal}$ and the lattice energy, ΔH^o_{latt}. The larger the lattice energy, the more negative the enthalpy of formation and so, more stable is the compound. All these terms become smaller on descending the series from lithium to caesium. The relative stabilities of the salts are, therefore, decided by the parameter which decreases more rapidly — the lattice energy or the sum of the metal enthalpies.

The enthalpy of atomisation of an element is the enthalpy change when one mole of gaseous atoms is formed from the element in the standard state, e.g.,

$1/2Cl_2(g) \longrightarrow Cl(g) + \Delta H_{atom}$ In this equation ΔH_{atom} is the enthalpy of atomisation.

In the salts having small anions of high charge density, e.g., F^-, N^{3-}, OH^-, O^{2-} etc., the change in lattice energy is much dependent on the size of the cation and decreases rapidly on descending the group. Thus, as the size of the cation increases, lattice energy decreases more than the change in the sum of the metal enthalpies. Therefore, as we go down the group, the stability of these salts having small anions decreases. Thus, in alkali metal fluorides, the stability decreases in the order LiF > NaF > KF > RbF > CsF.

The opposite trend is observed in the stability of the salts containing large anions of low harge density, e.g., Br^-, I^-, NO^-_3, etc. In such cases, the lattice energy is relatively insensitive to the change in cation size and there is more rapid decrease in ionisation energy nd atomisation enthalpy on descending the group. The lower values of these favour tability of the compounds. Thus, the stability of the compounds having large anions ncreases as we move down the group from lithium to caesium.

The stability of the compounds can also be explained by using the concept of polarising ower. The simple idea is that, as the charge density of the metal ion increases, the thermal tability of the salts of large polarisable anions, relative to some decomposition product lecreases. In general, the least polarising metal ions are those of the most electropositive netal ions and these form the most stable salts with large anions. In other words, small ations form stable salts with small anions and large cations form stable salts with large nions. Let us take the example of carbonates of Group 1 metals. The carbonates of sodium, otassium, rubidium and caesium are resistant to the heat of a bunsen burner flame, owever, lithium carbonate decomposes to its oxide and carbon dioxide under the same onditions:

$i_2CO_3 \longrightarrow Li_2O + CO_2$

he tendency of Li_2CO_3 to undergo thermal decomposition may be explained in terms of the in in electrostatic attraction that occurs when extremely small Li^+ ion combines with the naller oxide ion rather than the much larger carbonate ion. The other carbonates of roup 1(Na - Cs) are more stable because the cations have a lower charge density and are onsiderably larger in size and so, their decomposition is less favourable energetically.

ll the metals except lithium form stable bicarbonates (lithium bicarbonate is formed only in ueous solutions and has not been isolated). When we heat the alkali metal bicarbonates, ey are decomposed to carbonates and simultaneously, carbon dioxide and water are erated.

$aHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$

e thermal stability of Group 1 hydroxides also follows a similar trend as that of rbonates. Thus, except LiOH, which on heating decomposes to Li_2O, all other Group 1 droxides are stable. Similarly, lithium nitrate also decomposes on heating to give Li_2O, $_2$ and O_2 but all other alkali metal nitrates decompose on strong heating to nitrites erating oxygen:

$iNO_3 \longrightarrow 2Li_2O + O_2 + 4NO_2$

$aNO_3 \longrightarrow 2NaNO_2 + O_2$

b) Potassium nitrate on heating [illegible]

i) K_2O, O_2 & K ☐ iii) KNO_2, [illegible]

ii) KNO_2 & O_2 ☐ iv) K, KO_2 [illegible]

4.4 SOLVATION OF THE ALKALI METAL IONS

When a metal ion is surrounded by the solvent molecules, the phenomenon is called **solvation** of the metal ion. When the solvent is water it is called **hydration**. The alkali metal ions are highly hydrated. The smaller the size of the ion, the greater is its degree of hydration. This is because the smaller the size, the more will be its charge density and the more will be its attraction for the polar solvent molecules. Thus, Li^+ ion, which is the smallest gets more hydrated than the Na^+ ion and so on. The degree of hydration decreases on moving down the group. As a result of differences in their degree of hydration, the hydrated ionic radii of the alkali metal ions decrease as we go down the group from lithium to caesium. Li^+ ion has the largest hydrated radius while Cs^+ has the smallest hydrated radius in the first group. You will agree that the smaller the size of the ion and the lighter it is, the more will be its mobility and thus conductance. In this regard we should expect the highest conductance for Li^+ which is the smallest of the alkali metals but this is not so. We have explained above that the hydrated radius of Li^+ is the largest of all the alkali metal ions, in solution. Therefore, **Li^+ ion is the least conducting in solution.** The ionic conductance in solution actually decreases in the order $Cs^+>Rb^+>K^+>Na^+>Li^+$

SAQ 4

In the space given below, briefly explain how [illegible] metal salts and why.

....

....

4.5 SOLUTIONS OF ALKALI METALS IN LIQUID AMMONIA

All the alkali metals are highly soluble in liquid ammonia giving deep blue colour. Per 100g of NH_3, the solubilities are: Li, 10g; Na, 25g and K, 49g. The dissolution of the alkali metal is accompanied by its dissociation into the metal ions and the electrons. The metal ion and the electrons then get associated with ammonia solvent molecules. Electrons associated with the solvent are known as **solvated electrons.**

$$Na\,(s) + NH_3(l) \longrightarrow Na^+\,(NH_3)_x + e(NH_3)_y$$

The alkali metal solutions in liquid ammonia are highly conducting and behave almost as metals. Their specific conductivities are almost the same, because the anion, i.e., solvated electron in all the cases is the same. The small difference in the conductivity is due to the nature of the metal itself. The solution of alkali metals in liquid ammonia is blue in colour due to the presence of solvated electrons and, therefore, the solutions are also paramagnetic. With increasing concentration there is a decrease in paramagnetism suggesting that the electron can get associated to form diamagnetic electron pairs. Although, there may be other equilibria also:

$$Na(s)\ (\text{dispersed}) \rightleftharpoons Na(\text{in solution}) \rightleftharpoons Na^+ + e$$

$$2e \rightleftharpoons e_2$$

On increasing the concentration above 3M, the colour of the solution changes to copper bronze having metallic luster because the metal ions form clusters. Except lithium, other alkali metals can be recovered unchanged from solution. Lithium in ammonia solution forms a complex of the type $[Li(NH_3)_4]^+$. The blue solutions of alkali metals are moderately stable at temperatures where ammonia is still a liquid, but the reaction to give amide,

$$Na + NH_3(l) \rightleftharpoons NaNH_2 + \tfrac{1}{2}H_2$$

can occur photochemically and is catalysed by transition metal salts. The alkali metal solutions in liquid ammonia are powerful reducing agents and are used for this purpose in inorganic and organic reactions.

SAQ 5

Alkali metals dissolve in ammonia giving blue coloured solutions. The blue colour of the solution of sodium in liquid ammonia is due to one of the following reasons. Tick the correct answer in the boxes provided along side.

i) ammonia ☐

ii) solvated electron ☐

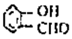
iii) sodium metal ☐

iv) all of the above ☐

v) none of the above ☐

4.6 COMPLEXATION BEHAVIOUR OF ALKALI METALS

Before discussing the complexation behaviour of alkali metals, let us first define 'what is a complex compound'. A completely satisfactory definition of this is difficult to give at this stage but we can define a complex compound as a compound having a central metal atom/ion surrounded by a group of ions or molecules called 'ligands'. These ligands are usually bound to the metal by the 'coordinate bond', i.e., the bond formed by the donation of a lone pair of electrons from one atom (of the ligand) to the other (metal atom/ion). Although both metal and the ligand are usually capable of independent existence as stable chemical species, yet when the complex is formed, it generally retains its identity in solution. For example, in solution Fe^{++} and CN^- can exist independently but once the complex $[Fe(CN)_6]^{4-}$ is formed it exists in solution as such, i.e., it does not dissociate appreciably into Fe^{++} and CN^-; as a result it will not give any test for Fe^{++} and CN^-. It is thus a complex species. **The most stable complexes would be formed by the highly polarising cations,** which have a strong tendency of interacting with electron clouds of other anionic or neutral electron rich species (ligands).

A ligand which occupies more than one coordination position, i.e., more than one atom of the ligand is bonded to the central metal is called a **chelating ligand**, e.g., salicylaldehyde,  can bind the metal by its both the oxygen atoms. A coordination compound formed with a chelating ligand is called a **chelate.**

According to the above model, a very weak coordinating ability is expected in the Group I metals because of their large size and low charge of the cations, M^+. According to this view, stability of the complexes of the alkali metals should decrease in the order Li>Na>K>Rb>Cs and this is the observed trend also. Alkali metals form few complexes, mostly **chelates** with the ligands like β-diketones, nitrophenols, nitrosonaphthols, etc. as shown in Fig. 4.6. They are of low stability.

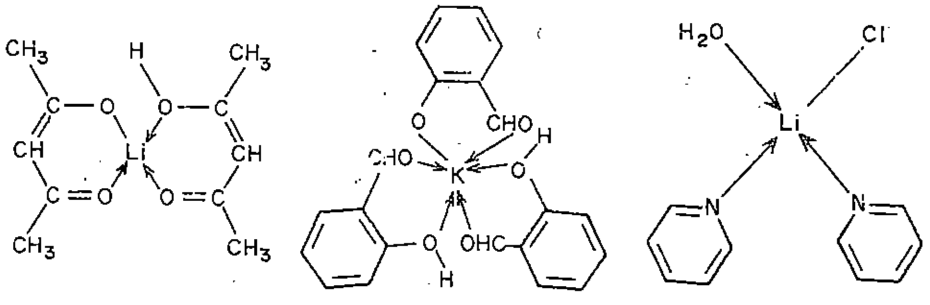


Fig. 4.6 : Some complexes of alkali metal ions

Lithium, being the most polarising cation of all the alkali metals, forms tetrahedral complexes with ligands like NH_3, C_5H_5N, etc. With ammonia it forms the complex of the type $[Li(NH_3)_4]I$, whereas with pyridine, a complex of the type $[LiCl\,(C_5H_5N)_2\,(H_2O)]$ is formed.

SAQ 6

Explain briefly, in the space given below, why alkali metals are poor complexing agents.

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....

4.7 ANOMALOUS NATURE OF LITHIUM

On descending any group of *s*- or *p*-block elements of the periodic table, there is a general decrease in electronegativity or increase in electropositivity. The difference in electronegativity between the first and the second elements of each group is much greater than that between any two successive elements. This is reflected in the properties of the elements. Thus, not only is the first element more electronegative than the other elements of the group, but it is much more electronegative than expected by simple extrapolations. The differences, therefore, between the first and rest of the Group 1 metals are those between a less electropositive metal and a more electropositive metal. We have discussed most of these properties at the appropriate places in earlier sections. Let us summarise them again.

Due to the very small size of lithium, the metallic bonding between the atoms in the metallic lattice is very strong giving rise to strong cohesive forces. This is shown in its relatively higher melting and boiling points, hardness and homonuclear bond energy.

The relatively higher attraction of lithium for its outer electron results in its relatively higher electronegativity, ionisation energy, hydration energy, electron affinity and of course smaller atomic radii relative to the other homologues.

Similar anomalies are also found in the chemical properties but the differences appear greater.

i) Lithium salts of large polarisable anions are thermally less stable than those of other alkali metals, e.g., lithium carbonate decomposes at 950 K, whereas no decomposition of sodium carbonate takes place below 1050 K.

ii) Lithium forms no solid bicarbonate, triiodide and superoxide as these are unstable at room temperature, whereas those of other alkali metals require a higher temperature to effect their decomposition.

iii) Lithium salts of anions of high charge density are less soluble than those of other alkali metals. The halides of lithium are more covalent than the other halides and are more soluble in organic solvents.

iv) Lithium forms stable salts with anions of high charge density owing to their high lattice energy. For example, in air, lithium forms the normal oxide, whereas the others form higher oxides. Lithium reacts with nitrogen to form nitride, Li_3N, the others do not react. Lithium hydride is more stable than the other hydrides and lithium carbide is formed more easily with acetylene.

v) Lithium reacts slowly with water.

vi) Lithium forms more stable covalent bonds than other alkali metals and, therefore, forms more stable complex compounds (Section 4.6). For example, lithium cannot be recovered unchanged from its liquid ammonia solution, owing to the formation of $[Li(NH_3)_4]^+$.

This correlation of properties with the concepts of electronegativity and electropositivity is only one way of rationalising the data.

Other way of looking at the anomalous nature of lithium is by considering the variation of the ionic radius down the Group 1 metals. This determines the energy of interaction of the alkali metal ions with other (negative) ions and polar molecules and determines such important factors as hydration energies, the complexing power, solubilities, stabilities, electrode potentials, etc.

4.8 SUMMARY

Let us recall what we have discussed in this unit. As far as the main trends in properties of alkali metals are concerned, we have seen that electropositivity, density, atomic radii, atomic volume, reactivity, reducing power and large anion stabilisation increase down the group, whereas m.p., b.p., hardness and ionisation energy decrease down the group. The elements of this group form carbonates, bicarbonates and nitrates, the stability of which increases on descending the group.

Li^+ being the smallest cation is heavily hydrated and is least conducting. Bigger cations are less solvated. All the alkali metals have good solubility in liquid NH_3 and their ammonia solutions are highly conducting. Since the metal ions are large and have low charge, they form less stable complexes. Some covalent compounds, e.g., methyllithium and ethylsodium have also been prepared.

We have also noticed that lithium behaves quite abnormally in many respects, e.g., it has high cohesive properties, high electronegativity, ionisation energy, electron affinity and small atomic radius.

4.9 TERMINAL QUESTIONS

1 Why the elements of Group 1 are called the alkali metals?

2 Why do alkali metals not occur as free elements in nature?

3 Explain why
   i) alkali metals are good conductors of electricity.
   ii) lithium has the highest ionisation energy in the group.
   iii) sodium forms +1 ion and not +2 ion.
   iv) Group 1 elements form ionic compounds.

4 Consider the elements Li, Na, K, Rb, Cs and Fr. List them in the order of
   i) decreasing atomic radius
   ii) decreasing hydrated ionic radius
   iii) increasing density
   iv) decreasing melting and boiling points
   v) increasing ionisation energy.

5 Explain how does the solubility of salts vary and why do hydroxides become stronger alkalies on descending the group.

6 Explain
   i) The trend in the solubility of alkali metal iodides.
   ii) Why lithium forms oxide, sodium forms peroxide and potassium, caesium and rubidium form superoxide. [Hint: discuss on the basis of the size of cation and anion.]
   iii) Why stability of carbonates increases down the group.
   iv) Why lithium compounds have more covalent character than potassium compounds.

7 Why do peroxides and superoxides oxidise in aqueous solution?

8 What will be the action of water on
   i) alkali metal oxides
   ii) alkali metal hydrides
   iii) alkali metal carbides
   Give equations only.

9 What will be the action of the following on lithium? Give equations only.
   i) H_2
   ii) N_2
   iii) O_2
   iv) NH_3
   v) Cl_2

10. Explain why lithium forms more complexes than the other elements of Group 1.

4.10 ANSWERS

Self Assessment Questions

1 i) T ii) T iii) F iv) T v) F
vi) F vii) T viii) T ix) T x) F

2 The outermost electron in alkali metals is very loosely bound so it can be removed easily. Thus, alkali metals are strong reducing agents.

3 a. (v) b. (ii)

4. Conductivity in solution decreases as the hydrated ionic radii of the metal ion

increases. Thus, for alkali metal salts conductivity varies as $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$.

5. (ii).

6. Because of the large size and low charge on the alkali metal ions, they have poor complexing power.

Terminal Questions

1 Group 1 elements form hydroxides which are strong alkalies so they are called alkali metals.

2 Alkali metals are very reactive, therefore, they do not occur as free elements in nature.

3 i) The outermost electron in alkali metals is very loosely bound and can go from one metal ion to other easily. Therefore, these metals are good conductors of electricity.

ii) Lithium, being the smallest metal in its group, holds its electrons most tightly. So maximum energy is required to remove its outermost electron among Group 1 metals. Thus it has the highest ionisation energy in the group.

iii) After losing one electron and forming Na^+ ion, sodium achieves noble gas configuration $1s^2 2s^2 2p^6$, from which removing an electron is extremely difficult. Thus, sodium forms +1 ion and not +2.

iv) Group 1 elements are large in size and are highly electropositive. They also have low charge to size ratio and thus they form ionic compounds mostly.

4 i) Fr > Cs > Rb > K > Na > Li

ii) Li > Na > K > Rb > Cs > Fr

iii) Li < Na > K < Rb < Cs < Fr

iv) Li > Na > K > Rb > Cs > Fr

v) Fr < Cs < Rb < K < Na < Li

5 For salts of alkali metals with the anions of high charge density (F^-, O^{2-}, OH^- etc.), the solubility increases on moving down the group. For salts having anions of low charge density (CO_3^{2-}, HCO_3^-, I^-, NO_3^-), solubility decreases on moving down the group.
As the hydroxides of the alkali metals which are lower in the group are more soluble, OH^- ions are released more readily. Therefore, the hydroxides become stronger alkalies on moving down the group.

6 i) LiI > NaI > KI > RbI > CsI.

ii) Small cations form stable compounds with small anions of high charge density and *vice versa*. The charge density of oxide ions varies as $O^{2-} > O_2^{2-} > O_2^-$ and that of alkali metals as Li > Na > K > Rb > Cs. Therefore, Li forms stable oxide, Li_2O, sodium forms peroxides, Na_2O_2 and potassium, rubidium and caesium form stable superoxides.

iii) The trend in stability of carbonates is $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$. When cations are large, salts with large anions are stable. Thus, stability of carbonates increases down the group. Lithium having high charge density, its carbonate decomposes to oxide which is much more stable.

iv) Lithium cation is much smaller than the potassium cation, therefore, the polarising power of lithium cation is much higher than that of potassium cation. So, the lithium compounds are more covalent than the potassium compounds.

7 Peroxides and superoxides in aqueous solution give H_2O_2 which is a strong oxidising agent. Thus, peroxides and superoxides are strong oxidising agents.

8. i) $Li_2O + H_2O \longrightarrow 2LiOH$

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

ii) $NaH + H_2O \longrightarrow NaOH + H_2$

iii) $Na_2C_2 + 2H_2O \longrightarrow 2NaOH + C_2H_2$

9. i) $2Li + H_2 \longrightarrow 2LiH$

ii) $6Li + N_2 \longrightarrow 2Li_3N$

iii) $4Li + O_2 \longrightarrow 2Li_2O$

iv) $Li + 4NH_3 \longrightarrow [Li(NH_3)_4]^+ + e$

v) $2Li + Cl_2 \longrightarrow 2LiCl$.

10. The most stable complexes would be formed by the highly polarising cations. Li^+ being the most polarising cation of all the alkali metals, forms larger number of complexes than the other Group 1 metals.

UNIT 5 ALKALINE EARTH METALS

Structure

5.1 Introduction
    Objectives
5.2 Occurrence, Extraction and Uses
5.3 General Characteristics
    Physical Properties
    Chemical Properties
    Complexation Behaviour
5.4 Anomalous Nature of Beryllium
5.5 Summary
5.6 Terminal Questions
5.7 Answers

5.1 INTRODUCTION

In the previous unit, you studied the general characteristics of Group 1 elements. i.e., alkali metals and their compounds. Group 1 and Group 2 elements belong to the *s*-block of the periodic table, as they have ns^1 and ns^2 outer shell electronic configuration, respectively. *s*-Block elements are known to be very reactive metals and generally form ionic compounds. In this unit you will study the elements of Group 2 consisting of beryllium, magnesium, calcium, strontium, barium and radium. Elements Ca, Sr, Ba and Ra are called **alkaline earth metals** because their earths (earth is the old name for a mineral oxide) are alkaline in nature. However, beryllium is not counted as an alkaline earth metal since its earth is not alkaline. Like the Group 1 elements, they show a distinct group relationship in which similarities between the elements are more pronounced than the differences between them. The first member of the group is 'anomalous' (cf. lithium). In this unit, we will study the general characteristics and chemistry of this group of elements.

Objectives

After studying this unit you should be able to:

- describe the general trend in the properties of the Group 2 elements,
- explain chemistry of the Group 2 elements,
- correlate the complexation behaviour of these elements, and
- explain why and how beryllium differs from the rest of the members of the group.

5.2 OCCURRENCE, EXTRACTION AND USES

The alkaline earth metals, like alkali metals are very reactive, therefore, do not occur free in nature. All of them are found in the form of their salts. These metals are strong reducing agents and, therefore, it is very difficult to obtain them by chemical reduction methods. All of these find some or the other use in industry. Let us now study their occurrence, extraction and uses in this section.

Occurrence

Beryllium, the first member of the group is found in small quantities in the silicate mineral, phenacite, Be_2SiO_4 and beryl, $3BeO.Al_2O_3.6SiO_2$. Magnesium (2.76%) and calcium (4.66%) are among the eight most abundant elements in the earth's crust. Magnesium (0.13%) is the second most abundant metallic element next only to sodium (chloride) in sea water. It occurs as magnesite, $MgCO_3$; dolomite, $MgCa(CO_3)_2$; kieserite, $MgSO_4.H_2O$ and carnallite, $KMgCl_3.6H_2O$ in the earth's crust. Calcium occurs extensively as calcite and lime-stone ($CaCO_3$) in many mountain ranges. Calcium and magnesium are very important biologically too. Calcium is found in the bones of animals and human beings. Magnesium is found in the green pigment, viz., chlorophyll of the plants. Strontium (0.038%) and barium (0.039%) are much less abundant and occur as carbonates and sulphates. These metals are well known because they occur as concentrated ores and are easy to extract. Radium is extremely scarce (10^{-10}%) and it is a radioactive element.

The gem stone, emerald, is beryl, the green colour being due to the presence of chromium.

Extraction

These metals are extracted by electrolysis of their fused chlorides, though magnesium has been manufactured by the carbon reduction of its oxide also. Thus, beryllium is obtained by the electrolysis of molten beryllium chloride. However, sodium chloride must be added to the melt as an electrolyte because $BeCl_2$ is covalent and, therefore, is a very poor electrical conductor. During the electrolysis, the less active metal, Be, is produced at the cathode and Cl_2 is evolved at the anode. Calcium is extracted from fused calcium chloride using anode of graphite and cathode of iron. Strontium chloride and barium chloride are used for the extraction of strontium and barium, respectively.

Uses

Beryllium is used for making atomic fuel containers because it absorbs very few neutrons and does not become radioactive. Being transparent to X-rays, it is used as a window material in X-ray apparatus. It has a number of uses as alloys, e.g., when mixed with Cu, Be increases the strength of Cu sixfold. Beryllium alloys are non-sparking, therefore, these are used in making hand tools for use in the petroleum industry. Magnesium, because of its lightness, is used as a construction alloy material. e.g., in aircrafts. For this purpose, it is alloyed with aluminium. Magnesium is used as a reducing agent in the extraction of some metals like titanium and uranium. It forms Grignard reagents, RMgX, which are important organic reagents. Calcium, strontium and barium as free metals do not find extensive uses because they are very reactive. Calcium oxide (quick lime) is a constituent of glass, mortar and portland cement. Thus, it finds extensive use in industry.

Mme. Marie Sklodowska Curie, 1867-1934. She got Nobel Prize in 1911 for discovering and isolating radium.

5.3 GENERAL CHARACTERISTICS

All the Group 2 elements have two electrons in their outermost orbital. Their outer orbital electronic structures may be written as $2s^2$, $3s^2$, $4s^2$, $5s^2$, $6s^2$ and $7s^2$ for Be, Mg, Ca, Sr, Ba and Ra, respectively. Because of their similar outermost electronic configuration, they show more or less similar properties. However, beryllium being the first element of the group, shows considerable differences from the rest of the elements of the group and exhibits diagonal relationship with aluminium in group 13. In this section we will discuss in brief the physical and chemical properties, solubility and complexation behaviour of these elements.

5.3.1 Physical Properties

The alkaline earth metals are quite soft metals, but are harder than the corresponding Group 1 elements. This is because of their two valence electrons which participate in metallic bonding. They are good conductors of electricity. In pure form they are silver coloured, but on exposure to atmosphere, the silvery lusture is lost, because of the formation of oxide layer on the surface of the metal. Their physical properties are given in Table 5.1.

Table 5.1: Properties of the Group 2 metals

Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	Radium Ra
Atomic Number	4	12	20	38	56 88	
Electronic configuration	$[He]2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$	$[Rn]7s^2$
Atomic weight	9.012	24.312	40.08	87.62	137.34	226.02
Ionic radius (pm)	31	65	99	113	135	
Covalent radius (pm)	89	136	174	191	198	
Boiling point (K)	3243	1380	1760	1607	1413	1700
Melting point (K)	1553	934	1118	1062	998	700
Enthalpy of hydration (kJ mol^{-1})	−2455	−1900	−1565	−1415	−1275	
Density (10^3 x kg m^{-3})	1.85	1.74	1.54	2.6	3.62	5.5
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9
Ionisation energy (kJ mol^{-1}) I	900	738	590	549	502	509
II	1757	1450	1146	1064	965	975

The atoms of the alkaline earth metals are smaller than those of the corresponding Group 1 elements. This is because of the increase in effective nuclear charge with the increase in atomic number. Due to increase in effective nuclear charge, valence shell electrons are pulled in more firmly by the nucleus, thereby reducing the size of the atom. Similarly, their ionic radii are also smaller than those of Group 1 elements, because the removal of two orbital electrons increases the effective nuclear charge even further.

These elements are denser than Group I metals because they have two valence electrons per atom for bonding the atoms into a metallic lattice and as a result more mass can be packed into a smaller volume. The density decreases slightly on moving down the group from Be to Ca but increases considerably thereafter up to Ra.

The atomic and ionic radii increase from Be to Ra due to the effect of extra shells of electrons being added. This outweighs the effect of increased nuclear charge.

Group 2 metals have higher melting points when compared to the Group 1 metals. The reason being +2 charge on the cations in the metallic lattice, causing them to be more strongly attracted to the 'sea of electrons' and making it difficult to pull them apart.

The first ionisation energy (Table 5.1) of alkaline earth metals is more than that of corresponding alkali metals. This is because the alkaline earth metals have higher effective nuclear charge and are smaller in size, thereby the electrons are more tightly held to the nucleus. The second ionisation energy of these elements is almost twice their first ionisation energy. This is because once one electron has been removed, the effective nuclear charge felt by orbital electrons is increased, so that the remaining electrons are more tightly held and hence, much more energy is needed to remove the second electron. However, their second ionisation energy is less than that of the corresponding alkali metals because of stability of a closed shell configuration of the univalent cations that are formed in the latter cases. The ionisation energy of alkaline earth metals also decreases on moving down the group.

Lower second ionisation energies of the alkaline earth metals as compared to those of alkali metals can be exemplified as below:

$\underset{(2,8,2)}{Mg} \rightarrow \underset{(2,8,1)}{Mg^+} + e$

$\underset{(2,8.1)}{Mg^+} \rightarrow \underset{(2.8)}{Mg^{++}} + e$

stable closed shell

(Electronic configuration of the metal and the ion is given in brackets.)

$\underset{(2,8,1)}{Na} \rightarrow \underset{(2.8)}{Na^+} + e$

$\underset{(2.8)}{Na^+} \rightarrow \underset{(2,7)}{Na^{++}} + e$

stable closed shell

The metals of this group (beryllium is an exception) form ionic compounds. This is because the assembly of positive and negative ions into a symmetrical crystal lattice results in the liberation of a large amount of energy. As a result of the exothermic process (refer to **Born Haber Cycle, Unit 3** of **Atoms and Molecules** course), there is the overall formation of ionic compounds.

Electropositive character and the reducing property (tendency to lose electrons) increase on moving down the group.

As the alkaline earth metals may lose electrons quite easily, they form divalent cations which have a noble gas structure with no unpaired electrons. Therefore, their compounds are diamagnetic and colourless, unless the anion is coloured. Ca, Sr and Ba compounds give characteristic flame colourations which are used to identify them — Ca (brick red flame), Sr (crimson red flame) and Ba (apple green flame).

SAQ 1

Write answers for the following questions in short in the given space.

a) Why are Group 2 elements smaller in size than their counterparts of Group 1?

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b) Why are Group 2 metals harder and have higher melting points as compared to the Group 1 metals?

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Solubility, Lattice Energy and Hydration Energy

We observe some interesting trends in the solubility of alkaline earth metal compounds. The metal ions are easily hydrated, e.g., $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $BaCl_2.2H_2O$. The hydration energies of these ions are much greater than those of alkali metal ions (Table 5.2), because of their smaller size and increased cationic charge (see Unit 4, Sec. 4.3). The lattice energies

(Table 5.2) of alkaline earth metal salts are also much higher than those of alkali metal salts. Hydration and lattice energies decrease with increase in size of metal ions. Decreasing lattice energy favours increased solubility, whilst decreasing hydration energy favours decreased solubility. If on moving down a group the hydration energy decreases more rapidly than the lattice energy, the compound becomes less soluble. This occurs with most of the compounds except for fluorides and hydroxides, for example, solubility of sulphates decreases from $BeSO_4$ to $BaSO_4$. Due to their small ionic radii, Be^{2+} and Mg^{2+} have high hydration energies. Thereby $BeSO_4$ and $MgSO_4$ are soluble in water. $CaSO_4$ is only slightly soluble in water, whereas $SrSO_4$ and $BaSO_4$ are almost insoluble in water. In case of fluorides and hydroxides, the lattice energy decreases more rapidly than their hydration energy. This causes a reverse trend, i.e., the fluorides and hydroxides increase in solubility on moving down the group.

For a substance to dissolve, the hydration energy must exceed the lattice energy

Table 5.2: Enthalpies of hydration, ΔH_{hyd}, of alkaline earth metal ions, M^{2+} and lattice energies, ΔH_{latt}, of their oxides, carbonates, fluorides and iodides in kJ mol^{-1}

	ΔH_{hyd}	ΔH_{latt}			
	M^{2+}	MO	MCO_3	MF_2	MI_2
Be	–2494	—	—	—	—
Mg	–1921	–3923	–3178	–2906	–2292
Ca	–1577	–3517	–2986	–2610	–2058
Sr	–1443	–3312	–2718	–2459	—
Ba	–1305	–3120	–2614	–2367	—

SAQ 2

On the basis of the data given in Table 5.2 predict the solubility behaviour of alkaline earth carbonates. Answer in about 60 words.

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5.3.2 Chemical Properties

You studied in the earlier sections about some of the physical properties of Group 2 elements. Let us now see how they behave chemically.

A few of the chemical reactions shown by alkaline earth metals are given in Table 5.3. These metals are less reactive than alkali metals as they are less electropositive than the latter. However, the reactivity increases with increasing atomic number down the group.

Table 5.3: Reactions of the Group 2 metals

$2M(s) + O_2(g) \rightarrow 2MO(s)$	All burn if heated. Some MO_2 formed.
$M(s) + S(s) \rightarrow MS(s)$	The sulphides are insoluble, but hydrolyse if heated in water.
$M(s) + 2H_2O(l) \rightarrow M(OH)_2(s) + H_2(g)$	Be does not react even at red heat; Mg reacts with steam only; others react with water at room temperature.
$M(s) + 2H^+(aq) \rightarrow M^{2+}(aq) + H_2(g)$	Be only slowly; others more quickly.
$M(s) + H_2(g) \rightarrow M^{2+}2H^-(s)$	Not with Be. With others at high temperatures only. With Mg under pressure.
$M(s) + X_2(g) \rightarrow MX_2(s)$	X = halogen. No polyhalides are formed.
$3M(s) + N_2(g) \rightarrow M_3N_2(s)$	At red heat. Stability: Be > Mg > Ca (hydrolyse to NH_3).
$3M(s) + 2NH_3(g) \rightarrow M_3N_2(s) + 3H_2(g)$	In liquid ammonia, Ca, Sr, Ba give blue solution because of solvated electrons (Unit 4, Section 4.4).
$Be + 2H_2O + 2OH^- \rightarrow [Be(OH)_4]^{2-} + H_2(g)$	Not with other alkaline earth metals.
$M(s) + 2C(s) \rightarrow MC_2(s)$	At high temperatures Be forms Be_2C. Ionic compounds.

- All the metals liberate hydrogen from acids, although beryllium reacts slowly. Beryllium also liberates hydrogen when treated with sodium hydroxide solution. The reaction can be given as:

$$Be + 2H_2O + 2OH^- \longrightarrow [Be(OH)_4]^{2-} + H_2(g)$$

This explains the anomalous behaviour of beryllium in having amphoteric properties. All the alkaline earth metals burn in oxygen to form oxides, MO. The oxides are also formed by thermal decomposition of MCO_3, $M(OH)_2$, $M(NO_3)_2$ and MSO_4. Beryllium oxide is covalent and all other oxides are ionic in nature. BeO has wurtzite (hexagonal ZnS) structure (Fig. 5.1),each ion has four nearest neighbours distributed tetrahedrally around it. Others have sodium chloride type of structure, i.e., each metal ion, M^{2+}, is surrounded by six O^{2-} ions and each O^{2-} is surrounded by six metal ions (Fig. 5.2). CaO is prepared on a large scale by heating calcium carbonate in lime kilns and is used in the manufacture of sodium carbonate, calcium carbide, bleaching powder, glass and cement.

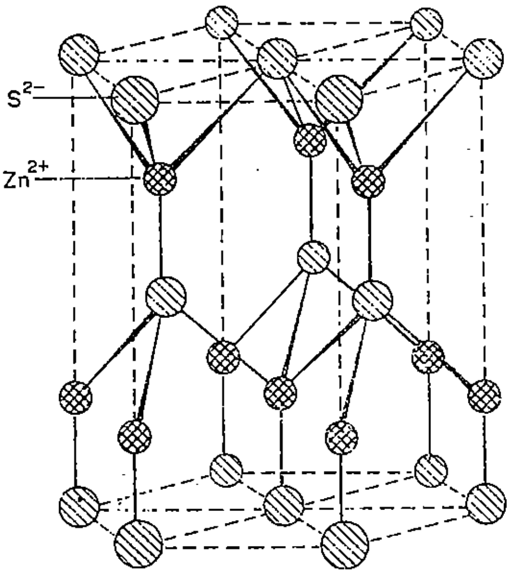


Fig. 5.1 : Wurtzite (ZnS) structure

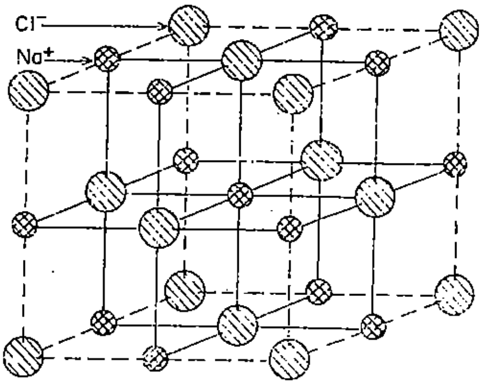


Fig. 5.2: Rock salt (NaCl) structure

- Barium peroxide, BaO_2, is formed by passing air over heated BaO, at ~800K, strontium peroxide, SrO_2, is obtained in a similar way at high temperature and pressure. Calcium peroxide, CaO_2, is obtained as a hydrate by treating $Ca(OH)_2$ with hydrogen peroxide, H_2O_2, and then dehydrating the product. Magnesium peroxide, MgO_2, is obtained only in the crude form by using hydrogen peroxide, but no peroxide of beryllium is known. These peroxides are ionic solids having $(O\text{-}O)^{2-}$ ion and can be considered as salts of very weak acid, H_2O_2. The peroxides on treatment with dilute acids form H_2O_2.
- Alkaline earth metals react with water less readily than alkali metals to give hydrogen and metal hydroxides. Beryllium does not react with water or steam even at red heat. Magnesium reacts with hot water and Ca, Sr and Ba react with cold water to form the corresponding hydroxides. Beryllium hydroxide, $Be(OH)_2$, is amphoteric; the basic strength increases in the order Mg to Ba. Aqueous solutions of calcium and barium hydroxides are known as lime water and baryta water, respectively. $Ca(OH)_2$ reacts with CO_2 to form first an insoluble $CaCO_3$ which further reacts with CO_2 to give soluble bicarbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{(insoluble white ppt.)}}{CaCO_3 \downarrow} + H_2O$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{\text{(soluble)}}{Ca(HCO_3)_2}$$

Stalactite: The downward growth of $CaCO_3$ formed on the roof of a cave by the trickling of water containing calcium compounds.

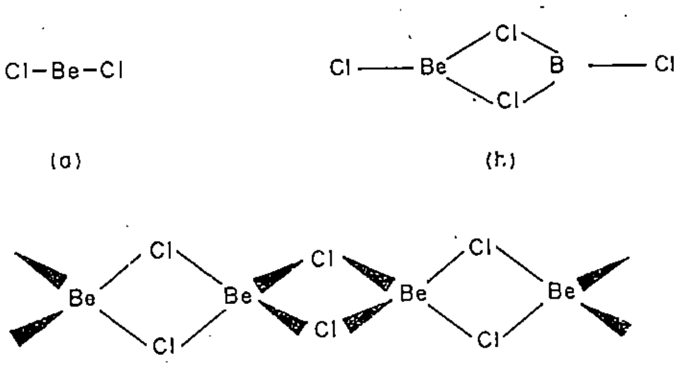
Stalagmite: The upward growth from the floor of a cave; of the same nature and origin as a stalactite.

Calcium and barium bicarbonates are stable only in solution and decompose on removal of water to give carbonates. This property of bicarbonates is the reason for **stalactite** and **stalagmite** formation (Fig. 5.3).

- Metal halides, MX_2, are obtained by direct combination with halogens as well as by the action of halogen acids on metals. Beryllium halides are covalent and other metal halides are ionic. Beryllium halides are hygroscopic and fume in air due to hydrolysis. They sublime and do not conduct electricity. Anhydrous beryllium halides are polymeric. Beryllium chloride vapours contain $BeCl_2$ and $(BeCl_2)_2$, but the solid is polymerised and can be represented as $(BeCl_2)_n$ (Fig. 5.4).

Fig. 5.3: The growth of stalactites and stalagmites (Cheddar Cave)

Sublimation is the conversion of a solid directly into vapour and subsequent condensation back to the solid. It occurs for a substance when at a particular pressure, its b.p. is lower than its m.p.



(a) (b)

(c)

Fig. 5.4: Beryllium chloride. (a) monomer (b) dimer and (c) polymer

The halides are hygroscopic and form hydrates. $CaCl_2$ is a well known drying agent and anhydrous $MgCl_2$ is important in the electrolytic extraction of Mg.

- All the Group 2 elements except beryllium form hydrides, MH_2, by direct combination with hydrogen. Beryllium hydride can be formed by reducing beryllium chloride with lithium aluminium hydride, $LiAlH_4$. All these hydrides are reducing agents which react with water and liberate hydrogen. Calcium, strontium and barium hydrides are ionic and contain the hydride ion, H^-. Beryllium and magnesium hydrides are covalent and polymeric, $(BeH_2)_n$ has an interesting structure. The polymeric solid contains hydrogen bridges between beryllium atoms, (Fig. 5.5).

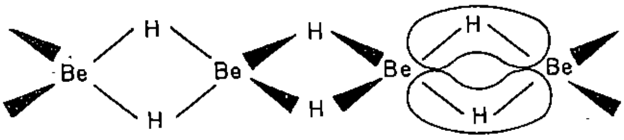


Fig. 5.5 : Beryllium hydride polymer

Each beryllium atom is bonded to four hydrogen atoms and each hydrogen atoms forms two bonds as it is bridging two Be atoms. Since Be has two valence electrons and H only one, it is apparent that there are not enough electrons to form the usual electron pair bonds in which two electrons are shared between two atoms. Instead of this, three-centre bonds are formed in which a 'banana-shaped' molecular orbital covers three atoms Be...H...Be, and contains two electrons. The monomeric molecule BeH_2, if formed with normal bonds, would have only four electrons in the outer shell of the beryllium atom and would be electron deficient.

This would make the molecule very unstable; that is why BeH_2 exists as a polymer. This is an example of a cluster compound in which each atom shares its electrons with several neighbours and receives a share in their electrons to acquire a stable configuration.

- All the metals in the Mg-Ba series or their oxides react directly with carbon to give the carbides (acetylides), MC_2. These carbides are ionic in nature and have a NaCl type of structure (Fig. 5.2) with M^{2+} replacing Na^+ and $C{\equiv}C^{2-}$ replacing Cl^-. Beryllium forms methanide, Be_2C, with carbon and acetylide, BeC_2, with acetylene. Magnesium on heating with carbon forms Mg_2C_3 also, which is an allylide since with water it liberates allylene (methylacetylene).
- The alkaline earth metals burn in nitrogen and form nitrides, M_3N_2. It requires a lot of energy to convert the stable N_2 molecule into nitride ion, N^{3-}, and this is recovered from the very high lattice energies of the alkaline earth metal nitrides. The beryllium compound is rather volatile while others are not. They are all colourless crystalline solids which decompose on heating and react with water to liberate ammonia and form either the metal oxide or hydroxide, e.g.,

$$3Mg(s) + N_2(g) \longrightarrow Mg_3^{2+}N_2^{3-}(s)$$

$$Mg_3^{2+}N_2^{3-}(s) + 6H_2O(l) \longrightarrow 3Mg^{2+}(OH^-)_2(s) + 2NH_3(g)$$

The carbides are named depending upon the hydrocarbon they liberate on reaction with water. If it liberates acetylene, it will be named acetylide, and if methane is liberated, it will be called as 'methanide', etc.

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + \underset{\text{acetylene}}{C_2H_2}$

$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + \underset{\text{methane}}{CH_4}$

$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + \underset{\text{allylene}}{CH_3{-}C{\equiv}CH}$

Thermal Stability of Oxysalts

All the Group 2 elements form oxysalts. The thermal stability of the oxysalts increases with the increase in electropositivity of the metals. Thus, it increases down the group. The thermal stabilities of the salts of Group 2 are less than those of the Group 1 metals. The carbonates of alkaline earth metals are stable at room temperature. On heating, they decompose into the corresponding oxides and carbon dioxide:

$$MCO_3 \longrightarrow MO + CO_2$$

The temperature at which the carbonates decompose are given as:

$BeCO_3$ < 400K ; $MgCO_3$, 800K ; $CaCO_3$, 1200K : $SrCO_3$, 1550K; $BaCO_3$, 1650K

The sulphates are more stable than the carbonates. On heating, they decompose into oxides and sulphur trioxide.

$$MSO_4 \longrightarrow MO + SO_3$$

The order of decomposition temperature of the sulphates is:

$BeSO_4$, 850K ; $MgSO_4$, 1150K; $CaSO_4$, 1400K ; $SrSO_4$, 1650K.

Alkali metal nitrates decompose into nitrites on heating whereas alkaline earth metal nitrates decompose on heating to metal oxide, nitrogen dioxide and oxygen, e.g.,

$$2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$$

SAQ 3

Explain in brief why is the hydride bridge in $(BeH_2)_n$ considered to be electron deficient but not the halide bridge in $(BeCl_2)_n$.

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5.3.3 Complexation Behaviour

Let us discuss another interesting property of these elements, i.e., their complexation behaviour. Complex formation is favoured by small, highly charged cations with suitable empty orbitals of approximately the right energy with which the ligand orbitals can combine (see Unit 4, Section 4.6).

Alkaline earth metals form more complexes as compared to alkali metals. The tendency to form complexes (mostly with O & N donors) decreases with increasing atomic number. Thus, of the heavier ions only Ca^{2+} forms a complex with ethanol. Beryllium having the smallest ion in the group tends to form complexes most readily. It mostly forms complexes with tetrahedral arrangement because of the available orbitals as shown below:

	1s	2s	2p	
Be atom in ground state	↑↓	↑↓		No unpaired electrons so no covalent bonds
Be atom in excited state	↑↓	↑	↑	Two unpaired electrons can form two covalent bonds
Be in $[BeF_4]^{2-}$	↑↓	↑↓	↑↓ ↑↓ ↑↓	Two fluoride ions each donate an electron pair into an empty orbital forming a coordinate bond
		sp^3 hybridisation		

The well known tetrafluoroberyllates have a tetrahedral structure as shown in Fig. 5.6.

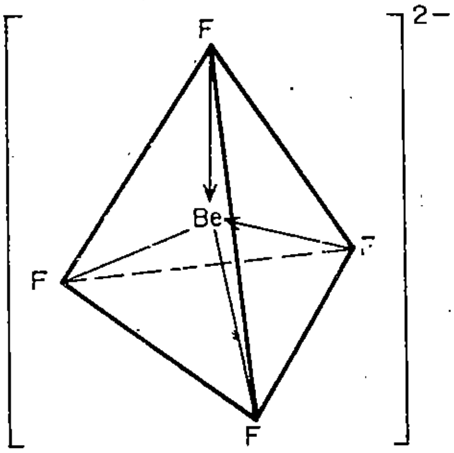

Fig. 5.6: Tetrafluoroberyllate complex ion, $[BeF_4]^{2-}$.

The arrows in the above figure indicate that two F^- ions form 'coordinate' bonds with BeF_2. However, once these are formed, all the Be–F bonds tend to become similar.

Beryllium forms white crystalline molecular oxide-carboxylates, of which **basic beryllium acetate,** viz., $[OBe_4(CH_3COO)_6]$ is typical and important for the purification of Be because of its volatility and solubility in organic solvents. Beryllium forms a number of chelates also with ligands like oxalates, $[Be(C_2O_4)_2]^{2-}$ (Fig. 5.7), and β - diketonate anions.

Chelates are the ring compounds formed as a result of coordination with ligands having more than one binding sites.

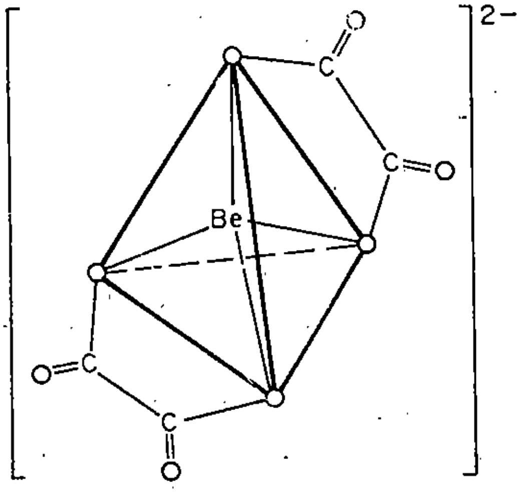

Fig. 5.7: Beryllium oxalate complex ion, $[Be(C_2O_4)_2]^{2-}$

In the hydrated salts, e.g., $BeCO_3.4H_2O$ and $BeSO_4.4H_2O$, beryllium ions exist in the form, $[Be(H_2O)_4]^{2+}$, where they show a coordination number of four.

Magnesium is known to form a very important complex occurring in nature, viz., chlorophyll; a green pigment of the plants which produces sugars for the plant in presence of sunlight, CO_2 and H_2O in a process called photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{Sunlight}]{\text{Chlorophyll}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

Magnesium, in chlorophyll, is coordinated by four nitrogen atoms in the heterocyclic porphyrin ring system (Fig. 5.8).

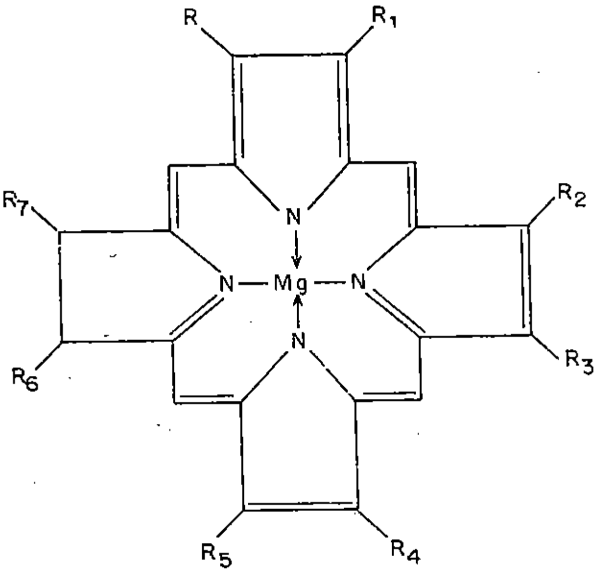

Fig. 5.8: Skeleton of chlorophyll molecule

When water does not form lather with soap, it is called as hard water. Hardness of water is due to the presence of heavy metal cations like Ca^{2+}, Mg^{2+} and Fe^{2+} etc.

The rest of the elements from calcium to barium form complexes only with strong complexation agents such as acetylacetone, ethylenediaminetetraacetic acid (EDTA), etc. In fact, titrations are performed using EDTA in buffer solutions to estimate the amounts of Ca^{2+} and Mg^{2+} present in water, to determine the hardness of water.

5.4 ANOMALOUS NATURE OF BERYLLIUM

Beryllium, the first member of the group, appears to be quite different from the other members, in the same way as lithium differs from the other alkali metals and for the same reasons as discussed for lithium in the previous unit. Beryllium differs more from magnesium than lithium does from sodium, in fact, the anomalous nature of the first member of *s*- and *p*-block groups becomes more pronounced towards the middle of the table. Also beryllium shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium. Also the properties in which beryllium differs from magnesium, it shares with aluminium in general. Let us now consider all the factors one by one.

a) The cohesive properties of beryllium are much greater than those of magnesium and other elements in the group. As a result it is much harder and has higher melting and boiling points.

b) It has smaller atomic radii, higher electron affinity and higher ionisation energy.

c) Its higher polarising power leads to all its compounds being largely covalent, with lower melting and boiling points and enthalpies of formation (e.g., BeF_2, m.p. 1073K, for rest of the group about 1573K). All the compounds of Be are more soluble in organic solvents than the corresponding magnesium compounds. They hydrolyse in water, and in this respect they rather resemble aluminium.

5.5 SUMMARY

Let us now summarise the main points that we have discussed in this unit.

- The general properties of the Group 2 elements are similar due to the similarity in the outer shell electronic configuration, i.e., ns^2.

- Like Group 1 elements, Group 2 elements also follow the group trends, i.e., increasing atomic size, density, electropositivity, reactivity, reducing power, hardness and conductivity. Their ionisation energy decreases down the group.
- The Group 2 metals are harder, have higher melting and boiling points, form hydroxides which are weaker alkalies and form carbonates which are less stable than those of corresponding Group 1 elements.
- The complexation behaviour in the group is mainly restricted to beryllium and very few complexes of the rest of the elements are known.
- Beryllium being the first number of the group exhibits anomalous properties and shows diagonal relationship with aluminium.

5.6 TERMINAL QUESTIONS

1 The first ionisation energy of beryllium is greater than that of lithium, but the position is reversed in the case of second ionisation energy. Why?

2 Why beryllium forms covalent compounds?

3 Describe the difference in the nature of bonding of BeH_2 and CaH_2.

4 What are the usual coordination numbers for Be^{2+} and Mg^{2+}? What is the reason for the difference?

5 Why do halides and hydrides of beryllium polymerise?

6 Which is more stable to heat, beryllium carbonate or barium carbonate, and why?

5.7 ANSWERS

Self Assessment Questions

1 a) Since the effective nuclear charge felt by the outer electrons in the atoms of Group 2 elements is comparatively higher, these elements are smaller in size than their counterparts of Group 1.

b) Since Group 2 elements have two valence electrons, they have stronger metallic bonding and show higher cohesive properties than their Group 1 neighbours. Thus they are harder and have higher melting points as compared to the Group 1 elements.

2 If you subtract the lattice energies from the hydration energies of MCO_3, you will find the difference increasing from Mg to Ca, decreasing from Ca to Sr and again increasing from Sr to Ba showing a decrease in solubility from Mg to Ca, an increase from Ca to Sr and a decrease again from Sr to Ba. The maximum solubility is shown by $MgCO_3$.

3 The hydrogen bridge in $(BeH_2)_n$ is held together by one electron pair only and is electron deficient in the sense that there is less than one electron pair for each pair of bonded atoms. But in $(BeCl_2)_n$, each pair of bonded pair of atoms has the normal electron pair and so, its bridge is not electron deficient.

4 As compared to the alkali metals, the alkaline earth metals form more complexes because they are smaller in size and have higher cationic charge.

Terminal Questions

Because of its smaller atomic size and higher effective nuclear charge, the first ionisation energy of Be is higher than that of Li. But the second ionisation energy of Be is smaller than that of Li because of the stability of a closed shell configuration of Li^+.

According to Fajan's rule, small size and high charge density favours covalency and therefore, Be has a strong tendency for covalency.

According to Fajan's rule, calcium forms ionic hydride while beryllium forms covalent hydride.

The usual coordination numbers for Be^{2+} and Mg^{2+} are 4 and 6, respectively. The difference is due to the very small size of Be^{2+} and non-availability of *d* orbitals in it.

The monomeric molecules BeH_2 and $BeCl_2$ formed with normal bonds will result in only four electrons in the outer shell of the beryllium atom making it electron deficient. By polymerising, each atom shares its electrons with several neighbours and receives a share in their electrons making the situation more favourable. Therefore, the halides and hydrides of Be polymerise.

6 $BaCO_3$ is more stable than $BeCO_3$.
(**Hint:** Relate size of cation to size of anion.)

FURTHER READINGS

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

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

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

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

Uttar Pradesh
Rajarshi Tandon Open University

UGCHE-03

INORGANIC CHEMISTRY

Block

2

p-BLOCK ELEMENTS – I

UNIT 6

Elements of Group 13 5

UNIT 7

Elements of Group 14 26

UNIT 8

Elements of Group 15 44

BLOCK 2 *p*-BLOCK ELEMENTS – I

In Block 1, you studied the development of the periodic table and the concept of periodicity in properties of elements. You also studied the chemistry of hydrogen, the alkali metals and the alkaline earth metals, which together constitute the *s*-block of the periodic table. You must have noticed that although the first element of each group of the *s*-block exhibits some anomalous behaviour, the similarity of the elements within a group is the most striking feature of the chemistry of the *s*-block elements. All the *s*-block elements, except hydrogen, are highly reactive metals and do not occur in nature in the elemental state; they exhibit only one stable oxidation state, which is equal to the number of electrons in the valence shell of their atoms. They show regular gradation in properties as a group is descended.

In this block and in the following block, you will study the chemistry of the *p*-block elements, which is very extensive and varied. The elements of a *p*-block group show less regular chemistry, less regular changes in properties and more than one stable oxidation state, halogens being an exception. The first element of each of the *p*-block groups also exhibits anomalous behaviour. The differences between successive elements of a *p*-block group become more pronounced on descending the group so that a change from non-metallic to metallic character is clearly observed. Nevertheless, some points of similarity between the elements in a group, for example, valence relations, are always present.

Unit 6 deals with the chemistry of the Group 13 elements comprising of boron, aluminium, gallium, indium and thallium. Boron, the first element of the group, is a nonmetal whereas the remaining elements are typical metals. The stable oxidation state in most elements of the group is III; only thallium and to some extent gallium and indium exhibit oxidation state of I; in thallium this is the more stable oxidation state.

In Unit 7, you will study the main features of the chemistry of Group 14 elements, namely, carbon, silicon, germanium, tin and lead. They exhibit a gradual change in their character. Carbon is a nonmetal; silicon and germanium are semimetals; tin and lead are distinctly metallic in nature. Their common oxidation states are II and IV.

In Unit 8, we will discuss the salient features of the chemistry of nitrogen, phosphorus, arsenic, antimony and bismuth which constitute Group 15 of the periodic table. The most striking feature of the chemistry of this group is the differences in the properties of the elements. The variation in properties is vast, the elements range from highly electronegative nonmetal, nitrogen, to the very weakly electropositive metal, bismuth, via the semimetals arsenic and antimony. These elements exhibit a wide range of oxidation states. You will study the chemistry of the remaining elements of the *p*-block in Block 3 of this course.

We expect that after studying this block, you should be able to :

- discuss the periodic trends in the properties of the *p*-block elements of Groups 13, 14 and 15,
- describe the main features of the chemistry of the *p*-block elements of Groups 13, 14 and 15,
- compare the properties of *p*-block elements of Groups 13, 14 and 15 with those of the *s*-block elements.

UNIT 6 ELEMENTS OF GROUP 13

Structure

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6.1 INTRODUCTION

In the previous two units, you studied the main features of the chemistry of Group 1 and Group 2 elements, i.e. the alkali and the alkaline earth metals. In this unit you will study the elements of Group 13, namely, boron, aluminium, gallium, indium and thallium. While studying the alkali and alkaline earth metals, you have seen that all the elements of these two groups are highly reactive metals and the first element of each group shows some differences from the rest. In Group 13, the differences between the first element and the remaining elements become so pronounced that the first member of the group, i.e. boron is a nonmetal whereas the rest of the elements are distinctly metallic in nature. In a way, this is the first group of the periodic table in which you observe a marked change in the nature of the elements down the group.

Objectives

After studying this unit, you should be able to:

- describe the occurrence, extraction and uses of Group 13 elements,
- explain the trends in the properties of the elements of this group,
- give reasons for the electron deficiency encountered in compounds of boron and aluminium,
- describe the chemistry of hydrides, halides and oxides of boron and aluminium,
- elucidate the structures of hydrides of boron and aluminium,
- discuss the chemistry of acids of boron, bo[illegible]ine and boron nitride,
- discuss the complexation behaviour of the Group 13 elements, and
- describe the anomalous nature of boron.

6.2 OCCURRENCE, EXTRACTION AND USES

Elements of Group 13 are sufficiently reactive. Therefore, none of them occurs in the native state. Some of these elements and their compounds find important uses in diverse areas of modern science and technology and even in every day life. Let us, therefore, first study their occurrence, extraction and uses.

6.2.1 Occurrence

Both boron and aluminium have a high affinity for oxygen, so neither of them is found native. Boron occurs principally in the earth's crust as boric acid, H_3BO_3 and as borates, such as, borax, $Na_2B_4O_7 \cdot 10H_2O$, kernite, $Na_2B_4O_7 \cdot 4H_2O$ and colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$. Aluminium is the most abundant metal (8.13%) in the earth's crust and is the third most abundant element, next only to oxygen (46.6%) and silicon (27.7%). It occurs widely in the complex alumino-silicates, such as, clay from which, however, it cannot be extracted economically. The important ores of aluminium are bauxite, $Al_2O_3 \cdot xH_2O$, where x = 1-3, cryolite, Na_3AlF_6 and corundum, Al_2O_3. Gallium (1.9×10^{-3}%), indium (2.1×10^{-5}%) and thallium (7.0×10^{-5}%) are much less abundant than aluminium. Gallium and indium are found in aluminium and zinc ores. But even the richest sources contain less than 1% gallium and still less indium. Thallium is widely distributed in nature and occurs in sulphide ores of zinc, lead, copper and iron.

6.2.2 Extraction

Boron is obtained by the reduction of B_2O_3 with magnesium or sodium. B_2O_3 is first prepared by strongly heating H_3BO_3 which is obtained by the action of HCl or H_2SO_4 on a concentrated solution of borax:

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

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

Pure crystalline boron may be obtained in small quantities by the reduction of BBr_3 with H_2 on a heated tantalum metal filament at 1275-1475 K.

Aluminium cannot be extracted economically from the silicate minerals. Therefore, bauxite is the most important ore for the extraction of aluminium, but this has many problems. Al_2O_3 is a very stable compound. It is not reduced by heating in hydrogen. On strong heating with carbon, Al_2O_3 gives the carbide, Al_4C_3. As Al_2O_3 does not melt below 2300 K, it cannot be electrolysed conveniently. However, electrolysis of a solution of Al_2O_3 in fused cryolite occurs at a much lower temperature of 1100-1300 K. Thus, aluminium is extracted by electrolysis of purified alumina in fused cryolite.

Bauxite approximately contains Al_2O_3=55%, Fe_2O_3=15%, TiO_2=2%, SiO_2=3% and H_2O=25%.

India is fortunate in having large deposits of bauxite in a reasonably pure state.

Pure alumina is obtained from bauxite ore. Powdered bauxite mineral is heated in a concentrated solution of sodium hydroxide under pressure when alumina and silica get dissolved:

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2\,NaAl(OH)_4$$

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

Iron oxide and titanium dioxide do not dissolve in the alkali and are filtered off as a sludge. The solution is cooled and most of the aluminium hydroxide is precipitated either by the passage of carbon dioxide or by seeding with some freshly precipitated aluminium hydroxide :

$$2NaAl(OH)_4 + CO_2 \longrightarrow 2Al(OH)_3\downarrow + Na_2CO_3 + H_2O$$

$$NaAl(OH)_4 \xrightarrow{Al(OH)_3} Al(OH)_3\downarrow + NaOH$$

The silicates remain in solution, since silica is a more acidic oxide than alumina. Aluminium hydroxide is filtered, washed and heated to give pure alumina.

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

Alumina is dissolved in fused cryolite to which calcium fluoride is added to lower the melting point. The solution is then electrolysed at 1100-1300 K in an iron cell, lined with graphite, which acts as the cathode and carbon rods suspended in the electrolyte acting as the anode (Fig. 6.1). Electrolysis of the solution gives aluminium at the cathode and oxygen at the anode. The discharged aluminium sinks to the bottom of the cell and is tapped off. Fresh alumina is added as required. The anode is slowly attacked by liberated oxygen to form carbon monoxide. Therefore, anode has to be continually replaced, adding substantially to the cost of the process. The temperature of the cell is maintained by the passage of electric current. Following reactions take place during electrolysis:

For each kg of Al produced, about 1.9 kg of Al_2O_3, 0.150 kg of NaOH, 0.50 kg of C and 6.0×10^7 kJ of electricity are consumed.

$$Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{2-}$$

$$3O^{2-} \longrightarrow 3/2O_2 + 6e, \text{ at anode}$$

$$2Al^{3+} + 6e \longrightarrow 2Al, \text{ at cathode}$$

Gallium, indium and thallium are usually obtained by electrolysing aqueous solutions of their salts. This method is not applicable in the case of aluminium salts as they are hydrolysed considerably by water.

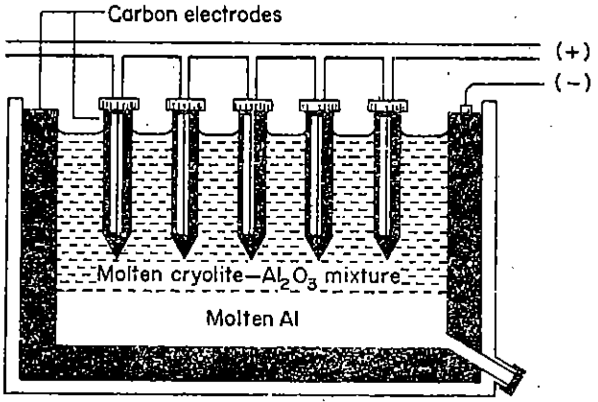

Fig. 6.1 : Manufacture of Al

6.2.3 Uses

Boron is used to increase the hardness of steels. Crystalline boron is used in transistors. Boron is a good neutron absorber and is used as shields and control rods in nuclear reactors. Boranes are used as high energy fuels, for example, in rockets. Boric acid is used as an antiseptic. Borax is used to make heat resistant borosilicate glass. It is also used for vitreous enamelling of baths, domestic appliances and for glazing tiles and pottery. Another use of borax is to make peroxyborates, e.g., $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, which are useful cleaning and bleaching agents. In the laboratory, borax is used for standardising acids and in the borax bead test in qualitative analysis.

Aluminium exhibits useful properties of low density, high thermal and electrical conductivity, good corrosion resistance with non-toxic nature of the metal and its compounds. Due to these properties, it is the most widely used non-ferrous metal. Aluminium is used for making electrical conductors, cooking utensils and wrapping materials. You must have seen milk bottles capped with aluminium foil. Aluminium is extensively used for structural purposes, either alone or alloyed, in aircraft, ship and building industries. Large amounts of aluminium are converted into alloys, such as, duralumin and magnalium containing a few per cent of copper or magnesium. These alloys are harder and stronger than pure aluminium but possess almost the same properties of lightness and corrosion resistance which can be further increased by anodising process. Aluminium beryllium alloys are harder and lighter than other alloys of aluminium and are extensively used in space-craft. However, toxic nature of beryllium makes their handling difficult. Due to its strong affinity for oxygen, aluminium is a good reducing agent and is used in aluminothermic process for extraction of metals and in welding. Suspension of finely powdered aluminium in oil is used as paint.

When an aluminium article is made the anode in the electrolysis of dil. sulphuric or chromic acid, a thick hard film of Al_2O_3 is formed on the surface of the article. This process is called anodising. Al_2O_3 layer adsorbs many dyes and takes a very high polish. You must have seen many bright, colourful articles made of anodised aluminium.

Anhydrous $AlCl_3$ is an important catalyst, used in organic synthesis and in the cracking of petroleum. $Al_2(SO_4)_3$ as such or as potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ is used for sizing paper, for tanning leather, for waterproofing cloth and as a mordant for dying cotton. It is extensively used for purification of water and in sewage treatment.

Because of its extreme hardness, high m.p., non-volatility, chemical inertness and good electrical insulating properties, corundum (Al_2O_3) finds many applications in abrasives, refractories and ceramics. Large crystals of α-Al_2O_3 when coloured with metal-ion impurities are prized as gemstones, e.g., ruby (Cr^{3+}, red), sapphire ($Fe^{2+/3+}/Ti^{4+}$, blue), oriental emerald (Cr^{3+}/V^{3+}, green), oriental topaz (Fe^{3+}, yellow), etc. Aluminates are important constituents of Portland cement. Gallium has the longest liquid range (303-2343 K) of any known substance and so finds use as a high temperature thermometer liquid.

Gallium is mainly used in semiconductor technology. It is used for doping other semiconductors and in solid state devices such as transistors.

Compounds of Ga with P and As, such as, GaP and GaAs have semiconductor properties similar to those of elemental Si and Ge. These are used as light emitting diodes (LEDs) familiar in pocket calculators, wrist watches, etc. They are also used in infrared emitting diodes, infrared detectors, photocathodes and photomultiplier tubes.

The most important applications of indium are in protection of bearings against wear and erosion, in low-melting alloys and in electronic devices. Thallous salts, being toxic, are used as fungicides, germicides and in ointments used for the treatment of ring-worms. Thallium compounds find applications in preparing optical glass on account of their high refractive power.

We will discuss the general characteristics of these elements in the next section but before that try this SAQ.

SAQ 1

a) Write the names and formulae of two important ores of the most abundant metallic element in the earth's crust.

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b) Match the following properties of Al with the uses to which the metal or its compounds are put:

i) Good thermal conductivity
ii) Good electrical conductivity
iii) Low density and resistance to corrosion
iv) Non-toxicity
v) Gel nature of $Al(OH)_3$

a) Building ships and aircrafts
b) Utensils
c) Electric wires
d) Adsorbent
e) Food packaging

6.3 GENERAL CHARACTERISTICS

All the elements of Group 13 have similar valence shell electronic configuration of ns^2np^1, but the underlying core varies. For B and Al, it is the preceding noble gas core, for Ga and In, it is noble gas plus d^{10} and for Tl, noble gas plus $4f^{14}5d^{10}$. This variation in the electronic configuration of the core is also reflected in the ionisation energies of these elements and has a strong influence on their properties.

6.3.1 Physical Properties

Elements of Group 13 are less-metallic than those of Groups 1 and 2. Within the group, there is a variation in metallic character. Boron, the smallest element in this group is a non-metal. The other elements in this group are fairly reactive metals. This is the first group in which change from non-metallic to metallic nature occurs. Some physical properties of Group 13 elements are listed in Table 6.1.

The elements of Group 13 have smaller atomic radii and higher electronegativities as compared to *s*-block elements of the same period. However, these properties do not vary in a regular way down the group, in contrast to the properties of the element of Groups 1 and 2. You know that the size and the ionisation energies of atoms depend on effective nuclear charge of the atom. B and Al follow immediately the *s*-block elements Be and Mg, respectively. Their size and ionisation energies are as expected. But between the *s*- and *p*-block elements of the fourth and successive rows, the *d*-block elements, i.e., the transition elements get inserted. The insertion of transition elements results in higher effective nuclear charge of the fourth row elements Ga, Ge, etc., than expected by simple extrapolation from the second and third row elements. In other words, the nuclei of these fourth row elements attract electrons more strongly than expected and this affects their properties. Thus, the atomic size of gallium is smaller; its electronegativity and ionisation energies higher than expected. Atoms with d^{10} inner shell, in general, are smaller and have higher ionisation energies. In a similar way, the inclusion of fourteen electrons in 4*f* orbital further affects the size and ionisation energy of Tl. As a result of this, irregularities in atomic radii, electronegativity and ionisation energies are seen from B to Tl.

Table 6.1 shows that densities of these elements show a gradual increase while melting and boiling points fall in value. The exceptionally low melting point of gallium (303 K). however. has, so far, no simple explanation.

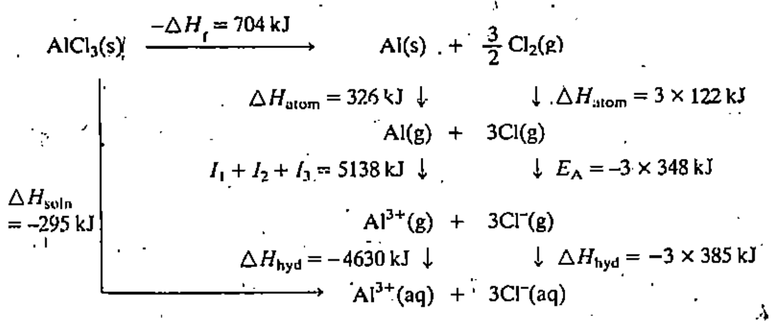
Table 6.1: Some properties of Group 13 elements

Property	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Atomic weight	10.81	26.98	69.72	114.82	204.38
Electronic structure	$[He]2s^22p^1$	$[Ne]3s^23p^1$	$[Ar]3d^{10}4s^24p^1$	$[Kr]4d^{10}5s^25p^1$	$[Xe]4f^{14}5d^{10}6s^26p^1$
Metallic radius (pm)	98	143	141	166	171
Covalent radius (pm)	82	125	125	144	155
Ionic radius M^{3+} (pm)	20	50	62	81	95
Melting point (K)	2573	933	303	429	576
Boiling point (K)	2823	2740	2343	2273	1730
Density ($10^3 \times$ kg m^{-3})	2.34	2.7	5.91	7.3	11.8
Ionisation 1st	800	577	579	558	589
energy 2nd	2427	1816	1979	1820	1970
($kJ\ mol^{-1}$) 3rd	3658	2745	2962	2703	2879
Electronegativity (A/R)	2.0	1.45	1.8	1.5	1.45
Electron affinity ($kJ\ mol^{-1}$)	–27	–44	–30	–30	–30
Common oxidation state	(2)*, 3	3	(1)*, 3	1, 3	1, (3)*
Common co-ordination numbers	3, 4	3, 4, 6	3, 6	3, 6	3, 6
Natural abundance (%)	1.0×10^{-3}	8.13	1.9×10^{-3}	2.1×10^{-5}	7.0×10^{-5}

* Comparatively less stable.

From Table 6.1 you will observe that these elements form small ions of high charge density and the value of the sum of their first, second and third ionisation energies is very high. These properties lead us to the conclusion that these elements will prefer to form covalent rather than ionic compounds. Boron is always covalent and does not form B^{3+} ions, because the energy required to remove three electrons is very high. Many simple compounds of Al and Ga like $AlCl_3$ and $GaCl_3$ are also covalent when anhydrous. However, in solution, the large amount of hydration energy evolved compensates the high ionisation energy and all the metal ions exist in a hydrated state.

This can be explained with the help of Born-Haber cycle as given below. However, this is a simplified approach given only on the basis of enthalpy changes, whereas the direction and extent of any reaction depend on the free energy changes which take into account changes both in enthalpy and entropy.



$$\begin{aligned}\Delta H_{soln} &= 704 + 326 + 366 + 5138 - 1044 - 4630 - 1155\\ &= 6534 - 6829\\ &= -295 \text{ kJ}\end{aligned}$$

Born-Haber cycle for formation of Al^{3+}(aq) ion

Thus, despite the large ionisation energies of aluminium, the enthalpy of solution of $AlCl_3$ has a large negative value. Therefore, in aqueous solution, $AlCl_3$ exists as Al^{3+}(aq) and Cl^-(aq). It might be thought that the same argument would apply to BCl_3. But to make the enthalpy of solution of BCl_3 negative, the enthalpy of hydration of B^{3+} should be −6009 kJ which is unlikely for the small B^{3+} cation. Therefore, BCl_3 hydrolyses in aqueous solution to give boric acid and not $B^{3+}(aq)$:

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

Unlike the s-block elements which show only one stable oxidation state, the elements of this group show more than one stable oxidation state. While the trivalent state is important for all the five elements, the univalent state becomes progressively more stable on descending the group. Thus, for B, Al and Ga, the +3 state is more stable than +1 state; for In, both are equally stable, and for thallium the univalent state is more stable than the trivalent state. Oxide, sulphide, carbonate, sulphate and halides, etc. of Tl(I) are well characterised, and are more stable in aqueous solution than Tl(III) compounds. This is due to the s electrons in the outer shell of thallium tending to remain paired and not participating in bonding because the energy required to unpair them is rather high. This is called the **inert pair effect.** This effect is noticeable particularly among the heavier elements in the p-block. In addition to the above, some compounds are known, in which the elements show +2 oxidation state, e.g., B_2F_4 and B_2Cl_4. However, these compounds are less stable.

SAQ 2

Covalent radius, ionisation energy and electronegativity of gallium are different from those expected by simple extrapolation of these properties from those of boron and aluminium. Discuss this anomaly briefly.

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6.3.2 Chemical Properties

Elements of Group 13 are comparatively less reactive than the alkali and alkaline earth metals of Groups 1 and 2. However, the reactivity of the elements increases on descending the group. The crystalline form of boron is black, very hard and inert. It reacts with other elements only at high temperatures. The more common amorphous form is brown and more reactive than the black crystalline form. Aluminium is a light and hard white metal. It reacts with atmospheric oxygen with the formation of a protective layer of aluminium oxide which prevents further attack. Amalgamation with mercury removes the oxide coating and a rapid reaction occurs with oxygen, water or dilute acids. Gallium, indium and thallium are relatively soft and more reactive than boron and aluminium.

- All the elements except thallium when heated with halogens, oxygen or chalcogens form halides (EX_3), oxides (E_2O_3), chalcogenides (E_2S_3, etc.). Thallium on the other hand forms TlX, Tl_2O, Tl_2S, etc.

The reaction of aluminium with Fe_2O_3 produces temperatures approaching 3300 K – enough to melt the iron metal produced. This is called the **thermite reaction** and is used to weld cracks in iron and steel articles.

- Aluminium has a very high affinity for oxygen; this is reflected in high exothermic heat of formation of Al_2O_3 (−1676 kJ mol^{-1}). This allows aluminium to extract oxygen from other metal oxides, and forms the basis of Goldschmidt's aluminothermic process for preparing Ca, Sr, Ba, Mn, Cr, Mo, etc.:

$$3MnO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Mn$$
$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe(l)$$

- Boron and aluminium when heated with nitrogen form the **nitrides** BN and AlN. Nitrides of Ga and In are formed by heating the elements with ammonia. Boron nitride can also be made by the action of ammonia on boron at 1300 K, or by passing nitrogen over a mixture of boron trioxide and carbon at a slightly higher temperature:

$$2B + 2NH_3 \xrightarrow{1300\,K} 2BN + 3H_2$$

$$B_2O_3 + 3C + N_2 \xrightarrow{>1300\,K} 2BN + 3CO$$

BN is isoelectronic with C_2, and like carbon, it exists in diamond and graphite forms. The latter is a useful lubricant with additional advantage of being inert. Boron nitride is a white solid. It is chemically rather inert, but is hydrolysed to NH_3 and $B(OH)_3$ by the action of steam or hot acids:

$$BN + 3H_2O \longrightarrow B(OH)_3 + NH_3$$

- Boron and aluminium on heating react with carbon to form the **carbides** $B_{12}C_3$ and Al_4C_3, respectively. Aluminium carbide is a colourless, high melting ionic solid and is decomposed by water to liberate methane. Therefore, it can be termed as aluminium methanide also:

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

On the other hand, the isolable form of boron carbide has the molecular composition $B_{12}C_3$. It is a black, extremely hard, high melting and chemically inert covalent compound. It is used as an abrasive for polishing and tool sharpening.

- Boron on heating reacts with many metals to form binary compounds called **borides**, e.g., MgB_2, VB and Fe_2B, whereas other elements of Group 13 form alloys. Metal borides are extremely hard, chemically inert, non-volatile, refractory materials. They have high melting points and high thermal and electrical conductivities. The diborides of Ti, Zr, Hf, Nb and Ta all have melting points higher than 3200 K. The thermal and electrical conductivities of TiB_2 and ZrB_2 are about ten times greater than those of Ti and Zr metals.

- Boron does not react with non-oxidising acids. Even hot concentrated oxidising acids react with boron only slowly to form boric acid:

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$
$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

- Al, Ga, In and Tl react with warm dilute HCl and H_2SO_4 to replace hydrogen and form M^{3+} except Tl which forms Tl^+:

$$2M + 6HCl \longrightarrow 2M^{3+} + 6Cl^- + 3H_2$$
$$2Tl + 2HCl \longrightarrow 2Tl^+ + 2Cl^- + H_2$$

- With hot and conc. H_2SO_4, SO_2 is liberated:

$$2M + 6H_2SO_4 \longrightarrow M_2(SO_4)_3 + 3SO_2 + 6H_2O$$

- Hot and conc. HNO_3 renders Al and Ga passive. The initial attack of the acid covers the metal with an impervious, coherent, unreactive layer of oxide which prevents further attack. In and Tl react with conc. HNO_3 to form metal trinitrates liberating NO_2:

$$M + 6HNO_3 \longrightarrow M(NO_3)_3 + 3NO_2 + 3H_2O$$

- Boron reacts with fused alkalies forming the borates:

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

Aluminium and gallium dissolve in aqueous alkalis to form aluminate and gallate ions, respectively:

$$M + 4NaOH \longrightarrow NaM(OH)_4 + 2H_2$$

Thus, you see that the elements of Group 13 are fairly reactive and form many useful compounds such as hydrides, halides, nitrides, oxides, oxoacids and their salts, etc. Let us now study some of the compounds of B and Al in detail. Compounds of Ga, In and Tl will be described only in brief, where appropriate, for the sake of comparison only.

SAQ 3

a) Explain in the space given below why the action of conc. nitric acid renders aluminium passive.

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....

b) Write the formulae of the compounds you would expect B and Al to form with halogens, oxygen, sulphur, nitrogen and carbon.

....

6.4 HYDRIDES OF BORON AND ALUMINIUM

Boron forms a series of volatile hydrides which resemble in some respects, e.g., volatility and covalent nature, the hydrides of carbon and silicon. The boron hydrides are generally called boranes by analogy with the alkanes and silanes. In view of its trivalency, boron is expected to form a simple hydride BH_3, but it is unstable. The simplest stable hydride of boron is diborane, B_2H_6. There are about a dozen well characterised boranes which correspond to the following two stoichiometries:

i) B_nH_{n+4} : B_2H_6, B_5H_9, B_6H_{10}, B_8H_{12}, $B_{10}H_{14}$, $B_{18}H_{22}$ and iso-$B_{18}H_{22}$

ii) B_nH_{n+6} : B_4H_{10}, B_5H_{11}, B_6H_{12}, B_9H_{15} and $B_{10}H_{16}$

Boranes are usually named by indicating the number of B atoms with a prefix and the number of hydrogen atoms by an arabic number in parenthesis. For example, B_4H_{10} is named as tetraborane(10) and B_9H_{15} as nonaborane(15). The hydride, B_2H_6 is simply called **diborane** as the compound of stoichiometry B_2H_8 is not known. Diborane is of special interest because it is the starting material for the preparation of various other boron hydrides and because of its synthetic uses. So, let us first discuss B_2H_6 in detail.

6.4.1 Diborane (B_2H_6)

The chemistry of diborane has aroused considerable interest because of its usefulness in many synthetic reactions and also because the elucidation of its structure helped to clarify the basic concepts about the structure of electron deficient compounds. We shall briefly discuss the chemistry of diborane below.

B_2H_6 has only 12 valence electrons; for ethane type structure 14 valence electrons are needed.

a) **Preparation:** Diborane can be prepared in almost quantitative yields by the reduction of boron trifluoride etherate ($BF_3{\cdot}OEt_2$) with lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$):

$$4BF_3{\cdot}OEt_2 + 3LiAlH_4 \xrightarrow{Et_2O} 2B_2H_6 + 3LiAlF_4 + 4Et_2O$$

$$4BF_3{\cdot}OEt_2 + 3NaBH_4 \xrightarrow{\text{diglyme}} 2B_2H_6 + 3NaBF_4 + 4Et_2O$$

where, diglyme is diethyleneglycol dimethyl ether, $(MeOCH_2CH_2)_2O$. Diborane can also be prepared by treating $NaBH_4$ with conc. H_2SO_4 or H_3PO_4:

$$2NaBH_4 + H_2SO_4 \longrightarrow B_2H_6 + 2H_2 + Na_2SO_4$$

$$2NaBH_4 + 2H_3PO_4 \longrightarrow B_2H_6 + 2H_2 + 2NaH_2PO_4$$

b) **Properties of diborane:** Diborane is a colourless gas (b.p., 183K). It is rapidly decomposed by water with the formation of H_3BO_3 and H_2:

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

Mixtures of diborane with air or oxygen inflame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. Therefore, it is used as a rocket fuel.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O, \Delta H = -2165 \text{ kJ mol}^{-1}$$

Pyrolysis of B_2H_6 in sealed vessels at temperatures above 375 K is an exceedingly complex process producing a mixture of various boranes, e.g., B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12} and $B_{10}H_{14}$. By careful control of temperature, pressure and reaction time, the yield of various intermediate boranes can be optimised. For example, by storing B_2H_6 under pressure for 10 days, B_4H_{10} is produced in 15% yield according to the following equation:

$$2B_2H_6 \longrightarrow B_4H_{10} + H_2$$

Diborane undergoes a facile addition reaction with alkenes and alkynes in ether solvents at room temperature to form organoboranes:

$$6RCH{=}CH_2 + B_2H_6 \longrightarrow 2B(CH_2CH_2R)_3$$

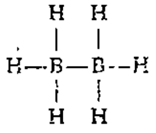
This reaction known as **hydroboration reaction** was discovered by Brown and Subba Rao in 1956. It is regiospecific, boron atom showing preferential attachment to the least substituted carbon atom. You may compare this addition with polar additions to the double bond, e.g., addition of HX, which obey Markownikoff's rule. Reaction of the resulting organoborane with an anhydrous carboxylic acid yields the alkane corresponding to the initial alkene whereas oxidative hydrolysis with alkaline H_2O_2 yields the corresponding primary alcohol:

$$B(CH_2CH_2R)_3 \xrightarrow{EtCO_2H} 3RCH_2CH_3$$

$$B(CH_2CH_2R)_3 \xrightarrow{NaOH/H_2O_2} 3RCH_2CH_2OH$$

Hydroboration reaction has proved to be of outstanding synthetic utility. H.C. Brown was awarded the 1979 Nobel Prize in chemistry for developing hydroboration reaction.

c) **Structure of diborane:** The structure of diborane is of great interest since it cannot be explained on the basis of simple theories of bonding. As mentioned earlier, there are not enough valence electrons in B_2H_6 to form the expected number of covalent bonds, in other words, B_2H_6 is an electron-deficient compound. Since boron atom has three unpaired electrons in the outermost orbit in the excited state, it can form three covalent bonds. If each of the boron atoms in diborane links itself to three hydrogen atoms, there will be no electrons left to form a bond between the two boron atoms. Thus, diborane cannot have an ethane type structure as shown in the margin.



$$\begin{array}{c} \quad H \quad H \\ \quad | \quad\; | \\ H—B—B—H \\ \quad | \quad\; | \\ \quad H \quad H \end{array}$$

Not possible

Diborane, B_2H_6, has been found to possess a bridge structure (Fig. 6.2) in which each B atom is bonded to two H atoms called terminal H atoms by regular electron-pair bonds. The resulting two BH_2 fragments are bridged by two H atoms as indicated by electron diffraction studies and by Raman and infrared spectroscopy. The two boron atoms and the four terminal hydrogen atoms lie in the same plane while the two bridging hydrogen atoms lie in a plane perpendicular to this plane as shown in Fig. 6.2. The bridging hydrogen atoms prevent rotation between the two boron atoms.

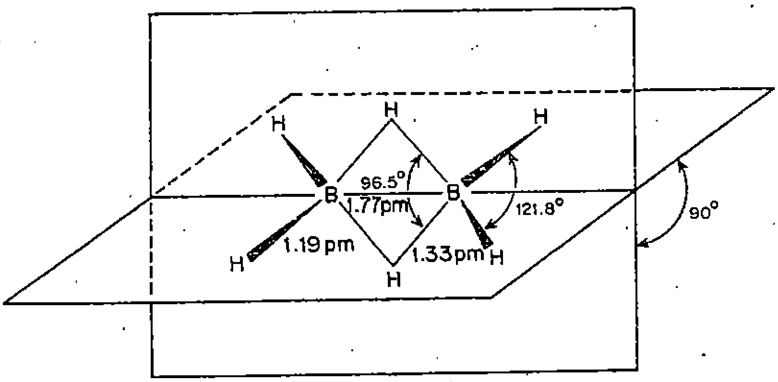


Fig. 6.2: Bridge structure of diborane

In the bridge structure, diborane has eight bonds but there are 12 electrons available for bonding, three per B and one per H. Hence, all the bonds in the molecule cannot be electron-pair bonds which would require 16 electrons for the structure in Fig. 6.2. The terminal B–H bond lengths are the same as the bond lengths in non-electron deficient compounds. This means that the four terminal B–H bonds are normal electron pair bonds accounting for a total of eight electrons. Thus, electron deficiency must be associated with the bridging B–H–B bonds in which a pair of electrons binds three atoms, viz., B, H and B. Therefore, these bridging B–H–B bonds are called three centre electron pair bonds abbreviated [illegible]

Alternatively, we can give a simple molecular orbital description of bonding in B_2H_6 as follows. Each boron atom is sp^3 hybridised giving four sp^3 hybrid orbitals, one of which is vacant and the other three are singly filled. Two of the sp^3 hybrid orbitals on each boron atom are used to form terminal B–H bonds with singly filled 1*s* orbital of hydrogen. Two BH_2 units are then brought together so that all six atoms are coplanar. Then one singly filled sp^3 hybrid orbital on one B atom and one vacant sp^3 hybrid orbital on the other B atom overlap with the singly filled 1*s* orbital on hydrogen atom to form a bonding orbital shaped like a banana and covering all three atoms, viz, B, H and B. Similarly the other bonding orbital is also formed (Fig. 6.3).

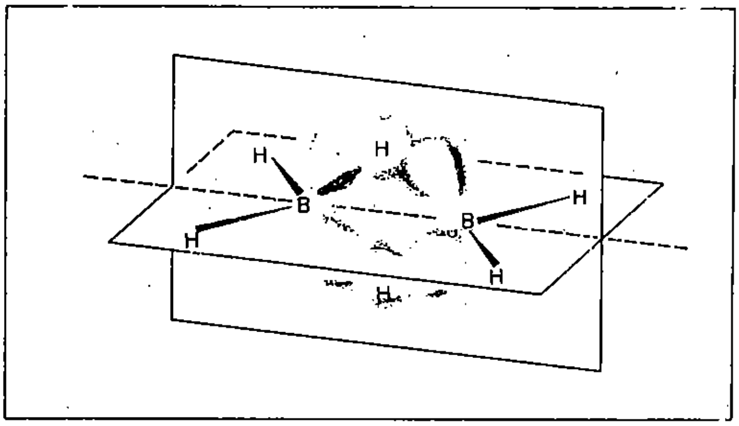


Fig. 6.3: Formation of bridging (3c–2e) B–H–B bonds in diborane.

This orbital binding three atoms contains only two electrons; the bonding between the bridging H atom and the B atom is thus only about half as strong as in the conventional two-centre two-electron terminal bonds. The B_2H_6 molecule contains two such three-centre electron pair bonds. Due to repulsion between the two H nuclei, the delocalised orbitals are bent away from each other giving it the banana shape.

6.4.2 Borohydrides

Borohydrides like $NaBH_4$, $Be(BH_4)_2$ and $Al(BH_4)_3$ are the salts of complex tetrahydridoborate anion, BH_4^-. Since in BH_4^-, boron has a complete octet, the borohydrides are more stable than the boranes. Sodium borohydride is obtained by the reaction of NaH and methyl borate:

$$4NaH + B(OMe)_3 \longrightarrow NaBH_4 + 3CH_3ONa$$

Other borohydrides are prepared from sodium borohydride. The alkali metal borohydrides are white, non-volatile, ionic solids which are stable in dry air. In contrast to the alkali metal borohydrides, $Be(BH_4)_2$ and $Al(BH_4)_3$ are covalent and volatile in nature. The alkali metal borohydrides react with water with varying ease. Thus, $LiBH_4$ reacts violently with water, $NaBH_4$ can be recrystallised from cold water while KBH_4 is even more stable.

$$LiBH_4 + H_2O \longrightarrow LiBO_2 + 4H_2$$

Tetrahydridoborate anion, BH_4^- has a tetrahedral structure, which can be explained on the basis of sp^3 hybridisation of boron. You have already studied that $NaBH_4$ is an important reagent for the preparation of B_2H_6. Solubility and stability of $NaBH_4$ in alcoholic and aqueous solutions make it a useful reagent in the reduction of aldehydes and ketones to primary and secondary alcohols, respectively. Other functional groups such as >C=C<, –COOH and $-NO_2$ are not attacked normally:

$$RCHO \xrightarrow{NaBH_4} RCH_2OH$$

6.4.3 Hydrides of Aluminium

The extensive chemistry of the boron hydrides finds no parallel with the hydrides of heavier elements of Group 13. Out of the four possible binary hydrides of Al, Ga, In and Tl, only aluminium hydride, $(AlH_3)_n$, is known. It is prepared by the action of either 100% pure H_2SO_4 or $AlCl_3$ on lithium aluminium hydride in an ethereal solvent:

$$2LiAlH_4 + H_2SO_4 \longrightarrow 2/n(AlH_3)_n + Li_2SO_4 + 2H_2$$

$$3LiAlH_4 + AlCl_3 \longrightarrow 4/n(AlH_3)_n + 3LiCl$$

•Protic reagents contain an easily replaceable proton; examples are acids, water, alcohols, etc.

Aluminium hydride is a colourless, nonvolatile, thermally unstable (above 425 K) solid. It is a strong reducing agent and reacts violently with water and other protic reagents to liberate H_2.

$$2(AlH_3)_n + 6nH_2O \longrightarrow 2nAl(OH)_3 + 9nH_2$$

Similar to B_2H_6, $(AlH_3)_n$ is also an electron deficient compound. Therefore, it is extensively polymerised by 3c-2e non-linear Al–H–Al bonds

6.4.4 Lithium Aluminium Hydride

Lithium aluminium hydride is much more useful than aluminium hydride. It is prepared in the laboratory by the action of LiH on $AlCl_3$ in diethyl ether:

$$4LiH + AlCl_3 \xrightarrow{ether} LiAlH_4 + 3LiCl\downarrow$$

Lithium aluminium hydride is a greyish-white solid which decomposes into its elements above 400 K. It is stable in dry air but reacts violently with water:

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2\uparrow$$

$LiAlH_4$ is readily soluble in ethers. It is a very important reducing agent for both inorganic and organic compounds. It reduces inorganic halides to hydrides, e.g.:

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$$

$$MCl_4 + LiAlH_4 \longrightarrow MH_4 + LiCl + AlCl_3$$

(M = Si, G , Sn)

$LiAlH_4$ is one of the most important reducing agents in organic chemistry because it reduces as many as 60 functional groups including ethylenic >C=C< double bonds. But, it is less selective than sodium borohydride. Before we discuss the halides of boron and aluminium, you may like to attempt the following SAQ based on the hydrides of boron and aluminium.

SAQ 4

a) Explain briefly the difference between a two centre electron pair bond and a three centre electron pair bond.

....

....

b) Compare $NaBH_4$ and $LiAlH_4$ as reducing agents.

....

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c) Which of the above two would you use in the following conversions:

i) $R\text{-}CH{=}CH\text{-}CHO \longrightarrow R\text{-}CH{=}CH\text{-}CH_2OH$

ii) $R\text{-}CH_2\text{-}COOEt \longrightarrow R\text{-}CH_2\text{-}CH_2OH$

6.5 HALIDES OF BORON AND ALUMINIUM

All the elements of Group 13 form binary halides. All the four trihalides of each element are known, with one exception. The compound TlI_3 is not thallium(III) iodide, but rather thallium(I) triiodide $Tl^+(I_3)^-$, which is similar to potassium triiodide, $K^+I_3^-$. You will learn more about triiodides in Unit 10. Thallium(III) chloride and bromide are also very unstable and decompose into the thallium(I) halides and the free halogen. Thus, the only stable trihalide of thallium in +3 oxidation state is the trifluoride, TlF_3, which is an ionic solid. This is in keeping with the general trend that Tl(I) compounds are more stable than Tl(III) compounds. Let us now briefly discuss the halides of B and Al.

6.5.1 Halides of Boron

Boron trihalides of the type BX_3 exist for all the four halogens. Boron trifluoride can be prepared on a large scale by the fluorination of boric oxide or borax with fluorspar and conc. H_2SO_4:

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

$$Na_2B_4O_7 + 6CaF_2 + 8H_2SO_4 \longrightarrow 4BF_3 + 6CaSO_4 + 6NaHSO_4 + 7H_2O$$

In the laboratory, pure BF_3 is best prepared by thermal decomposition of benzene diazonium tetrafluoroborate, PhN_2BF_4:

$$PhN_2BF_4 \longrightarrow PhF + N_2 + BF_3$$

BCl_3 and BBr_3 are prepared on a large-scale by direct halogenation of B_2O_3 in the presence of C, e.g.:

$$B_2O_3 + 3C + 3Cl_2 \xrightarrow{775\ K} 2BCl_3 + 6CO$$

In the laboratory BCl_3 and BBr_3 are prepared by halogen exchange reaction between BF_3 and Al_2X_6:

$$2BF_3 + Al_2X_6 \longrightarrow 2BX_3 + 2AlF_3, \text{ where } X = Cl \text{ and } Br$$

BI_3 is prepared in good yield by reacting $LiBH_4$ or $NaBH_4$ with I_2 at 400 K and 475 K, respectively:

$$LiBH_4 + 4I_2 \longrightarrow BI_3 + LiI + 4HI$$

The boron trihalides are highly volatile; BF_3 (b.p., 173 K) and BCl_3 (b.p., 260.5 K) are gases, BBr_3 a volatile liquid (b.p., 319 K) and BI_3 a low melting solid (m.p., 323 K). Boron halides are all hydrolysed by water giving H_3BO_3, and hydrohalic acids, HX or hydrofluoboric acid, HBF_4:

$$BX_3 + 3H_2O \longrightarrow H_3BO_3 + 3HX, (X = Cl, Br, I)$$

$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HBF_4$$

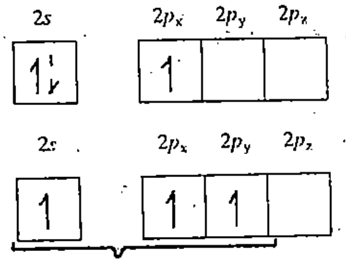
In addition to the trihalides, boron forms lower halides of formula, B_2X_4. But only B_2F_4 and B_2Cl_4 have been studied in some detail. B_2F_4 is a colourless gas whereas B_2Cl_4 is a colourless liquid at room temperature. These halides are much less stable than the corresponding trihalides. B_2F_4 is the most stable of all the B_2X_4 compounds. These are spontaneously inflammable in air and react with H_2, H_2O, ROH, Cl_2, etc.

Unlike BH_3 which is unstable, boron trihalides are monomeric molecular compounds and have no tendency to dimerise. In this respect boron trihalides resemble organoboranes, BR_3, but differ from diborane, B_2H_6 and the aluminium halides, Al_2X_6. Thus, boron trihalides having three electron pair B–X bonds are electron deficient. However, the interatomic distances, B–X, are substantially shorter than those expected for single bonds. For example, the B–F bond length in BF_3 is 130 pm which is shorter than the sum of the covalent radii of B (80 pm) and F (72 pm). This shortening of bonds has been explained in terms of appreciable $p\pi$–$p\pi$ bonding between an empty p orbital of the sp^2 hybridised boron atom and filled p orbitals of one of the fluorine atoms.

All the four trihalides are trigonal planar molecules. This can be explained on the basis of sp^2 hybridisation of the boron atom.

Electronic configuration of boron atom in ground state

Electronic configuration of boron atom in excited state



sp^2 – hybridisation — trigonal planar structure

The three hybrid orbitals of boron overlap with singly filled $2p$ orbitals of three halogen atoms giving rise to three B–X bonds. The empty $2p$ orbital of boron which is not involved in hybridisation in perpendicular to the plane of the triangle. Its energy is comparable to that of the filled $2p$ orbitals of halogen atom. Thus it can accept a pair of electrons from a filled $2p$ orbital of any one of the three halogen atoms, forming a dative π bond. This makes an octet of electrons around the boron atom. The BX_3 molecule exists as a resonance hybrid of the following three structures as shown in Fig. 6.4.

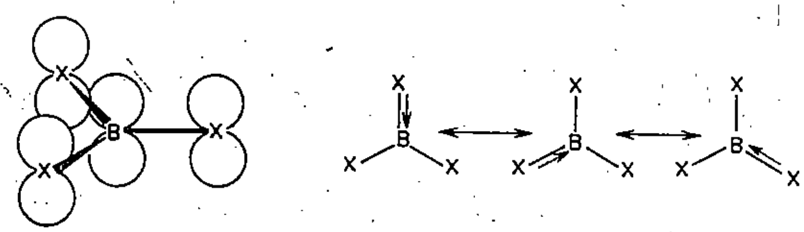


Fig. 6.4: Structure of boron trihalides

Because of lack of efficient overlapping, the extent of π bonding decreases as the size of atoms involved in bonding increases. Thus, the extent of π bonding in boron halides decreases from BF_3 to BI_3.

6.5.2 Halides of Aluminium

All the four trihalides of aluminium, i.e. AlF_3, $AlCl_3$, $AlBr_3$ and AlI_3 are known. AlF_3 is made by treating Al_2O_3 with HF gas at 1000K and the other trihalides are prepared by the direct exothermic reaction of the elements, e.g.:

$$Al_2O_3 + 6HF \xrightarrow{1000\ K} 2AlF_3 + 3H_2O$$
$$2Al + 3X_2 \longrightarrow 2AlX_3, (X = Cl, Br, I)$$

$AlCl_3$ is also obtained by heating a mixture of alumina and coke in a current of Cl_2:

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

Aluminium trifluoride differs from the other trihalides of Al in being ionic and nonvolatile in nature. Other halides of Al, as also of Ga and In, are covalent in nature when anhydrous and are relatively more volatile. $AlCl_3$, $AlBr_3$ and AlI_3 exist as dimeric species formed by pairing of two AlX_3 units as shown in Fig. 6.5. The pairing occurs by formation of a coordinate covalent bond from the halogen on one AlX_3 unit to the Al atom of another. Thus, for $AlCl_3$, the species Al_2Cl_6 is formed. This is similar to the linking together of $BeCl_2$ units in solid $BeCl_2$ which you have already studied in the preceding unit.

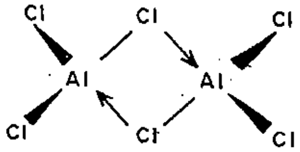


Fig. 6.5: Structure of Al_2Cl_6

The dimerisation of AlX_3 occurs because these halides are electron deficient. By dimerisation, the halides attain an octet of electrons. You have studied that the trihalides, BX_3 are also electron deficient and attain an octet by $p\pi$–$p\pi$ bonding. This is not possible in case of Al and other larger elements because of lack of efficient π-overlap, and hence, they dimerise. This dimerisation is retained when the halides dissolve in non-polar solvents such as C_6H_6 and CCl_4. In coordinating solvents, such as, diethyl ether, trimethyl amine and phosphorus oxochloride, $AlCl_3$ forms complexes like $AlCl_3{\cdot}OEt_2$, $AlCl_3{\cdot}NMe_3$ and $AlCl_3{\cdot}OPCl_3$, e.g.:

$$Al_2Cl_6 + 2\,(C_2H_5)_2O \longrightarrow 2\,(C_2H_5)_2O{\cdot}AlCl_3$$

Alkyl and acyl chlorides, RCl and RCOCl, react with $AlCl_3$ to form complexes of the type $R^+AlCl_4^-$ and $RCO^+AlCl_4^-$, respectively; these are formed as intermediates in Friedel-Crafts alkylation and acylation reactions.

As explained in Section 6.3, due to high heat of hydration of Al^{3+}, the covalent dimers are broken into $[Al(H_2O)_6]^{3+}$ and $3X^-$ (aq) ions, when the halides dissolve in water. Aqueous solutions of aluminium halides and other aluminium salts are acidic in nature. This is because the hexa-aquo complex or the aqua ion $[Al(H_2O)_6]^{3+}$ dissociates readily in solution giving hydroxonium ions by a series of changes as shown below:

Aqueous solutions of salts of most heavy metals are acidic in nature because of dissociation of their aqua ions as shown in the case of aluminium.

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$$
$$[Al(H_2O)_5OH]^{2+} + H_2O \rightleftharpoons [Al(H_2O)_4(OH)_2]^+ + H_3O^+$$

If a base like NH_4OH is added to an aqueous solution of salts of aluminium, the H_3O^+ ions are neutralised and hydrated aluminium hydroxide is precipitated as a gelatinous precipitate:

$$[Al(H_2O)_4(OH)_2]^+ + OH^- \longrightarrow [Al(H_2O)_3(OH)_3]\downarrow + H_2O$$

Gelatinous nature of $Al(OH)_3$ is due to its hydrated nature. Because of its gelatinous nature, $Al(OH)_3$ is used for purifying water and as a mordant in dyeing.

An excess of a strong alkali like NaOH, causes the above reaction to continue further with the formation of the soluble aluminate anion, $[Al(H_2O)_2(OH)_4]^-$:

$$[Al(H_2O)_3(OH)_3] + NaOH \longrightarrow Na[Al(H_2O)_2(OH)_4]$$

The above reactions can be reversed by the addition of an acid. Thus, when a basic solution containing aluminate ion is slowly neutralised, the hydroxide

$[Al(H_2O)_3(OH)_3]$ precipitates and then redissolves as more acid is added:

$$[Al(H_2O)_2(OH)_4]^- + H_3O^+ \longrightarrow [Al(H_2O)_3(OH)_3]\downarrow + H_2O$$

$$[Al(H_2O)_3(OH)_3] + 3H_3O^+ \longrightarrow [Al(H_2O)_6]^{3+} + 3H_2O$$

This explains the amphoteric nature of $Al(OH)_3$.

SAQ 5

Explain briefly why boron trichloride is a gas and aluminium trichloride is a dimeric solid.

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6.6 OXIDES OF BORON AND ALUMINIUM

All the elements of Group 13 form trioxides also known as sesquioxides of the formula, M_2O_3. Thallium forms stable Tl_2O also. The basic character of oxides increases down the group with increase in the atomic number. Thus, B_2O_3 is acidic, Al_2O_3 and Ga_2O_3 are amphoteric whereas In_2O_3 and Tl_2O_3 are basic. Tl_2O is soluble in water and the resulting hydroxide TlOH is, in fact, as strong a base as KOH. Let us now study the oxides of boron and aluminium in a little more detail, this will be followed by a discussion of the acids of boron and the borates.

6.6.1 Boric Oxide

Boric oxide, B_2O_3, is the principal oxide of boron. It is also known as boron trioxide, boron sesquioxide and boric anhydride. It is prepared by burning boron in oxygen or by heating boric acid to red heat:

$$2B + 3O_2 \longrightarrow B_2O_3$$

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

Boric oxide is a white hygroscopic solid. It is acidic in nature and dissolves in water to form boric acid:

$$B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$$

When fused with metal salts, it forms metaborates known as borate glasses. Metaborates of coloured cations have characteristic colours. This forms the basis of the borax-bead test in qualitative inorganic analysis, e.g.:

$$CoO + B_2O_3 \longrightarrow Co(BO_2)_2, \text{ deep blue}$$

$$CuSO_4 + B_2O_3 \longrightarrow Cu(BO_2)_2, \text{ blue}$$

$$Cr_2(SO_4)_3 + B_2O_3 \longrightarrow 2Cr(BO_2)_3, \text{ green}$$

The bond energy of the B–O single bond is very high (523 kJ mol^{-1}). Therefore, unlike carbon and nitrogen, boron does not form stable BO double bonds to oxygen. Instead of forming small volatile covalent molecule, $B_2O_3(g)$ and small anion, BO_3^{3-}, it forms polymers having –B–O–B–O–B–O– chains. Thus, boric oxide is a polymeric solid.

6.6.2 Aluminium Oxide

Aluminium oxide, Al_2O_3 is a highly ionic compound of aluminium. It is also known as alumina. As you have studied earlier, it occurs in nature not only as bauxite and colourless corundum, but also as coloured gem stones like ruby, emerald, sapphire and topaz, etc. Colours of these gem stones are due to the presence of transition metal ions. Anhydrous aluminium oxide can exist in two forms both of which are white. These are α-Al_2O_3 and τ-Al_2O_3. The τ-Al_2O_3 is formed by dehydrating $Al(OH)_3$ below 750 K:

$$2Al(OH)_3 \longrightarrow \tau\text{-}Al_2O_3 + 3H_2O$$

The τ-Al_2O_3 is quite reactive. It dissolves readily in both acids and bases. If the τ-Al_2O_3 is heated to 1500 K, it changes to the α-Al_2O_3, which is called corundum. Corundum has a very high melting point (about 2328 K). It is very hard and inert, especially towards acids.

SAQ 6

Discuss briefly the nature of oxides of Group 13 elements.

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6.7 OXOACIDS OF BORON AND BORATES

Orthoboric acid H_3BO_3 commonly known as boric acid and metaboric acid HBO_2, are two well-known and important oxoacids of boron. On a large scale, H_3BO_3 is prepared by the action of HCl or H_2SO_4 on a concentrated solution of borax:

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

Boric acid is a flaky, white crystalline solid. It is moderately soluble in water. Boric acid is a very weak monobasic acid (pK = 9.25), because it acts as an electron pair acceptor (Lewis acid) from OH^- rather than as a proton donor (Arrhenius acid).

$$H_3BO_3 + 2H_2O \rightleftharpoons [B(OH)_4]^- + H_3O^+$$

Its acid strength is considerably enhanced on complex formation with polyhydric alcohols such as glycerol and mannitol. With mannitol pK drops to 5.15 indicating an increase in acid strength by a factor of more than 10^4:

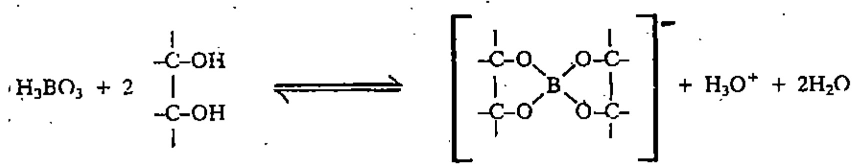

Fig. 6.6: Complex formation between boric acid and a 1:2-diol

On heating boric acid at 375 K, metaboric acid, HBO_2 is formed. On further heating above 500 K, B_2O_3 is formed:

$$H_3BO_3 \xrightarrow{375\ K} HBO_2 + H_2O$$

$$2HBO_2 \xrightarrow{500\ K} B_2O_3 + H_2O$$

In solution metaboric acid changes into orthoboric acid.

Boric acid has a two dimensional layer structure in which planar BO_3 units are linked to each other by unsymmetrical hydrogen bonds as shown in Fig. 6.7. In contrast to the short O–H....O distance of 272 pm within the plane, the distance between consecutive layers is 318 pm. This is the cause of slippery and waxy feel of boric acid which is also a good lubricant.

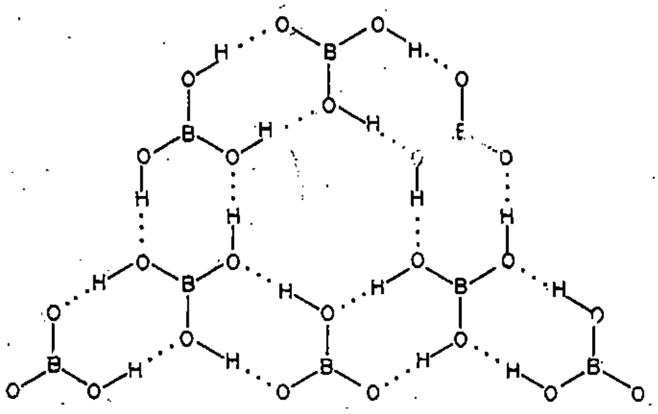

Fig. 6.7: Layer structure of H_3BO_3

Borax

Salts of boric acids are known as borates. As said earlier, hydrated borates occur naturally, e.g., borax, $Na_2B_4O_7 \cdot 10H_2O$, kernite, $Na_2B_4O_7 \cdot 4H_2O$, colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$, etc. Anhydrous borates can be made by fusion of boric acid and metal oxides.

Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$, is commonly known as borax. It occurs in certain lakes in India, Tibet and U.S.A. It is obtained by extracting impure borax with water and concentrating the solution until crystals of borax separate out.

Borax can also be prepared from the mineral colemanite by boiling it with Na_2CO_3 solution:

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3\downarrow$$

Borax is crystallised from the filtrate after removing insoluble $CaCO_3$. By passing CO_2, $NaBO_2$ present in the mother liquor is converted into borax:

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

Borax is a white crystalline solid. It is hydrolysed by water to give an alkaline solution:

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons 4H_3BO_3 + 2NaOH$$

On heating, borax loses water to become anhydrous. Anhydrous borax on strong heating with NH_4Cl gives boron nitride and boron trioxide:

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2BN + B_2O_3 + 2NaCl + 4H_2O$$

On heating alone, it decomposes to form $NaBO_2$ and B_2O_3

$$Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

Borax possesses an anion $[B_4O_5(OH)_4]^{2-}$ having both three- and four-coordinated boron as shown in Fig. 6.8.

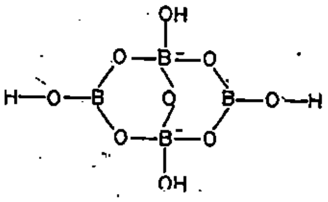

Fig. 6.8: Structure of $[B_4O_5(OH)_4]^{2-}$ an.

SAQ 7

a) Explain why boric acid behaves as a weak monobasic acid.

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b) Boric acid can be estimated by titration with standard alkali solutions, in the presence of glycerol using phenolphthalein as an indicator. What is the function of glycerol in this titration?

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6.8 BORAZINE

Reaction of ammonia with diborane at 475 K gives a compound $B_3N_3H_6$ known as borazine or borazole:

$$3B_2H_6 + 6NH_3 \xrightarrow{475\,K} 2B_3N_3H_6 + 12H_2$$

Borazine is best prepared by reducing B-trichloroborazine with sodium borohydride, $NaBH_4$. B-trichloroborazine is first prepared by heating BCl_3 with NH_4Cl.

$$3BCl_3 + 3NH_4Cl \xrightarrow{425\ K} B_3N_3Cl_3H_3 + 9HCl$$
$$B_3N_3Cl_3H_3 + 3NaBH_4 \longrightarrow B_3N_3H_6 + 3NaCl + 3/2B_2H_6$$

Borazine has many physical properties closely similar to those of isoelectronic benzene as shown in Table 6.4. Therefore, sometimes it is also called as inorganic benzene.

Table 6.4: Comparison of physical properties of borazine and benzene

Property	$B_3N_3H_6$	C_6H_6
Mol. wt.	80.5	78.1
MP (K)	216	279
BP (K)	328	353
Density ($10^3 \times kg\,m^{-3}$)	0.81	0.81

Borazine, however, is more reactive than benzene. It readily reacts with H_2O, MeOH and HX to yield 1:3 adducts which eliminate H_2 on being heated to 373 K, e.g.:

$$B_3N_3H_6 + 3H_2O \longrightarrow [BH(OH)NH_2]_3 \longrightarrow [B(OH)NH]_3 + 3H_2$$
$$B_3N_3H_6 + 3HCl \longrightarrow [BH(Cl)NH_2]_3 \longrightarrow B_3N_3H_3Cl_3 + 3H_2$$

Borazine has a regular plane hexagonal ring structure. The B–N bond distance of 144 pm in borazine molecule is less than the sum of single-bond covalent radii of B (82 pm) and N (70 pm). This indicates the presence of π bonding involving the lone pair of electrons on nitrogen and an empty p orbital on boron. Thus, in valence bond terminology, the structure of borazine can be written as shown in Fig. 6.9.

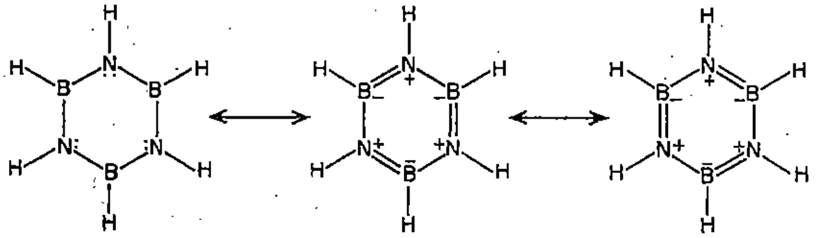

Fig. 6.9: Valence bond structures for borazine

Molecular orbital calculations, which are beyond the scope of discussion in this course, indicate that in borazine the π electrons are only partially delocalised. This is because of the difference in the energy of the π orbitals of B and N.

The experimental results of the reactions of water and HCl with borazine indicate that the reactions proceed by nucleophilic attack on boron atom. This suggests that the actual sign of net charges on B and N atoms in borazine should be opposite to that indicated in Fig. 6.9. This apparent paradox is explained by the existence of considerable polarity in the B–N σ-bond (electronegativity B, 2.0, N, 3.05) in a direction opposite to that in the B–N π-bond. In fact the drift in electron density in B–N σ-bond outweighs the drift in electron density in the B–N π-bond so that the nitrogen atoms are relatively negative.

Nucleophiles are the electron donating molecules or ions that lose or share electrons with another atom or ion.

SAQ 8

Borazine is isoelectronic with benzene but it is much more reactive than benzene. Explain briefly why this is so and what will be the nature of reagent attacking the borazine molecule.

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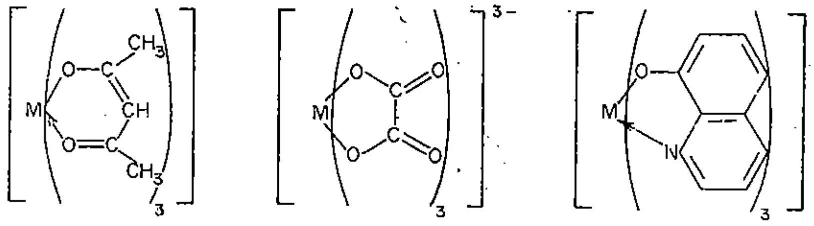
6.9 COMPLEXATION BEHAVIOUR

As compared to the elements of Groups 1 and 2, elements of Group 13 show a greater tendency of complex formation. Because of lack of *d*-orbitals, boron is invariably tetrahedrally coordinated in these compounds. For example, in compounds like $NaBH_4$, $NaBF_4$, $NaB(C_6H_5)_4$, $BH_3\cdot NMe_3$, $BF_3\cdot NH_3$ as well as in chelates such as $[B(o\text{-}C_6H_4O_2)_2]^-$ and $[B(o\text{-}OC_6H_4COO)_2]^-$ the coordination number of boron atom is four. Due to the presence of *d*-orbitals, the higher members of the group can expand their coordination number even up to six. Thus, Al, Ga, In and Tl form complexes such as (i) $AlCl_3\cdot NMe_3$, $RCO^+AlX_4^-$(X=Cl, Br), $Et_4N^+MX_4^-$ (M=Al, Ga, X=Cl, Br) in which the coordination number is four, (ii) $AlCl_3\cdot 2NMe_3$, in which the coordination number is five, and (iii) $Na_3[AlF_6]$ in which the coordination number is six. With chelating ligands like β-diketones, pyrocatechol, dicarboxylic acids and 8-quinolinol, Al, Ga, In and Tl form anionic or neutral complexes in which the coordination number of the metal is six. Structures of some of these complexes are shown in Fig. 6.10.

You know that the formation of $AlCl_4^-$ is important in Friedel-Crafts reaction whereas the 8-quinolinol complex of aluminium is used in gravimetric estimation of aluminium.



acetyl acetone complex

oxalate complex

8-quinolinol complex

Fig. 6.10: Some chelates of Al, Ga, In and Tl

In addition to coordination complexes, aluminium forms a number of double sulphates of general formula $MAl(SO_4)_2\cdot 12H_2O$, where M is usually K, Rb, Cs or NH_4. These double sulphates are known as alums. For example, potash alum, $KAl(SO_4)_2\cdot 12H_2O$ and ammonium alum, $NH_4Al(SO_4)_2\cdot 12H_2O$. In alums, Al can also be replaced by a number of cations of the same charge and not too different in size, e.g., Ga, In, Ti, V, Cr, Mn, Fe and Co. For example, chrome alum, $KCr(SO_4)_2\cdot 12H_2O$ and ferric alum, $NH_4Fe(SO_4)_2\cdot 12H_2O$. The alums are isomorphous with each other. It is important to realise that the alums are double salts and not complex salts. In solution they behave simply as a mixture of component sulphates and give reactions of their individual cations.

SAQ 9

a) Explain why boron cannot expand its coordination number beyond four.

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b) Work out the coordination number of the metal in the chelates given in Fig. 6.10.

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6.10 ANOMALOUS BEHAVIOUR OF BORON

Just like lithium and beryllium in Groups 1 and 2, boron also shows anomalous behaviour. In general, the boron chemistry resembles that of silicon (occupying a diagonal position in the periodic table) more closely than that of Al, Ga, In and Tl. This is because of the small size and high electronegativity of boron as compared to those of Al, Ga, In and Tl. Boron resembles silicon and differs from Al, Ga, In and Tl in the following manner:

- Both B and Si are nonmetals whereas Al, Ga, In and Tl are distinctly metallic in nature.
- $B(OH)_3$ and $Si(OH)_4$ are acidic in nature, $Al(OH)_3$ and $Ga(OH)_3$ are amphoteric and $In(OH)_3$ and $Tl(OH)_3$, basic in nature.
- The hydrides of B and Si are volatile, spontaneously inflammable liquids. These are readily hydrolysed by water and acids whereas aluminium hydride is a nonvolatile polymeric solid. Hydrides of Ga, In and Tl are not stable.
- BCl_3 and $SiCl_4$ are monomeric covalent compounds which are readily hydrolysed by water to $B(OH)_3$ and $Si(OH)_4$. Anhydrous $AlCl_3$ is also a covalent compound and exists in the form of a dimer, i.e. Al_2Cl_6. On dissolving in water, it readily gives $Al^{3+}(aq)$ and $Cl^-(aq)$ whereas $B^{3+}(aq)$ does not exist.
- Both B_2O_3 and SiO_2 are acidic in nature and react with metallic oxides on fusion to form borate and silicate glasses. On the other hand, Al_2O_3 is amphoteric.
- Boron reacts with more electropositive elements, i.e. metals to form borides which are very hard substances; Al, Ga, In and Tl form alloys with metals.

SAQ 10

List four properties in which boron differs from rest of the elements of the group.

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6.11 SUMMARY

Let us now summarise the main points of the chemistry of Group 13 elements which you have studied in this unit.

- Boron, aluminium, gallium, indium and thallium are members of Group 13 of the periodic table. You have studied occurrence, extraction, uses and the general characteristics of these elements and gradations in their properties.
- Boron the first member of the group exhibits anomalous behaviour showing resemblance to silicon and differing from other members of the group.
- Hydrides of boron and aluminium are electron deficient compounds and exhibit three centre electron pair bonding in addition to normal electron pair bonding. Complex hydrides of boron and aluminium are important reducing agents.
- Halides of boron are monomeric covalent compounds which are hydrolysed by water. Boron halides exhibit $p\pi$–$p\pi$ bonding.
- Aluminium trifluoride is an ionic solid whereas its other halides when anhydrous are dimeric covalent compounds. In aqueous solution, the halides furnish $Al^{3+}(aq)$ ions.
- Boron forms two stable acids, viz., orthoboric acid and metaboric acid. In solution metaboric acid changes into orthoboric acid which behaves as a weak monobasic acid. Salts of these acids are known as borates.
- Boron forms borides, boron nitride and borazine. Borides are extremely hard compounds. Boron nitride which is isoelectronic with C_2 can exist in diamond and graphite forms. Borazine is isoelectronic with benzene and is also known as inorganic benzene.
- Aluminium oxide is an extremely stable ionic compound which can exist in two different forms: $\alpha\text{-}Al_2O_3$ and $\tau\text{-}Al_2O_3$.
- Boron and aluminium form a large number of addition complexes and chelate complexes with various nitrogen and oxygen donor ligands.

6.12 TERMINAL QUESTIONS

1 Describe various steps involved in the extraction of aluminium from bauxite. Explain why it cannot be prepared by reduction of Al_2O_3 with C.

2 While Al, Ga, In and Tl form both covalent and electrovalent compounds, boron forms mostly only covalent compounds. How would you explain this behaviour?

3 Describe the structure of diborane molecule. What is the nature of bonding in this molecule?

4 Write chemical equations showing amphoteric nature of Al_2O_3 and $Al(OH)_3$.

5 How would you explain the anomalous nature of boron?

6 How would you prepare borazine? Compare its properties with those of benzene.

7 Diborane is added to $CH_3{-}CH{=}CH_2$ and the product treated with (a) CH_3COOH (b) H_2O_2/OH^-. What will be the product formed in each case?

6.13 ANSWERS

Self Assessment Questions

1 a) Aluminium is the most abundant metallic element in the earth's crust. Its two important ores are bauxite, $Al_2O_3{\cdot}xH_2O$ and cryolite, Na_3AlF_6.

b) i) — b), ii) — c), iii) — a), iv) — e), v) — d).

2 Due to insertion of ten 3*d* elements between Ca and Ga, the effective nuclear charge of Ga is higher. Consequently its atomic radius is smaller as well as its ionisation energies and electronegativity are higher than expected.

3 a) By the action of conc. HNO_3, a thin impervious, coherent, unreactive layer of Al_2O_3 is deposited over the surface of Al metal. This coating protects Al from further attack and thus Al becomes passive.

b) With halogens, oxygen, sulphur, nitrogen and carbon, boron and aluminium form compounds having the formulae BX_3 and AlX_3, B_2O_3 and Al_2O_3, B_2S_3 and Al_2S_3, BN and AlN, $B_{12}C_3$ and Al_4C_3, respectively.

4 a) In a two centre electron pair bond, a pair of electrons binds two atoms, whereas in a three centre electron pair bond a pair of electrons binds three atoms together.

b) $LiAlH_4$ is a more versatile reducing agent than $NaBH_4$; it reduces as many as sixty functional groups in organic chemistry. On the other hand, $NaBH_4$ is more selective. For example, $NaBH_4$ reduces $>C{=}O$ group in aldehyde and ketones to alcohols, but functional groups such as $>C{=}C<$, $-COOH$ and $-NO_2$ are not normally attacked.

c) i) $NaBH_4$ ii) $LiAlH_4$

5 In BCl_3 boron attains an octet of electrons by means of $p\pi{-}p\pi$ bonding between B and Cl atoms. Thus it exists as a monomeric gas. Due to the larger size of aluminium in aluminium trichloride, efficient $p\pi{-}p\pi$ bonding cannot take place between Al and Cl atoms. Consequently, aluminium trichloride dimerises to attain an octet of electrons around Al by forming a dative bond between Cl and Al atoms. Thus, it exists as a solid.

6 The elements of Group 13 form oxides of the type M_2O_3 which become more basic on moving down the group. Thus, B_2O_3 is acidic, Al_2O_3 and Ga_2O_3 are amphoteric, whereas In_2O_3 and Tl_2O_3 are basic.

7 a) Boric acid behaves as a weak monobasic acid because it ionises in water by accepting a pair of electrons from the hydroxyl ion as given below:

$$H_3BO_3 + 2H_2O \rightleftharpoons [B(OH)_4]^- + H_3O^+$$

b) As explained above, boric acid is a weak monobasic acid. On addition of glycerol to boric acid, a chelate complex is formed due to which the strength of boric acid increases by a factor of 10^4. Thus, in the presence of glycerol, boric acid can be used as a primary standard using phenolphthalein as indicator.

8 In benzene, the π electrons are completely delocalised over all the carbon atoms whereas in borazine these are only partially delocalised. Due to the difference in electronegativities of B and N atoms, there is a drift in the electron density in both

σ– and π– B–N bonds. The drift in B–N σ– bond is from B to N and it outweighs the drift in B–N π– bond which is from N to B. Thus, nitrogen acquires a net negative charge whereas boron acquires a net positive charge. This results in a nucleophilic attack on boron in borazine.

9 a) As boron can accommodate at the most eight electrons in its outermost shell ($n = 2$), it cannot form more than four electron pair bonds and expand its coordination number beyond four.

b) The coordination number of the metal in all the chelates shown in Fig. 6.10 is six.

10 i) Boron is a nonmetal, whereas Al, Ga, In and Tl are metals.

ii) $B^{3+}(aq)$ does not exist, whereas Al, Ga, In and Tl easily furnish $M^{3+}(aq)$.

iii) $B(OH)_3$ is acidic whereas $Al(OH)_3$ and $Ga(OH)_3$ are amphoteric and $In(OH)_3$ and $Tl(OH)_3$ are basic in nature.

iv) The halides of boron exhibit $p\pi - p\pi$ bonding whereas those of Al, Ga, In and Tl do not.

Also see other differences in Section 6.10.

Terminal Questions

1 Purification of bauxite and electrolysis of fused Al_2O_3 in cryolite are the two steps involved in extraction of Al. Aluminium cannot be prepared by reduction of Al_2O_3 with C, because on heating Al_2O_3 with C, Al_4C_3 is formed.

2 Because of their high ionisation energies, all the elements of Group 13 form covalent compounds. But due to their high enthalpies of hydration, compounds of Al, Ga, In and Tl ionise in aqueous solution to furnish $M^{3+}(aq)$ ions, also.

3 See sub-section 5.4.1(c).

4 $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$

$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

$Al(OH)_3 + NaOH \longrightarrow NaAl(OH)_4$

5 Because of its extremely small size and high electronegativity boron exhibits anomalous behaviour.

6 See sub-sec. 6.8.1.

7 $6CH_3CH{=}CH_2 + B_2H_6 \longrightarrow 2B(CH_2CH_2CH_3)_3$

a) $B(CH_2CH_2CH_3)_3 \xrightarrow{CH_3COOH} 3CH_3CH_2CH_3$

b) $B(CH_2CH_2CH_3)_3 \xrightarrow{H_2O_2/OH^-} 3CH_3CH_2CH_2OH$

UNIT 7 ELEMENTS OF GROUP 14

Structure

7.1 Introduction
  Objectives
7.2 Occurrence, Extraction and Uses
  Occurrence
  Extraction
  Uses
7.3 General Characteristics
  Physical Properties
  Multiple Bonding
  Catenation
  Chemical Properties
  Complex Formation
7.4 Anomalous Behaviour of Carbon
7.5 Silica and Silicates
  Silica
  Silicates
  Silicones
7.6 Chemistry of Divalent Silicon, Germanium, Tin and Lead Compounds
7.7 Summary
7.8 Terminal Questions
7.9 Answers

7.1 INTRODUCTION

In Units 4 and 5 you have studied the general characteristics of the elements of *s*-block, as well as the periodicity in their properties. You have also studied in Unit 6 these aspects of the chemistry of elements of Group 13, which belongs to *p*-block. You would have noticed that while *s*-block elements show a regular gradation in properties down the group, the elements of Group 13 show some irregularities. It was also pointed out that the first element in each group shows some anomalous behaviour.

Now we extend our study to another group of *p*-block elements, namely, Group 14, which consists of carbon, silicon, germanium, tin and lead. This is the first group in which the transition from non-metals, C and Si through typical metalloid, Ge, to weakly electropositive metals, Sn and Pb, can be clearly seen. However, this does not imply that the properties of carbon are completely non-metallic; its crystalline forms are lustrous, one allotrope (graphite) conducts electricity. Tin and lead, on the other hand, form amphoteric oxides and volatile chlorides. We will discuss these properties in this unit. In the next unit you will study the chemistry of Group 15 elements.

Objectives

After studying this unit you should be able to :

- explain the occurrence, extraction and uses of the elements of carbon family,
- explain allotropy and describe different forms in which these elements exist,
- compare the general characteristics of the elements of carbon family,
- explain catenation with special reference to carbon,
- describe internal π-bonding and the concept of complex formation by elements of this group,
- explain the nature of bonding in carbides,
- describe the chemistry of halides, hydrides and oxides of these elements,
- describe the structure and uses of silicates and silicones, and
- describe the chemistry of divalent compounds of these elements.

7.2 OCCURRENCE, EXTRACTION AND USES

All the elements of this group are important in some manner or another. While carbon is an essential constituent of all living beings, silicon is present in rocks as well as many minerals. Both silicon and germanium are important components of semiconductors and transistors. Tin and lead also find various uses in everyday life. In the following paragraphs you will study the occurrence, extraction and uses of elements of this group.

You may be aware that a new form of element carbon called fullerenes in which the atoms are arranged in closed shells was discovered in 1985 by Dr.Robert F. Curl, Dr.Harold W.Croto and Dr. Richard F. Smalley who have incidently won the 1996 Nobel Prize in Chemistry jointly. A detailed information of the discovery, properties and uses of fullerenes has been given in App.-I.

7.2.1 Occurrence

Amongst all elements of this group, carbon is the only one to occur in the elemental state as diamond and graphite. These are the two naturally occurring allotropic forms of carbon. As stated above, carbon, in the combined form, is an essential constituent of all living systems, you will study about such carbon compounds in courses on Organic Chemistry and Biochemistry. The inorganic carbonates of sodium, calcium and magnesium are widely distributed in the rocks, soil and water. Air contains about 0.03% of carbon dioxide. Coal and petroleum, which are called fossil fuels, because of their origin from the prehistoric plant and animal life, are mixtures of complex compounds of carbon with hydrogen containing small amounts of oxygen or sulphur.

Silicon is the second most abundant element in the earth's crust forming about 27.7%. Oxygen with its relative abundance of 46.6% ranks first. Silicates are present in the rocks. Clays are essentially alumino-silicates of Na or Ca. Common sand is an impure form of silica. Glass which is a mixture of silicates has been known since antiquity. Germanium is a rare element. It occurs in traces in coal, in rare mineral argyrodite, $4Ag_2S{\cdot}GeS_2$, in germanite, $Cu_3(Ge,Fe)S_4$, and as admixture in zinc and tin ores. Tin occurs mainly as cassiterite or tin stone, SnO_2 and lead as galena, PbS.

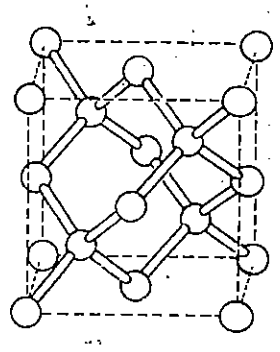


Fig. 7.1: Structure of diamond

Allotropy

Many elements exist in more than one form. These forms are called allotropes, and the phenomenon is called allotropy. The two common allotropic forms of carbon, viz., diamond and graphite are well-known. These are, in fact, giant macromolecules consisting of C atoms linked by a network of covalent bonds (Figs. 7.1 and 7.2). Each carbon in diamond is tetrahedrally bonded to four other carbons with a bond distance of 154 pm. Here you may note that SiC also has the same structure but the alternate atom in it is Si in place of carbon. In diamond, the strong covalent bonds formed within the giant macromolecule result in a structure which is without any mobile electrons and thus it behaves as an insulator. The rigid, three dimensional linkages make diamond one of the hardest substances known. In contrast to diamond, graphite is very soft because it has a two dimensional sheet structure with regular planar hexagons (Fig. 7.2). The bond length is 142 pm showing some multiple bond character, intermediate between a double and a single bond. Different layers are at a distance of 335 pm from each other and are thus held by weak van der Waals forces only. These layers can slide over one another easily, imparting softness to graphite. In graphite, each carbon forms three bonds with other carbon atoms leaving one electron which is delocalised over the whole planar structure. These delocalised electrons make graphite a good conductor of electricity. Metallic lustre can also be attributed to these delocalised electrons. Carbon exists in amorphous form also; for example, as lampblack.

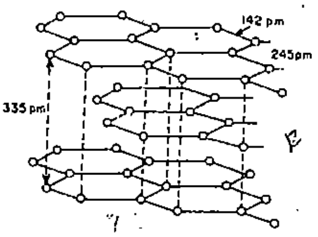


Fig. 7.2: Structure of graphite

Silicon and germanium exist only in one form, i.e., the diamond form. Tin shows polymorphism and exists in two crystalline forms: grey or α-tin, which is a semimetallic form, stable below 286 K, and white or β-tin, the stable metallic form, which is a good conductor of electricity. Grey tin has a diamond structure whereas the white tin has a tetragonal structure. Due to a close-packed lattice, density of β-tin, 7.31×10^3 kg m^{-3}, is considerably higher than that of α-tin, 5.75×10^3 kg m^{-3}. The two forms are interconvertible as shown in following equilibrium:

$$\text{Grey}\ (\alpha\text{-tin}) \xrightleftharpoons{286\ \text{K}} \text{White}\ (\beta\text{-tin}) \xrightleftharpoons{505\ \text{K}} \text{tin(liq)}$$

Tin has many peculiar properties. It is known to be able to cry. It produces a special characteristic sound when bent. Tin is sensitive to cold. In severe winter it turns grey, begins to crumble and breaks up into a powder. This serious disease is called Tin Plague. In fact, Napoleon's retreat from Russia has been attributed to this 'Tin Plague'

Lead, again, exists only in one crystalline form [illegible] distorted cubic close packed structure.

7.2.2 Extraction

As said above, diamond and graphite occur in nature. However, diamond can also be formed when carbon is subjected to high temperature and pressure. Moissan

In India, diamond mines are found in Panna district of Madhya Pradesh. Panna Mines have produced some famous diamonds like the kohinoor. This historic diamond weighs 186 carats. Weight of diamonds is usually quoted in carats:
1 carat = 0.200 g.

(1896) got artificial diamonds by quick quenching of a solution of carbon in iron. The sudden expansion of iron led to tremendous pressure which resulted in the separation of carbon in crystalline form. Though small in size, these artificial diamonds find many uses in industry. Artificial graphite can be manufactured on a large scale by heating coke with silica at ~ 2775 K for 25-35 hours.

$$SiO_2 + 3C \xrightarrow{-2CO} [SiC] \xrightarrow{2775\,K} Si(g) + C\,(\text{graphite})$$

Three other forms of carbon are manufactured on a large scale because of their vast industrial uses. These are coke, charcoal and carbon black or lampblack. The first two are formed by the destructive distillation or pyrolysis of coal and hardwood or bones in the absence of air. Carbon black is formed when petroleum gases or natural gas is burnt in a limited supply of air.

Destructive distillation is heating a substance to high temperatures in the absence of air and distilling off the volatile substances so formed.

Commercial form of silicon is obtained by reduction of SiO_2 with C or CaC_2 in an electric furnace. High purity silicon is obtained either from $SiCl_4$ or from $SiHCl_3$. These volatile compounds are purified by exhaustive fractional distillation and then reduced with very pure Zn or Mg. The resulting spongy Si is melted, grown into cylindrical single crystals, and then purified by zone refining. Ge is also obtained by the reduction of GeO_2 with C or H_2. Tin is obtained by the reduction of its oxide with carbon. Lead is normally obtained from PbS. The ore is roasted in air to give the oxide which is then mixed with coke and limestone and reduced in a blast furnace.

Zone refining, applied mainly to metals, is based on the principle that the solubility of an impurity B in a main component A in the solid state may differ from the solubility of B in A in the liquid state; when a narrow molten zone is made to pass (e.g., by movement of a heater outside a tube containing a long bar of the material) along a bar of impure A, the distribution of B between the solid and liquid material alters so that the impurity B tends to segregate towards one end of the bar, with pure material at the other end.

7.2.3 Uses

Diamonds are used in jewellery on account of their high refractive and dispersive power. Due to their exceptionally hard nature, inferior quality diamonds are used for industrial purposes mainly in the form of grit and powder in cutting, drilling, grinding and polishing tools. Graphite electrodes are used in the extraction of aluminium. Graphite is also used for making crucibles, as a lubricant in heavy machines and as pencil lead, etc. Very pure graphite is used as a neutron moderator in nuclear reactors. Coke is mainly used in metallurgy. Carbon black is used to strengthen rubber, as a pigment in inks, paints, paper and plastics. Activated carbon has enormous surface area and is used extensively in sugar industry as a decolorising agent. Amongst the compounds of carbon, CO_2 finds an important use as a fire extinguisher and in refrigeration as dry ice.

Moderator is the material used in a nuclear reactor to moderate or slow down neutrons from the high velocities at which they are created in the fission process.

Silicon finds uses in both elemental and combined forms. Very pure silicon is used in making semiconductors and in solar cells which are becoming increasingly important. Hyperfine Si is one of the purest materials used in the production of transistors. Silicates are used in glass and cement manufacture. Silicones (cf. sub-section 7.5.3) are also widely used as lubricants. Their inert nature makes them ideal for use in gas chromatography, e.g., methylphenyl silicones. Germanium is used largely in transistor technology. However, its use in optics is growing; germanium is transparent in infrared region and is, therefore, used in infrared windows, prisms and lenses.

Due to its resistance to corrosion, tin is used to coat mild steel plate. Tinning of copper and brass utensils has been an age old practice in India. Tin is also used for making various alloys like bronze, pewter, gun metal, etc. Tin-lead alloys are fusible and low melting. Solders, which are low melting alloys, are used to join pieces of metal together. Soldering is a very common practice for joining components of an integrated circuit. Sn-Pb alloys are also used as bearing metal or type metal. Lead is used as an inert material, e.g., for building roofs, and for cable sheathing. Lead gets covered with a layer of $PbSO_4$, which is insoluble and does not get attacked by common reagents. Lead pipes were used in municipal water supply at one time. Soft water, however, tends to dissolve lead and may cause lead poisoning. Therefore, galvanised iron (GI) pipes are now used for water supply. Due to their low chemical reactivity, lead coated chambers are used in many industrial preparations like that of sulphuric acid. In view of its high density, lead is also used in making shielding blocks for radioactivity experiments. Organolead compounds, e.g., tetraethyllead, Et_4Pb and tetramethyllead, Me_4Pb, are used as antiknock additives to petrol for internal combustion engines. However, in recent times, because of their polluting nature, many countries have reduced or altogether stopped their use. One of the major uses of lead still is in the storage batteries. Storage batteries also called lead-acid batteries have a supporting grid of lead-tin alloy (91:9) with PbO_2 as the oxidising agent and spongy Pb as the reducing agent. The electrolyte is dilute H_2SO_4.

SAQ 1

Tick √ on the correct answer.

Diamond is not a conductor of electricity because,

i) it is very hard in nature.
ii) it has a tetrahedral arrangement of atoms.
iii) it does not have a layer structure.
iv) it does not have delocalised electrons.

7.3 GENERAL CHARACTERISTICS

The outer shell electronic configuration of all the elements is given in Table 7.1. It shows that the elements of this group can attain a closed shell configuration by gain, loss or sharing of four electrons. Therefore, they may be expected to show a valency of four. Let us discuss their physical properties, chemical properties and some of their important compounds.

Table 7.1: Physical properties of Group 14 elements

	Elements				
Property	Carbon (C)	Silicon (Si)	Germanium (Ge)	Tin (Sn)	Lead (Pb)
Electronic configuration	$[He]2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]3d^{10}4s^2 4p^2$	$[Kr]4d^{10}5s^2 5p^2$	$[Xe]4f^{14}5d^{10}6s^2 6p^2$
Atomic number	6	14	32	50	82
Atomic weight	12.01	28.08	72.59	118.69	207.19
*Ionic radius (pm)	15 (+4) 260 (−4)	41 (+4) 271 (−4)	93 (+2) 53 (+4)	112 (+2) 71 (+4)	120 (+2) 84 (+4)
Covalent radius (pm)	77	117	122	140	154
Boiling point (K)	5100	2628	3103	2543	2017
Melting point (K)	3823	1683	1210	505	600
Density ($10^3 \times kg\ m^{-3}$)	2.22 (gr**) 3.51 (d**)	2.33	5.32	7.3	11.3
Electronegativity (A/R)	2.5	1.74	2.0	1.7	1.55
Ionisation energy I	1086	787	760	707	715
($kJ\ mol^{-1}$) II	2352	1577	1534	1409	1447
III	4619	3230	3308	2943	3087
IV	6220	4355	4409	3821	4081

* Oxidation states are given in brackets ** gr = graphite, d = diamond

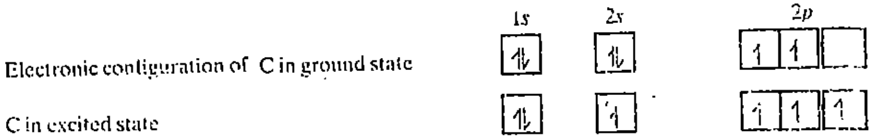
7.3.1 Physical Properties

You must have noticed in case of Group 13, that *p*-block elements show more than one stable oxidation state. The elements of Group 14 show oxidation states of +2 and +4, which are also the valencies shown by these elements, except carbon where oxidation state varies from −4 to +4. However, the valency and the stable oxidation state for a given element may not be the same. Valency, as you know, can be defined in terms of the number of electrons lost, gained or shared in bond formation. Oxidation state or oxidation number, on the other hand, is equal to the charge the atom would have if all the electrons in a covalent bond it forms were assigned to the more electronegative atom in the bond. Table 7.2 gives some simple rules to deduce the oxidation state.

Table 7.2 : Rules to deduce the oxidation state

Species	Oxidation state
Uncombined element	0
Combined O except peroxides	−2
Combined O in peroxides	−1
Combined H except hydrides	+1
Combined H in hydrides	−1
Alkali metals (Group 1)	+1
Alkaline earth metals (Group 2)	+2
Sum of all oxidation numbers in a neutral molecule	0

The ionisation energies (Table 7.1) indicate that a very large amount of energy is required to form a M^{4+} ion, therefore, not many ionic compounds are formed by Group 14 elements in the +4 oxidation state. On the other hand, the promotion of one of the *ns* electrons to the *np* vacant orbital, as shown below, can allow a tetracovalency. In fact, most of the tetravalent compounds formed by elements of this group are covalent in nature. Electronic configuration of carbon in the ground and excited state is given as an example.



4 unpaired electrons can form four equivalent covalent bonds – a case of sp^3 hybridisation.

Lead (IV) oxide converts hot HCl to Cl_2:
$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2 \uparrow$

It loses oxygen on heating to give lead (II) oxide :
$2PbO_2 \longrightarrow 2PbO + O_2$

As we go down the group, the stability of +4 oxidation state decreases, the heavier elements of the group have a tendency to change from +4 to +2 state. This is reflected in the oxidising power of their tetravalent compounds. For example, CO_2, SiO_2 and GeO_2 do not act as oxidants, SnO_2 is a mild oxidising agent while PbO_2 is a strong one. In fact, stannous salts are reducing agents. The tendency to form ionic compounds in the +2 oxidation state increases as we go down the group; PbF_2 and $PbCl_2$ are well defined ionic compounds.

The increasing stability of the divalent state down the group, especially in the case of lead compounds is attributed to the **"inert pair effect"**. This effect has been ascribed to an increase in the stability of ns^2 electrons in the ionic compounds. However, the higher stability of covalent compounds such as tetraalkyllead, R_4Pb, compared to the dialkyllead species, R_2Pb, points to the ready participation of the *s* pair electrons in covalently bonded tetravalent compounds of these elements.

Since the sum of the first two ionisation energies also decreases down the group, it becomes increasingly favourable thermodynamically, for Sn and Pb to form compounds in oxidation state +2 which are more ionic in character.

The covalent radii of the elements, as expected, increase with increase in atomic number. This increase, however, is not uniform. You may have noticed in Table 7.1, that when we move from carbon to silicon the covalent radius increases sharply, and then the increase is gradual. This can be explained as follows. A large increase in the size of silicon is due to the introduction of the 3rd shell. When we go down to germanium, the 4th shell is introduced, no doubt, but the effective nuclear charge resulting from addition of eighteen protons to the nucleus outbalances the effect of the additional shell leading to only a marginal increase in size. Similarly, in case of Pb, the increase in covalent radius is very small in comparison to that in Sn. This is further reflected in the ionisation energies and electron affinities of these elements.

Going through the data given in Table 7.1, you will notice that carbon has higher electronegativity as compared to other elements of the group. As a result, it can accept (gain) electrons and can form negative ions of the kind C_2^{2-} in acetylides and C^{4-} in methanides, while the other elements in the group are unable to do so. When we see the electronegativity trends in the group, we find that the value decreases down the group as expected, with Ge as an exception whose electronegativity is slightly higher than that of Si. As explained above, this could be due to the higher effective nuclear charge in case of Ge.

If we go through the data for ionisation energies given in Table 7.1, we find that the first and second ionisation energies decrease down the group from C to Sn as expected, but they increase slightly when we move to Pb. On the other hand, both the 3rd and the 4th ionisation energies vary irregularly, their sequence is C > Ge > Si > Pb > Sn.

The decrease in the 1st and 2nd ionisation energies from C to Sn is because of the increase in atomic size down the group. The 3rd and 4th ionisation energies increase from Si to Ge because of poor shielding of 4*s* electrons offered by the 3*d* electrons against the increased nuclear charge in Ge. All the ionisation energies are slightly higher in case of Pb. This increase can again be attributed to the poor shielding effect of the 4*f* and 5*d* orbital electrons. Further, the *s*-electrons being more penetrating, experience higher nuclear charge which makes it difficult to remove them.

SAQ 2

Making use of the rules given in Table 7.2, find out the oxidation state and valency of C in the following compounds:

CH_4, CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl.

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7.3.2 Multiple Bonding

In Group 14, carbon is the only element capable of forming comparatively stable multiple bonds with another C atom and also with N, O, etc. Examples are alkenes ($>C=C<$), alkynes($-C\equiv C-$), imines ($>C=N-$), nitriles ($-C\equiv N$), ketones ($>C=O$), etc. None of the other elements of the group forms stable compounds containing multiple bonds. Recently, some success has been achieved in synthesising compounds with $>Si=Si<$ and $>Si=C<$ double bonds, but their details are beyond the scope of this course. Stoichiometric analogues like SiO_2, SnO_2 and $(Me_2SiO)_n$ are known which are giant macromolecules containing M–O–M linkages.

The tendency of formation of multiple bonds easily, in case of carbon, is because of the high bond energy (Table 7.3) and a small atomic radius of carbon as compared to other elements of the group. So its *p*- orbitals can approach the *p*-orbitals of the other C, O or N atom for an effective overlap essential for π-bond formation.

A π bond is formed by the lateral overlap of two dumb-bell shaped orbitals, e.g., $p\pi$-bond can be represented as:

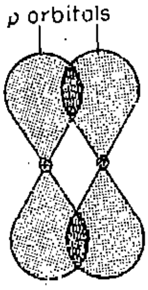

Table 7.3: Bond energies of Group 14 elements (kJ mol^{-1})

Bond	C	Si	Ge	Sn	Pb
E–E*	347	226	118	150	–
E=E	611	318	–	–	–
E≡E	837	–	–	–	–
E–H	414	318	285	251	–
E–O	360	464	360	–	–
E=O	736	640	–	–	–

*E=Element, C, Si, Ge, Sn or Pb.

pπ-dπ Bonding

You are familiar with a π bond formed by the lateral overlap of *p* orbitals. It is called a *pπ-pπ* bond. A lateral overlap of *p* and *d* orbitals under favourable conditions can also lead to the formation of a π bond. Such a π bond formation is called *pπ-dπ* bond. Let us understand this in case of C and Si compounds with nitrogen as the central atom, e.g., in trimethyl amine, $(CH_3)_3N$, and trisilyl amine, $(SiH_3)_3N$, (Fig. 7.3). From your previous knowledge of hybridisation and the corresponding structures formed, you understand that trimethylamine has a pyramidal structure. Nitrogen being sp^3 hybridised, the three methyl groups occupy three vertices of the pyramid and the 4th position is occupied by the lone pair on nitrogen. The structure of trisilyl amine, $(SiH_3)_3N$, is unexpectedly different. It has a trigonal planar structure with nitrogen in sp^2 hybridised state. The three silyl groups are at the three corners of the triangle and the p_z orbital of N which is perpendicular to the plane of the molecule is left with an electron pair. The arrangement of electrons of nitrogen in both the compounds can be shown as given below :

Electronic structure of N atom in $(CH_3)_3N$

$$\begin{array}{cc} 2s & 2p \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow} \end{array}$$

sp^3 hybridisation – tetrahedral structure, three unpaired electrons form bonds with three CH_3 groups; 3 bond pairs and 1 lone pair.

Electronic structure of N atom in $(SiH_3)_3N$

$$\begin{array}{cc} 2s & 2p \\ \boxed{\uparrow} & \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow\downarrow} \end{array}$$

sp^2 hybridisation – trigonal planar structure, three unpaired electrons form bonds with three SiH_3 groups, lone pair in p_z orbital.

In case of $(SiH_3)_3N$, the p_z orbital of N with a lone pair overlaps with the empty d-orbital of silicon and forms a π-bond. It may be noted that p_z orbital of N has energy comparable to d-orbital of Si. This kind of a π bond is called $p\pi$-$d\pi$ bond. Since donation of lone pair is within the molecule, this is called internal π-bonding. This type of bonding is possible to some extent in Ge but not in case of Sn and Pb. Since C does not have any d orbitals, therefore, it does not show this type of bonding. The $p\pi$-$d\pi$ overlap is indicated in the Fig. 7.3.

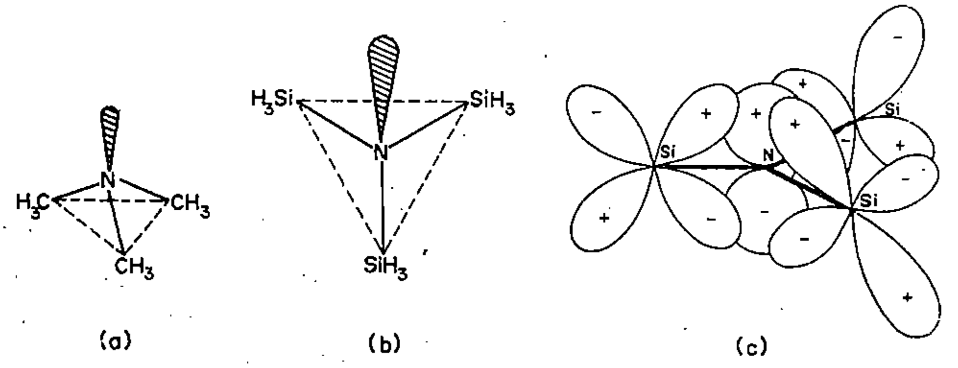

Fig. 7.3: a) structure of trimethylamine b) structure of trisilylamine c) $p\pi$-$d\pi$ bond between N and Si in trisilylamine

7.3.3 Catenation

Catenation is a property by virtue of which elements form long chain compounds by single or multiple bond formation between atoms of the same element. Carbon shows this tendency to a remarkable extent because of its small size and high bond energy (Tables 7.1 and 7.3), Si and Ge to a lesser extent and Sn and Pb to a very small extent. A few examples of their hydrides and halides can be cited here. In case of carbon we have alkanes, e.g., ethane, propane, butane, pentane, etc. These are chains of carbon hydrides having the general formula C_nH_{2n+2}, where n can be a large number, alkanes with n=100 are known. Carbon also forms a number of catenated halides, e.g., polyvinylchloride (PVC). Silicon forms silanes having the general formula Si_nH_{2n+2}, but n does not exceed 8. Its halides also show catenation and have a general formula Si_nX_{2n+2}, where if X=F, n=1–14; if X=Cl, Br or I, n=1–10. Germanium forms germanes, with general formula Ge_nH_{2n+2}, where n=1–9. Germanium halides form dimers, e.g., Ge_2Cl_6. Hydrides of Sn and Pb are much less stable, while SnH_4 and Sn_2H_6 have been prepared, analogous methods fail for the preparation of PbH_4. No catenated halides are known for Sn and Pb.

SAQ 3

Discuss briefly in the given space why tin and lead compounds do not show $p\pi$-$d\pi$ bonding.

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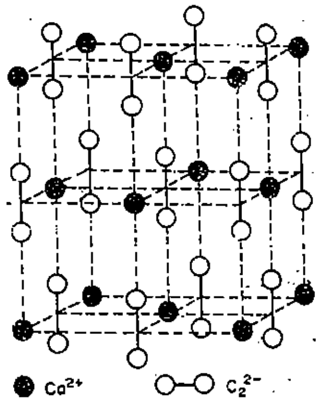


Fig. 7.4: Structure of ionic carbides

7.3.4 Chemical Properties

In general, the chemical reactivity of Group 14 elements increases down the group. Their chemical reactions are listed in Table 7.4, followed by a brief description of carbides, halides, fluorocarbons, hydrides and oxides.

Carbides

When carbon is linked to elements of lower or approximately the same electronegativity, the binary compounds so formed are termed as **carbides**, e.g., CaC_2, Al_4C_3, Be_2C, etc. However, compounds of carbon with hydrogen, oxygen, sulphur, phosphorus, nitrogen and halogens are excluded from this definition. Depending upon the bonding between the element and carbon, carbides are classified into three groups, viz., salt-like or ionic carbides, interstitial carbides and covalent carbides.

a) Salt-like or Ionic Carbides

Ionic carbides are formed by elements of Group 1, 2, 3, 11, 12 and 13 except boron. Most of these are colourless and non-conducting in the solid state. These carbides are decomposed by water and dilute acids liberating either acetylene or methane. They are named as acetylides and methanides, respectively.

$$\underset{\text{(Calcium acetylide)}}{CaC_2(s)} + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(s)$$

$$\underset{\text{(Aluminium methanide)}}{Al_4C_3(s)} + 12H_2O(l) \longrightarrow 3CH_4(g) + 4Al(OH)_3(s)$$

Most of the acetylides have cubic structure similar to the sodium chloride structure. One cell axis is, however, elongated to accommodate the $(C{\equiv}C)^{2-}$ ion making the symmetry of the crystal tetragonal and not cubic. In Fig. 7.4, you will observe that the coordination number of each ion is six.

Table 7.4: Some chemical reactions of Group 14 elements.

Reagent	Reaction	Remarks
Hot concentrated HCl	$M + 2HCl \longrightarrow MCl_2 + H_2$	M = Sn, and Pb, but not C, Si, Ge. Reaction with Pb is also slow because of insoluble $PbCl_2$ formed.
Hot concentrated H_2SO_4.	$M + 2H_2SO_4 \longrightarrow MO_2 + 2SO_2 + 2H_2O$ $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$	M = Pb, Sn; Ge (slow): not Si. In case of lead, insoluble $PbSO_4$ slows down the reaction.
Concentrated HNO_3	$3M + 4HNO_3 \longrightarrow 3MO_2 + 4NO + 2H_2O$ $3Pb + 2HNO_3 \longrightarrow 3PbO + 2NO + 4H_2O$	M ≠ Si, Pb. Ge and Sn give hydrated oxides. Fuming nitric acid renders lead passive.
HF	$Si + 6HF \longrightarrow 2H_2 + H_2SiF_6$	Only HF attacks Si, stability of SiF_6^{2-}.
Aqueous alkali	$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$	Not C, Ge, Pb; SiO_3^{2-} is formed fast. $Sn(OH)_6^{2-}$ is formed very slow.
Molten alkali		Not C, SiO_4^{4-}, GeO_4^{4-}, $Sn(OH)_6^{2-}$, $Pb(OH)_4^{2-}$ are formed.
O_2 or air, heat	$M + O_2 \longrightarrow MO_2$ $Pb \xrightarrow{O_2} PbO \xrightarrow{H_2O} Pb(OH)_2 \xrightarrow{CO_2}$ basic carbonate. molten $Pb + O_2 \longrightarrow PbO \xrightarrow[O_2]{743\,K} Pb_3O_4$	M = C, Si, Ge, Sn. Lead reacts slowly with cold, moist air.
H_2O, 293K	lead + soft water $\xrightarrow[O_2]{}$ $Pb(OH)_2$ lead + hard water $\xrightarrow[O_2]{}$ protective layer of insoluble $PbSO_4$ or $PbCO_3$	Poisonous.
Steam, heat (strongly)	$M + 2H_2O \longrightarrow MO_2 + 2H_2$ $C + H_2O \longrightarrow CO + H_2$	M = Sn, Si. Not Ge.
S, heat	$M + 2S \longrightarrow MS_2$	All except lead, which gives PbS.
Cl_2, heat	$M + 2Cl_2 \longrightarrow MCl_4$	All except lead which gives $PbCl_2$.
Metals, heat		Carbides and silicides, lead and tin alloys.

b) Interstitial Carbides

These are formed by combination of carbon with some transition metals like Ti, W, V, etc. These carbides resemble interstitial hydrides which you have studied in Unit 3. They are non-stoichiometric compounds. Carbon atoms are adjusted in the interstitial spaces of the metal lattices without causing any appreciable distortion. At the same time carbon atoms further stabilise the lattice, resulting in very high melting points, high conductivity and increased hardness of these carbides. The ability of carbon atoms to enter the interstices without appreciably distorting the metal lattice requires that the interstices and hence the metal atoms should be relatively large. Lattices of metals with atomic radius less than 130 pm get distorted, e.g., iron, cobalt and nickel do not form typical interstitial carbides. Their carbides are intermediate in properties between ionic and interstitial. The transition metals mentioned above have atomic radii 126, 125 and 125 pm, respectively.

c) Covalent Carbides

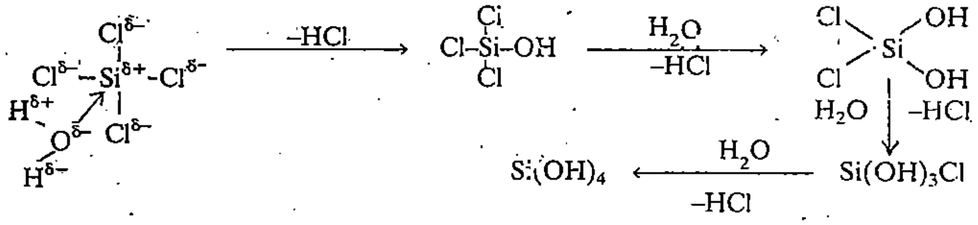
These are formed by combination of carbon with elements of almost equal electronegativity like boron and silicon. Silicon carbide, SiC, known as carborundum and boron carbide, $B_{12}C_3$ are giant macromolecules having covalent bonding all through. Both carbides are very hard, infusible and chemically stable substances. You have already studied the characteristics of $B_{12}C_3$. Boron carbide, is harder than silicon carbide and is used as an abrasive.) The structure of SiC, which is similar to that of diamond, is shown in Fig. 7.1.

Halides

All the elements of the group form dihalides (except carbon) and tetrahalides. All the four tetrahalides, namely, fluorides, chlorides, bromides and iodides are known for all the elements of the group, except $PbBr_4$ and PbI_4. The tetrahalides are volatile covalent compounds with tetrahedral structure. The mixed halides of carbon, i.e., chlorofluorocarbons form an important class of compounds, these are discussed after halides. The tetrahalides of carbon are relatively inert to hydrolysis while $SiCl_4$ gets readily hydrolysed to give silicic acid:

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

The tetrahalides of Ge are hydrolysed less readily, while in case of Sn and Pb halides, the reaction is often incomplete and can be suppressed on addition of appropriate halogen acid. The suggested mechanism for hydrolysis is the formation of a complex between the halide and water molecule. This complex dissociates to give the hydroxy compound. The process continues till the completely hydrolysed product is obtained. To form such a complex, the central atom in the tetrahalide has to extend its octet to accommodate the incoming water molecule. This requires the presence of *d*-orbitals. Since *d*-orbitals are not available in case of carbon, carbon halides are inert towards hydrolysis. A plausible mechanism for hydrolysis of $SiCl_4$ can be illustrated as given below:



Hydrolysis in the presence of alkali will be faster because of the stronger nucleophile, i.e., OH^-, now available. It may be mentioned that in acidic solutions, water gets protonated and thus does not remain an effective nucleophile.

The formation, stability and properties of the dihalides are discussed later in Section 7.6.

Fluorocarbons

Fluorocarbons are the synthetic equivalents of hydrocarbons in which some or all of the hydrogens have been replaced by fluorine atoms, e.g., CF_4, C_2F_4, C_2F_6, etc. Replacement of H by F greatly increases both the thermal stability and the chemical inertness because of the greater strength of the C–F bond and the larger size of the fluorine compared to hydrogen atoms. The bond energy of C–F bond is 489 kJ mol^{-1} compared with C–H bond energy of 414 kJ mol^{-1}. Fluorocarbons are resistant to attack by acids, alkalis, oxidising and reducing agents.

It is possible to synthesise a number of fluorocarbons and their derivatives by reacting hydrocarbons with fluorine either directly or in the presence of catalyst, or by using other fluorinating agents, like CoF_3, AgF_2 and MnF_3:

$$C_8H_{18} + 9F_2 \longrightarrow C_8F_{18} + 18HF$$
$$C_6H_6 + 6F_2 \xrightarrow{\text{Cu at 538 K}} C_6F_{12} + 12HF$$

Like hydrocarbons, fluorocarbons are capable of forming carbon chains of indefinite lengths. They are not oxidised by oxygen because carbon bonded to fluorine can be considered to be effectively oxidised. However, they are attacked by hot metals like molten sodium. On burning, they split at C–C bond rather than at C–F bond.

CF_4 is the simplest fluorocarbon. It is a colourless gas obtained by the reaction of carbon tetrachloride with silver fluoride at 575 K. Perfluoroethane, C_2F_6, is analogous to ethane, C_2H_6. Tetrafluoroethene, C_2F_4, can be polymerised thermally or in aqueous emulsions to a chemically inert plastic, polytetrafluoroethene (PTFE), commercially known as **Teflon.**

$$nC_2F_4 \xrightarrow[\text{heat}]{\text{pressure}} (-CF_2.CF_2-)_n$$

Teflon has an extremely low coefficient of friction. It is used as a protective coating in non-stick kitchen utensils, razor blades, bearings, etc. Mixed chlorofluorocarbons such as CCl_2F_2, $CFCl_3$ and CF_3Cl are known as '**Freons**'. They are volatile, thermally stable and chemically inert compounds with low viscosity. Therefore, they are used in refrigeration, in aerosol propellants and in heat transfer processes. $CF_3CHBrCl$ is a safe anaesthetic.

Hydrides

All the elements in the group form covalent hydrides. The stability of the hydrides decreases down the group, because of decreasing M–H bond energies (Table 7.3). Thus while CH_4 and other alkanes are stable compounds, PbH_4 has not even been properly characterised, so far. We have already discussed the catenation in hydrides of these elements.

The availability of *d*-orbitals coupled with lower bond energy of the M–H bond makes hydrolysis of the hydrides of heavier elements easier as compared to that of alkanes. For example, methane does not undergo hydrolysis at all due to non-availability of *d*-orbitals in C, but silanes do so in presence of dilute alkali. Hydrolysis of the hydrides of heavier elements follows a complicated pattern depending upon factors such as stability of the parent hydride to side-reactions, like oxidisability, etc.

Oxides

All the elements in the group form mainly mono and dioxides. The dioxides are all thermally stable except for PbO_2, the reason being an increase in stability of +2 oxidation state down the group (see sub-section 7.3.1). Acidic character of the dioxides decreases down the group; CO_2 and SiO_2 are acidic oxides, while GeO_2, SnO_2 and PbO_2 are amphoteric. Carbon is exceptional in forming gaseous mono and dioxides; CO and CO_2.

Carbon monoxide is obtained on passing steam over red hot coke. The product, a mixture of CO and H_2, is called **water gas** and is used as a fuel.

$$C(s) + H_2O(g) \longrightarrow \underbrace{CO(g) + H_2(g)}$$

The electronic structure of CO has been debated. The molecule is expected to show a large dipole moment because of the electronegativity difference between carbon and oxygen. But the molecule has only a small dipole moment of 0.112 D. The sign of the dipole moment has been found to be $C^{\delta-}–O^{\delta+}$ which is opposite to that expected in view of the higher electronegativity of oxygen as compared to carbon. To explain this, in addition to the normal double bond, oxygen is supposed to form a coordinate bond with C by donating and sharing its lone pair of electrons. As a result oxygen gets a partial positive charge on it decreasing the electronegativity difference. The valence bond structure is represented below. It may be mentioned that CO is the most stable diatomic molecule, with the highest bond energy of 1071 kJ mol^{-1}.

$${}^{\times}_{\times}C^{\times}_{\times}\underset{\leftarrow :}{:}O: \text{ usually written as } :C\overset{}{\underset{\leftarrow}{\equiv}}O \text{ or } {}^{-}C\equiv O^{+}$$

Carbon monoxide is a colourless and odourless gas. Because of its lack of smell, it is very dangerous. If inhaled it forms a very stable compound, carboxyhaemoglobin, with haemoglobin. Haemoglobin is the oxygen carrying protein in blood. Formation of carboxyhaemoglobin prevents it from acting as an oxygen carrier and death eventually occurs from asphyxia. Carbon monoxide has reducing properties. It is an important reducing agent, reducing metallic oxides to the metals at high temperatures forming carbon dioxide.

Carbon dioxide is the other important oxide of carbon. It is formed whenever carbon or any of its compounds is completely burnt in air. In the laboratory, the gas is made by the action of an acid on a carbonate. $CaCO_3$ in the form of marble chips is usually taken:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2\uparrow$$

CO_2 is a colourless gas with a faint smell. Its structure can be represented by O=C=O. It can be easily liquified by application of pressure even at the ordinary ambient temperatures. If liquid CO_2 is allowed to expand rapidly, solid CO_2 is obtained. Solid CO_2 is known as **dry ice**. When it is used as a refrigerant, it does not pass through the liquid phase (*cf.*, water). Solid carbon dioxide is also used as a freezing mixture in organic solvents like acetone or methanol.

Increase in the concentration of CO_2 in the atmosphere has recently been causing concern. Trapping of earth's thermal radiation by CO_2 can lead to a general warming up of the planet and expose it to the dangers of green house effect. Lowering of the pH of the surface ocean water can also have disastrous consequences for marine life.

Carbon dioxide is an acidic oxide which forms carbonates and bicarbonates with bases:

$$NaOH(aq) + CO_2 \longrightarrow NaHCO_3(aq)$$

$$2NaOH(aq) + CO_2 \longrightarrow Na_2CO_3(aq) + H_2O$$

In presence of sunlight and chlorophyll, plants are able to synthesise carbohydrates from water and carbon dioxide. You have read about this process called photosynthesis in Unit 5. Being a non-supporter of combustion, CO_2 is used in fire extinguishers.

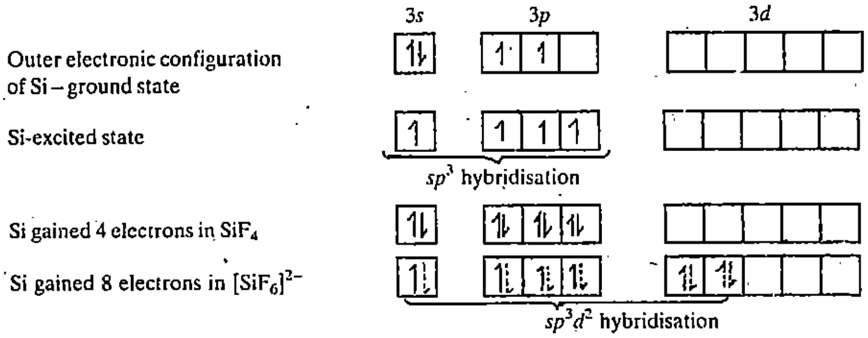
Silicon forms an important acidic oxide, silicon dioxide discussed in detail in Section 7.5 and an unstable monoxide, SiO. Germanium and tin form amphoteric oxides. GeO_2 is mainly acidic, while SnO and SnO_2 are amphoteric in nature, dissolving both in alkalies and acids. As explained in sub-section 7.3.1, PbO_2 being unstable behaves as an oxidant; the lower oxide, PbO, is quite stable. If PbO is carefully heated in air to a temperature between 675 and 750 K, it is converted into trilead tetraoxide, Pb_3O_4 or $2PbO{\cdot}PbO_2$, also called 'red lead':

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$

Red lead is used as a pigment in paints and in the manufacture of crystal glass.

7.3.5 Complex Formation

Carbon, can have a maximum coordination number of four, since, after gaining four electrons, it attains a stable noble gas configuration with 8 electrons in the outer shell. Therefore, carbon compounds do not form complexes. Other elements of the group also acquire a noble gas configuration in a similar manner but even then they have empty *d*-orbitals available for bonding. Therefore, they can form complexes by expanding the coordination number to six or even eight in the case of heavier elements. This can be shown taking Si as an example:



It can be assumed that the four singly filled hybrid orbitals are used in forming covalent bonds with four F atoms. The two vacant hybrid orbitals are utilised in forming coordinate bonds by accepting a pair of electrons each from the two F^- ions. However, once the complex is formed all the bonds become equivalent.

The tetravalent compounds of the heavier elements function as Lewis acids and are able to accept electron pairs from bases. This is possible because of the availability of *d* orbitals, e.g.,

$$GeF_4 + 2NMe_3 \longrightarrow [GeF_4{\cdot}(NMe_3)_2]$$

$$SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$$

SAQ 4

a) Why is C–H bond essentially non-polar? Explain in the space given below.

....

....

....

b) Using the concept of hybridisation, predict the shape of $[SiF_6]^{2-}$ ion

....

....

....

....

7.4 ANOMALOUS BEHAVIOUR OF CARBON

We have discussed in the earlier sections how and in what ways carbon behaves differently from the rest of the elements in the group; the reasons have also been discussed. Let us list all of them here:

- Carbon has a maximum covalency of 4 and is not able to form complex compounds.
- Carbon is the only element in the group to form stable derivatives with double and triple bonds, which show special characteristics.
- Carbon forms gaseous oxides, i.e., CO and CO_2 whereas others form solid oxides.
- Carbon has a much higher electronegativity and higher ionisation energy than other elements in the group.
- Carbon has a unique capacity of catenation and forms a very large number of stable compounds, with long chains or rings of carbon atoms, which can occur in many isomeric forms.
- Carbon forms stronger bonds not only with itself but also with elements like halogens, oxygen, nitrogen and sulphur than any other element in the group.

7.5 SILICA AND SILICATES

The earth's crust is largely composed of silica and silicates, which are the principal constituents of all rocks and the sands, clays and soils that are the breakdown products of rocks. Most inorganic building materials are based on silicate minerals. These include natural silicates such as sandstone, granite and slate, and manufactured materials such as cement, concrete and ordinary glass. Some of the properties and mportant uses of silica and silicates are described below.

7.5.1 Silica

ilicon dioxide, SiO_2, is commonly known as silica. Its amorphous as well as crystalline forms are known. Flint is the amorphous form of silica. The crystalline orms are quartz, tridymite and cristobalite which have different structures. Quartz the purest and the most stable form of silica. It is a colourless solid having a specific density of 2.65 and is also called **rock crystal.** Each crystalline form can exist in two odifications, one stable at lower temperatures while the other at high temperatures. hese forms can be interconverted with change in temperature.

Quartz gets coloured due to the presence of some impurities and is prized as a gemstone, e.g., amethyst which is purple.

On hydrolysis of silicon tetrachloride, silicic acid is obtained which on drying and gnition gives silica as a fine white powder.

$$SiCl_4 + 4H_2O \xrightarrow{-4HCl} Si(OH)_4 \xrightarrow{-2H_2O} SiO_2$$

Silica is insoluble in water and acids except hydrofluoric acid with which it forms volatile silicon tetrafluoride, SiF_4. When passed in water, SiF_4 is hydrolysed to give soluble H_2SiF_6 and silicic acid as an insoluble white solid:

$$\begin{array}{lcl} SiF_4 + 4H_2O & \longrightarrow & Si(OH)_4 + 4HF \\ 2SiF_4 + 4HF & \longrightarrow & 2H_2SiF_6 \\ \hline 3SiF_4 + 4H_2O & \longrightarrow & 2H_2SiF_6 + Si(OH)_4 \downarrow \end{array}$$

These reactions are used in analytical chemistry.

Silica is acidic in nature and gives silicates when fused with alkalies.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

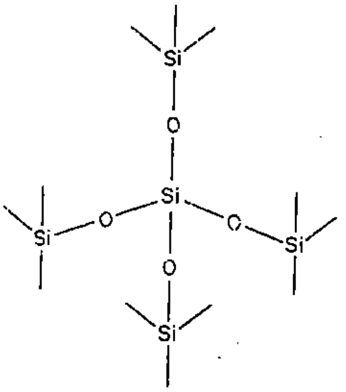


Fig. 7.5: Structure of Silicon dioxide.

SiO_2 differs from CO_2 in an important respect that it is a solid at room temperature whereas CO_2 is a gas. You know that CO_2 is a simple linear molecule in which carbon is attached to two oxygen atoms by means of two double bonds. On the other hand, SiO_2 forms a giant or macromolecular structure in which each silicon atom is surrounded tetrahedrally by four covalently bonded oxygen atoms and each oxygen, in turn, is bonded to two silicon atoms (Fig. 7.5). However, the overall stoichiometry or the silicon-oxygen ratio remains the same, i.e. SiO_2.

Silica is the chief constituent of glass. **Silica gel** is an amorphous form of SiO_2 with a porous structure. It is used as a dehydrating agent as well as a catalyst. Silica gel is being increasingly used as an adsorbent in chromatography.

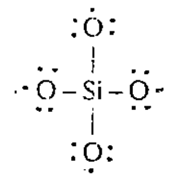
Silica when fused with sodium carbonate gives sodium silicate (water glass):

$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$$

7.5.2 Silicates

Silicates are regarded as the salts of silicic acid, H_4SiO_4. All the silicates are comprised of SiO_4 units. These units have a tetrahedral structure formed as a result of sp^3 hybridisation (cf. SiF_4, Sub-sec. 7.3.5). Since 4 valence electrons from silicon and 6 valence electrons from each oxygen are insufficient to complete the octet of all the atoms, therefore, oxygens acquire electrons from other atoms and become negatively charged to produce discrete anion $[SiO_4]^{4-}$. This can be made clear by writing the electronic formula as given below:

Silicon atom has its octet completed but each oxygen atom is still short of one electron to complete its octet. As said above, they can complete their octet by taking up 4 electrons from a metal, getting converted to an anion $[SiO_4]^{4-}$



The $[SiO_4]^{4-}$ tetrahedra can be represented in three ways as shown in Fig. 7.6. One silicate differs from the other only in the manner in which the units are linked together. The simple silicates are salts of orthosilicic acid, H_4SiO_4, and contain the orthosilicate ion, $[SiO_4]^{4-}$, e.g., $Zr^{4+}SiO_4^{4-}$.

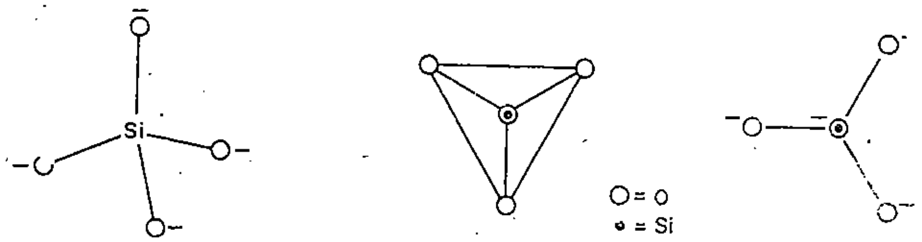


Fig. 7.6: Representations of SiO_4^{4-} tetrahedra.

In some silicates, the oxygen atoms of SiO_4 units tend to complete their octet by sharing electrons with other silicon atoms, the oxygen atoms, thus, form bridges of the type Si–O–Si to other silicon atoms. The number of such bridges can vary from one to four. This leads to the formation of complex silicates. Any oxygen which fails to pick up electrons from the other silicon atom is not able to complete its octet. The resulting silicate chains are, therefore, negatively charged anions. The metal cations generally present in silicate minerals are Li^+, Na^+, K^+, Ca^{2+}, Al^{3+}, etc. Depending upon the way these SiO_4 units are linked, silicates of different structure and complexity are obtained. Some representative types are given in Fig. 7.7.

In addition to the types where linkages between SiO_4 units are two-dimensional, complex silicates result from three dimensional linkages between SiO_4 tetrahedra.

Silicate industry is a very important industry and it plays an important role in national economy. From these mineral silicates, glass, ceramics, cement, etc. are manufactured. Let us study, in brief the uses of some mineral silicates.

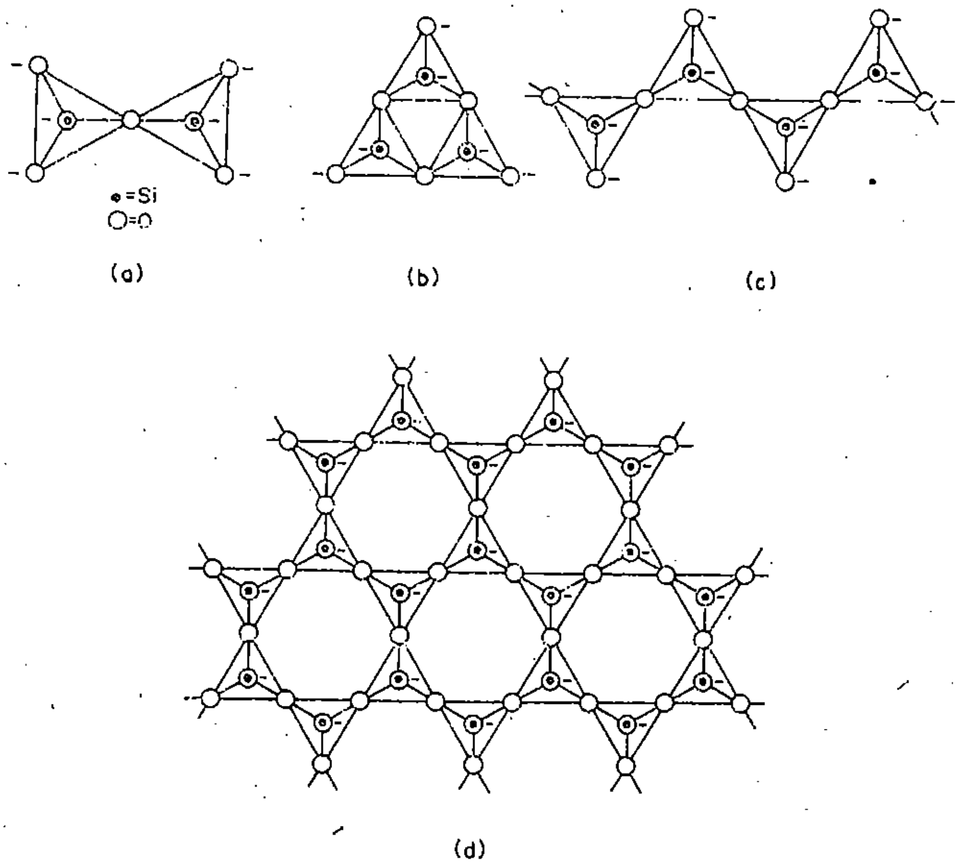


Fig. 7.7: Structure of (a) Pyrosilicates, e.g., Thortveitite, $Sc_2Si_2O_7$

(b) Cyclic silicates, e.g., Wollastonite, $Ca_2(Si_3O_9)$

(c) Chain silicates, e.g., Spodumene, LiAl $(SiO_3)_2$

(d) Sheet Silicates, e.g., Talc, $Mg_3(OH)_2(Si_2O_5)_2$

Mica

Micas are layer structured silicates. They have toughness, elasticity, transparency, high dielectric strength, chemical inertness and thermal stability up to 775 K. Therefore, mica sheets are used for furnace windows, for electrical insulation and in vacuum tubes.

In some silicates, Si^{4+} ion in the lattice is replaced by Al^{3+} ion. Aluminosilicates resulting from this isomorphous replacement have negatively charged macro anions. Micas and Zeolites are some of the common aluminosilicates.

Asbestos

Asbestos are fibrous silicates. They have high tensile strength, great flexibility, resistance both to heat and flame and also to corrosion by acids or alkalies and are low cost materials. Asbestos is used as a thermal insulator for lagging steam pipes, for making fire proof textiles and as an insulator. Prolonged exposure to airborne suspensions of asbestos fibre dust can be very dangerous and there has been increasing concern at the incidence of asbestosis.

Clay

Clays are essential components of soils, formed by weathering and decomposition of igneous rocks. When mixed with water, clays become soft, plastic and mouldable. Clays have been used since times immemorial for pottery and for making bricks, tiles, etc. Some clays like fuller's earth have high adsorptive capacity and marked cation exchange properties. They are extensively used as oil and grease absorbents in petroleum industry. Talc is valued for its softness, smoothness, dry lubricating properties and chemical inertness. Its whiteness makes it suitable for use in cosmetic and toilet preparations as well as in ceramics and paper industry.

Cement

The basic raw materials for cement manufacture are lime, silica and alumina. Portland cement is obtained by calcining a suitable mixture of limestone and clayey material and adding small amounts of gypsum and powdering the mixture. This powdered mixture hardens into a solid mass on reacting with water and gives a water resistant product. Cement slurry alone or mixed with sand or concrete can be made to set in any desired shape. This property makes it an excellent building material.

Zeolites

Zeolites, also called Permutits, are sodium aluminosilicates used in softening of water. These are used as cation exchangers and remove the Ca^{2+} and Mg^{2+} ions from hard water.

Zeolites are also aluminosilicates with open pore structure and contain equal number of anions and cations.

$$Na_2Z + Ca^{2+} \longrightarrow CaZ + 2Na^+ \text{ (Water softening)}$$
$$CaZ + 2Na^+ \longrightarrow Na_2Z + Ca^{2+} \text{ (recharging or regenerating)}$$

The calcium and magnesium salts of permutit can be converted back into the sodium salt by treatment with a concentrated solution of sodium chloride.

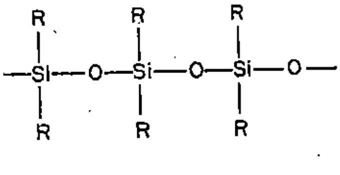
Glass

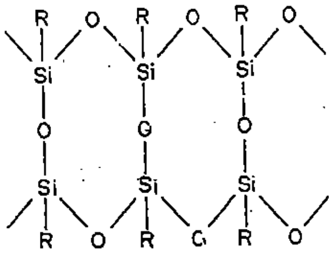
When a mixture of silicates mainly of sodium and calcium is melted and then supercooled, i.e. cooled immediately to a low temperature, a transparent solid is obtained which is called **glass**. There are different varieties of glass but most of them are a mixture of either only different silicates or mixture of borates and silicates. Borates make glass heat resistant. Borate glasses like Borosil are used for making laboratory and kitchen ware. Lead glasses have a very high refractive power and are used for making optical components like lenses, prisms, etc. Sodium glasses are soft, replacement of sodium by potassium makes glass hard. Introduction of a suitable amount of different coloured metallic oxides makes the glass coloured. Metallic oxides used are Cu_2O, Fe_2O_3, U_3O_8, MnO_2, NiO, Co_2O_3, etc. giving red, green, yellow, violet, black and blue colours to the glass, respectively.

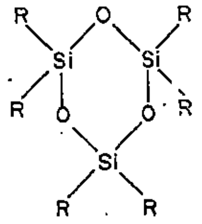
The method of melting glass was discovered about 5.000 B.C. in Egypt or Mesopotamia probably by some potters when they were firing their pots. The first articles of glass were probably the glass beads.

7.5.3 Silicones

Silicones are a group of organosilicon polymers. Unlike $SiCl_4$ which on complete hydrolysis gives SiO_2, alkylsubstituted chlorosilanes on hydrolysis do not give the expected silicon compound analogous to ketone but get hydrolysed to long chain polymers or silicones. While the hydrolysis of trialkylmonochlorosilane yields hexalkyldisiloxane, the alkyldichlorosilane gives straight chain polymers with active hydroxyl groups at each end of the chain and trichlorosilane gives complex cross-linked polymers. The chain size is limited by the size of alkyl group and the amount of cross-linking is regulated by the relative amounts of di- and tri-methyl-chlorosilanes. Thus silicones with desired properties can be obtained as oils, greases or rubbers. They are chemically inert, heat resistant upto ~500 K, water repellent, good electrical insulators and show little viscocity change with temperature. They are used as lubricants, insulators, protective coating and heating oils.


Linear silicone polymer


Cross linked silicone polymer


Cyclic silicone

SAQ 5

Which silicon compound is used as a:

i) dehydrating agent

ii) cation exchanger

iii) lubricant

iv) thermal insulator

7.6 CHEMISTRY OF DIVALENT SILICON, GERMANIUM, TIN AND LEAD COMPOUNDS

The trend in Group 14 is in keeping with the general trend in *p* block elements that the lower oxidation state becomes more stable as we go down the group. In other words, the stability of oxidation state IV decreases and that of oxidation state II increases on going from silicon to lead. This is reflected in a decrease in the reducing property of the +2 state and an increase in the oxidising property of +4 state. Ge(II) is a strong reducing agent, Sn(II) is a mild reducing agent and Pb(II) is not a reducing agent. On the other hand Ge(IV) has no oxidising property. Sn(IV) is a mild oxidant and Pb(IV) is a strong oxidant. Reasons for this we have already discussed in Sec.

7.3. However, you remember that divalent lead compounds are predominantly ionic while tetravalent lead compounds are covalent. Vapours of tin and lead halides have been shown to contain monomers, MX_2. This is expected since both metals are weakly electropositive, tin less than lead. $SnCl_2$ is, in fact, soluble in organic solvents and does not conduct electricity in the molten state, whereas $PbCl_2$ is only sparingly soluble in alcohol and molten $PbCl_2$ is a good conductor. Thus $SnCl_2$ is best regarded as covalent and $PbCl_2$ mainly as ionic. The following brief discussion about divalent compounds of these elements highlights the trends indicated above.

Divalent silicon compounds are thermodynamically unstable under normal conditions. But, some SiX_2 compounds have been formed in high temperature reactions and have been trapped by rapid chilling to liquid nitrogen temperature.

Divalent germanium halides are stable. When anhydrous HF is passed over germanium metal at 475 K, GeF_2 is formed. It is polymeric having fluorine bridges. Other dihalides are less stable than the fluoride and can be prepared by reacting the corresponding tetrahalide with germanium.

$$GeX_4 + Ge \longrightarrow 2GeX_2$$

GeF_2 and $GeCl_2$ react exothermically with solutions of alkali metal halides to give the hydrolytically stable GeX_3^- ion.

Divalent tin halides, SnF_2 and $SnCl_2$, are important compounds. When Sn is heated with gaseous HF or HCl, SnF_2 or $SnCl_2$ is obtained. SnF_2 is less soluble in water. $SnCl_2$ hydrolyses in water to the basic chloride. However, if a slightly acidic solution of $SnCl_2$ is taken, $SnCl_2 \cdot 2H_2O$ crystallises out. It is soluble in organic solvents, which shows its covalent nature. Despite their covalent nature, in aqueous halide solutions, SnF_2 and $SnCl_2$, like the corresponding germanium halides, give complex ions, $[SnX_3]^-$. Divalent tin halides act as Lewis acids and form adducts with donor solvents, such as acetone, pyridine, etc.

In the presence of air or oxygen, Sn(II) compounds are oxidised to Sn(IV). Stannous chloride is used as a mild reducing agent. It reduces ferric salts to ferrous, cupric to cuprous, chromates to chromic salts, and mercury, gold and silver salts to the metals, e.g.,

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$
$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$

Stannous fluoride is used in tooth pastes as a source of fluoride ions to harden dental enamel. Stannous chloride is widely used as a mild reducing agent and as a mordant in calico printing.

Divalent Lead : Of the four elements, only lead forms stable, well defined ionic compounds in the divalent state. The oxide, PbO has two forms. The red one is called litharge and the yellow one massicot. The halides unlike those of tin are always anhydrous. Except acetate and nitrate, lead(II) salts are generally insoluble in water giving characteristic properties and are thus used for characterisation of many anions like halides, sulphates, chromates, etc. All lead(II) salts are poisonous.

SAQ 6

Categorise the following compounds into oxidising and reducing agents:
CO, GeO, PbO_2, $SnCl_2$ and $PbCl_4$

7.7 SUMMARY

Let us recollect what we have studied in Unit 7 about different aspects of the elements of carbon family. The members of this family, carbon, silicon, germanium, tin and lead have been studied from the points of view of the trends in physical and chemical properties:

- An increase in tendency of ionic bond formation and covalent radii of the elements has been observed down the group.

- Electronegativity and ionisation energies show a decrease on moving from carbon to lead. Heavier elements in the group show metallic character also. Going down the group, the lower oxidation state, +2, becomes more stable. Silicon compounds are supposed to have internal π–bonding.
- Allotropic forms of carbon and tin have been described.
- Carbon is unique in having the important property of catenation. It also possesses the ability to form multiple bonds. This ability is responsible for the formation of a large number of carbon compounds. Carbon forms a number of binary compounds called carbides. It forms fluorocarbons which find a number of uses in industry.
- Tin and lead are closely related elements. They can be tetravalent forming covalent compounds such as hydrides and tetrahalides. They can also be divalent forming compounds containing the ions Sn^{2+} and Pb^{2+}. Sn and Pb show inert pair effect. Both of them find their uses as alloys and in metal coating.
- Different types of silicates and their structures have also been discussed. Silicates, in Permutit and glass have special importance industrially. Structures and some important uses of organosilicon compounds or silicones have been described.

7.8 TERMINAL QUESTIONS

1 Diamond and graphite both are allotropic forms of carbon; still only graphite is used as a lubricant. Why?

2 What are the properties responsible for the anomalous behaviour of carbon?

3 Why are tin and lead incapable of showing the property of catenation?

4 Why is trisilylamine a very weak and trimethylamine a good Lewis base?

5 Give reactions to show that CO_2 is an acidic oxide and SnO_2 is an amphoteric oxide.

6 Explain the following briefly :

i) SiC is as hard as diamond.

ii) CCl_4 is not hydrolysed while $SiCl_4$ or $SnCl_4$ get hydrolysed easily.

iii) $PbBr_4$ and PbI_4 do not exist.

iv) SiO_2 is a solid whereas CO_2 is a gas.

7.9 ANSWERS

Self Assessment Questions

1 iv

2

Compound	Oxidation state
CH_4	−4
CCl_4	+4
$CHCl_3$	+2
CH_2Cl_2	0
CH_3Cl	−2

3 Tin and lead do not show $p\pi$–$d\pi$ bonding because the *d* orbitals of Sn and Pb are of much higher energy than that of the element with which they form a bond in the compound.

4 a) The ionic character (polarity) of a bond depends upon the difference in electronegativity of the elements involved. The electronegativities of carbon and hydrogen (C = 2.5 and H = 2.1) are quite close, as a result they form essentially non-polar bonds.

b) $[SiF_6]^{2-}$ will have an octahedral structure (see sub-sec. 7.3.5).

5 i) Silica gel

ii) Zeolites

iii) Silicones

iv) Asbestos

6 Oxidising agents: $PbCl_4$ and PbO_2

Reducing agents: CO, GeO and $SnCl_2$

Terminal Questions

1 Graphite has a sheet structure where the carbon atoms are arranged in layers. The two layers are bonded by weak van der Waals forces, and can slide over each other. This gives graphite softness and makes it useful as a lubricant, while the tetrahedral geometry of diamond makes it very hard.

2 Small size, very high electronegativity and high ionisation energy are some of the main properties of carbon which lead to its anomalous behaviour in the group.

3 The bond between two Sn or two Pb atoms is not strong enough (Table 7.3). Therefore Sn_2 or Pb_2 are not formed and they do not show the property of catenation.

4 A Lewis base is the one which can donate a pair of electrons. You read in the case of trisilylamine, the orbital containing the lone pair of N overlaps with the empty *d* orbital of Si to form a $p\pi$–$d\pi$ bond. The lone pair thus becomes unavailable for donation. While in case of trimethyl amine, which has a pyramidal structure, the 4th position of the pyramid is occupied by the lone pair of N. This lone pair is easily available for donation and makes trimethylamine a good Lewis base.

5 CO_2 reacts with a base as shown by the following reaction:

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

The following reactions show the amphoteric nature of SnO_2:

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

6 i) **Hint :** Structure of SiC is similar to that of diamond.

ii) Participation of *d* orbitals is responsible for the hydrolysis of $SiCl_4$ and $SnCl_4$. This is not possible in CCl_4 due to non-availability of *d*-orbitals.

iii) Low stability of +4 state in case of Pb and large sizes of Br and I make $PbBr_4$ and PbI_4 very unstable.

iv) In CO_2, a carbon atom is bound to two oxygen atoms through double bonds. The interaction between different molecules of CO_2 is weak van dar Waals type. Therefore, CO_2 is gaseous in nature. On the other hand, in case of SiO_2 Si and O are bound to each other in long chains which are further cross-linked to give a three dimensional structure. The structure leads to a solid form.

UNIT 8 ELEMENTS OF GROUP 15

Structure

8.1 Introduction
  Objectives
8.2 Occurrence, Extraction and Uses
8.3 General Characteristics
  Physical Properties
  Allotropic Forms of Phosphorus
  Chemical Properties
8.4 Hydrides
  Ammonia
  Hydrazine
  Hydrazoic Acid HN_3, and Azides
  Phosphine
  Arsine, Stibine and Bismuthine
8.5 Halides
  Trihalides
  Pentahalides
8.6 Oxides
  Oxides of Nitrogen
  Oxides of Phosphorus, Arsenic, Antimony and Bismuth
8.7 Oxoacids of Nitrogen, Phosphorus, Arsenic and Antimony
  Oxoacids of Nitrogen
  Oxoacids of Phosphorus, Arsenic and Antimony
8.8 Nitrogen Cycle, Nitrogen Fixation and Phosphate Fertilisers
  Nitrogen Cycle
  Nitrogen Fixation
  Phosphate Fertilisers
8.9 Anomalous Behaviour of Nitrogen
8.10 Summary
8.11 Terminal Questions
8.12 Answers

8.1 INTRODUCTION

We now extend our study to another group of the periodic table, namely, Group 15 consisting of nitrogen, phosphorus, arsenic, antimony and bismuth. Like the preceding groups, elements of this group also exhibit regular gradation in the physical and chemical properties. Nitrogen and phosphorus are distinctly non-metallic, arsenic and antimony are metalloids, while in bismuth metallic characteristics predominate. The first element in the group, nitrogen shows some exceptional behaviour. We will briefly discuss the chemistry of these elements and some of their important compounds in this unit.

Objectives

After studying this unit you should be able to :

- describe the occurrence, extraction and uses of the Group 15 elements,
- discuss the general characteristics of the Group 15 elements,
- discuss the properties of hydrides, halides, oxides and oxoacids formed by these elements,
- explain how nitrogen-nitrate balance is maintained through nitrogen cycle,
- explain how atmospheric nitrogen is fixed,
- describe the use of phosphorus in fertilisers, and
- list the differences of nitrogen from rest of the Group 15 elements.

8.2 OCCURRENCE, EXTRACTION AND USES

Group 15 of the periodic table contains some very important elements. Nitrogen is a major component of the earth's atmosphere. Both nitrogen and phosphorus are essential constituents of all plant and animal tissues. They are also put to a variety of uses as elements and in the form of their compounds. Let us see, how these elements occur in nature and how they are extracted from their natural sources.

8.2.1 Occurrence

Nitrogen is the most abundant uncombined element accessible to man. It comprises 78.1% of the atmosphere by volume. Despite its readily availability in the atmosphere, nitrogen is relatively less abundant (1.9×10^{-3}%) in the crustal rocks and soils of earth. A few major minerals are saltpetre, KNO_3 and Chile saltpetre, $NaNO_3$. Phosphorus is the eleventh element in order of abundance in the crustal rocks of the earth, its occurrence being to the extent of 0.112%. All its known terrestrial minerals are orthophosphates. The major minerals of the phosphate family are the apatites, $Ca_5(PO_4)_3X$ and the common members are fluorapatite, $Ca_5(PO_4)_3F$, chlorapatite, $Ca_5(PO_4)_3Cl$ and hydroxyapatite, $Ca_5(PO_4)_3OH$. In addition, there are vast deposits of amorphous phosphate rock, phosphorite, $Ca_3(PO_4)_2$. As we have said above, both nitrogen and phosphorus occur in all living beings. They are present in the proteins and in the genetic material deoxyribonucleic acid or DNA. Phosphorus as $Ca_3(PO_4)_2$ is also present in bones and teeth. Arsenic, antimony and bismuth are comparatively less abundant in the earth's crust, their abundances being 1.8×10^{-4}%, 2.0×10^{-5}% and 8.0×10^{-8}%, respectively. They mostly occur as sulphides.

8.2.2 Extraction

Nitrogen is obtained commercially from air. Initially air is cooled to remove water vapour and carbon dioxide and then it is repeatedly compressed to about 2×10^4 kPa and allowed to expand rapidly. This causes the temperature to fall and eventually, the air liquefies. Fractional distillation of liquid air enables separation of nitrogen, oxygen and the noble gases.

Phosphorus is extracted from the phosphate rock by heating it with sand and coke in an electric furnace (Fig. 8.1) at a temperature of about 1800 K. The nonvolatile silicon dioxide displaces the more volatile phosphorus pentoxide which is then reduced by coke.

$$2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + 10C \longrightarrow P_4 + 10CO$$

Arsenic, antimony and bismuth can be obtained from their sulphide ores. The ore is roasted in air to convert the sulphide to the oxide which is then reduced by heating with coke.

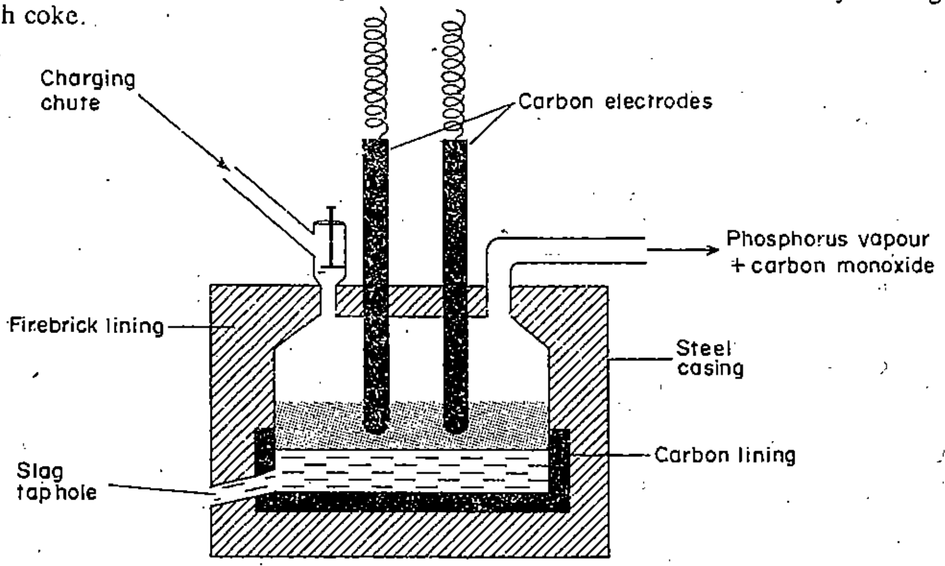


Fig. 8.1 : Electric furnace for extracting phosphorus

8.2.3 Uses

The main use of elemental nitrogen is to create an inert atmosphere in the iron and steel industry and in many other metallurgical and chemical processes where the presence of air would involve fire, explosion hazards or undesirable oxidation products. It is also used in the packaging of processed foods and pharmaceuticals and to pressurise electric cables, telephone wires and rubber tyres, etc. Liquid nitrogen is also frequently used for freezing of foodstuffs, freeze grinding of normally soft and rubbery materials like meat, preservation of biological specimens and for in-transit refrigeration.

Red phosphorus is used in matches, fire works and as a component of phosphor-bronze alloys used for making bearings. The main use of elemental arsenic, antimony and bismuth is in the production of various alloys.

Besides the use of elemental nitrogen, compounds of nitrogen have extensive applications in various fields. Ammonia is used in various forms as a fertiliser, e.g., as NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, etc. Its applications also include refrigeration, as a pH controller in food and beverage industry, pharmaceuticals and in water purification. Nitric acid is another important compound of nitrogen. Its major uses include manufacture of NH_4NO_3, explosives like nitroglycerine, nitrocellulose and TNT. Hydrazine, N_2H_4 and its methyl derivatives, $MeNHNH_2$ and Me_2NNH_2, are used as rocket fuels. Nitrous oxide, N_2O, is used as an anaesthetic.

Sulphides of phosphorus, P_4S_3 and P_4S_{10} are used in match industry. Phosphoric acid is used in fertilisers, cleaning of metals, rust proofing, pharmaceuticals, etc. Disodium hydrogen phosphate, Na_2HPO_4, is widely used as an emulsifier in the manufacture of pasteurised cheese. Sodium dihydrogen phosphate, NaH_2PO_4, is used as a constituent in the undercoat for metal paints. Calcium phosphates are used in baking powders and tooth-pastes. Synthetic $Ca_5(PO_4)_3OH$ (1 – 2%) is added to table salt to impart free flowing properties. Sodium tripolyphosphate, $Na_5P_3O_{10}$, is used in detergents and in softening water. Phosphorus compounds like malathion, parathion, etc., are used as pesticides.

Arsenic compounds find extensive use in agriculture as herbicides for weed and pest control, e.g., monosodium methyl arsenate, MSMA and disodium methyl arsenate, DSMA. Arsenic acid is used as a wood preservative. Sodium arsenite is used for aquatic weed control. Arsenic oxide, As_2O_5, is used to decolourise bottle glass. Antimony compound, antimonial lead, is used in storage batteries. Compounds of antimony with aluminium, gallium and indium, AlSb, GaSb and InSb, find applications in infrared devices and in diodes.

8.3 GENERAL CHARACTERISTICS

Elements of this group have ns^2np^3 electronic configuration in their outermost shell. However, the electronic configuration of the core differs. In the case of nitrogen and phosphorus, it is that of the preceding noble gas, whereas for arsenic and antimony it is noble gas plus d^{10} and for bismuth it is noble gas plus $d^{10}f^{14}$. This is reflected in the properties of these elements which we will discuss below.

8.3.1 Physical Properties

As we have said earlier, the elements of this group show a systematic gradation of properties (Table 8.1). Nitrogen is gaseous in nature and exists as a diatomic molecule N≡N. This is due to the very high bond energy of the N≡N bond, 946 kJ mol^{-1}, which is nearly six times the N–N bond energy, 160 kJ mol^{-1}. On the contrary P≡P bond is quite weak, its energy of 490 kJ mol^{-1} is only ~ 2.5 times the P–P bond energy, 209 kJ mol^{-1}. Therefore, phosphorus exists as tetra-atomic P_4 molecules in the gaseous state. In the solid state, it exists in different allotropic forms about which you will study in the following sub-section.

The change from non-metallic to metallic character with increase in the atomic number is well illustrated in this group. The first two elements, nitrogen and phosphorus, are nonmetals, arsenic and antimony are metalloids whereas bismuth is predominantly metallic in nature. In keeping with this trend, the electronegativity of these elements decreases gradually on moving down the group. The density, melting and boiling points of the elements increase with increase in atomic number.

Atomic radii, as expected, increase with increase in atomic number. As a consequence, ionisation energies decrease on descending the group. Nitrogen shows an exceptionally high ionisation energy which is due to its small atomic size. As discussed above, all the elements of this group have five electrons in their valence shell, they exhibit a highest oxidation state of +5 by using all five electrons in forming bonds. As one goes down the group, the tendency of the pair of *s* electrons to remain inert increases and only *p* electrons are used in bonding, resulting in an oxidation state of +3. The stability of +3 state relative to the +5 state thus increases on moving down the group. In the case of nitrogen, a very wide range of oxidation states exists:

–3 in NH_3, –2 in N_2H_4, –1 in NH_2OH, 0 in N_2, +1 in N_2O, +2 in NO, +3 HNO_2, +4 in NO_2 and +5 in HNO_3. The negative oxidation states of nitrogen arise because of its higher electronegativity (3.05) than that of hydrogen (2.1). As you can see from the Table 8.1, the energy required to produce M^{5+} is so immense that it is never formed. The compounds formed by these elements in +5 oxidation state are thus predominantly covalent. However, in case of Sb and Bi, the sum of the first three ionisation energies is just low enough to form M^{3+} ions. But fluorine is the only element which gives an electronegativity difference enough to permit the formation of ionic bonds. Thus SbF_3 and BiF_3 exist as ionic solids.

Table 8.1: Some physical properties of Group 15 elements

Property	Nitrogen N	Phosphorus P	Arsenic As	Antimony Sb	Bismuth Bi
Atomic number	7	15	33	51	83
Electronic configuration	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
Ionic radius (pm)	171 (–3)	212 (–3)	222 (–3)	62 (+5)	120 (+3)
Covalent radius (pm)	70	110	121	141	148
van der Waals radius (pm)	150	180	200	220	
Bond energy (E–E, kJ mol^{-1})	160	209	180	142	–
Melting point (K)	63	317^w	1090	903	544
Boiling point (K)	77	553^w	883	1653	1833
Density ($10^3 \times$ kg m^{-3})	0.81^a	1.82^w	5.73	6.7	9.8
Electronegativity (A/R)	3.05	2.05	2.2	1.8	1.65
Electron affinity (kJ mol^{-1})	+9	–72	–77	–101	–110
Ionisation energy (kJ mol^{-1})					
(I + II + III)	8,839	5,864	5,478	4,866	4,766
(I + II + III + IV + V)	25,755	17,090	16,357	14,469	14,490
Common oxidation states*	–3, –2, –1, 0, 1, 2, 3, 4, 5	–3, (1), 3, 5	–3, 3, 5	(–3), 3, 5	3, (5)

a = density of liquid at boiling point; w = white; * the oxidation states in bracket correspond to less stable oxidation state of the element.

Since, it is not easy from energy considerations to gain three electrons to achieve stable noble gas configuration, the formation of the tri-negative ion (M^{3-}) is rare. But, nitrogen being the smallest and the most electronegative of all the members of the group, forms trivalent anion with reactive metals which have low ionisation energies. Thus, nitrogen forms ionic nitrides such as Li_3N, Be_3N_2, Mg_3N_2, Ca_3N_2. As the electronegativity of the other elements of the group, i.e., P, As, Sb and Bi, is low, most of their compounds are covalent in nature.

Nitrogen is not able to extend its coordination number beyond four, the other elements have coordination numbers of five as well as six. The extension of coordination number is due to the availability of *d*-orbitals in P, As, Sb and Bi, using which these elements can attain sp^3d and sp^3d^2 hybridisation, e.g., in PCl_5 and PCl_6^-, respectively. Thus, nitrogen does not function as a Lewis acid whereas phosphorus, arsenic, antimony and bismuth do so. The hydrides of this group and their alkyl derivatives act as Lewis bases, forming a number of addition complexes, e.g., $NH_3.BF_3$, $CaCl_2.4NH_3$, etc.

Nitrogen forms strong $p\pi$–$p\pi$ **multiple** bonds but other elements of the group do not show this behaviour. This property also differentiates nitrogen from other elements of the group. Apart from the nitrogen molecule, $N{\equiv}N$, compounds having $p\pi$–$p\pi$ multiple bonding include nitrates, NO_3^-, nitrites, NO_2^-, azides, N_3^-, cyanides, $C{\equiv}N^-$, oxides of nitrogen, etc. Thus, the oxides N_2O_3 and N_2O_5 are monomeric due to the presence of multiple bonds but analogous P_2O_3 and P_2O_5 exist as dimers, P_4O_6 and P_4O_{10}. However, phosphorus and the heavier elements of the group show $d\pi$–$p\pi$ bonding.

8.3.2 Allotropic Forms of Phosphorus

Phosphorus exists as discrete tetrahedral P_4 molecules in the gaseous and liquid states and also in the solid state as **white phosphorus.** Because of angular strain in the P_4 molecule in which the angles are only 60°, it is reactive. It spontaneously catches fire in air. White phosphorus is soft, appreciably volatile and poisonous, soluble in organic solvents but not in water. In fact, it is stored under water to protect it from oxygen. Phosphorus glows in the dark with faint green glow, due to **phosphorescence.**

Phosphorescence is a form of luminescence in which a substance emits light of one wavelength after having absorbed electromagnetic radiation of a shorter wavelength. It may continue for a considerable time after excitation.

Above 1600 K, P_4 molecules begin to dissociate into P_2 molecules. Rapid cooling of this vapour gives **brown phosphorus** which probably contains P_2 molecules. If white phosphorus is heated above 1000 K for sometime, one of the P–P bonds in P_4 is broken and a polymeric form of phosphorus known as **red phosphorus** is formed. Because of its polymeric structure in which angles are less strained, it is less reactive. Heating white phosphorus under high pressure results in **black phosphorus** which is inert and has layer structure (Fig. 8.2), resembling graphite. Like graphite it has metallic lustre and is a conductor of heat and electricity. Black phosphorus is the most metallic of the allotropes of phosphorus and is often called **metallic phosphorus.**

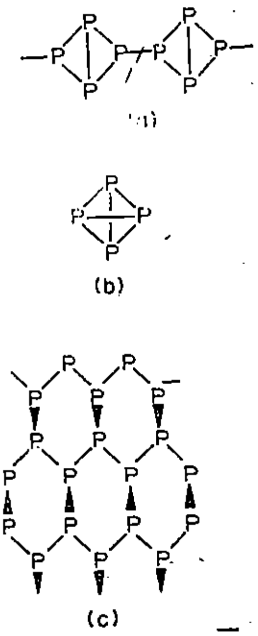


Fig. 8.2: Allotropes of phosphorus: (a) red phosphorus, (b) white phosphorus, and (c) black phosphorus

Reactivity of the various allotropic forms of phosphorus towards other substances decreases in the order, brown > white > red > black, the last one being almost inert. Similarly, arsenic, antimony and bismuth also have a number of allotropic forms. Generally, the metallic allotropes become more stable with increasing atomic number.

8.3.3 Chemical Properties

Nitrogen is quite inert at room temperature because of the great strength of the N≡N bond, 946 kJ mol^{-1}. It is a blessing, in the sense that our atmospheric oxygen might otherwise disappear with some of the nitrogen to form oceans of nitric acid. White phosphorus is very reactive while red and black allotropes are not. Arsenic, antimony and bismuth are fairly reactive.

- With oxygen, nitrogen combines only at very high temperatures to yield nitric oxide; white phosphorus combines so readily giving trioxide and pentoxide that it is stored under water.
- Arsenic, antimony and bismuth on heating in air form the trioxides As_2O_3, Sb_2O_3 and Bi_2O_3, respectively. All except nitrogen react with halogens to form halides EX_3 and EX_5; bismuth yields only BiX_3 (inert pair effect).
- All react with sulphur, except nitrogen, to form the sulphides.
- Only nitrogen reacts with hydrogen under suitable conditions to form ammonia.
- All the elements of Group 15 react with metals; nitrogen forming nitrides, phosphorus and arsenic giving phosphides and arsenides whereas antimony and bismuth form alloys.
- Hot concentrated sulphuric acid converts phosphorus, arsenic, antimony and bismuth to H_3PO_4, H_3AsO_3 (arsenious acid), $Sb_2(SO_4)_3$ and $Bi_2(SO_4)_3$, respectively. With nitric acid, phosphorus forms phosphoric acid, arsenic forms arsenious and arsenic acids, antimony and bismuth form Sb_2O_5 and $Bi(NO_3)_3$, respectively.
- The action of alkalies is different on different elements — phosphorus forms alkali hypophosphites and phosphine, arsenic forms alkali arsenites, AsO_3^{3-}, whereas antimony and bismuth remain unaffected.

These reactions are summarised in Table 8.2

Table 8.2: Some reactions of Group 15 elements

$E + O_2 \xrightarrow{\text{Heat}} E_xO_y$	Nitrogen forms NO when a mixture of N_2 and air is passed through an electric arc; P gives P_2O_3 and P_2O_5; As, Sb and Bi yield As_2O_3 and Bi_2O_3.
$E + F_2 \longrightarrow E_xF_y$	Not N and P; As, Sb and Bi form AsF_5, SbF_5 and BiF_3, respectively.
$E + X_2 \longrightarrow E_xX_y$ (X = Cl, Br, I)	Not N; P gives PX_3 and PX_5; As, Sb and Bi form EX_3.
$E + S \longrightarrow E_xS_y$	Not N; P gives P_4S_3; As, Sb and Bi form As_2S_3, Sb_2S_3 and Bi_2S_3, respectively.
$P + KOH + H_2O \longrightarrow PH_3 + KH_2PO_2$	Not N, Sb and Bi; As reacts with fused alkalies to form Na_3AsO_3 and H_2.
$As + \underset{\text{hot \& conc.}}{H_2SO_4} \longrightarrow H_3AsO_3$	Not N; P forms H_3PO_4 whereas Sb and Bi yield $Sb_2(SO_4)_3$ and $Bi_2(SO_4)_3$, respectively.
$As + \underset{\text{dil}}{HNO_3} \longrightarrow H_3AsO_3$	Conc. HNO_3 oxidises P, As, Sb and Bi to H_3PO_4, H_3AsO_4, Sb_2O_5 and $Bi(NO_3)_3$, respectively.

Before we discuss the compounds of Group 15 elements, try the following SAQ.

SAQ 1

Explain briefly in the space given below, why

a) nitrogen exists as N_2 whereas phosphorus exists as P_4 molecules in the gaseous state.

....

....

....

b) white phosphorus is more reactive than red phosphorus.

....

....

8.4 HYDRIDES

All elements of Group 15 form trihydrides of the type EH_3. In addition to these, nitrogen also forms N_2H_4 and N_3H, and phosphorus gives P_2H_4. Bond energy of the M–H bond decreases from NH_3 to BiH_3 because of increase in the size of the element on descending the group. Consequently, the stability of the hydrides decreases from NH_3 to BiH_3; bismuth hydride decomposes quite rapidly at room temperature. As you have studied in Unit ?, the variation in boiling point of trihydrides is one of the strongest pieces of evidence for hydrogen bond formation by nitrogen. Properties of these trihydrides are summarised in Table 8.3.

Table 8.3: Properties of Group 15 hydrides, EH_3

Property	Ammonia NH_3	Phosphine PH_3	Arsine AsH_3	Stibine SbH_3	Bismuthine BiH_3
Melting point (K)	195	139	157	185	–
Boiling point (K)	240	186	211	256	295
Solubility in water (V/V at 293 K)	739	0.26	0.20	0.20	–
Odour	pungent	decaying fish	garlic-like	–	–
Bond energy, E–H ($kJ\ mol^{-1}$)	389	322	297	255	–
Bond angle	106°47′	93°30′	92°	91°30′	–
Dipole moment (D)	1.44	0.55	0.15		
Decomposition to elements (K)	775	on gentle heating	295	295	very unstable

The central atom in the trihydrides is sp^3 hybridised. As one of the positions in the tetrahedron is occupied by a lone pair, the structure of these hydrides is pyramidal, (Fig. 8.3). The tetrahedron is distorted due to repulsion between the lone pair of electrons and the bond pairs. With the decrease in the electronegativity of the central atom, the bond pairs of electrons go further away from the central atom. This results in a decrease in the repulsion of the bonding pairs in the vicinity of the central atom resulting in a decrease in the bond angles which become close to 90° (Table 8.3). E–H bond then consists of almost pure p-orbitals and the lone pair is almost in a pure s-orbital. As we go down the group, lone pair resides mainly in the s-orbital from where it is more difficult to be removed. This is the reason why ammonia acts as a better donor than other hydrides of the group. Thus, NH_3 readily forms ammonium salts with H^+. Phosphonium salts are formed with H^+ only under anhydrous conditions but other hydrides, AsH_3, SbH_3 and BiH_3 do not form such salts. Let us now discuss the hydrides of nitrogen in brief.

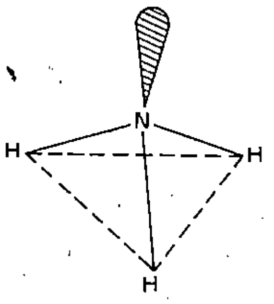


Fig. 8.3: Structure of ammonia

8.4.1 Ammonia

As described earlier, ammonia is an important industrial chemical. Of all the nitrogen compounds, it is produced in the largest quantities. Ammonia can be obtained in the laboratory by heating ammonium salts with an alkali:

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

Ammonia is manufactured industrially by **Haber process.** Nitrogen from air and hydrogen from **synthesis gas,** are reacted together at a high pressure of about 250 atmosphere and at a temperature of 800 K in the presence of a finely divided catalyst.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3, \ \Delta H^\circ = -92.0 \text{ kJ mol}^{-1}$$

A mixture of carbon monoxide and hydrogen, obtained from methane, CH_4, naphtha, C_7H_{16} and water at 1175 K and 30 atm. pressure in presence of a catalyst is known as synthesis gas.

Le Chatelier's Principle:
If the conditions controlling the equilibrium of a system are changed, the system moves in such a way as to oppose the effects of the change.

As Le Chatelier's principle would tell you, high pressure will favour the forward reaction, which proceeds with reduction in volume. Since the forward reaction is exothermic, high temperatures would favour the back reaction resulting in dissociation of ammonia. However, to enable the reaction to proceed at a reasonable rate, the reaction is carried out at 800 K in the presence of a finely divided iron catalyst containing traces of oxides of Mo, K and Al. The above pressure and temperature is optimum to give about 15% yield of NH_3. The unreacted gases are recycled.

Ammonia has a strong characteristic pungent smell. It is a colourless gas at room temperature and can be easily liquefied by either increasing the pressure or decreasing the temperature. It is highly soluble in water, it is more soluble than any other gas because of hydrogen bonding with water. The ammonia solution in water is generally called ammonium hydroxide. The name ammonium hydroxide is, however, misleading and the solution should better be called 'aqueous ammonia'. The solution has $NH_3(aq)$, $NH_4^+(aq)$ and $OH^-(aq)$ ions:

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The equilibrium constant K for the above reaction is only 1.81×10^{-5}. This value is quite low, suggesting that the aqueous solution is a weak alkali. Ammonia solution, in the presence of NH_4Cl, is used as a buffer solution in the pH range of 10. This mixture is also used for precipitation of metal hydroxides selectively. You must have studied simple reactions of ammonia, e.g., with HCl in your school chemistry.

As we have discussed earlier, NH_3 molecule has a pyramidal structure, having a lone pair of electrons at the apex. The ammonium ion formed on reaction with H^+ has a tetrahedral structure. Ammonia functions as a donor molecule towards Lewis acids and many complex ions having ammonia as a ligand are known, e.g., $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$, $[Ni(NH_3)_6]^{2+}$, etc. Ammonia is linked to the metal ions through its lone pair.

Liquid Ammonia as a Non-aqueous Solvent

Liquid ammonia functions as a good solvent for many substances and many types of reactions. In this behaviour, it resembles water as a solvent. Both are self-ionising, the difference being in the lower degree of ionisation of ammonia :

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

As you know, all those substances, which on dissolving in water produce hydronium ion, are acids and all those which produce hydroxide ion are bases, e.g., HCl, HNO_3 are acids in water and NaOH, $Ca(OH)_2$ are bases. Similarly, all those substances which dissolve in liquid ammonia to give NH_4^+ ions are acids and those which give amide ions, NH_2^-, are bases. Thus, NH_4Cl, NH_4NO_3 are acids and $NaNH_2$ is a base in liquid ammonia. Acid-base neutralisation reaction in liquid ammonia, thus, can be a reaction giving a salt and the solvent. Compare the corresponding reaction in water, e.g.,

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$
$$NaNH_2 \rightleftharpoons Na^+ + NH_2^-$$

$$NH_4Cl + NaNH_2 \xrightarrow{NH_3} NaCl + 2NH_3$$
$$HCl + NaOH \xrightarrow{H_2O} NaCl + H_2O$$

Similarly,

$$2NH_4Cl + \underset{\text{lead imide}}{PbNH} \xrightarrow{NH_3} PbCl_2 + 3NH_3$$

$$3NH_4Cl + \underset{\text{Aluminium nitride}}{AlN} \xrightarrow{NH_3} AlCl_3 + 4NH_3$$

Thus, we see that imides like PbNH, and nitrides such as AlN, also function as bases in liquid ammonia. Liquid ammonia is a basic solvent because it can easily accept a proton. Therefore, those acids which are weak in water will be highly acidic in liquid ammonia. Thus, acetic acid is a weak acid in water (pka = 5) but will function as a strong acid in liquid ammonia:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

Reactions accociated with complex formation are also comparable in water and liquid ammonia.

$$ZnCl_2 + 2NaOH \xrightarrow{\text{water}} \underset{\text{precipitate}}{Zn(OH)_2} \xrightarrow[\text{NaOH}]{\text{excess}} \underset{\text{soluble complex}}{[Zn(OH)_4]^{2-}}$$

$$ZnCl_2 + 2NaNH_2 \xrightarrow{\text{liquid } NH_3} \underset{\text{precipitate}}{Zn(NH_2)_2} \xrightarrow[NaNH_2]{\text{excess}} \underset{\text{soluble complex}}{[Zn(NH_2)_4]^{2-}}$$

As you have learnt in Units 4 and 5, liquid ammonia dissolves alkali and alkaline earth metals giving blue solutions. This reaction is, however, less vigorous than the reaction of these metals with water.

8.4.2 Hydrazine, N_2H_4

Hydrazine is prepared by the action of sodium hypochlorite on ammonia in the presence of a small amount of gelatin, which helps to suppress the side reactions:

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$
$$NH_3 + NH_2Cl + NaOH \longrightarrow NH_2NH_2 + NaCl + H_2O$$
$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl \text{ (side reaction)}$$
$$3NH_2Cl + 2NH_3 \longrightarrow N_2 + 3NH_4Cl \text{ (side reaction)}$$

Anhydrous hydrazine may be obtained by distillation over NaOH or by precipitating $N_2H_6SO_4$, which is then treated with liquid NH_3 to precipitate $(NH_4)_2SO_4$:

$$N_2H_4(aq) + H_2SO_4(aq) \longrightarrow N_2H_6SO_4 \xrightarrow{2NH_3} N_2H_4 + (NH_4)_2SO_4$$

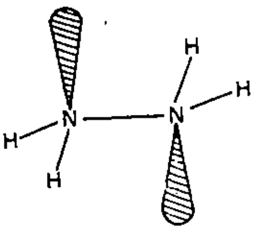


Fig. 8.4: Structure of hydrazine

Hydrazine is a colourless, fuming liquid. It forms a dihydrate, $N_2H_4{\cdot}2H_2O$ and two series of salts, e.g., N_2H_5Cl and $N_2H_6Cl_2$. Hydrazine burns in air giving nitrogen and water. As this reaction is highly exothermic ($\Delta H^\circ = -622$ kJ), hydrazine is used as a **rocket fuel** along with liquid air or oxygen as an oxidant.

Hydrazine has a structure (Fig. 8.4) similar to that of hydrogen peroxide having two lone pairs of electrons and can act as a coordinating ligand forming complexes with metal ions like Co^{2+}, Ni^{2+}, etc. The bond energy of N–N bond in hydrazine is very small due to the repulsion of the nonbonding electrons which weaken the N–N bond. Thereby hydrazine is unstable, it decomposes to N_2, NH_3 and H_2 at 500 K.

8.4.3 Hydrazoic Acid, HN_3, and Azides

Hydrazoic acid is also known as hydrogen azide. It is a colourless, highly explosive liquid. When sodamide is reacted with N_2O at 450 K, sodium azide is formed which on treatment with sulphuric acid gives hydrazoic acid :

$$2NaNH_2 + N_2O \longrightarrow NaN_3 + NaOH + NH_3$$
$$2NaN_3 + H_2SO_4 \longrightarrow 2HN_3 + Na_2SO_4$$

It is a weak acid and dissociates only slightly in water. With electropositive metals it forms azides. $Pb(N_3)_2$ is covalent and explosive in nature and it is used as a **detonator.** NaN_3 is ionic and non-explosive. For the azide ion, N_3^-, three resonance structures can be drawn :

$$:\ddot{N}^-=N^+=\ddot{N}^-: \longleftrightarrow :\ddot{N}^{2-}-N^+\equiv N: \longleftrightarrow :N\equiv N^+\ \ \ddot{N}^{2-}:$$

For covalent azides and hydrazoic acid, which is largely covalent, three resonance structures may also be drawn. But, according to Pauling's adjacent charge rule, one structure is excluded, since in it, two adjacent atoms have the same charge.

$$H\dot{N}=N^+=\ddot{N}^-: \longleftrightarrow H\ddot{N}^-\ \ N^+\equiv N: \qquad \underset{\text{Not possible}}{HN\equiv N^+\ -\ddot{N}^{2-}:}$$

Thus the increased stability of the ionic azides may be due to a larger number of resonance forms.

8.4.4 Phosphine, PH_3

Phosphine, PH_3, is the most stable hydride of phosphorus. It is intermediate in thermal stability between ammonia and arsine. Phosphine can be easily prepared by any of the following methods:

- hydrolysis of metal phosphides such as AlP or Ca_3P_2:

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$

- Pyrolysis of phosphorus acid at 480 – 485 K:

$$4H_3PO_3 \longrightarrow PH_3 + 3H_3PO_4$$

- Alkaline hydrolysis of phosphonium iodide:

$$PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$$

- Alkaline hydrolysis of white phosphorus (industrial process):

$$P_4 + 3KOH + 3H_2O \longrightarrow PH_3 + 3KH_2PO_2$$

Phosphine is a colourless, extremely poisonous gas having a faint garlic odour. As the P–H bond is not polar enough to form P–H-----P or P–H-----O bonds, unlike ammonia, phosphine is not associated in the liquid state and is much less soluble in water. In contrast to the basic nature of solutions of ammonia in water, aqueous solutions of phosphine are neutral, which is due to the much weaker tendency of PH_3 to protonate in water. However, it does react with HI to form phosphonium iodide:

$$PH_3 + HI \longrightarrow PH_4I$$

Pure phosphine ignites in air at about 435 K, but when contaminated with traces of P_2H_4 it is spontaneously inflammable:

$$PH_3 + 2O_2 \longrightarrow H_3PO_4$$

8.4.5 Arsine, Stibine and Bismuthine

he thermal instability of AsH_3 is ilised in the detection of arsenic isoning.

AsH_3, SbH_3 and BiH_3 are exceedingly poisonous, thermally unstable, colourless gases whose physical properties are compared with those of NH_3 and PH_3 in Table 8.3. As pointed out earlier, the thermal stability and basic character of these hydrides decrease from NH_3 to BiH_3.

AsH_3 and SbH_3 can be prepared by acid hydrolysis of arsenides and antimonides of electropositive elements like Na, Mg, Zn, etc.:

$$Mg_3As_2 + 6HCl \longrightarrow 2AsH_3 + 3MgCl_2$$
$$Zn_3Sb_2 + 6HCl \longrightarrow 2SbH_3 + 3ZnCl_2$$

Bismuthine is extremely unstable and is best prepared by the disproportionation of methylbismuthine at 230 K:

$$3MeBiH_2 \longrightarrow 2BiH_3 + BiMe_3$$

SAQ 2

Explain briefly:

a) Why ammonia acts as a Lewis base?

....

....

b) What type of substances act as acids or bases in liquid ammonia?

....

....

c) Why hydrazine is unstable?

....

....

8.5 HALIDES

We have already discussed that Group 15 elements form compounds mainly in two oxidation states, +3 and +5. Both types of their halides, i.e. trihalides as well as pentahalides are known. We will discuss the trihalides first and then the pentahalides.

8.5.1 Trihalides

All the elements of Group 15 form trihalides, MX_3. Of all nitrogen halides, only NF_3 is stable due to strong N–F bonds. All other trihalides of nitrogen, NCl_3, NBr_3 and NI_3 are unstable. Of these, NCl_3 is explosive and NBr_3 and NI_3 exist only as their ammoniates, i.e., as ammonia adducts and detonate on removing ammonia.

Except NX_3, all the trihalides hydrolyse rapidly to either hydrated oxides, e.g., $As_2O_3{\cdot}nH_2O$ or acids, H_3PO_3 or oxochloride, SbOCl and BiOCl. NCl_3 on hydrolysis gives NH_3 and HOCl instead of HNO_2 (nitrous acid) and HCl:

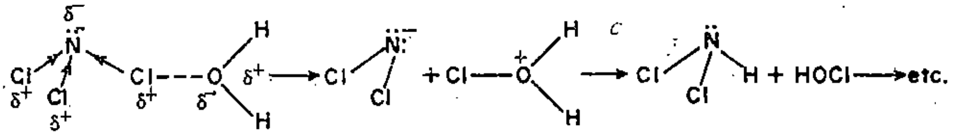
$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The mechanism of the hydrolysis of phosphorus trichloride is similar to that of silicon tetrachloride, explained in the preceding unit. It involves the formation of an intermediate four coordinate species $H_2O{\rightarrow}PCl_3$. The formation of this type of intermediate is impossible for nitrogen because of the non-availability of *d*-orbitals. NCl_3, therefore, hydrolyses by a different mechanism, which involves the attack of the Lewis base, water, on the partially positive chlorine to remove it in the form of a protonated hypochlorous acid molecule. Proton exchange with the Cl_2N^- anion then generates one molecule of HOCl and $NHCl_2$ each. Replacement of two more chlorine atoms with hydrogen produces the NH_3 molecule:



The trihalides, except NX_3, act as Lewis acids, i.e. electron pair acceptors, forming haloanions, $SbCl_4^-$, $BiCl_4^-$, etc. The trihalides can be oxidised to pentahalides. The ease of oxidation decreases from PX_3 to BiX_3. However, NX_3 is not oxidised at all. The trihalides function as halogenating agents. PCl_3 reacts with NH_3, halogens, HI, S, O_2 and AgNCO to give $P(NH_2)_3$, PX_2Cl_3, PI_3, $PSCl_3$, $POCl_3$ and $P(NCO)_3$, respectively. The following chemical equations represent these reactions :

$$PCl_3 + 3NH_3 \longrightarrow P(NH_2)_3 + 3HCl$$

$$PCl_3 + Br_2 \longrightarrow PBr_2Cl_3$$

$$PCl_3 + HI \longrightarrow PI_3 + 3HCl$$

$$PCl_3 + S \longrightarrow PSCl_3$$

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

$$PCl_3 + 3AgNCO \longrightarrow P(NCO)_3 + 3AgCl$$

Trihalides of the lighter elements of the group are predominantly covalent in nature, therefore, they can exist as discrete molecules which have a pyramidal structure, like NH_3. The trihalides of heavier elements, e.g., BiF_3, are ionic in nature.

8.5.2 Pentahalides

Nitrogen does not form any pentahalides. The stability of other pentahalides of the group decreases in the order P > Sb > As > Bi and in the order F > Cl > Br for halogens. PF_5, PCl_5, PBr_5, AsF_5, SbF_5, $SbCl_5$ and BiF_5 are stable. However, PBr_5 and $SbCl_5$ readily lose halogen forming trihalides. The pentahalides get more oxidising as we go down in the group, except arsenic pentahalides, AsX_5, which are unexpectedly more oxidising than those of the element following it in the group. All the pentahalides have trigonal bipyramidal structure in the gas phase (Fig. 8.5). However, their structures differ in the solid state, e.g., PCl_5 splits into $[PCl_4]^+[PCl_6]^-$ which have tetrahedral and octahedral structures, respectively; PBr_5 splits to give $[PBr_4]^+Br^-$. Pentahalides are obtained by the action of excess of halogen on trihalides:

$$PX_3 + X_2 \longrightarrow PX_5$$

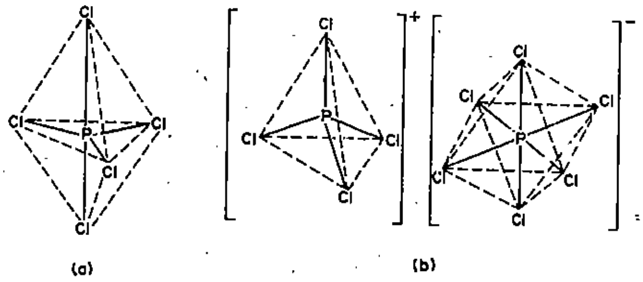


Fig. 8.5: Structure of PCl_5 in (a) gaseous state (b) solid state

Pentahalides are good halogenating agents, e.g., PCl_5 is used for conversion of alcohols to alkyl halides and acids to acylchlorides as shown below:

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

They hydrolyse to give either oxoacids, H_3PO_4, H_3AsO_4, or hydrated oxides like $Sb_2O_5.nH_2O$ or oxohalides like BiOCl; partial hydrolysis of PCl_5 gives $POCl_3$. Almost all pentahalides can accept an electron pair and act as Lewis acids, as in PF_6, PF_5. L, etc.

SAQ 3

Explain briefly why trihalides of nitrogen cannot be oxidised to pentahalides.

....

....

....

8.6 OXIDES

As stated earlier, nitrogen forms a number of oxides, N_2O, NO, N_2O_3, NO_2 or N_2O_4 and N_2O_5, and also very unstable NO_3 and N_2O_6. All these oxides of nitrogen exhibit $p\pi$–$p\pi$ multiple bonding between nitrogen and oxygen. This does not occur with the heavier elements in the group and consequently nitrogen forms a number of oxides which have no P, As, Sb or Bi analogues. The oxides of this group will be discussed briefly in this section.

8.6.1 Oxides of Nitrogen

Important characteristics of oxides of nitrogen are listed in Table 8.4. Let us first describe the preparation, properties and structures of these oxides.

Table 8.4 : Oxides of nitrogen

Formula	Name	Colour	Remarks
N_2O	Nitrous oxides	Colourless	Rather unreactive
NO	Nitric oxide	Colourless	Moderately reactive
N_2O_3	Dinitrogen trioxide	Dark blue	Extensively dissociated as gas
NO_2	Nitrogen dioxide	Brown	Moderately reactive
N_2O_4	Dinitrogen tetroxide	Colourless	Extensively dissociated to NO_2 as gas and partly as liquid
N_2O_5	Dinitrogen pentoxide	Colourless	Unstable as gas; ionic solid
NO_3, N_2O_6			Not well characterised and quite unstable

Preparation

N_2O is obtained generally by heating NH_4NO_3:

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

NO is best prepared by the reduction of 8M HNO_3 with reducing agents like Cu or by reduction of nitrous acid or nitrites by Fe^{2+} or I^- ions:

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$2NaNO_2 + 2NaI + 4H_2SO_4 \longrightarrow 4NaHSO_4 + 2NO + I_2 + 2H_2O$$

As you will study later, NO is formed as an intermediate in the manufacture of nitric acid by oxidation of NH_3.

N_2O_3 is obtained as an intense blue liquid or a pale blue solid on cooling an equimolar mixture of NO and NO_2:

$$NO + NO_2 \longrightarrow N_2O_3$$

On warming, its colour fades due to its dissociation into these two oxides.

NO_2 can be prepared by reduction of conc. HNO_3 with Cu or by heating heavy metal nitrates:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

N_2O_5 is an anhydride of HNO_3. It is best prepared by dehydrating HNO_3 with P_4O_{10} at low temperatures:

$$4HNO_3 + P_4O_{10} \xrightarrow{250\ K} 2N_2O_5 + 4HPO_3$$

N_2O is also known as laughing gas because it induces laughter. Mixed with N_2, it is used as an anaesthetic by dentists.

Properties and Structure

Oxides of nitrogen are all oxidising agents, N_2O even supporting the combustion of S and P. NO which is thermally more stable, supports the combustion of Mg and P but not of S. Sulphur flame is not hot enough to decompose it. N_2O and NO are neutral, while the other oxides are acidic.

N_2O is isoelectronic with CO_2 and also has a linear structure. However, unlike CO_2, N_2O has a small dipole moment. The resonance structures of the molecule are given in Fig. 8.6.

$$:\ddot{N}^-{=}N^+{=}\ddot{O}: \longrightarrow :N{\equiv}N^+{-}\ddot{O}^-:$$

Fig. 8.6: Resonance structures of nitrous oxide

NO has a total of 15 electrons. It is impossible for all of them to be paired and hence this is an odd electron molecule. In the gaseous state, it is paramagnetic. However, the liquid and the solid states are diamagnetic because loose dimers (Fig. 8.7) are formed cancelling out the magnetic effect of unpaired electrons.

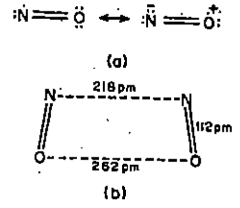
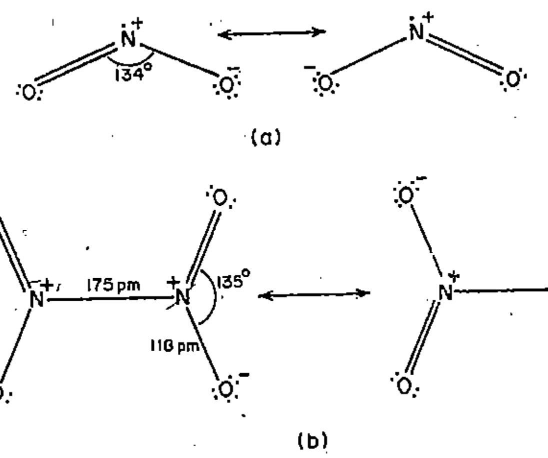


Fig. 8.7: (a) Resonance structures of nitric oxide, and (b) Molecular structure of crystalline nitric oxide

The bonding in NO is best described by the molecular orbital theory which you have studied in Unit 5 of the "Atoms and Molecules" course. Molecular orbital electronic configuration of NO molecule can be represented as σs^2, σ^*1s^2, $\sigma 2s^2$, σ^*2s^2, $\sigma 2p_x^2$, $\pi 2p_y^2{=}\pi 2p_z^2$, $\pi^*2p_y^1$. This gives a bond order of 2.5. If the unpaired electron occupying the antibonding π^*2p_y orbital is removed, nitrosonium ion, NO^+, is formed and the bond order becomes 3. This is reflected in the shortening of the bond length from 115 pm in NO to 106 pm in NO^+. Nitrosonium ion is stable and forms salts like NO^+Cl^-. It is isoelectronic with CO and forms complexes with transition elements. The brown ring formed in the test for nitrates is due to the formation of a complex of iron, $[Fe(H_2O)_5NO]^{2+}$.

NO_2 with 23 electrons is again an odd electron molecule. In the gaseous state it is paramagnetic. On cooling, the gas condenses to a brown liquid and eventually to a colourless solid both of which are diamagnetic due to dimerisation. NO_2 molecule is angular with ONO angle of 134°. The O–N bond length is 120 pm, intermediate between a single and a double bond. The odd electron is on nitrogen. The dimer has been shown to have a planar structure. The N–N bond length is very large, 175 pm, making this a very weak bond (Fig. 8.8).



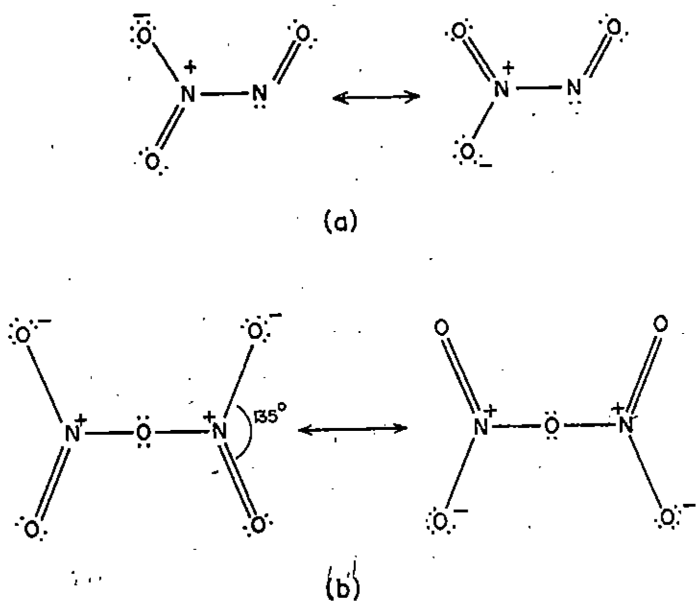
(a)

(b)

Fig. 8.8: Resonance structures of (a) NO_2, and (b) N_2O_4

Liquid N_2O_4 undergoes self-ionisation to form NO^+ and NO_3^- ions and therefore, it has been extensively studied as a non-aqueous solvent. Resonance structures of N_2O_3 are shown in Fig. 8.9(a).

Solid N_2O_5 exists in the ionic form, $NO_2^+NO_3^-$. In the gaseous form, the discrete N_2O_5 molecules have a N–O–N bond angle close to 180°, Fig. 8.9(b).



(a)

(b)

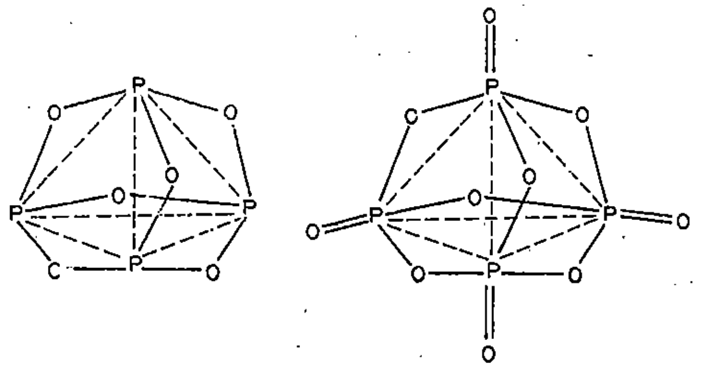
Fig. 8.9: Resonance structures of (a) N_2O_3, and (b) N_2O_5

8.6.2 Oxides of Phosphorus, Arsenic, Antimony and Bismuth

As discussed earlier, P, As and Sb form oxides in both +3 and +5 oxidation states whereas only one oxide of bismuth, Bi_2O_3 is known. Remember the stability of higher oxidation states decreases on going down the group. Except Bi_2O_3 others exist in dimeric form. Structures of oxides of phosphorus are shown in Fig. 8.10. As expected, the basic character of oxides increases on descending the group. The oxides of P and As are acidic, those of Sb amphoteric and of Bi wholly basic. Also the higher oxidation states are more acidic.

As^{III} is quantitatively oxidised to As^{V} by I_2. Therefore, As_2O_3 is used as a primary standard in iodimetric titrations.

$$\tfrac{1}{2} As_2O_3 + I_2 + H_2O \longrightarrow \tfrac{1}{2} As_2O_5 + 2H^+ + 2I^-$$



P_4O_6 P_4O_{10}

Fig. 8.10: Structures of oxides of phosphorus

SAQ 4

Explain briefly why NO is paramagnetic whereas NO^+ is diamagnetic.

....

....

....

8.7 OXOACIDS OF NITROGEN, PHOSPHORUS, ARSENIC AND ANTIMONY

An oxoacid is the acid in which ionisable hydrogen atoms are attached to the central atom through oxygen atoms, e.g., Cl–OH. N, P, As and Sb form a number of oxoacids as also do S, Se and Te in Group 16, and Cl, Br and I in Group 17. Let us, therefore, first familiarise ourselves with the nomenclature of oxoacids.

To distinguish between the oxidation states of the central atom in oxoacids, suffixes, **ous** and **ic** are used. The acids in which the central atom is in a lower oxidation state are termed **ous** acids, whereas those having central atom in a higher oxidation state are called **ic** acids. The oxoacids having halogens in their highest oxidation states are termed as **peracids**. In **hypo-ous** and **hypo-ic** acids the oxidation state of the central atom is lower than that in **ous** and **ic** acids, respectively.

The prefixes ortho, meta and pyro are used to distinguish acids differing in the content of water. The most highly hydroxylated acid of an element in a particular oxidation state is called the **ortho** acid. The acid which has one water molecule less than the ortho acid is called **meta** acid. The **pyro** acid corresponds to the loss of one water molecule between two molecules of the ortho acid. You will find examples of all these types while you study the oxoacids in this unit and in the following two units.

8.7.1 Oxoacids of Nitrogen

Nitrogen forms a number of oxoacids. Most of them are known only in aqueous solutions or as their salts. We will discuss here the two better known oxoacids, i.e., nitrous acid and nitric acid.

Nitrous Acid, HNO_2

It is an unstable, weak acid which is known only in aqueous solution. It can be obtained by acidifying an aqueous solution of a nitrite or by passing an equimolar mixture of NO and NO_2 into water:

$$Ba(NO_3)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4\downarrow$$

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2$$

On trying to concentrate, the acid decomposes :

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

Nitrous acid and nitrites are good oxidising agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates, e.g.,

$$2KI + 2HNO_2 + 2HCl \longrightarrow 2H_2O + 2NO + 2KCl + I_2$$

With strong oxidising agents, like $KMnO_4$, nitrous acid and nitrites function as reducing agents and get oxidised to NO_3^- ions:

$$2KMnO_4 + 5KNO_2 + 6HCl \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCl$$

Structures of nitrous acid and nitrite ion are shown in Fig. 8.11.

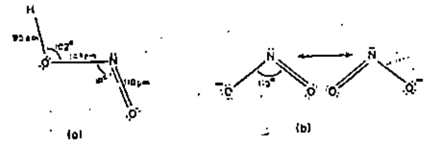


Fig. 8.11 : (a) Molecular structure of HNO_2; (b) Resonance structures of nitrite ion

Nitrite ion is a good coordinating agent. Both nitrogen and oxygen have lone pairs capable of forming coordinate bond with metal ions. Nitrite ion can coordinate either through N or through O. Thus, isomerism occurs between $M \leftarrow NO_2$ and $M \leftarrow ONO$ structures. Analogous organic derivatives are also known, the nitrites, R–ONO and the nitro compounds, $R–NO_2$ where R is any alkyl or aryl group. Such ligands which can coordinate in two different ways are called ambidentate.

Nitric Acid, HNO_3

Nitric acid is one of the major acids of modern chemical industry. It has been known as a corrosive solvent for metals since the thirteenth century. HNO_3 is now almost exclusively manufactured by Ostwald process. In this process NH_3 is catalytically oxidised to give NO:

$$4NH_3 + 5O_2 \xrightarrow[1200\,K]{Pt–Rh\ catalyst} 4NO + 6H_2O, \ \Delta H = -904\ kJ\ mol^{-1}$$

In the above reaction, about 96-98% of NH_3 is converted into NO. Since, the reaction is exothermic, reaction temperature can be maintained without external heating provided a heat exchanger is used. The mixture of gases is cooled and diluted with air. NO combines with O_2 to give NO_2 which is absorbed in water to give HNO_3 and NO, which is then recycled. The following equations represent various steps in this process:

$$2NO + O_2 \longrightarrow 2NO_2$$
$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Nitric acid can be concentrated to 68% by distillation, when a **constant boiling mixture** is formed. More concentrated acid can be made by distilling the mixture with concentrated sulphuric acid.

Constant boiling mixture or **azeotrope** is a mixture of two or more liquids that distils at a certain temperature and has a constant composition at a given pressure. Its boiling point may be lower or higher than the boiling points of pure components.

Pure nitric acid is a colourless liquid (b.p. 359 K). It decomposes readily in light giving a yellow colour due to the formation of nitrogen dioxide. It is a strong acid and is almost completely dissociated into ions in solution. It reacts with metals and with metal oxides, hydroxides and carbonates forming salts called nitrates.

The reaction of HNO_3 with metals is of particular interest because of the great variety of products obtained, e.g., H_2, N_2, NH_4NO_3, N_2O, NO and NO_2 in addition to the nitrate or oxide of the metal. The nature of products formed depends upon the nature of the metal and reaction conditions, like concentration of the acid and temperature.

With very dilute acid, magnesium and manganese give hydrogen:

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2\uparrow$$

Other metals like Zn, Sn, Fe, etc., which also lie above hydrogen in the electrochemical series, liberate hydrogen from dilute nitric acid. But, since nitric acid is a strong oxidising agent and hydrogen a reducing agent, secondary reactions take place resulting in the reduction of nitric acid to NH_3, N_2O or N_2. Thus, Zn reacts with dilute HNO_3 in cold giving N_2O or N_2 according to the following equations:

$$\begin{aligned}
Zn + 2HNO_3 &\longrightarrow Zn(NO_3)_2 + 2H] \times 4\\
2HNO_3 + 8H &\longrightarrow N_2O + 5H_2O\\
\hline
4Zn + 10HNO_3 &\longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O
\end{aligned}$$

$$\begin{aligned}
Zn + 2HNO_3 &\longrightarrow Zn(NO_3)_2 + 2H] \times 5\\
2HNO_3 + 10H &\longrightarrow N_2 + 6H_2O\\
\hline
5Zn + 12HNO_3 &\longrightarrow 5Zn(NO_3)_2 + N_2 + 6H_2O
\end{aligned}$$

Very dilute HNO_3 reacts with Zn to give NH_3, which is of course neutralised to form NH_4NO_3:

$$\begin{array}{lcl}
Zn + 2HNO_3 & \longrightarrow & Zn(NO_3)_2 + 2H] \times 4 \\
HNO_3 + 8H & \longrightarrow & NH_3 + 3H_2O \\
HNO_3 + NH_3 & \longrightarrow & NH_4NO_3 \\
\hline
4Zn + 10HNO_3 & \longrightarrow & 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O
\end{array}$$

Similarly, iron and tin also give NH_4NO_3 with dilute HNO_3 in cold.

As you know, metals such as Cu, Bi, Hg, Ag, etc., lying below hydrogen in the electrochemical series do not liberate hydrogen from acids. With these metals, the action of nitric acid involves the oxidation of metals into the metallic oxides which dissolve in the acid to form nitrates accompanied by evolution of NO or NO_2 depending upon whether the acid is dilute or concentrated. For instance, Cu, Ag, Hg and Bi react with dilute acid liberating NO:

$$\begin{array}{lcl}
3Cu + 2HNO_3 & \longrightarrow & 3CuO + 2NO + H_2O \\
CuO + 2HNO_3 & \longrightarrow & Cu(NO_3)_2 + H_2O] \times 3 \\
\hline
3Cu + 8HNO_3 & \longrightarrow & 3Cu(NO_3)_2 + 2NO + 4H_2O
\end{array}$$

With concentrated acid NO_2 is given off:

$$\begin{array}{lcl}
Cu + 2HNO_3 & \longrightarrow & CuO + 2NO_2 + H_2O \\
CuO + 2HNO_3 & \longrightarrow & Cu(NO_3)_2 + H_2O \\
\hline
Cu + 4HNO_3 & \longrightarrow & Cu(NO_3)_2 + 2NO_2 + H_2O
\end{array}$$

Concentrated nitric acid behaves essentially as an oxidising agent and metals like Al, Fe, Cr, etc., are rendered passive due to the formation of a layer of insoluble oxide on the metal surface.

Noble metals like Au, Pt, Rh and Ir are not attacked by nitric acid. However, a 1:3 mixture of conc. HNO_3 and conc. HCl known as **aqua regia,** dissolves Au and Pt as it contains free chlorine:

$$\begin{array}{lcl}
HNO_3 + 3HCl & \longrightarrow & 2H_2O + 2Cl + NOCl \\
Au + 3Cl + HCl & \longrightarrow & HAuCl_4 \\
Pt + 4Cl + 2HCl & \longrightarrow & H_2PtCl_6
\end{array}$$

Conc. HNO_3 readily oxidises the solid nonmetals and metalloids to their respective oxoacids or hydrated oxides. Thus, P, As, Sb, S, I and Sn are oxidised to phosphoric acid, H_3PO_4, arsenic acid, H_3AsO_4, antimony pentoxide, Sb_2O_5, sulphuric acid, H_2SO_4, iodic acid, HIO_3 and metastannic acid, H_2SnO_3, respectively, e.g.,

$$\begin{array}{lcl}
2HNO_3 & \longrightarrow & 2NO_2 + H_2O + O] \times 10 \\
P_4 + 10O & \longrightarrow & P_4O_{10} \\
P_4O_{10} + 6H_2O & \longrightarrow & 4H_3PO_4 \\
\hline
P_4 + 20HNO_3 & \longrightarrow & 4H_3PO_4 + 20NO_2 + 4H_2O
\end{array}$$

Dilute nitric acid also acts as an oxidising agent. Hence, reducing agents, such as, H_2S, HI and $FeSO_4$ are oxidised to S, I_2 and $Fe_2(SO_4)_3$; respectively:

$$\begin{array}{lcl}
2HNO_3 & \longrightarrow & 2NO + H_2O + 3O \\
H_2S + O & \longrightarrow & S + H_2O] \times 3 \\
\hline
2HNO_3 + 3H_2S & \longrightarrow & 2NO + 4H_2O + 3S
\end{array}$$

Nitric acid also oxidises many organic compounds. It converts a mixture of cyclohexanol and cyclohexanone to adipic acid which is the starting material for nylon polymers. Nitric acid also oxidised *p*-xylene to terephthalic acid which is used for the manufacture of terylene.

Concentrated nitric acid, in the presence of concentrated sulphuric acid, reacts with certain aromatic compounds forming nitro compounds, e.g., benzene is converted into nitrobenzene:

$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$$

This process known as **nitration** is of great industrial importance because of usefulness of nitro compounds. Nitronium ion, NO_2^+, which is formed in the presence of the conc. H_2SO_4, is believed to be the active nitrating agent:

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$$

The molecular structure of nitric acid is shown in Fig. 8.12. In nitric acid the nitrogen and the three oxygen atoms are coplanar. Terminal N–O bonds are equivalent, the other N–O bond is much longer and corresponds to a single bond.

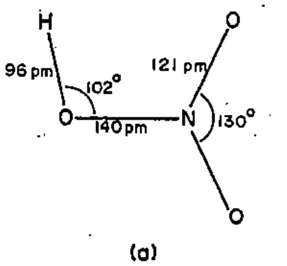
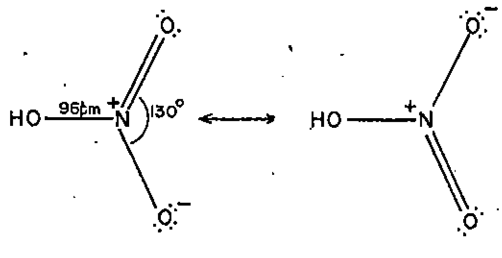


Fig. 8.12 (a): Molecular structure of HNO_3



8.12 (b): Resonance Structures of HNO_3

The nitrate ion is planar with equal N–O bonds. Its structure can be represented as a resonance hybrid as shown in Fig. 8.13.

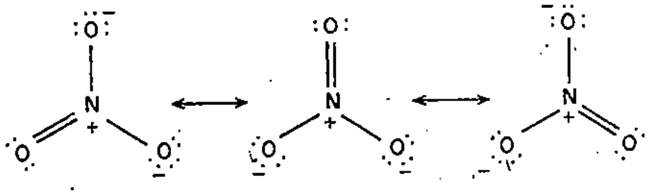


Fig. 8.13: Resonance structures of nitrate ion

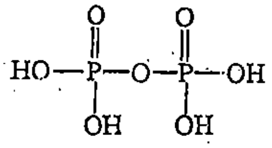
8.7.2 Oxoacids of Phosphorus, Arsenic and Antimony

Phosphorus, arsenic and antimony also form a number of oxoacids. Oxoacids of arsenic and antimony are not well characterised. Their salts, however, are known. Phosphorus forms two series of oxoacids, the phosphoric and the phosphorous acids. The oxidation state of phosphorus is +5 in phosphoric acids whereas it is +3 in phosphorous acids. You may notice that hypophosphorous and phosphorous acids have direct P–H bond(s) also. However, this P–H bond is not ionisable, it does not give H^+, and hence, it does not confer acidity. These acids are, therefore, monobasic and dibasic, respectively. Table 8.5 summarises the properties of oxoacids of phosphorus.

Table 8.5: Oxoacids of phosphorus and their properties

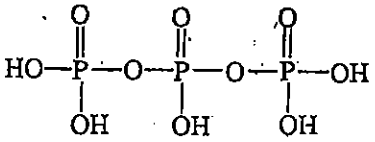
Acid	Nature	Preparation	Anion	Remarks
H_3PO_2 or $H_2P(OH)O$ Hypophosphorous	crystalline white solid	white P_4 + alkali	$H_2PO_2^-$ hypophosphite	strongly reducing, monobasic p$K \sim 2$
H_3PO_3 or $HPO(OH)_2$ Orthophosphorous	deliquescent colourless solid	P_4O_6 or $PCl_3 + H_2O$	$H_2PO_3^-$, HPO_3^{2-} phosphite	reducing, but slow, dibasic p$K_1 \sim 2$ p$K_2 \sim 6$
$H_4P_2O_3$ Pyrophosphorous	white solid	$PCl_3 + H_3PO_3$	$H_2P_2O_5^{2-}$ pyrophosphite	reducing, dibasic
$H_4P_2O_6$ Hypophosphoric	white solid	red P + alkali	$P_2O_6^{4-}$ hypophosphate	not reducing or oxidising, tetrabasic p$K_1 \sim 2$
H_3PO_4 Orthophosphoric	white solid	$P_4O_{10} + H_2O$	$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, phosphate	not oxidising, tribasic
$H_4P_2O_7$ Pyrophosphoric	colourless solid	heat phosphates or phosphoric acid	$P_2O_7^{4-}$ pyrophosphate	tetrabasic p$K_1 \sim 2$
HPO_3 Metaphosphoric	deliquescent solid	heat H_3PO_4 to 600 K		

A large number of condensed phosphoric acids or their salts are known which have rings or chains of PO_4 tetrahedra linked together through P–O–P linkages, e.g., di or pyrophosphoric acid, $H_4P_2O_7$ and triphosphoric acid, $H_5P_3O_{10}$:



$$HO-P(=O)(OH)-O-P(=O)(OH)-OH$$

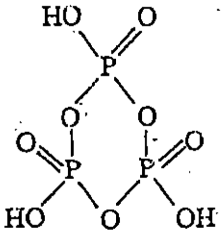
Diphosphoric acid



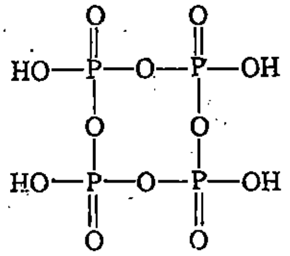
$$HO-P(=O)(OH)-O-P(=O)(OH)-O-P(=O)(OH)-OH$$

Triphosphoric acid

Sodium salt of triphosphoric acid, $Na_5P_3O_{10}$, forms stable chelate complexes with alkaline earth metal cations. It is, therefore, used in water softening. What is known as metaphosphoric acid and given the empirical formula HPO_3 is in fact a mixture of cyclo-polyphosphoric acids containing -P-O-P-O- linkages. Two important cyclo-polyphosphoric acids are cyclotriphosphoric acid, $H_3P_3O_9$ and cyclo-tetraphosphoric acid, $H_4P_4O_{12}$.



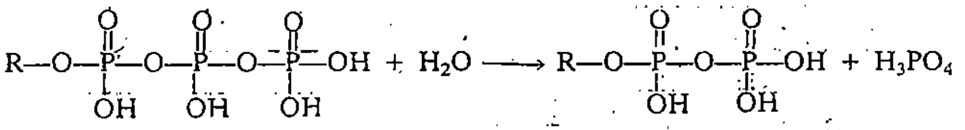
Cyclo-triphosphoric acid



Cyclo-tetraphosphoric acid

Salts of cyclo-polyphosphoric acids having 3-8 phosphorus atoms are known. Sodium cyclo-hexaphosphate, $Na_6P_6O_{18}\cdot 6H_2O$, known as calgon is a useful compound. It forms soluble complexes with alkaline earth metal cations. Therefore, it is used in water softening.

The phosphate link, P–O–P, is very important in biological systems, as it is supposed to be the prime store of energy. The energy of the bond (29 kJ mol^{-1}) is released to the system when needed, by enzyme catalysed hydrolysis of the phosphate link in adenosine triphosphate (ATP), the high energy molecule:



$$R-O-P(=O)(OH)-O-P(=O)(OH)-O-P(=O)(OH)-OH + H_2O \longrightarrow R-O-P(=O)(OH)-O-P(=O)(OH)-OH + H_3PO_4$$

Adenosine triphosphate (ATP) **Adenosine diphosphate (ADP)**

SAQ 5

a) Write one reaction each showing oxidising and reducing properties of HNO_3

....

....

....

b) Describe briefly the manufacture of nitric acid.

....

....

....

8.8 NITROGEN CYCLE, NITROGEN FIXATION AND PHOSPHATE FERTILISERS

We have, so far, studied the compounds of Group 15 elements. Now we will see some other aspects of their chemistry. You have already learnt about the nitrogen cycle in detail in the Foundation Course in Science and Technology. We will discuss it here briefly.

8.8.1 Nitrogen Cycle

Nitrogen cycle as you know, is the continuous exchange of nitrogen between the atmosphere and the biosphere. Though, the atmosphere contains large reserves of nitrogen, most plants and animals cannot utilise it in the elemental form. Plants can utilise nitrogen in the form of ammonium salts or as nitrates, so atmospheric nitrogen has to be converted to this form or '**fixed**' so that plants can utilise it.

One way of nitrogen fixation is by lightning discharges in the atmosphere, when nitrogen gets converted to nitric oxide and then to nitric acid. This nitric acid is washed down by rain into the soil, where it is neutralised by lime present in the soil to form calcium nitrate.

There is also a biological mode of nitrogen fixation. Certain bacteria, both free living or symbiotic, convert atmospheric nitrogen into ammonium salts. In the latter category is rhizobium which lives in the root nodules of leguminous plants like peas, beans, soya, etc. Such bacteria are called nitrogen fixing bacteria. It has been estimated that about 90–175 × 10^6 tonnes of nitrogen is fixed biologically per year. The comparable figures for industrial fixation are about 85 × 10^6 tonnes per annum.

The ammonium salts and nitrates are taken up from the soil by plants which convert them into proteins and nucleic acids, essential components of all living beings. From plants these are passed on to the herbivores, the animals which live on plants and then on to the carnivores along the food chain.

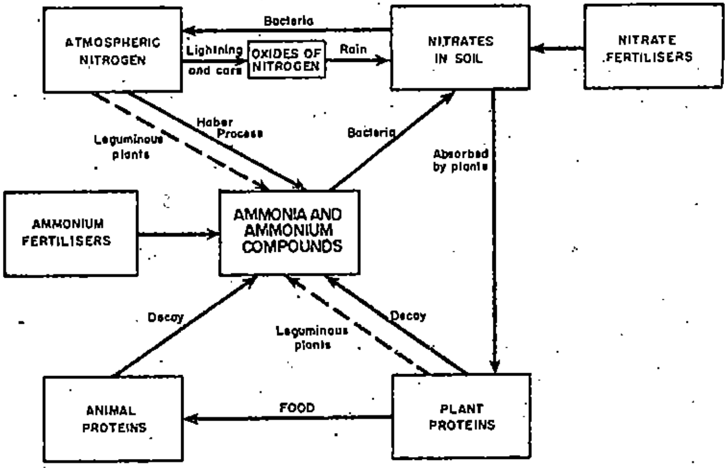


Fig. 8.14: Nitrogen cycle in nature

When the plants and animals die, their bodies decay, the nitrogenous compounds in their bodies get decomposed to ammonia and ammonium compounds by ammonifying bacteria present in the soil. The ammonium salts are converted to the nitrites by nitrosifying bacteria, and the nitrites oxidised to nitrates by nitrifying bacteria. An alternate path way is the conversion of nitrogenous compounds to elementary nitrogen by denitrifying bacteria. Release of nitrogen into the atmosphere, in a way, completes this cycle (Fig. 8.14).

8.8.2 Nitrogen Fixation

To meet the needs of the increasing world population, agricultural productivity needs to be increased. When the same soil is cropped intensively year after year, it gets depleted in nitrogen content which must be supplemented by artificial fertilisers to enhance production. In addition to the fertilisers there is also a great demand for other nitrogen compounds like polymers, explosives, etc. To meet these demands, we have to draw upon the atmospheric nitrogen. Atmospheric nitrogen can be fixed artificially by a variety of methods. One important method for the fixation of nitrogen is its conversion into NH_3 by Haber process which you have already studied. Formation of calcium cyanamide is another such method. **Calcium cyanamide**, is obtained by passing atmospheric N_2 over calcium carbide at 1400 K:

$$CaC_2 + N_2 \xrightarrow{1400\,K} CaCN_2 + C$$

Calcium cyanamide is used in large amounts as a nitrogenous fertiliser because it is slowly hydrolysed in the soil to ammonia :

$$CaCN_2 + 5H_2O \longrightarrow CaCO_3 + 2NH_4OH$$

It is also used as a source of organic chemicals such as melamine.

You can see that the conversion of atmospheric nitrogen into ammonia by Haber process and by Cyanamide process is expensive because these processes need the use of high temperature and pressure. Therefore, considerable research is going on to discover catalytic reactions which will convert nitrogen into ammonia under normal conditions, as in the case of biological processes.

8.8.3 Phosphate Fertilisers

As mentioned earlier also, phosphorus like nitrogen is an essential constituent of living organism. Plants and animals take phosphorus for their growth through different sources. Plants assimilate phosphorus from the soil which contains small quantities of phosphorus as phosphates. Phosphates are very important fertilisers. Animals get their phosphorus from plants as well as from other non-vegetarian sources, e.g., eggs, meat, etc. Some of this phosphorus is returned to the soil on death and decay of plants and animals. To make up for the phosphorus deficiency in the soil, especially in view of intensive agricultural activity, artificial fertilisers are needed. Phosphorite rock itself can be pulverised and used as a phosphate fertiliser, but because $Ca_3(PO_4)_2$ has a very low solubility it is able to deliver phosphate only slowly and in small amounts. However, treatment of $Ca_3(PO_4)_2$ with dilute sulphuric acid gives a fertiliser known as superphosphate of lime, a mixture of $CaSO_4$ and $Ca(H_2PO_4)_2$:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \longrightarrow \underbrace{Ca(H_2PO_4)_2 + 2(CaSO_4{\cdot}2H_2O)}_{\text{superphosphate of lime}}$$

Because $Ca(H_2PO_4)_2$ is water soluble, this mixture is a more effective fertiliser than phosphorite rock, hence, the name superphosphate. There are other phosphate fertilisers also, e.g., a mixture of $(NH_4)_2HPO_4$ and $CaHPO_4$. In the manufacture of steel, a by-product **phosphatic slag** is obtained. This slag is also a very good fertiliser.

SAQ 6

Fill in the blanks in the following sentences:

a) Continuous exchange of nitrogen between the atmosphere and the biosphere is called ....

b) Conversion of nitrogen into its compounds is known as ....

c) Bacteria which convert nitrogen into its compounds are called ....

d) Bacteria which convert nitrogen compounds into free nitrogen are known as ....

e) The ammonium compounds are converted into the nitrites by ....

f) The nitrites are oxidised to the nitrates by ....

g) Superphosphate of lime is a mixture of .... and ....

8.9 ANOMALOUS BEHAVIOUR OF NITROGEN

As usual, nitrogen, the first element of Group 15 differs considerably from rest of the family members. These differences are due to the small size of nitrogen, its high electronegativity, tendency to form stable multiple bonds and non-availability of *d*-orbitals in the valence shell. These differences have been highlighted in various sections of this unit. Let us bring them together here and see how many of these you can recollect.

- The elemental form of nitrogen is a stable gaseous molecule, N≡N, whereas other elements exist as solids. In the gaseous state, P, As and Sb exist in the form of tetra-atomic molecules, P_4, As_4 and Sb_4. This is due to the fact that bond energy of triply bonded nitrogen is much greater than that of phosphorus, i.e., $E_{N\equiv N} >> E_{P\equiv P}$; but the reverse is true for the single bonds. $E_{P-P} >> E_{N-N}$.

- Nitrogen is very inert as a consequence of the high bond strength of $N\equiv N$. The heavier elements are, however, comparatively more reactive.
- Nitrogen exhibits a large number of oxidation states such as –3, –2, –1, 0, +1, +2, +3, +4, +5. Other elements do not exhibit such a variety of oxidation states.
- Except for NF_3, the halides of nitrogen, NCl_3, NBr_3, NI_3 are unstable and highly explosive. The halides of other elements of this group are fairly stable.
- The oxides of nitrogen are gaseous, whereas the oxides of phosphorus, arsenic, etc. are solids.
- Nitrogen cannot expand its octet, whereas phosphorus and other elements can; the latter elements can, therefore, have coordination numbers greater than four. Thus, compounds like PF_5, PF_6^- have no nitrogen analogues. This has other effects also on the chemistry of nitrogen; for example, hydrolysis of NCl_3 is slow and yields a different product from the hydrolysis of PCl_3, which is fast.
- Since nitrogen is one of the most electronegative elements, it extensively enters into hydrogen bond formation. Other elements having comparatively low electronegativities, do not form hydrogen bonds.

8.10 SUMMARY

Let us now summarise what you have learnt about Group 15 elements in this unit.

- We have seen that these elements show a wide range of properties. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a metal.
- The principal method of industrial preparation of nitrogen is the fractionation of liquid air. Phosphorus is obtained commercially by treating a mixture of phosphorite rock, sand and coke in an electric furnace. Arsenic, antimony and bismuth are obtained by carbon reduction of their oxides at elevated temperatures. The uses of Group 15 elements have been reviewed.
- These elements form hydrides. Of these hydrides, ammonia is most important and is prepared commercially by direct reaction of nitrogen and hydrogen (Haber process). Other important hydrides of nitrogen include hydrazine, and hydrazoic acid. All the Group 15 elements form trihalides, some pentahalides are also known. The elements, N, As, Sb and Bi, also form oxohalides of the type MOX, phosphorus forms oxohalides of the type POX_3.
- Oxides of nitrogen are known for every positive oxidation state of nitrogen from +1 to +5. The important oxides of phosphorus contain phosphorus in oxidation states of +3 (P_4O_6) and +5 (P_4O_{10}). Arsenic, antimony and bismuth also form +3 oxides (As_4O_6, Sb_4O_6 and Bi_2O_3) and +5 oxides (As_2O_5 and Sb_2O_5).
- The most important oxoacid of nitrogen is nitric acid, HNO_3. It is an important industrial chemical. Another important oxoacid of nitrogen is nitrous acid which is unstable, except in solution. Phosphorus forms a large number of oxoacids, e.g., orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid, etc. These acids form phosphates which are important ingredients of fertilisers.
- Oxoacids of arsenic and antimony are not well characterised. However, the corresponding salts are known.
- In nature, nitrogen is constantly being taken up from the atmosphere and returned to it. This is called the nitrogen cycle. A brief account of nitrogen cycle and the fixation of nitrogen is also given.
- As in the other groups, the first element of Group 15, i.e., nitrogen shows some anomalous behaviour. This has been highlighted.

8.11 TERMINAL QUESTIONS

1 Write the electronic configuration of nitrogen and phosphorus in the ground state.

Point out the major difference between the two, that is responsible for differences in various properties.

2 Explain why nitrogen is chemically less reactive.

3 Explain why NF_3 is stable, while NCl_3 and NI_3 are explosives.

4 Why are PBr_5 and PI_5 less stable despite the fact that phosphorus(V) is not an oxidising state?

5 Why are the oxides of nitrogen so different from those of phosphorus?

6 For the three hydrides, NH_3, PH_3 and AsH_3.

a) give the shape of the molecule and state how the bond angle varies from $NH_3 \rightarrow PH_3 \rightarrow AsH_3$?

b) state which is the strongest and which is the weakest base? Why?

c) give an explanation, in terms of bonding, for the difference in the boiling points of ammonia and phosphine which are 240 K and 186 K, respectively.

7 Explain briefly why the hydrolysis of NCl_3 and PCl_3 yields different types of products.

8.12 ANSWERS

Self Assessment Questions

1 a) Because the bond energy of N≡N bond is about six times the energy of N–N bond, nitrogen exists as a diatomic molecule. On the contrary, P≡P bond energy is only 2.5 times the P–P bond energy. Therefore, phosphorus prefers to exist as a P_4 molecule having six P–P bonds.

b) White phosphorus is more reactive than red phosphorus because of higher angular strain in the former.

2 a) Ammonia has a lone pair of electrons on the nitrogen atom, therefore, it acts as a Lewis base.

b) The substances which furnish NH_4^+ and NH_2^-, act as acids and bases, respectively in liquid ammonia, e.g., NH_4Cl acts as an acid whereas $NaNH_2$ acts as a base.

c) In hydrazine, there is N–N single bond with a lone pair on each nitrogen. Due to the small size of nitrogen, there is considerable repulsion between these nonbonding electrons, thus weakening the N–N single bond. This makes hydrazine unstable.

3 Because of the nonavailability of *d*-orbitals, nitrogen atom cannot accommodate more than eight electrons in its valence shell, therefore, its trihalides cannot be oxidised to pentahalides.

4 Nitric oxide is paramagnetic because of the presence of an unpaired electron. On losing this unpaired electron, nitrosonium ion, NO^+, is formed, which is diamagnetic.

5 a) i) $2KI + 2HNO_2 + 2HCl \longrightarrow 2KCl + 2NO + 2H_2O + I_2$

ii) $2KMnO_4 + 5HNO_2 + 6HCl \longrightarrow 2MnCl_2 + 5HNO_3 + 2KCl + 3H_2O$

b) Nitric acid is manufactured by Ostwald process. Ammonia is first oxidised to NO by air in the presence of a Pt–Rh catalyst. NO is then mixed with more air to convert it to NO_2 which is dissolved in water to give HNO_3. (See reactions in sub-section 8.7.1).

6 a) Nitrogen cycle b) Fixation of nitrogen
c) Nitrogen fixing bacteria d) Denitrifying bacteria
e) Nitrosifying bacteria f) Nitrifying bacteria
g) $Ca(H_2PO_4)_2$ and $CaSO_4 \cdot 2H_2O$

Terminal Questions

1 N; $1s^2 2s^2 2p^3$

P; $1s^2 2s^2 2p^6 3s^2 3p^3 3d^0$

The main difference between N and P in terms of electronic configuration is the availability of *d*-orbitals in P. Because of the availability of *d*-orbitals in P, it can expand its octet and thus form many compounds which are not known for nitrogen.

2 The bond energy of N≡N is very high due to which nitrogen is much less reactive under ordinary conditions.

3 The N–F bond is very strong compared to N–Cl and N–I. Thus, NF_3 is very stable while NCl_3 and NI_3 decompose explosively.

4 In PBr_5 and PI_5, the atomic size of halogens is very large compared to the small size of phosphorus, so five halogens cannot be packed around phosphorus. Therefore, PBr_5 and PI_5 are less stable.

5 Nitrogen forms weak N–O bonds and strong N=O bonds with oxygen, its oxides exist as monomeric gaseous species. On the other hand, phosphorus forms strong P–O bonds and weak P=O bonds, its oxides exist as dimeric species.

6 a) Shape of all the hydrides is pyramidal, the bond angle being $\angle HNH > \angle HPH > \angle HAsH$. This is because the electro-negativity of the central atom decreases as we go down the group, thus forcing bonding electrons to be away from the central atom. This reduces the repulsion of bonding pairs in PH_3 and AsH_3, thus decreasing the bond angle HEH in the order given above.

b) The strongest base is NH_3 while the weakest is AsH_3. This is because as we go down the group, the bond angle decreases such that the bonded orbitals have more *p* character and the lone pair has more *s* character. We know that it is difficult to remove *s* electrons so the donor property decreases as we go down the group from NH_3 to AsH_3 and thus base strength also decreases.

c) The boiling point of ammonia is much higher than that of phosphine because there is strong hydrogen bonding in ammonia.

7 In the hydrolysis of PCl_3, a four coordinate intermediate is formed, it hydrolyses forming H_3PO_3. Due to the nonavailability of *d*-orbitals, nitrogen cannot form this intermediate so the hydrolysis of NCl_3 takes place by a different mechanism. In this mechanism, water attacks the chlorine atom of NCl_3 resulting in the formation of NH_3 and hypochlorous acid.

FURTHER READINGS

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

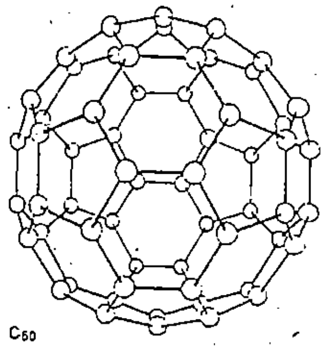
2 *Chemistry : Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

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

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

APPENDIX - I

FULLERENES - Great Balls of Carbon



C_{60}

As was mentioned in Unit 7 fullerenes are the new form of element carbon in which carbon atoms are 'symmetrically arranged in closed shells. They are formed when vapourised carbon condenses in an atmosphere of inert gas and produces clusters with 60 carbon atoms and clusters with 70. The C_{60} cluster has a great symmetry and it was thought to be a truncated icosahedron cage' structure i.e, a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5 - angled) surfaces (see Fig. in the margin). The pattern of a football has exactly this structure therefore, the C_{60} molecule is sometimes called as football molecule also. The diameter of a C_{60} molecule is only 0.7 mm. The structure also resembles the geodesic dome designed by the American architect R.Buckminster Fuller for the 1967 Montreal world exhibition. The researchers, therefore named this allotrope of carbon as ***Buckminsterfullerene*** after him.

The physicists who first discovered fullerenes had a very simple method for making them, they vapourised a graphite rod by passing a very high current through it. The vapour was prevented from reacting with the air by enclosing the rod in an inert helium atmosphere. The product obtained by this method was a fluffy, black soot. This carbon condensate was extracted with an organic solvent to get a mixture of C_{60} and C_{70}. The structure was confirmed using X-ray crystallography and other spectroscopic techniques. The chemists proposed its structure corresponding to an aromatic three dimensional system in which single and double bonds alternated.

Properties

As you might guess fullerenes have very different properties from diamond and graphite. For instance, C_{60} dissolves in benzene to form a wine-red solution and has mustard colour crystals. It is stable in the dark.. If kept in air and exposed to ultraviolet light, the cage breaks into fragments.

Birch reduction was done to confirm the presence of double bonds in fullerenes. It uses lithium metal dissolved in liquid ammonia to reduce(or hydrogenate) the fullerene double bonds leading to $C_{60}H_{36}$. Osmium tetraoxide (OsO_4) reacts with one of the double bonds in the cage and if an excess of 4-tert-butylpyridine is present in the reaction mixture, a stable compound can be isolated.

The C_{60} structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. Potassium, lanthanum and various other metals have been used for this purpose.

Uses

Fullerenes are now finding use in organic chemistry, electrochemistry and semiconductor technology. They act as superconductors when doped with alkali metals. Fullerenes may find use as optical limiters since C_{60} is transparent to low intensity but opaque to high intensity light. This property can be used to protect optical sensors from intense light. Some researchers think that fullerenes will make excellent lubricants by acting like tiny ball bearings. Many more applications will now be found owing to the aromatic and highly stable form of these molecules.

NOTES

Uttar Pradesh
Rajarshi Tandon Open University

UGCHE-03

Inorganic Chemistry

Block

3

p–BLOCK ELEMENTS–II

UNIT 9

Elements of Group 16 5

UNIT 10

Elements of Group 17 27

UNIT 11

Elements of Group 18 48

BLOCK 3 p-BLOCK ELEMENTS – II

In Block 2, you studied the salient features of the chemistry of p–block elements of Groups 13, 14 and 15. You learnt that the elements of these groups have a very extensive and varied chemistry. They exhibit more than one stable oxidation state, the lower oxidation state becomes progressively more stable down the group. A change from non-metallic to metallic nature is clearly observed on descending a group.

In this block, you will study the main features of the chemistry of the elements of remaining three groups of the p-block, namely, Groups 16, 17 and 18.

Unit 9 deals with the elements of Group 16 comprising of oxygen, sulphur, selenium, tellurium and polonium. Oxygen and sulphur are non-metals, selenium and tellurium are metalloids, whereas polonium is a weakly electropositive metal. The atoms of these elements are just two electrons short of the configuration of the next noble gas. They may acquire the noble gas configuration by forming oxide, sulphide, selenide and telluride ions. In addition to such divalent species, S, Se, Te and Po also form compounds in oxidation states IV and VI by using d orbitals in their valence shell.

In Unit 10 you will study the chemistry of Group 17 elements, namely, fluorine, chlorine, bromine, iodine and astatine. These elements are collectively called halogens. As their atoms are only one electron short of the noble gas configuration, the elements readily form halide ions, X^- or a single covalent bond. Halogens are the most electronegative elements in their respective periods and their chemistries are essentially non–metallic. Although first member of the group, i.e., fluorine exhibits anomalous behaviour, the elements of this group in general, show similar chemistries.

Unit 11 is about the elements of Group 18, namely, helium, neon, argon, krypton, xenon and radon. All these elements, except radon which is radioactive and rare, are constituents of air. The closed shell electronic structures of the atoms of these elements are extremely stable. Only krypton, xenon and radon form a few compounds. By analogy with the noble metals gold and platinum, these elements are now known as noble gases.

We expect that after studying this block, you should be able to :

- discuss the periodic trends in properties of the elements of Groups 16, 17 and 18,
- describe the main features of the chemistry of the elements of Groups 16, 17 and 18,
- compare the properties of p-block elements with those of the s-block elements.

UNIT 9 ELEMENTS OF GROUP 16

Structure

9.1 Introduction
  Objectives
9.2 Occurrence, Extraction and Uses
  Occurrence
  Extraction
  Uses
9.3 General Characteristics
  Physical Properties
  Chemical Properties
9.4 Compounds of Group 16 Elements
  Hydrides
  Halides
  Oxides
9.5 Oxoacids of Sulphur
  Sulphurous Acid
  Sulphuric Acid
  Peroxoacids of Sulphur
  Thiosulphuric Acid
9.6 Anomalous Behaviour of Oxygen
9.7 Summary
9.8 Terminal Questions
9.9 Answers

9.1 INTRODUCTION

In the previous unit, you studied the Group 15 elements. In this unit, we shall discuss Group 16 elements, viz., oxygen, sulphur, selenium, tellurium and polonium. These elements are called **chalcogens** or the ore forming elements. This name was derived from the Greek name for copper, since most of the copper ores contain members of this group. Compared to Groups 14 and 15 elements, the elements of this group are even more non-metallic in their behaviour. These also exhibit a gradual change towards metallic characteristics down the group. Thus polonium, the last member of the group, is almost metallic. We will describe the occurrence and extraction of these elements and also their allotropic modifications. Uses of these elements and some of their compounds will also be described. We shall then go on to discuss the general behaviour of these elements and their important compounds like hydrides, halides, oxides and oxoacids. In the next unit, you will study Group 17, which consists of halogens.

Objectives

After studying this unit, you should be able to :

- describe the occurrence, extraction and uses of the elements of Group 16,
- describe the allotropic forms of all these elements,
- discuss the general characteristics of Group 16 elements,
- describe the general properties of hydrides, halides and oxides of Group 16 elements, and
- list different oxoacids of Group 16 elements with an emphasis on the oxoacids of sulphur.

9.2 OCCURRENCE, EXTRACTION AND USES

Except oxygen and sulphur, other elements of the group are relatively scarce. While oxygen sustains all life on this planet, other elements and their compounds also find a variety of uses. We shall discuss the occurrence, extraction and uses of these elements in this section.

9.2.1 Occurrence

Oxygen is the most abundant of all elements on earth. Dry air contains 20.946% oxygen by volume in the free form. Oxygen forms about 46.6% by weight of the earth's crust including the oceans and the atmosphere. Most of this combined oxygen is in the form of silicates, oxides and water. Water is one of the most abundant compounds on earth, present not only in oceans which cover three fourths of the earth's surface but also in the atmosphere as vapour and in the subterranean aquifers. Living organisms also contain large amounts of water. Water contains 88.8% of oxygen by weight.

By contrast, the abundance of sulphur in the earth's crust is only 0.03–0.1%. It is often found as the free element near volcanic regions in Japan, Sicily, Mexico and Luisiana in USA. Combined sulphur exists primarily in sulphates and sulphides, such as gypsum, $CaSO_4 . 2H_2O$, barite, $BaSO_4$ and epsom salt, $MgSO_4 . 7H_2O$. The sulphides include galena, PbS, zinc blende, ZnS, chalcopyrite, $CuFeS_2$, iron pyrite, FeS_2 and cinnabar, HgS, etc. It also occurs in mineral springs as H_2S. Along with C, H, O, N and P, sulphur is one of the twenty-three odd elements essential for life. It is a constituent of substances such as eggs, wool, hair and also mustard, garlic, cabbage, etc. Selenium and tellurium also occur as sulphide ores. Polonium occurs naturally as a decay product in thorium and uranium minerals.

Allotropic forms

All the elements of the group show allotropy. Oxygen exists in two allotropic forms. Dioxygen, O_2, is a diatomic gas, paramagnetic in nature. Lewis structure of oxygen molecule with a pair of covalent bonds between two oxygen atoms, as shown in the margin is inadequate in explaining its paramagnetic nature (Fig.9.1). This structure with all paired electrons is expected to be diamagnetic rather than paramagnetic. Paramagnetism of oxygen can be explained on the basis of Molecular Orbital Theory. This theory has been explained in detail in Unit 5 of the 'Atoms and Molecules' course. The molecular orbital configuration of O_2 molecule can be represented as :

$$KK, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{matrix} \pi 2p_y^2 & \pi^* 2p_y^1 \\ \pi 2p_z^2, & \pi^* 2p_z^1 \end{matrix}$$

Selenium has been named after the goddess of moon 'Selene'

Polonium was named after Marie Curie's home country, Poland. She was also the discoverer of this element.

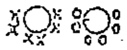


Fig 9.1 : Lewis structure of O_2 molecule.

The presence of two unpaired electrons in the antibonding orbitals explains the experimentally observed paramagnetic behaviour.

Ozone, O_3, the other allotropic form of oxygen is a triatomic, pale blue gas. The only method used to make ozone commercially is to pass gaseous oxygen or air through a high voltage electric discharge called a silent electric discharge.

Perhaps you know that the earth is covered by a layer of ozone which protects us from injurious ultraviolet rays coming from the sun. In the upper atmosphere at altitudes ranging from about 15–24 km, ozone is formed in appreciable amounts from oxygen by absorption of ultraviolet radiation from the sun. This radiation first splits O_2 molecule into oxygen atoms, which react with O_2 molecules to give O_3.

$$O_2 \xrightarrow{hv} 2O$$

$$O_2 + O \longrightarrow O_3$$

Ozone also absorbs ultraviolet light. This causes the O_3 to decompose and form O_2 again.

$$2O_3 \longrightarrow 3O_2$$

The absorption of uv radiation by O_3 serves a twofold purpose. It protects the inhabitants of our planet from injurious radiation and maintains an equilibrium between the concentrations of O_2 and O_3. Recently there has been a serious concern about the depletion of this layer. Nitric oxide from emissions of supersonic jets and chlorofluorocarbons used as aerosol propellants and as refrigerants have been identified as the main culprits. There is considerable international effort to save the protective ozone layer.

Sulphur displays allotropy to a remarkable degree, existing both in a variety of different molecular and physical forms. The molecular species, viz., S_2, S_4, S_6 and S_8 are in equilibrium in gaseous sulphur, their proportions varying with the temperature. The commonest and the most stable allotrope of sulphur at room temperature is known as rhombic sulphur or α–sulphur, S_α. In rhombic sulphur, S_8 rings are arranged in a way, Fig. 9.2, that gives a rhombic crystal structure. At 369 K, rhombic sulphur gets converted into monoclinic sulphur or β–sulphur, S_β. In monoclinic sulphur, S_8 rings are arranged in a monoclinic structure. It is stable between 369 and 392 K. At 392 K it melts to produce a liquid containing S_8 molecules, S_λ. At about 433 K the S_8 rings open up and join together into long spiral-chain molecules resulting in a thick viscous liquid, μ-sulphur, S_μ. Liquid sulphur boils at 718 K to give gaseous sulphur containing S_8 molecules, which dissociate to S_6, S_4, S_2 and finally to sulphur atoms at 2273 K. If liquid sulphur at 463 K is poured into cold water, **plastic sulphur** or **γ-sulphur** is formed. The allotropy of sulphur as a function of temperature is summarised as follows :

$$\begin{tikzcd}
 & & & & S_\gamma & \\
S_\alpha \arrow[r, "369\ K"] & S_\beta \arrow[r, "392\ K"] & S_\lambda \arrow[r, "433\ K"] & S_\mu \arrow[r, "718\ K"] \arrow[ur, "\text{cold water}"] & S_8(g) \arrow[r] & S_6
\end{tikzcd}$$

$$\longrightarrow S_4 \xrightarrow{1273\ K} S_2 \xrightarrow{2273\ K} S$$

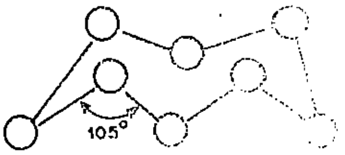


Fig. 9.2 : Structure of S_8 molecule.

Selenium, tellurium and polonium also exhibit allotropy. Amorphous as well as crystalline forms of selenium and tellurium are known.

9.2.2 Extraction

Oxygen is separated from air on a large scale by the fractional distillation of liquid air. It is obtained as a by-product along with hydrogen during electrolysis of water for the manufacture of heavy water. Ordinary water, H_2O, electrolyses faster with the result that residual water is richer in D_2O. In laboratory, O_2 can be prepared by thermal decomposition of $KClO_3$ in presence of MnO_2 as a catalyst :

$$2KClO_3 \xrightarrow[MnO_2\ \text{catalyst}]{\text{heat}} 2KCl + 3O_2$$

The most important method for the extraction of sulphur from native deposits is the **Frasch Process** developed by Herman Frasch in 1891. It consists of boring a hole from the ground surface to the sulphur bearing calcite deposit and lowering three concentric pipes to the ore bed (Fig. 9.3). Superheated steam, 438 K is forced down the outer pipe into the ore bed where it melts the sulphur. Compressed hot air is pumped down through the innermost pipe when a frothy mixture of molten sulphur, water and air is forced to the surface through the middle pipe. As it comes out from the well, sulphur has a purity of 99.5-99. 9% and contains virtually no As, Se or Te.

Sulphur is also obtained as a by-product in the production of coal gas and in refining crude oil and natural gas. Biotechnological techniques have now been developed for winning sulphur from sulphide ores.

Selenium and tellurium are obtained in concentrated form from anode mud obtained in the electrolytic refining of copper. Polonium is made artificially by neutron irradiation of bismuth in a nuclear reactor.

$$^{209}_{83}Bi + ^{1}_{0}n \longrightarrow ^{210}_{83}Bi \longrightarrow ^{210}_{84}Po + e$$

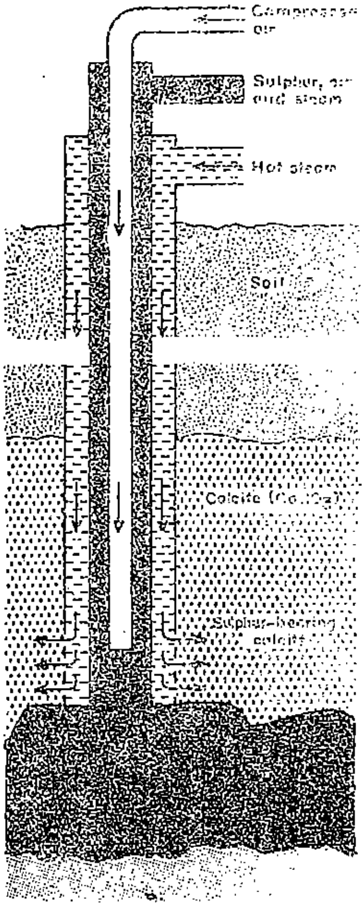


Fig. 9.3 : The Frasch process for extracting sulphur.

9.2.3 Uses

Oxygen is essential for life. Most life processes are based on oxidative metabolism. While the terrestrial beings take up oxygen through respiration, the aquatic plants and animals survive on oxygen dissolved in water. It is an important oxidant used in various energy generation processes through combustion of wood or of fossil fuels like coal, natural gas and petroleum. Rocket fuels have liquid oxygen as the oxidant. Since oxyacetylene and oxy-hydrogen flames have very high temperatures, they are used in cutting metals and in welding. Many chemical industries also use oxygen as an oxidant, e.g., in manufacture of ethylene and propylene oxides, vinyl acetate for polymer industry and oxidation of ammonia for manufacture of nitric acid. Ozone which is an allotropic form of oxygen is also a powerful oxidising agent. Ozone undergoes a characteristic reaction with unsaturated organic compounds where it attacks a double or triple bond. It can, therefore, be used for the detection and characterisation of the double or triple bond. It is also used in the treatment of drinking water.

Detergents are sodium salts of alkyl benzene sulphonic acids where alkyl groups are linear. Heavy metal salts of these benzene sulphonic acids are soluble, therefore, detergents can be used in hard water.

Sulphur is used in the manufacture of sulphur dioxide, sulphuric acid, gunpowder, matches, fertilisers, drugs, bleaching agents, leather and other products. Large quantities of elemental sulphur are used in the vulcanisation of rubber, in certain ointments and medicines. Sulphuric acid of varying concentrations is used in the manufacture of fertilisers, paints, pigments, dye-stuffs, fibres, plastics, detergents and soaps. It also finds its use in refining petroleum. In recent years nitrogen-sulphur compounds have aroused considerable interest because of their superconducting properties. A binary polymer, $(SN)_x$, exhibits metallic characteristics and becomes superconducting below 0.33 K.

Uses of selenium include photocopying process of xerography, decolorisation of glasses and as a catalytic agent particularly in the isomerisation of certain petroleum products. Selenium dioxide is used as an oxidising agent in organic reactions.

Tellurium is used primarily as an additive to steel to increase its ductility. It is also used as an additive to some catalysts, used in cracking of petroleum, as a colouring material for glasses and as an additive to lead to increase its strength and make it corrosion resistant: Polonium – 210 is used mainly for the production of neutron sources; for these, polonium is alloyed with elements such as beryllium.

SAQ 1

On the basis of molecular orbital diagram given for O_2 molecule, find out the number of unpaired electrons in the following:

(i) O_2^+ (ii) O_2^- (iii) O_2^{2-}

....

....

....

9.3 GENERAL CHARACTERISTICS

The valence shell electronic configuration of Group 15 elements is ns^2, np^4. These elements tend to gain inert gas configuration by accepting two electrons and forming E^{2-} anions (E=O, S, Se & Te) or by sharing two electrons in forming two covalent bonds. Let us see how their physical properties are related to their electronic configuration and how do they behave chemically.

9.3.1 Physical Properties

Similar to the groups discussed earlier, the metallic character in Group 16 increases with increasing atomic number. Oxygen and sulphur are entirely non-metallic in their chemical behaviour. Selenium and tellurium, though essentially non-metallic, assume increasing metallic character and are termed as metalloids. Polonium is most metallic in the group. Some physical properties of Group 16 elements are listed in Table 9.1, and the trends in these properties are shown graphically in Figures 9.4 – 9.7.

Density, Fig. 9.4, melting and boiling points, Fig. 9.5, covalent and ionic radii, Fig 9.6 show a regular increase from oxygen to polonium. The large difference in melting and boiling points between oxygen and sulphur can be explained on the basis of their structure. Oxygen exists mostly as a diatomic molecule held together by weak van der Waals forces while others exist as polyatomic molecules, e.g., S_8, Se_8, etc., where the atoms are bonded by covalent bonds associated with high dissociation energy. Their existence as diatomic and polyatomic molecules can be explained as follows. The bond energy of the oxygen-oxygen double bond, O=O, is 498 kJ mol^{-1}. This makes the O=O bond more than three times as strong as the O–O bond (bond energy for O–O is 142 kJ mol^{-1}). By comparison the S=S bond is less than twice as strong as the S–S single bond (bond energy for S=S, 431 kJ mol^{-1}; S–S, 264 kJ mol^{-1}). This results in catenated –O–O–O– chains being unstable relative to O=O; but catenated –S–S–S– chains being stable relative to the molecule S=S.

The elements of Group 16 are characterised by high ionisation energies, Fig. 9.7, decreasing gradually from oxygen to polonium. The high values indicate reluctance of these elements to form cations. Their electronegativities decrease with increasing atomic number. Thus, in view of the fall in electronegativity, metallic character within the group increases with increasing atomic size.

Table 9.1 : Some physical properties of Group 16 elements

Property	O	S	Se	Te	Po
Atomic Number	8	16	34	52	84
Electronic configuration	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]3d^{10}4s^24p^4$	$[Kr]4d^{10}5s^25p^4$	$[Xe]4f^{14}5d^{10}6s^26p^4$
Covalent radius (pm)	66	104	117	137	146
Ionic radius, E^{2-}(pm)	140	184	198	221	230
Electron affinity, E^- (kJ mol^{-1})	−141	−200	−195	−190	−183
Ionisation energy 1st (kJ mol^{-1})	1314	1000	941	869	813
Electronegativity (A/R)	3.5	2.45	2.5	2.0	1.75
Density ($10^3 \times kg\,m^{-3}$)	1.14	2.07	4.79	6.25	9.4
Melting point (K)	55	392	490	723	527
Boiling point (K)	90	717.6	957.8	1263	1235
Oxidation states*	−2,−1,1,2	−2,2,4,6	−2,2,4,6	−2,2,4,6	2,4

* Oxygen shows oxidation states of +1 and +2 in oxygen fluorides OF_2 and O_2F_2.

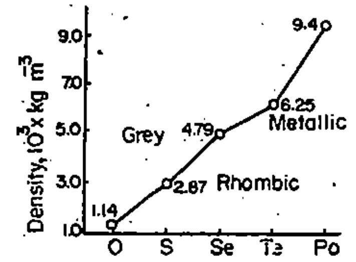


Fig. 9.4 : Densities of the oxygen family

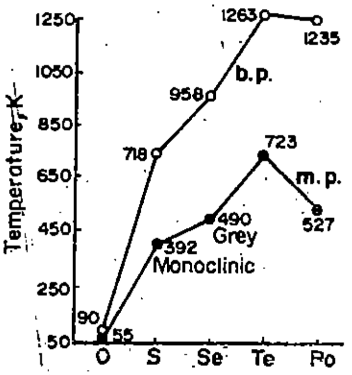


Fig. 9.5 : Melting and boiling points of the oxygen family

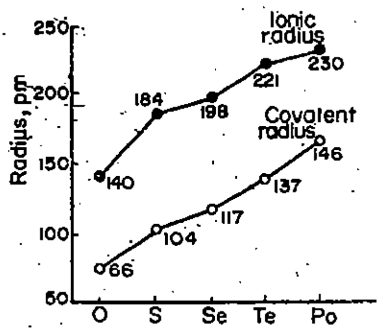


Fig 9.6 : Covalent and ionic radii of the oxygen family

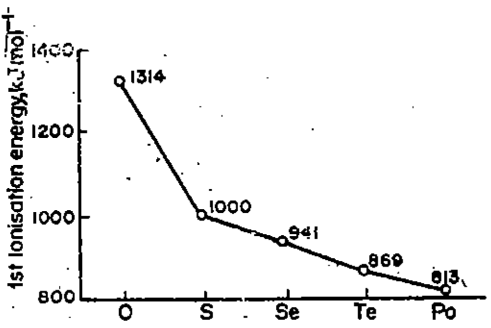


Fig.9.7: Ionisation energies of the oxygen family

Oxygen, the second most electronegative element, fluorine being the first, has a strong tendency to accept two electrons and give O^{2-} ion. Thus, almost all metal oxides are ionic and contain O^{2-} ions. Usually oxygen exhibits an oxidation state −2 in its other compounds also. It exhibits positive oxidation states only in a few compounds formed with fluorine, i.e., OF_2 and O_2F_2. The tendency for the formation of divalent anions decreases from sulphur downwards because of the increasing size and decreasing electronegativity of the elements. Sulphur, selenium and tellurium show a tendency for covalency with form. oxidation states +2, +4 and +6 in compounds in which they are combined with more electronegative elements such as oxygen and halogens. You may note that in the higher oxidation states of +4 and +6 of these elements electrons are unpaired and promoted to vacant *d* orbitals.

Oxygen, and to a greater extent, sulphur differ from the other members of the group in their ability to catenate and form peroxides, H-O-O-H and polysulphides, H_2S_n, n=1–8, respectively. The strong tendency of catenation in sulphur is evident from the fairly high bond dissociation energy of S–S single bond (264 kJ mol^{-1}). As discussed earlier it is also reflected in the high melting and boiling points of sulphur.

Bond Lengths and $p\pi - d\pi$ Bonding

The bonds between S and O are much shorter than expected for a single bond in its oxides and therefore, may be considered as double bonds. Along with a sigma bond between S and O, a π–bond is also formed by overlap of an oxygen *p*–orbital and sulphur *d* –orbital, forming a $p\pi - d\pi$ bond. Oxygen and sulphur have comparable energy and the size of *p* and *d* orbitals and, therefore, have effective $p\pi–d\pi$ overlap. But going from Se to Te, weaker bonds are formed because of difference in the size and energy of the *p* and *d* orbitals.

9.3.2 Chemical Properties

Oxygen is slightly less reactive than the halogens but reacts directly with nearly all the elements except the noble gases, the halogens and a few noble metals. Despite the high bond dissociation energy of O_2(498 kJ mol^{-1}), these reactions are frequently highly exothermic and, once initiated, can continue spontaneously or even explosively. For example, its reactions with carbon and hydrogen producing CO_2 and H_2O, respectively.

$$C(s) + O_2(g) \longrightarrow CO_2(g),\ \Delta H = -394\ kJ\ mol^{-1}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O\ (l),\ \Delta H = -568\ kJ\ mol^{-1}$$

Sulphur is also a very reactive element, particularly at slightly high temperatures. It reacts slowly with H_2 at 390 K, more rapidly above 473 K. Hot concentrated HNO_3 oxidises S to H_2SO_4.

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2\uparrow + 2H_2O$$

Sulphur dissolves in hot alkali giving a mixture of sulphide and sulphite as the first products. These react with excess of S giving polysulphides of the type Na_2S_n and some thiosulphate, $Na_2S_2O_3$:

$$3S + 6NaOH \longrightarrow 2Na_2S + Na_2SO_3 + 3H_2O$$

$$Na_2S + Na_2SO_3 + nS \longrightarrow Na_2S_2O_3 + Na_2S_n$$

It reacts with halogens to give compounds like SF_6, SF_4, S_2Cl_2, S_2Br_2, etc. The non-metals react with sulphur mostly at elevated temperatures. Sulphur compounds exhibit numerous possible oxidation states, from –2 to +6. You will study about them in the next section.

Selenium, tellurium and polonium combine directly with most elements, though less readily than do O and S, the most stable compounds are the selenides, tellurides and polonides (M^{2-}).

They form compounds with electronegative elements O, F and Cl in which the oxidation states are +2, +4 and +6.

SAQ 2

List the elements O, S, Se and Te in the order of decreasing

(i) b.p. (ii) m.p. (iii) electronegativity and (iv) ionisation energy.

(i) b.p.

....

(ii) m.p.

....

(iii) electronegativity

....

(iv) ionisation energy

....

9.4 COMPOUNDS OF GROUP 16 ELEMENTS

We will now discuss some compounds like the hydrides, halides and oxides of the Group 16 elements.

9.4.1 Hydrides

All elements of this group form simple volatile binary hydrides of the type H_2X ($X = O, S$, etc.). The simple hydride of oxygen is H_2O or water. The other known hydride of oxygen is H_2O_2, hydrogen peroxide. Sulphur forms the most extensive series of catenated hydrides such as H_2S, H_2S_2, H_2S_3, H_2S_4, etc. Hydrides of sulphur, other than H_2S, are all yellow oils which readily decompose into H_2S and free sulphur. Selenium, tellurium and polonium form H_2Se, H_2Te and H_2Po, respectively.

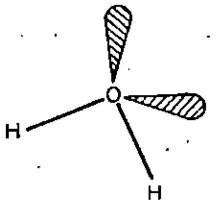


Fig 9.8: Structure of H_2O molecule

The reducing power of hydrides increases whereas their thermal stability decreases in the order H_2O; H_2S; H_2Se; H_2Te; H_2Po. In fact H_2Se and H_2Te are better reducing agents than hydrogen.

Some of the physical properties of the hydrides are summarised in Table 9.2.

Table 9.2: Some physical properties of binary hydrides

Hydride	M.P. (K)	B.P. (K)	Heat of formation ΔH_f (kJ mol^{-1})	Bond dissociation energy for E–H (kJ mol^{-1})
H_2O	273	373	–242	466.2
H_2S	187.5	212.5	–20.2	340.6
H_2Se	207	231	+85.8	277.6
H_2Te	222	271	+154.4	241.5

The hydride molecules are angular in shape. The bond angles in H_2O, H_2S, H_2Se and H_2Te being 104.5°, 92°, 91° and 89.0°, respectively. In case of H_2O, oxygen is supposed to be sp^3 hybridised with two lone pairs occupying two positions on the tetrahedron, Fig. 9.8. The distortion from the tetrahedral angle (109°28′) is supposed to be due to stronger repulsion between lone pairs of electrons compressing the bond angle. In the case of other hydrides, bond angles are close to 90° suggesting that almost pure p – orbitals are involved in bonding to hydrogen.

Water and Heavy Water

Water, H_2O, the simple hydride of oxygen is a unique compound. It has extraordinarily high melting and boiling points compared to the other hydrides of the group, Fig. 9.9. This is attributed to the high polarity of the molecule due to the large electronegativity difference between oxygen and hydrogen atoms. The high polarity of the molecule leads to very extensive association in water due to hydrogen bonding (see Unit 3).

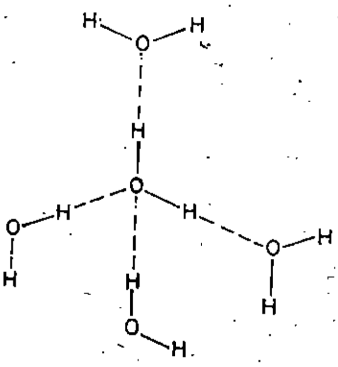


Fig. 9.10 : Structure of ice

Polarity of water is responsible also for it being a very good solvent, especially for ionic compounds. Most reactions in nature take place in aqueous solutions, including the very complex reactions in the living systems. Ice, the solid state of water is a giant polymeric molecule formed by tetrahedrally placed water molecules, held together by hydrogen bonds. Each oxygen atoms is surrounded by four hydrogen atoms, two covalently linked and two hydrogen bonded. In turn, each hydrogen atom is surrounded by four oxygen atoms. Because of this arrangement of water molecules, ice has a cage structure (Fig. 9.10) with lot of empty spaces. It is lighter than liquid water. Ice, in fact, floats on the surface of water. The density of water varies with temperature and is maximum at 277 K. These two factors in an unique way are related with the sustenance of aquatic life. The ice once formed protects lower layers of water from further cooling, and the highest density at 277 K ensures that water at the lower depths will never get cooler than that. So, you can see that in a way water has

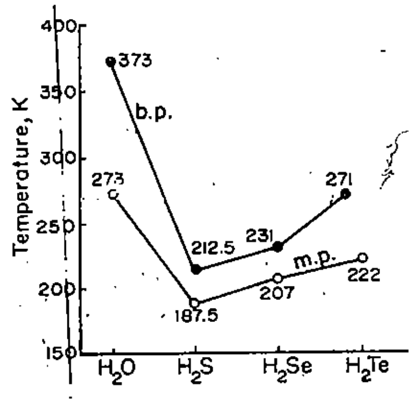


Fig 9.9 : Melting and boiling points of the hydrides of the elements of Group 16.

made the earth as we know it. Its geographical features have been shaped by various processes in which water is an active agent. The living beings also owe their existence to water.

Imagine a scenario, where ice formed sinks to the bottom, the whole oceans would freeze over a period of time, and the summer sun will not be able to melt them.

You know that, if the hydrogen atoms in water molecule are replaced by deuterium, an isotope of hydrogen with mass number = 2, then we get what is called heavy water or D_2O. Melting point, 276.81 K, boiling point, 374.42 K, density, 1.1044×10^3 kg m^{-3} and viscosity, 1.107 centipoise, of D_2O are higher than those of H_2O. This is attributed to higher molecular weight of D_2O.

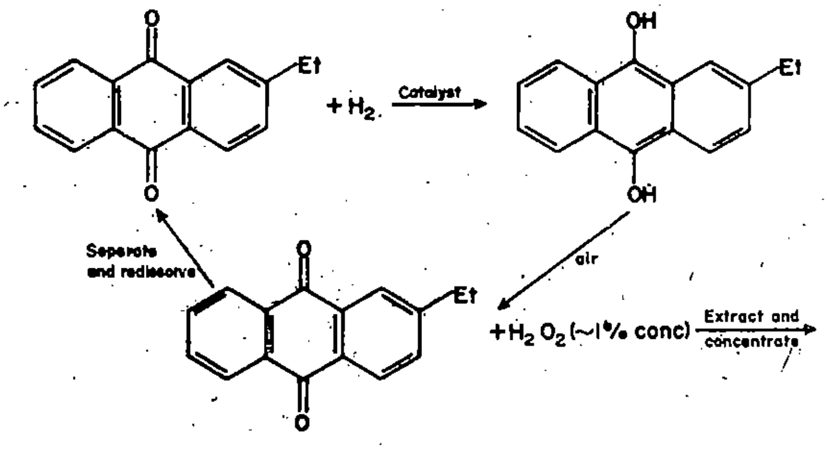
Water is the only practical source of deuterium, where it is present to the extent of 0.0145%. D_2O can be produced by electrolysis or repeated fractional distillation of water. These two processes are quite expensive as a large amount of energy is required for these processes. Heavy water is used on a large scale as a moderator in nuclear reactors.

Hydrogen Peroxide

Hydrogen peroxide is the other important hydride of oxygen. The oldest method of its preparation is by the action of dilute sulphuric acid on barium peroxide:

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

On an industrial scale, it is almost exclusively prepared by auto-oxidation of 2–ethyl anthraquinol as shown below:



H_2O_2 when pure, is an almost colourless liquid, freezing at 272.1 K. It is less volatile (b.p. 423 K) than water and somewhat more dense and viscous. It is miscible with water in all proportions. The concentration of aqueous solutions of H_2O_2 is expressed in terms of volumes of oxygen that will be liberated by a unit volume of H_2O_2 sample. The two largely used concentrations are 6 volume and 30 volume. Let us calculate the percentage of H_2O_2 in a 6 volume sample.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$0.068\ \text{kg} \longrightarrow 22.4\ \text{dm}^3\ \text{(at STP)}$$

Since the strength of the sample is 6 volume, 1 dm³ of H_2O_2 will produce 6 dm³ of O_2 at STP. According to the above relationship 6 dm³ of O_2 would be produced by,

$$\frac{0.068 \times 6}{22.4} = 0.0182 \text{ kg } H_2O_2$$

Thus, 1 dm³ of a 6 volume sample of H_2O_2 will have 0.0182 kg of H_2O_2. Hence, its concentration will be 0.0182 × 100 = 1.82 kg per 100 dm³ of sample = 1.82 % *w/v*.

Because of its oxidising property, H_2O_2 is used in Restoring paintings'. It converts the black PbS, formed from PbO in the original paint, to white $PbSO_4$.

Pure liquid H_2O_2 is highly unstable. It decomposes easily, even a speck of dust can initiate explosive decomposition of concentrated solutions.

H_2O_2 can act both as an oxidising and a reducing agent. For example, it oxidises ferrous sulphate and lead sulphide to ferric sulphate and lead sulphate, respectively :

$$2FeSO_4 + H_2SO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$$

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

It reduces chlorine to HCl as shown below:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$H_2O_2 + HOCl \longrightarrow HCl + H_2O + O_2$$

In industry, H_2O_2 is used mainly for bleaching cotton, wood pulp and other fibers. In the household it finds application as a mild antiseptic and as a bleaching agent.

The hydrogen peroxide molecule contains an O–O bond and has got a skewed configuration as shown in Fig. 9.11.

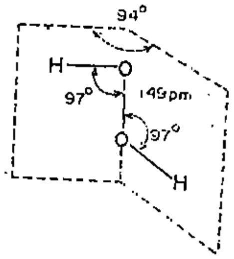


Fig. 9.11: Structure of hydrogen peroxide.

Hydrogen Sulphide

Hydrogen sulphide is the only thermodynamically stable sulphane. It is a foul smelling and poisonous gas.

H_2S is prepared in the laboratory by treating FeS with dilute HCl in Kipp's apparatus. Some of its physical properties are given in Table 9.2. In aqueous solution H_2S is a weak acid. At 293 K. it dissociates as shown below :

$$H_2S\,(aq) = H^+\,(aq) + SH^-\,(aq)\ ;\ pKa_1 = 6.88 \pm 0.02$$

$$SH^-\,(aq) = H^+\,(aq) + S^{2-}\,(aq);\ pKa_2 = 14.15 \pm 0.05$$

You must have used H_2S in qualitative identification and separation of cations. This separation is based on selective precipitation of the sulphides in acidic and alkaline medium. In the acidic medium the ionisation of H_2S, which is a weak acid, is further suppressed and the solubility product of sulphides of relatively less soluble cations of Group II, namely, Pb^{2+}, Hg^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+} Sb^{3+}, Sn^{2+} is exceeded :

$$H_2S = 2H^+ + S^{2-}$$

$$HCl = H^+ + Cl^-$$

In Group IV, in the presence of ammonia, a higher concentration of S^{2-} ions is obtained leading to the precipition of the more soluble sulphades of Zn, Mn, Ni and Co.

$$H_2S = 2H^+ + S^{2-}$$

$$NH_4OH = NH_4^+ + OH^-$$

SAQ 3

a) Explain briefly why is H2S a gas and water a liquid.

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b) Express the strength of a 9% w/v sample of H_2O_2 in volume.

(**Hint:** Look up the problem given in Sec 9.4.1, for finding out the percentage of a 6 volume sample of H_2O_2.)

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9.4.2 Halides

The elements of this group form a number of compounds with halogens. Some of them are listed in Table 9.3.

Table 9.3: Binary halides of Group 16 elements

Element	**Fluorides**	**Chlorides***	**Bromides***	**Iodides***
O	OF_2, O_2F_2	Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7	Br_2O, BrO_2, BrO_3	I_2O_4, I_2O_5, I_2O_9
S	S_2F_2, SF_2, SF_4, SF_6, S_2F_{10}	S_2Cl_2, SCl_2, SCl_4	S_2Br_2	–
Se	Se_2F_2, SeF_4, SeF_6	Se_2Cl_2, $SeCl_2$, $SeCl_4$	Se_2Br_2, $SeBr_2$, $SeBr_4$	–
Te	TeF_4, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Po	–	$PoCl_2$, $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

* In case of oxygen, oxides.

The halogen compounds of S, Se, Te and Po are called as halides. For oxygen, only the fluoro compounds are called as fluorides while the chloro, bromo and iodo compounds are designated as oxides. This is because of the high electronegativity of oxygen which is exceeded only by fluorine. You will study the oxides of halogens in the following unit.

All binary compounds of oxygen with halogens are covalent. They are unstable except OF_2 and I_2O_5. All, except fluorides of oxygen, are formally acid anhydrides or mixed acid anhydrides. Many of the halogen oxides react with water to give the corresponding oxoacid or a mixture of oxoacids. They also react with bases to give the salt or a mixture of salts of the corresponding oxoacids :

$$Cl_2O + H_2O \longrightarrow 2HOCl$$

$$2ClO_2 + 2NaOH \longrightarrow NaClO_3 + NaClO_2 + H_2O$$

As shown in Table 9.3, S, Se, Te and Po compounds with all the halogens are known except iodides of S and Se and fluorides of Po. The salient features of these and structures of some important compounds are given here.

Monohalides: Monohalides of the type M_2X_2 (where X = F, Cl and Br) are formed only by O, S and Se. Oxygen monofluoride decomposes above 225 K. These monohalides have got structures similar to H_2O_2 having E–E bonds.

Monohalides of Te and Po are not formed because Te–Te and Po–Po bonds are not stable. The monohalides are slowly hydrolysed to give the oxoacid.

$$2Se_2Cl_2 + 2H_2O \longrightarrow H_2SeO_3 + 3Se + 4HCl$$

Sulphur can readily be dissolved into sulphur monochloride, S_2Cl_2, to give chlorosulphanes, such as, S_3Cl_2, S_4Cl_2 and so on upto $S_{100}Cl_2$.

Dihalides: Dichlorides and dibromides are formed by the lower members of the group, viz., Se, Te and Po. These are formed mainly by dissociation of the corresponding tetrahalides. Sulphur dichloride can also be formed by chlorination of S_2Cl_2, preferably, in presence of a trace of a catalyst such as $FeCl_3$. However, due to the decomposition of SCl_2 into S_2Cl_2, it is rather unstable. While the dihalides of Se are gaseous, those of Te and Po are solids. These dihalides are hydrolysed by H_2O according to following equation for $TeBr_2$:

$$2TeBr_2 + 3H_2O \longrightarrow H_2TeO_3 + 4HBr + Te$$

Dissolution of chlorine in sulphur monochloride, S_2Cl_2 gives sulphur dichloride, SCl_2, an unstable liquid which dissociates back.

Tetrahalides: S, Se, Te and Po form tetrahalides with all the halogens. However, tetrafluoride of polonium, tetrabromide of sulphur and tetraiodides of sulphur and selenium are not formed. The tetrahalides are formed mainly by the reaction between the corresponding elements, e.g.,

$$Te + 2Cl_2 \longrightarrow TeCl_4$$

These are covalent compounds which hydrolyse to give the corresponding dioxides.

$$SeBr_4 + 2H_2O \longrightarrow SeO_2 + 4HBr$$

$$SF_4 + 2H_2O \longrightarrow SO_2 + 4HF$$

As stated above, the tetrahalides dissociate in solution or in the vapour state to the corresponding dihalides.

$$SeCl_4 \longrightarrow SeCl_2 + Cl_2$$

The tetrahalides also form complex anions of the type EX_6^{2-} in the presence of excess of the corresponding halogen acid.

$$SeCl_4 + 2HCl \longrightarrow H_2SeCl_6$$

There has been much controversy concerning the structure of tetrahalides. The presently accepted structure of SF_4 and SeF_4 is see-saw with one equatorial position occupied by an electron pair as shown in Fig. 9.12.

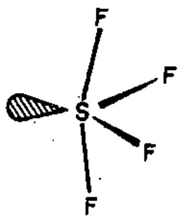
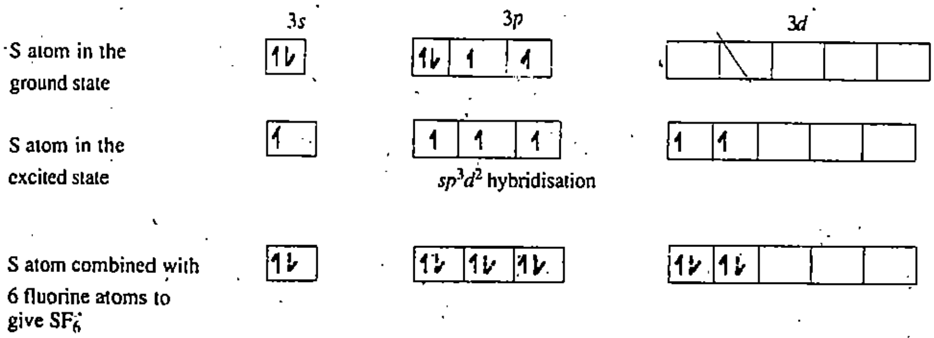


Fig. 9.12 : Structure of sulphur tetrafluoride.

Hexahalides: S, Se and Te react with excess of fluorine to give the corresponding hexafluorides. Fluorine being the most electronegative, oxidises the other elements to their highest oxidation states. Therefore, hexahalides other than fluorides are not formed. In hexafluorides the central atom uses its *d*–orbitals for bonding. The structure of SF_6 can be explained on the basis of sp^3d^2 hybridisation as shown below:



The sp^3d^2 hybridisation gives rise to a symmetrical structure with fluorine atoms octahedrally arranged around the hexavalent sulphur as shown in Fig. 9.13. The other hexafluorides also have similar structures.

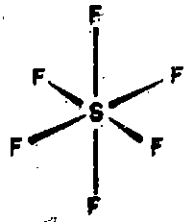


Fig 9.13 : Structure of sulphur hexafluoride.

While SF_6 and SeF_6 are quite inactive, TeF_6 gets slowly hydrolysed in the presence of water.

$$TeF_6 + 6H_2O \longrightarrow 6HF + H_6TeO_6$$

9.4.3 Oxides

As said before, oxygen reacts practically with all the elements in the periodic table, except lighter noble gases, to form binary compounds called oxides. An element can form more than one oxide of varied compositions, depending on the method of preparation, reaction conditions, etc. The oxides can be classified on the basis of the oxidation state of oxygen in the oxide or on the basis of their chemical nature. The first classification categorises oxides into the following five categories :

i) **Normal oxides** contain oxygen in its normal oxidation state of –2, e.g., MgO, O=C=O, etc.

ii) **Peroxides** contain the peroxide ion, O_2^{2-}, e.g., Na–O–O–Na, H–O–O–H, etc.

iii) **Suboxides** involve bonds between atoms of the element in addition to bonds between the element and oxygen, e.g., O=C=C=C=O.

iv) **Superoxides** contain O_2^- ion and are formed by alkali metals, e.g., KO_2, CsO_2, etc.

v) **Mixed oxides** are regarded as composed of two simpler oxides, e.g., Pb_3O_4 $(2PbO \cdot PbO_2)$.

A broader classification is based on the reaction of the oxide with water. According to this, oxides are classified as acidic, basic, neutral or amphoteric.

Acidic oxides dissolve in water to give acidic solutions. These react with alkalis forming a salt and water, e.g., CO_2. NO_2, SO_2, etc.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

Basic oxides dissolve in water to give alkaline solutions. These react with acids forming salt and water, e.g., Na_2O, CaO, MgO, etc.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

$$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$$

Neutral oxides have neither acidic nor basic properties and when dissolved in water, they give neutral solutions, e.g., CO, N_2O, etc.

Amphoteric oxides show both acidic and basic properties. They react with acids as well as with alkalis to give salt and water, e.g., Al_2O_3, ZnO, PbO, etc.

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \longrightarrow Na_2ZnO_2 + H_2O$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$$

Elements of Group 16 form a number of oxides. These are given in Table 9.4.

Table 9.4 : Oxides of Group 16 elements

Element	Oxides			
	Mono	Di	Tri	Others
S	SO	SO_2	SO_3	S_2O, S_2O_3, S_2O_7, SO_4
Se	SeO	SeO_2	SeO_3	SeO_3
Te	TeO	TeO_2	TeO_3	–
Po	PoO	$PoPO_2$	–	–

The important stable oxides are the di and trioxides. Their salient feature are briefly discussed here :

Dioxides

These are generally obtained by heating the element in air. The dioxides of Se and Te can also be prepared by treating the element with conc. HNO_3 followed by heating the oxoacid formed, e.g.,

$$Se + 4HNO_3 \longrightarrow H_2SeO_3 + 4NO_2 + H_2O$$

$$H_2SeO_3 \longrightarrow SeO_2 + H_2O$$

SO_2 is a gas, SeO_2 is a white volatile solid while TeO_2 is a non-volatile white solid. Gaseous SO_2 and SeO_2 have discrete symmetrical molecules which are bent or angular Fig. 9.14 (a). On solidification SeO_2 forms long polymeric chains, Fig. 9.14(b).

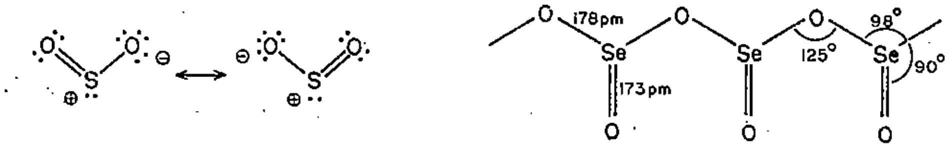


Fig. 9.14: (a) Structure of SO_2 molecule in gaseous state (b) Structure of SeO_2 polymer in solid state

SO_2 and SeO_2 are acidic oxides as they form acids when dissolved in water, whereas TeO_2 is slightly soluble in water and is an amphoteric oxide.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \text{ (sulphurous acid)}$$
$$SeO_2 + H_2O \longrightarrow H_2SeO_3 \text{ (selenous acid)}$$

SO_2 combines reversibly with oxygen in the presence of platinised asbestos or vanadium pentoxide to give sulphur trioxide. This reaction forms the basis of the Contact Process for manufacturing sulphuric acid as you will study later.

$$2SO_2 + O_2 \overset{\text{catalyst}}{\rightleftharpoons} SO_3$$

Precipitation of dissolved acidic oxides along with rains is called as **acid rain.**

Volatile sulphur compounds, mainly SO_2, are released into the atmosphere as a result of combustion of sulphur containing fossil fuels. SO_2, released in densely populated areas does great damage to the respiratory organs of human beings and animals, to buildings and perhaps most seriously to plants and aquatic life as a result of "acid rain".

SO_2 is a strong reducing agent in aqueous solution. The following reactions show this :

$$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$
$$Cl_2 + SO_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$$
$$2KMnO_4 + 2H_2O + 5SO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

Presumably the bleaching effect of SO_2 also depends upon its reducing properties.

SO_2 oxidises hydrogen sulphide to S provided moisture is present. At 1273 K it oxidises carbon to carbon dioxide.

$$2SO_2 + H_2S \longrightarrow H_2SO_4 + 3S$$
$$SO_2 + C \longrightarrow CO_2 + S$$

Trioxides

The selenium and tellurium trioxides are not stable, SO_3 is the only important trioxide in the group. Its preparation has been described above.

Sulphur trioxide exists in several polymorphic forms. The solid form, m.p. 290 K has a trimeric cyclic structure, in which four oxygen atoms are arranged approximately tetrahedrally around each sulphur atom, Fig. 9.15(c). This form gradually changes into a linear polymerised structure in the presence of moisture. The latter has a fibrous needle-like appearance, Fig.9.15(b). On heating, the polymeric form dissociates into discrete SO_3 molecules present in the vapour. These have a triangular, symmetrical and planar structure, Fig. 9.15(a).

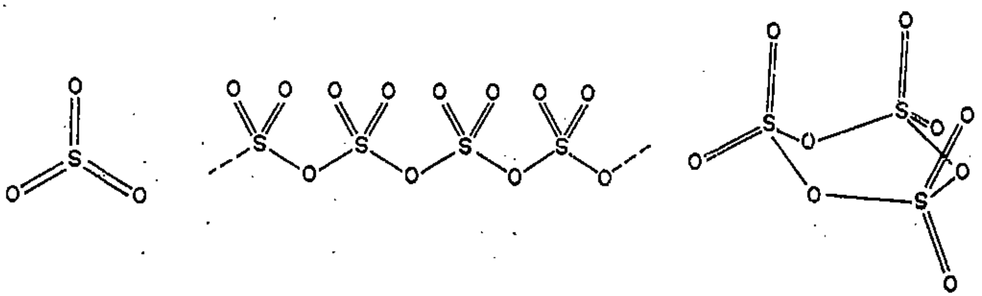


Fig 9.15 : Sulphur trioxide : a) trigonal structure ; b) linear polymerised structure; and c) cyclic structure

SO_3 is a powerful acidic oxide, it fumes in moist air and reacts explosively with water to form sulphuric acid.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

With excess SO_3, H_2SO_4 gives pyrosulphuric acid or oleum

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7 \text{ (oleum)}$$

In some reactions it acts as an oxidising agent, e.g., it oxidises HBr to free bromine.

$$2HBr + SO_3 \longrightarrow H_2O + Br_2 + SO_2$$

SAQ 4

Find out the oxidation states of sulphur in the following :

S_2O, S_2O_3, SO_2, SO_3.

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9.5 OXOACIDS OF SULPHUR

As you know, oxoacid is an acid in which the ionisable hydrogen atom is bonded through an oxygen atom to the central nonmetal atom, e.g., E–OH.

S, Se and Te all form oxoacids. The oxoacids of sulphur are by far the most numerous and important as compared to Se and Te. Many of the oxoacids do not exist as such but their salts are known. Oxoacids of sulphur are given in Table 9.5. It is evident from Table 9.5 that sulphur forms oxoacids in which its oxidation number varies from –2 to +6. We will now discuss sulphurous, sulphuric, peroxosulphuric and thiosulphuric acids and their salts in brief.

9.5.1 Sulphurous Acid

Sulphurous acid, H_2SO_3, is known only in solution. It exists mainly as a hydrate of sulphur dioxide, $SO_2 . 7H_2O$. Two series of salts, the bisulphites, containing HSO_3^-, and sulphites containing SO_3^{2-} ions are well known.

Sulphurous acid possesses both oxidising as well as reducing properties. It owes its reducing nature to the ease with which it can get oxidised to sulphuric acid. It reduces I_2 to HI, $KMnO_4$ to $MnSO_4$ and $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$:

$$H_2SO_3 + H_2O + I_2 \longrightarrow H_2SO_4 + 2HI$$

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

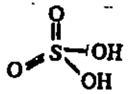
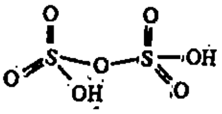
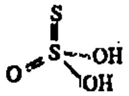
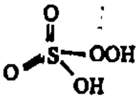
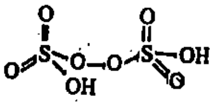
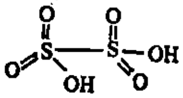
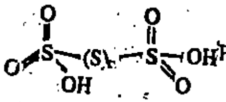
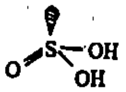
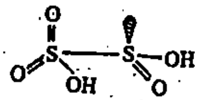
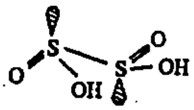
$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

In the presence of strong reducing agents like H_2S, it can behave as an oxidising agent.

$$2H_2S + H_2SO_3 \longrightarrow 3H_2O + 3S$$

Sodium and calcium bisulphite solutions are used in making paper from wood because they dissolve fibrous material lignin and facilitate pulping of cellulose.

Table 9.5: Oxoacids of sulphur

Formula	Name	Oxidation states	Schematic Structure	Salt
H_2SO_4	Sulphuric	VI		Sulphate, SO_4^{2-}, H-sulfate, $HOSO_3^-$
$H_2S_2O_7$	Pyrosulphuric	VI		Pyrosulphate, $O_3SOSO_3^{2-}$
$H_2S_2O_3$	Thiosulphuric	VI, –II		Thiosulphate, SSO_3^{2-}
H_2SO_5	Peroxomonosulphuric	VI		Peroxomonosulphate, $OOSO_3^{2-}$
$H_2S_2O_8$	Peroxodisulphuric	VI		Peroxodisulphate, $O_3SOOSO_3^{2-}$
$H_2S_2O_6$	Dithionic*	V		Dithionate, $O_3SSO_3^{2-}$
$H_2S_{n+2}O_6$	Polythionic	V,0		Polythionate, $O_3S(S)_nSO_3^{2-}$
H_2SO_3	Sulphurous*	IV		Sulphite, SO_3^{2-}, H-sulphite, $HOSO_2^-$
$H_2S_2O_5$	Disulphurous*	V,III		Disulphite, $O_3SSO_2^{2-}$
$H_2S_2O_4$	Dithionous*	III		Dithionite, $O_2SSO_2^{2-}$

* Unstable oxoacids

9.5.2 Sulphuric Acid

Sulphuric acid is one of the most important chemicals, both in industry as well as in the laboratory. We shall discuss its preparation and properties in detail now.

Two methods are industrially used for the manufacture of H_2SO_4. These are : i) lead chamber process and ii) contact process. Both these processes involve three basic steps namely,

i) Production of SO_2

ii) Oxidation of SO_2 to SO_3

iii) Conversion of SO_3 to H_2SO_4

We shall discuss as to how these steps are carried out in the two industrial processes.

a) **Lead chamber process,** is the older of the two processes. In this process SO_2 is produced by burning S or roasting pyrites.

$$S + O_2 \longrightarrow SO_2$$

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

The oxidation of SO_2 to SO_3 is carried out by using oxides of nitrogen. These are produced by oxidation of NH_3 using platinum as catalyst.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

A mixture of air, SO_2 and the nitrogen oxides is passed into a set of chambers lined with lead sheets from the top of which water is sprayed. The exact nature of the reactions which take place in the lead chambers is not fully understood. The following scheme of reactions seems to be operative:

$$NO_2 + NO + 2SO_2 + H_2O + O_2 \longrightarrow 2(NO{\cdot}HSO_4)$$

$$2\,(NO{\cdot}HSO_4) + H_2O \longrightarrow 2H_2SO_4 + NO_2 + NO$$

Nitrosyl hydrogen sulphate formed as an intermediate reacts with H_2O to give H_2SO_4 and the nitrogen oxides. The oxides play the rôle of a catalyst.

Though chamber process involves relatively simpler steps, yet it is not the method of choice where high purity of the acid is required. The chamber acid contains As_2O_3 (from pyrites), $PbSO_4$ (from chamber) and some oxides of nitrogen as impurities. This acid finds use in the preparation of fertilisers where removal of impurities is not necessary. The second drawback with chamber method is that it gives dilute acid (60-78%), since the process of concentration of the acid is expensive.

Contact process

The fact that SO_2 can be oxidised to SO_3 by air in the presence of platinum catalyst is the basis of the contact process which is used the world over for the manufacture of H_2SO_4. SO_2 is obtained in a manner similar to the chamber process. But before oxidation it requires thorough purification in order to avoid the poisoning of the catalyst, particularly by the arsenic impurities. The purified SO_2 is then oxidised directly according to the following reaction :

$$SO_2 + 1/2O_2 \longrightarrow SO_3\ ;\ \Delta H^\circ = -98\ \text{kJ mol}^{-1}$$

It is a reversible and exothermic reaction proceeding with a reduction in the volume. According to Le Chatelier principle, the yield of SO_3 would increase under the following conditions :

i) high pressure

ii) high concentration of O_2

iii) low temperature

iv) continuous removal of SO_3 from the reaction

Theoretical considerations require that the reaction be carried out at low temperature and high pressure. However, at low temperature, the reaction is too slow and high pressure makes the cost of plant uneconomical. The yields of SO_3 are optimised by using a suitable catalyst, an excess of O_2 and removing SO_3 formed, the latter two shift the equilibrium to the right. Optimally the reaction is carried out at 700 – 725 K and one atmosphere pressure using vanadium pentoxide as catalyst and an excess of oxygen.

The purified SO_2 is mixed with air (1:5) and is passed through a four stage catalytic converter operating between a range of temperatures, Fig. 9.16. After conversion of SO_2 to SO_3 to the extent of 99.5% or so, the gases come out of the converter.

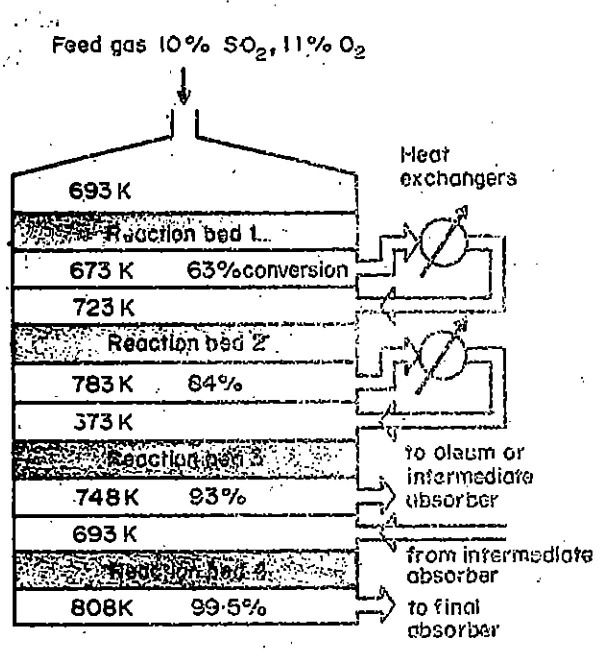


Fig. 9.16: Schematic diagram of converter

Reaction of SO_3 with H_2O is violent and gives a fog of dilute sulphuric acid. Therefore, SO_3 is passed through concentrated H_2SO_4 to give oleum. From oleum, H_2SO_4 of any required concentration can be prepared by appropriately diluting it.

The concentration of oleum is expressed in terms of the percentage of free SO_3 in it.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \text{ (oleum)}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

Concentrated sulphuric acid is a colourless, thick, oily liquid having sp.gr. 1.838 at 288 K, m.p. 283.4 K and b.p. 613 K. At its boiling point, it gives dense white fumes of SO_3. H_2SO_4 is a strong acid which is almost completely ionised in aqueous solution. It behaves as adibasic acid, forming two distinct series of salts, namely, hydrogen sulphates, containing HSO_4^- and sulphates, containing SO_4^{2-}. The dilute acid attacks many metals forming sulphates and hydrogen, but it does not react with lead, copper, mercury and silver :

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

Concentrated H_2SO_4 dissolves many metals giving sulphur dioxide. But there is no action on gold, platinum, glass, silica and silicon-steel, the latter is used for making distillation vessels.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2$$

Hot concentrated H_2SO_4 is a good oxidising agent. It oxidises H_2, C, P, S, HI, HBr to H_2O, CO, H_3PO_3, SO_2, I_2 and Br_2, respectively. It is also a good sulphonating agent.

$$C + H_2SO_4 \longrightarrow CO + SO_2 + H_2O$$

$$\underset{}{C_6H_6} + H_2SO_4 \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H + H_2O}$$

Concentrated H_2SO_4 has a great affinity for water and is used as a dehydrating agent. This property of concentrated sulphuric acid is used in drying gases like O_2, N_2, SO_2, etc. H_2SO_4 chars organic substances, by removing elements of water, leaving black carbon behind, e.g.,

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow[\text{conc. } H_2SO_4]{-11H_2O} 12C$$

It is due to the dehydrating power of sulphuric acid that it is highly corrosive to skin. First of all, it removes water and the heat produced in the action causes further damage.

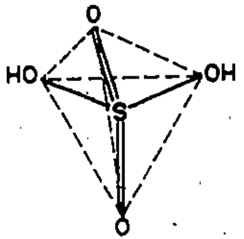
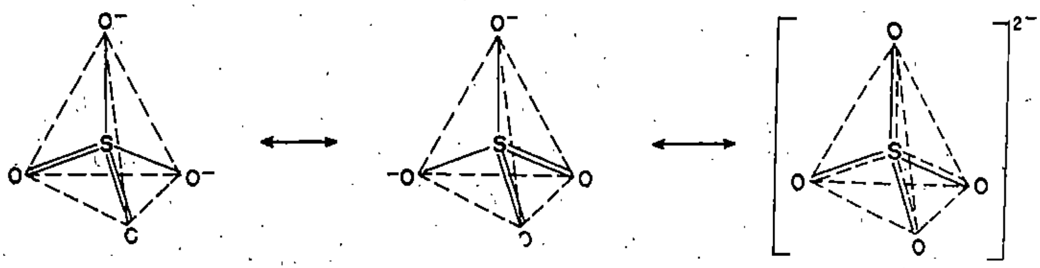


Fig. 9.17 : Structure of sulphuric acid

Below its melting point, anhydrous sulphuric acid is a white crystalline solid consisting of a three-dimensional hydrogen-bonded network, which persists in the liquid state and makes the liquid viscous. The two hydroxyl groups and two oxygens are tetrahedrally arranged around the S atom in H_2SO_4 as shown in Fig. 9.17 with S–OH and S–O bond lengths being 154 pm and 147 pm, respectively. This shortening of S–O bond shows $p\pi - d\pi$ bonding between sulphur and oxygen. The bond, as a result, has appreciable double bond character. In SO_4^{2-} ion all the four S–O bond lengths are 149 pm. This indicates extensive delocalisation of bonding electrons.



9.5.3 Peroxoacids of Sulphur

There are two peroxoacids of sulphur, viz., peroxomonosulphuric acid, H_2SO_5 and peroxodisulphuric acid, $H_2S_2O_8$. These acids are known also as **Caro's acid** and **Marshall's acid,** respectively, after the names of their discoverers. These acids can be considered as derived from hydrogen peroxide by the replacement of one or both the hydrogen atoms by sulphonic group, $-SO_2OH$:

HO–OH	HO–O–SO$_2$OH	HO–SO$_2$–O–O–SO$_2$–OH
Hydrogen peroxide	Peroxomonosulphuric acid	Peroxodisulphuric acid

Peroxomonosulphuric Acid

It is also known as permonosulphuric acid. It is obtained by the action of chlorosulphuric acid on cold anhydrous hydrogen peroxide :

$$H_2O_2 + ClSO_2\cdot OH \longrightarrow H{-}O{-}O{-}SO_2\cdot OH + HCl$$

It may also be prepared by the action of concentrated sulphuric acid on 5% hydrogen peroxide:

$$H_2O_2 + H_2SO_4 \longrightarrow H{-}O{-}O{-}SO_2\cdot OH + H_2O$$

Peroxomonosulphuric acid may also be obtained by hydrolysis of peroxodisulphuric acid at 273 K or by grinding potassium peroxodisulphate crystals with sulphuric acid in a freezing mixture.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$

$$K_2S_2O_8 + H_2SO_4 \longrightarrow H_2SO_5 + K_2S_2O_7$$

Peroxomonosulphuric acid is a white crystalline solid, m.p. 318 K. However, the salts of this acid are unstable in the solid state. The acid is a strong oxidising agent. It oxidises SO_2 to SO_3, sulphites to sulphates, ferrous salts to ferric salts and liberates iodine immediately from a solution of potassium iodide :

$$2KI + H_2SO_5 \longrightarrow K_2SO_4 + H_2O + I_2$$

$$2FeSO_4 + H_2SO_5 \longrightarrow Fe_2(SO_4)_3 + H_2O$$

Peroxodisulphuric Acid

It is also known as perdisulphuric acid or simply persulphuric acid. The acid can be obtained by the action of chlorosulphonic acid on H_2O_2:

$$H_2O_2 + 2ClSO_2OH \longrightarrow H_2S_2O_8 + 2HCl$$

This acid is obtained by the electrolysis of 50% sulphuric acid in cold using high current density and a platinum anode. The following reactions are supposed to take place during the process :

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

$$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e \quad \text{at anode}$$

$$2H^+ + 2e \longrightarrow H_2 \quad \text{at cathode}$$

The peroxodisulphuric acid is a colourless solid, m.p. 338 K. The acid is highly soluble in water. In aqueous solution it slowly changes to peroxomonosulphuric acid.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2O_2$$

Potassium and ammonium peroxodisulphate are the most important salts of this acid. These are freely soluble in water. These salts are, in fact, easier to prepare than the acid and both are made on an industrial scale by anodic oxidation of the corresponding sulphates under controlled conditions.

Peroxodisulphuric acid and its salts are powerful oxidising agents. They liberate iodine from KI slowly. This distinguishes $H_2S_2O_8$ from H_2SO_5, which liberates iodine immediately.

$$2KI + K_2S_2O_8 \longrightarrow 2K_2SO_4 + I_2$$

Both the acids are distinguished from H_2O_2 by their failure to react with $KMnO_4$.

The peroxodisulphates also oxidise ferrous salts to ferric, manganous salts to permanganates and chromic salts to dichromate in presence of a trace of silver nitrate :

$$2MnSO_4 + 5K_2S_2O_8 + 8H_2O \longrightarrow 2KMnO_4 + 4K_2SO_4 + 8H_2SO_4$$

$$Cr_2(SO_4)_3 + K_2S_2O_8 + 7H_2O \longrightarrow K_2Cr_2O_7 + 7H_2SO_4$$

Some metals, e.g., copper and zinc dissolve in an aqueous solution of persulphates giving metal sulphates :

$$Cu + K_2S_2O_8 \longrightarrow CuSO_4 + K_2SO_4$$

$$Zn + K_2S_2O_8 \longrightarrow ZnSO_4 + K_2SO_4$$

9.5.4 Thiosulphuric Acid

Thiosulphuric acid, $H_2S_2O_3$, has never been isolated but its salts are well known which contain the thiosulphate ion, $S_2O_3^{2-}$. The best known thiosulphate is the sodium salt, $Na_2S_2O_3 \cdot 5H_2O$. It is obtained by boiling a solution of sodium sulphite with sulphur followed by filtration and crystallisation.

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

Sodium thiosulphate is a colourless, crystalline solid highly soluble in water and commercially known as **hypo.** The thiosulphate ion is unstable in the presence of acids breaking to give H_2O, SO_2 and S.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + S + H_2O$$

It functions as a reducing agent, reducing chlorine to chloride. This reaction is utilised for removing excess chlorine from bleached fabrics.

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$

The milder oxidising agent iodine behaves rather differently giving sodium tetrathionate instead of Na_2SO_4, though it is also converted into iodide.

$$Na_2S_2O_3 + I_2 \longrightarrow 2NaI + \underset{\text{sodium tetrathionate}}{Na_2S_4O_6}$$

This reaction is used in iodometric titrations for determination of copper. Sodium thiosulphate is used in photography for 'fixing' the negative. It removes the unreacted light sensitive silver bromide from photographic plates to avoid further reaction of light.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

SAQ 5

Explain, in the space given below, how do you account for high b.p. and high viscosity of sulphuric acid.

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9.6 ANOMALOUS BEHAVIOUR OF OXYGEN

Oxygen differs considerably from the rest of the family members. Small size, very high electronegativity and non-availability of *d*-orbitals in the valence shell are the factors responsible for these differences. The main differences are as given below :

- Oxygen is a gas while other members are solids.
- Oxygen is diatomic whereas rest of the members are polyatomic.
- Being highly electronegative, oxygen shows only negative oxidation states of −2 and −1 except in OF_2 in which its oxidation state is +2.
- It shows paramagnetic behaviour in gaseous, liquid and solid states.
- Oxygen has a tendency towards extensive hydrogen bond formation. H_2O is a liquid, whereas hydrides of the other elements of this group are gases.

9.7 SUMMARY

Let us recall what all we have discussed in this unit :

- Members of oxygen family show the usual gradation in properties from non-metallic oxygen and sulphur to metallic polonium, in between being selenium and tellurium, the metalloids. Oxygen is the only element in the group existing as a diatomic molecule. Rest of the members are polyatomic. However, all of them show allotropy. Oxygen differs in many ways from other elements of the group and these differences have been discussed.

- All of them form bivalent anions like O^{2-} and S^{2-}. Due to the availability of *d*-orbitals in S, Se, Te and Po, the oxidation state of these elements increases from 2 to 4 and then to 6.

- The hydrides and halides of these elements have been discussed. One hydride of oxygen, namely, H_2O is very important for life and has unique properties. Except oxygen, which forms only dihalides, rest of the members form tetra and hexavalent compounds also with halogens.

- The Group 16 elements form a number of oxides. Di-and trioxides being more important have been discussed in detail. All the elements in the group form a number of oxoacids, the more important and useful being those of sulphur. Therefore, preparation of sulphuric acid, a very common chemical, has been discussed in detail explaining the contact and the lead chamber processes.

9.8 TERMINAL QUESTIONS

1 Why does oxygen exist as a diatomic molecule and sulphur as a polyatomic molecule at normal temperatures?

2 Oxygen usually does not exhibit a positive oxidation state in its compounds. Comment.

3 Explain why ice has a lower density as compared to that of water?

4 Arrange the hydrides of Group 16 elements in the decreasing order of:

   i) acidity
   ii) hydrogen bonding
   iii) stability
   iv) reducing power

5 Why is H_2S a stronger acid as compared to H_2O ?

6 Halogens form various types of compounds with oxygen. Is it justified to call them halides of oxygen? Give reason for your answer.

7 Give reasons for the following :

   i) Why is SO_3 not dissolved in water directly during the preparation of sulphuric acid ?
   ii) Why is the contact process preferred over lead chamber process for the preparation of H_2SO_4?

9.9 ANSWERS

Self-assessment Questions

1

Species	No. of unpaired electrons
i) O_2^+	1
ii) O_2^-	1
iii) O_2^{2-}	0

2 i) Te > Se > S >>> O

   ii) Te > Se > S >>> O

   iii) O >>> Se > S > Te

   iv) O >> S > Se > Te

3 (a) Water molecules are highly associated with one another by hydrogen bonding because of the presence of highly electronegative oxygen atoms. Whereas the hydrogen sulphide molecules are associated with one another by weak van der waals forces. As a result water exists as a liquid and H_2S exists as a gas.

   (b) The strength of the sample of H_2O_2 is 9% *w/v*. It means 100 dm^3 of H_2O_2 sample would have 9 kg of H_2O_2. Hence 1 dm^3 of H_2O_2 sample would have 0.09 kg of H_2O_2. From the equation,

$$\begin{array}{ccc} 2H_2O_2 & \longrightarrow & 2H_2O + O_2 \\ 2 \times 0.034 \text{ kg} & & 22.4 \text{ dm}^3 \end{array}$$

We know that 0.068 kg of H_2O_2 gives 22.4 dm^3 of O_2 at STP. Hence, 0.09 kg of H_2O_2 should give $\frac{22.4 \times 0.09}{0.068}$ dm^3 of O_2 at STP or 1 dm^3 of H_2O_2 should give 29.65 dm^3 of O_2 at STP.

Hence, the strength of a 9% *w/v* sample of H_2O_2 would be 29.65 volume.

4

Oxide	S_2O	S_2O_3	SO_2	SO_3
Oxidation state of sulphur	1	3	4	6

5 The high boiling point and viscosity of sulphuric acid are due to the presence of hydrogen bonding which binds a number of simple molecules into clusters.

Terminal Questions

1 Oxygen–oxygen double bond in O_2 molecule has bond energy three times that of oxygen-oxygen single bond. The molecule, therefore, prefers to be in the diatomic form. While the bond energy of sulphur-sulphur double bond is less than twice the sulphur-sulphur single bond energy. The S–S bond being stable makes the element exist in polyatomic form.

2 Oxygen has a very high electronegativity. In fact, it is the second most electronegative element, as a result it does not show a positive oxidation state.

3 Ice has a caged structure because of a network of tetrahedrally placed water molecules. This structure has a lot of empty space which makes ice lighter than water.

4 i) $H_2Po > H_2Te > H_2Se > H_2S > H_2O$

ii) $H_2O >> H_2S > H_2Se > H_2Te > H_2Po$

iii) $H_2O >> H_2S > H_2Se > H_2Te >> H_2Po$

iv) $H_2Po > H_2Te > H_2Se > H_2S > H_2O$

5 Due to high electronegativity of oxygen, the O–H bond in H_2O is stronger than the S–H bond of H_2S. Therefore, it is relatively easy to take out a proton from H_2S than from H_2O. Hence, H_2S is more acidic.

6 You know that in naming a covalent compound containing two elements, as a rule, the more metallic element's name appears first followed by non or less metallic one. Of the various halogens, only fluorine is more non-metallic and more electronegative than oxygen thereby the compounds of oxygen and fluorine are termed as fluorides. Since oxygen is more non-metallic and more electronegative than all other halogens, its compounds with Cl, Br and I are termed as oxides.

7 (i) In the preparation of H_2SO_4, SO_3 is not dissolved directly in H_2O as it reacts violently with water forming a dense white fog of dilute sulphuric acid.

(ii) The contact process is preferred over lead chamber process for two reasons.

(a) Contact process gives pure H_2SO_4 while chamber acid has got impurities of arsenic and lead.

(b) Sulphuric acid of any concentration can be obtained by contact process while the acid obtained from lead chamber process is quite dilute (60 – 78%).

UNIT 10 ELEMENTS OF GROUP 17

Structure

10.1 Introduction
    Objectives
10.2 Occurrence, Extraction and Uses
    Occurrence
    Extraction
    Preparation of Fluorine
    Uses
10.3 General Characteristics
    Physical Properties
    Oxidation States
    Oxidising Power
    Chemical Properties
    Basic Properties of Halogens
10.4 Compounds of Halogens
    Hydrogen Halides
    Halogen Oxides
    Oxoacids of Halogens
    Interhalogen Compounds
    Polyhalides and Polyhalonium Ions
10.5 Pseudohalogens and Pseudohalides
10.6 Anomalous Behaviour of Fluorine
10.7 Summary
10.8 Terminal Questions
10.9 Answers

10.1 INTRODUCTION

In Unit 1 you studied the periodic table which gives the classification of elements into various periods and groups. You have seen that in any period the element in Group 1 is the most electropositive and metallic in nature. As we go across a period from Group 1 to Group 17 of the main group elements, nonmetallic nature, ionisation energy, electron affinity and electronegativity increase, reaching a maximum at Group 17. In this way, at one extreme we have Group 1 comprising alkali metals and at the other we have Group 17 comprising non-metals, namely, fluorine, chlorine, bromine, iodine and astatine, collectively called the **halogens.** Halogens derive their name from the Greek words, halos + gens meaning salt producers, as they form salts in combination with metals. The most common of the salts being sodium chloride or the common salt. Halogens find a wide variety of uses in everyday life. In view of their nature and usefulness, it will be interesting to study the chemistry of halogens.

Objectives

After studying this unit, you should be able to:

- explain the occurrence, extraction and uses of halogens,
- describe the isolation of fluorine,
- list the general characteristics of halogens and describe their reactions,
- describe the chemistry of hydrogen halides, halogen oxides and oxoacids,
- describe the chemistry and geometry of interhalogen compounds and polyhalides, and
- explain the anomalous behaviour of fluorine.

10.2 OCCURRENCE, EXTRACTION AND USES

Chemistry of halogens is very interesting and has varied applications in our daily life. Due to their high reactivity, halogens do not occur free in nature. In the combined form, however, they are fairly abundant. In this section you will study their occurrence, extraction and some important uses.

10.2.1 Occurrence

Fluorine is the first element of this group; it constitutes nearly 0.054% of earth's crust, where it occurs as fluorspar (CaF_2), cryolite ($AlF_3 \cdot 3NaF$) and fluorapatite $[CaF_2 \cdot 3Ca_3(PO_4)_2]$.

Small amounts of fluorides occur in sea water and in some mineral springs. Bones also contain small amounts of fluorine. A six mile long belt of fluorspar has been recently discovered in Dungarpur (Rajasthan) and is considered to be sufficient to meet the needs of the country.

Chlorine, which forms 0.013% of earth's crust, occurs mainly as chlorides of sodium and other alkali and alkaline earth metals in salt mines as well as in sea water. Sea water is almost a 3% solution of various salts, of which sodium chloride forms ~83%. Bromine, as bromides, occurs in sea water and dry salt lakes and constitutes about $2.0 \times 10^{-4}\%$ of earth's crust. Iodine is the rarest of all the halogens, forming only $4.6 \times 10^{-5}\%$ of earth's crust. Its main source used to be **kelp,** or the ash obtained on burning sea weeds, and **Chile saltpetre** in which it occurs as iodates. However, now it is mostly extracted from brine. Astatine is a radioactive element. The naturally occurring isotopes of astatine have half-lives of less than one minute. Therefore, it occurs in negligible amounts in nature. The isotope $^{211}_{85}\mathrm{At}$ having the longest half-life of 7.21 hours, is made by bombarding bismuth with α particles.

$$^{209}_{83}\mathrm{Bi} + ^{4}_{2}\mathrm{He} \longrightarrow ^{211}_{85}\mathrm{At} + 2^{1}_{0}\mathrm{n}$$

10.2.2 Extraction

The only practicable method of preparing fluorine gas is Moissan's original procedure based on the electrolysis of KF dissolved in anhydrous HF. The details of this method along with some other methods for the isolation of fluorine have been given separately in Section 10.2.3. You have already studied in Unit 3 that chlorine is obtained as a byproduct along with hydrogen in the manufacture of sodium hydroxide by electrolysis of brine. Electrolysis of molten sodium chloride also gives chlorine and sodium. In some parts of the world, it is produced by the electrolysis of aqueous HCl. Bromine is made on an industrial scale by reaction of bromides with chlorine. A mixture of air and chlorine is blown through an aqueous solution of a bromide at a pH of 3.5. Chlorine displaces bromine and air blows it out of the solution.

Iodine can also be prepared similarly by the oxidation of iodides by chlorine. Iodine is also prepared by treating brine with $AgNO_3$ to precipitate AgI. This is possible because AgI is the least soluble of all the silver halides. Precipitated AgI is treated with clean scrap iron or steel to form metallic silver and a solution of FeI_2. This solution is then treated with chlorine to liberate I_2. Precipitated silver is redissolved in dil. HNO_3 to give $AgNO_3$ which is used again to precipitate AgI.

$$\mathrm{I^-\,(brine)} \xrightarrow{\mathrm{AgNO_3}} \mathrm{AgI}\downarrow \xrightarrow{\mathrm{Fe}} \mathrm{Ag}\downarrow + \mathrm{FeI_2}$$

$$\mathrm{FeI_2} \xrightarrow{\mathrm{Cl_2}} \mathrm{FeCl_2} + \mathrm{I_2}$$

$$3\mathrm{Ag} + 4\mathrm{HNO_3} \longrightarrow 3\mathrm{AgNO_3} + \mathrm{NO} + 2\mathrm{H_2O}$$

10.2.3 Preparation of Fluorine

Isolation of fluorine presented a tough problem to chemists for about a century. Though its existence was first shown by Davy in 1813, yet it could not be isolated before 1886. All attempts at isolation of fluorine failed due to the following reasons :

i) High chemical reactivity of fluorine towards other elements.

ii) It attacked the apparatus whether made of glass, carbon, platinum or any other metal in which its preparation was tried.

iii) In view of fluorine being the most powerful oxidant, no oxidising agent could be available which could bring about the oxidation of HF to F_2. Therefore, the only method available was that of electrolysis.

iv) The method of electrolysis was not fruitful. Aqueous HF on electrolysis yields hydrogen and oxygen. On the other hand anhydrous HF was found to be a non-conductor of electricity.

v) Exceedingly poisonous and corrosive character of anhydrous HF proved fatal to early chemists.

All the above mentioned reasons were very disheartening. However, Moissan picked up courage and entered this field. He electrolysed a cooled solution of KF in anhydrous liquid HF at 250 K using platinum-iridium electrodes sealed with fluorspar caps in a platinum U-tube. In this reaction, the actual electrolyte is KF while HF acts as an ionising solvent, F_2 is evolved at the anode and H_2 at the cathode as indicated below :

$$KF \rightleftharpoons K^+ + F^-$$

At the anode

$$F^- \longrightarrow F + e$$

$$F + F \longrightarrow F_2$$

At the cathode

$$K^+ + e \longrightarrow K$$

$$2K + 2HF \longrightarrow 2KF + H_2 \uparrow$$

Potassium fluoride thus formed again undergoes electrolysis. As the hydrogen fluoride is used up, more is added to prevent the melting point of the mixture from rising. The outgoing gases, F_2 and H_2, are not allowed to mix up in the electrolytic cell. The fluorine gas is collected in plastic receivers.

Moisson's original method has been modified. In place of the expensive Pt/Ir alloy, cells made of copper, steel or Monel metal, which is a nickel-copper alloy, have been used. These get covered by a thin protective film of the fluoride just as aluminium is protected by the thin film of oxide. Anode is a carbon rod impregnated with copper to render it inert and cathode is made of steel or copper. A mixture of KF and HF in the molar ratio of 1:1 or 1:2 is used as electrolyte giving a working temperature of 515 K or 345 K, respectively.

10.2.4 Uses

The main use of halogens is in the halogenation of organic and inorganic compounds. You must have heard of or used the tincture of iodine (iodine dissolved in alcohol) as an antiseptic. Iodine is present in the thyroid hormone. A deficiency of iodine causes goitre and leads to stunted growth and cretinism. To prevent this, common salt is routinely iodised. You must have used toothpastes containing fluorides in order to prevent tooth decay by dental caries. You are aware that naturally occurring uranium is a mixture of two isotopes – ^{238}U (99.3%) and ^{235}U (0.7%). Of the two, the latter is fissionable and is used for the generation of nuclear power. Fluorine is used for the production of uranium hexaflouride, the compound used for separation of ^{235}U and ^{238}U isotopes by gaseous diffusion method. Besides this, liquid fluorine was used as an oxidant in rocket fuels but this has now been discontinued. Teflon, so familiar to modern housewife in the form of its coating on kitchenware to make them nonsticking, is a polymer of fully fluorinated ethylene. You have already studied in Unit 7, the use of chlorofluorocarbons or CFCs as refrigerants, in aerosol sprays and in micro-electronics. Freons, e.g., CCl_2F_2 (Freon-12) and CCl_3F(Freon-11) used as refrigerants also contain fluorine. Bleaching powder, $CaOCl_2$, is used for bleaching paper pulp and textiles. Bleaching powder or liquid chlorine is used for disinfection of water on a large scale. Chlorine was used in the chemical warfare in World War I. The most important use of chlorine is in the manufacture of polyvinylchloride or PVC, which because of its non-inflammability and insulating properties is used as an electrical insulator, for covering electric wires, making conduit pipes, etc. Dichlorodiphenyltrichloroethane (DDT) is used widely as an insecticide. Methyl bromide is the most effective nematocide known. It is also used as a general pesticide. The use of silver bromide in making photographic plates or films is a common knowledge.

AQ 1

Why can't fluorine be obtained by electrolysis of an aqueous solution of NaF ?

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10.3 GENERAL CHARACTERISTICS

All elements of Group 17 have seven electrons in their outermost shell, with configuration ns^2, np^5. Thus, they are just one electron short of the electronic configuration of noble gases. The single unpaired electron in p-orbital is responsible for chemical bonding with other elements. Let us now discuss some of their physical and chemical properties.

10.3.1 Physical Properties

Halogens exist as non-polar diatomic molecules which are coloured. Fluorine is pale yellow, chlorine is yellowish green, bromine is brown and iodine is violet in the gaseous state. Solid iodine is almost black with a shiny metallic lustre. Except iodine which has some useful biological applications, halogens are very hazardous and toxic, fluorine being the most. Their vapours produce a choking sensation when inhaled.

Some of the physical properties of the halogens are listed in Table 10.1

Table 10.1: Some physical properties of halogens

Property	Fluorine F	Chlorine Cl	Bromine Br	Iodine I
Atomic number	9	17	35	53
Electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$
Atomic weight	18.9984	35.453	79.909	126.904
Density (liquid) ($10^3 \times$ kg m^{-3})	1.11	1.56	3.1	4.94
Ionic radius X^-(pm)	136	181	195	216
Covalent radius (pm)	64	99	114	133
Melting point (K)	53	172	266	386
Boiling point (K)	85	238.5	332	456
Enthalpy of fusion (kJ mol^{-1})	0.26	3.2	5.27	7.8
Enthalpy of vaporisation (kJ mol^{-1})	3.27	10.2	15	30
Enthalpy of atomisation (kJ mol^{-1})	79.1	122	111	106
Enthalpy of hydration $X^-(g)$ (kJ mol^{-1})	460	-385	-351	305
Electronegativity (A/R)	4.10	2.85	2.75	2.20
Ionisation energy (kJ mol^{-1})	1681	1255	1142	1007
Electron affinity (kJ mol^{-1})	333	348	340	297
Electrode potential $1/2X_2(g) + e \longrightarrow X^-(aq)$	+2.87	+1.36	+1.07	+0.54
Oxidation states	–I	–I, I, III, V, VII	–I, I, III, V	–I, I, III, V, VII
Lattice energy (kJ mol^{-1}) (Potassium salt)	817	718	656	615
Bond dissociation energy (X–X) (kJ mol^{-1})	158	244	192	152

Physical properties like melting and boiling points are related to the size and mass of the molecules as well as intermolecular attraction. The effect of size and mass, which gradually increase as we go down the group, is easy to understand. As for the intermolecular attraction in non-polar homonuclear diatomic molecules like halogens, which do not have any permanent polarity, the only forces of attraction are the weak van der Waals forces. The polarisability of halogens increases as we go down the group, begin maximum in iodine and least in fluorine. So, van der Waals forces of attraction are maximum in iodine and least in fluorine, with bromine and chlorine coming in between. As a consequence of this, fluorine and chlorine are gases at ordinary temperature, bromine is a liquid and iodine a solid. This is also reflected in the trends observed in their enthalpies of fusion and vaporisation (Table 10.1).

You have already learnt in Unit 2 that as we move along a period, the effective nuclear charge increases reaching a maximum at the noble gases. Halogens which immediately precede the noble gases have a very high effective nuclear charge coupled with small size and thus have the highest ionisation energies in the respective periods, next only to the noble gases. Like the trend in other groups, ionisation energy of halogens also decreases in going down the group from fluorine to iodine.

Halogens have seven electrons in their valence shell, they have a very strong tendency of gaining an electron to acquire a stable noble gas configuration. Therefore, they have very high electron affinities. In fact, their electron affinities are the highest in their respective periods. Their electron affinity follows the order Cl > F > Br > I. As explained in Unit 2, the smaller electron affinity of fluorine than that of chlorine is a consequence of its small size.

You know that as we go across the *p*–block elements in a period, the electronegativity increases reaching a maximum at the halogen group. Thus, halogens are the most electronegative elements in their respective periods. Electronegativity decreases on moving down a group, making fluorine the most and iodine the least electronegative among the halogens.

In going down the group from chlorine to iodine, the X–X bond dissociation energy gradually decreases (Table 10.1). This is easily explained by considering once again the size factor. In the chlorine molecule, which is the smallest of the three, viz., Cl_2, Br_2, I_2, the two bonding electrons are nearer to both the nuclei and are held strongly, while in bromine and iodine, the distance of the bonding electrons from the nuclei gradually increases resulting in lesser attraction and consequent weakening of the bond. Furthermore, as the size of the atom increases, it results in a less effective overlap of the orbitals and therefore, progressively weaker bonds are formed as we go down the group. The bond dissociation energy increases in the order $I_2 < Br_2 < Cl_2$ and if this trend was to continue, you should expect the F–F bond dissociation energy to be greater than the bond energy of chlorine, 244 kJ mol^{-1}. But this is not so. The actual bond dissociation energy of fluorine molecule is, however, surprisingly low and has the value of 158 kJ mol^{-1} only. The anomalously low bond dissociation energy of fluorine molecule is attributed to the fact that fluorine atom is very small and the non-bonding electrons on fluorine are near to each other, resulting in a much greater lone pair-lone pair repulsion, which weaken the covalent bond and lowers its dissociation energy. This repulsion is not so great in relatively larger halogen molecules like chlorine, bromine and iodine where the lone pairs are at a greater average distance from each other.

SAQ 2

Fill the name of the appropriate halogen in the space provided against each of the following:
Which of the halogens

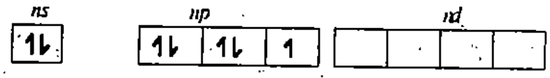
i) has two complete electron shells below the valence shell ....
ii) is solid at room temperature ....
iii) has highest electronegativity value ....
iv) lowest ionisation energy ....

10.3.2 Oxidation States

Fluorine is always univalent. Since it is the most electronegative element, it always has the oxidation number –1. Fluorine has no *d*–orbital in its valence shell, hence it cannot have any excited states or any other oxidation number.

Oxidation state of –1 is the most common and stable one for other halogens also. However, consistent with the decreasing electronegativity, –1 oxidation state becomes gradually less stable in going down the group. As chlorine, bromine and iodine are less electronegative than fluorine and oxygen, they exhibit an oxidation state of +1 in their fluorides and oxides. In addition, except fluorine all the other halogens exhibit oxidation states of +3, +5 and +7 due to the availability of vacant *d*-orbitals as shown below:

Halogen (except F)
atom in ground state



Oxidation state = ± 1,
e.g., HCl, HBr & HI
(oxidation = –1),
HClO, HBrO & HIO
(oxidation state = +1)

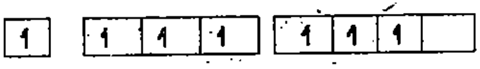
Halogen atom in
1st excited state

oxidation state = +3,
e.g., ClF_3, BrF_3

Halogen atom in the
2nd excited state

oxidation state = +5,
e.g., $HClO_3$, $HBrO_3$, HIO_3

Halogen atom in the
3rd excited state



oxidation state = +7
e.g., $HClO_4$; HIO_4.

Chlorine and bromine also exhibit oxidation state + 4 (ClO_2 and BrO_2) and + 6 (Cl_2O_6 and BrO_3). Iodine exhibits an oxidation state + 4 in I_2O_4.

10.3.3 Oxidising Power

Oxidation may be regarded as the removal of electrons, so that the oxidising agent gains electrons. Since halogens have a greater tendency to pick up electrons, they act as strong oxidising agents. Their oxidising power, however, decreases on moving down the group. The strength of an oxidising agent or its ability to accept electrons, depends on several energy terms. The reaction,

$$^{1}/_{2}\,X_2\,(\text{standard}) + e \longrightarrow X^-(aq) \qquad \ldots \text{(I)}$$

representing the oxidising action of a halogen, is actually a complicated process. It involves the following steps:

$$^{1}/_{2}\,X_2(\text{standard}) \xrightarrow{\Delta H_{\text{V}}} \frac{1}{2}\,X_2(g) \qquad \ldots \text{(II)}$$

$$^{1}/_{2}\,X_2(g) \xrightarrow{\Delta H_{\text{d}}} X\,(g) \qquad \ldots \text{(III)}$$

$$X(g) + e \xrightarrow{E_{\text{A}}} X^-(g) \qquad \ldots \text{(IV)}$$

$$X^-(g) + aq \xrightarrow{\Delta H_{\text{hyd}}} X^-(aq) \qquad \ldots \text{(V)}$$

The above changes are represented in the form of Born–Haber cycle, as shown below :

$$\begin{tikzcd}
\frac{1}{2}X_2(\text{standard}) \arrow[r, "\Delta H\text{v}", "\text{II}"'] \arrow[d, "\Delta E", "\text{I}"'] & \frac{1}{2}X_2(g) \arrow[r, "\Delta H\text{d}", "\text{III}"'] & X(g) \arrow[d, "E_{\text{A}}", "\text{IV}"'] \\
X^-(aq) & & X^-(g) \arrow[ll, "\Delta H_{\text{hyd}}"', "\text{V}"]
\end{tikzcd}$$

Evidently, since energy is invariably absorbed in steps (II) and (III), enthalpy of vapourisation, ΔH_{V} and enthalpy of dissociation, ΔH_{d}, always have positive values. However, energy is released in steps (IV) and (V), hence, electron affinity, E_{A}, and enthalpy of hydration, ΔH_{hyd} are negative. Consequently, from Hess's law, the net enthalpy change, ΔE for the reduction reaction (I) is given by the expression:

Hess's Law:
The amount of heat evolved in a chemical process is always the same irrespective of whether the process goes as a one or many step reaction.

$$\Delta E = \Delta H_{\text{V}} + \Delta H_{\text{d}} + E_{\text{A}} + \Delta H_{\text{hyd}}$$

For fluorine and chlorine which are gases at room temperature, the enthalpy of evaporation is omitted. Enthalpy changes associated with each of the above steps and the net enthalpy change, ΔE are given in Table 10.2.

You can see from Table 10.2 that ΔE, or the net enthalpy change associated with the reaction (I) decreases from fluorine to iodine. Considering that the difference in entropy changes are small and mainly enthalpy changes determine the free energy change, it can be inferred that the free energy change for reaction (I) becomes less negative on descending the group. In other words, fluorine is the strongest oxidising agent of the four. Thus, you may note that despite the electron affinity of chlorine being highest, fluorine is the strongest oxidising agent because of its low enthalpy of dissociation and high enthalpy of hydration.

Thus, it is the total enthalpy change and not the electron affinity which controls the strength of an oxidising agent.

Table 10.2 : Enthalpy values for $^1/_2 X_2 \longrightarrow X^-(aq)$

Molecule	Enthalpy of vapourisation, ΔH_v kJ mol^{-1}	Enthalpy of dissociation, ΔH_d kJ mol^{-1}	Electron affinity, E_A kJ mol^{-1}	Enthalpy of hydration, ΔH_{hyd} kJ mol^{-1}	ΔE kJ mol^{-1}
F_2	–	+79.2	–333	–460	–714
Cl_2	–	122.0	–348	–385	– 611
Br_2	15	96.0	–340	–351	–580
I_2	30	76.0	–297	–305	– 496

The oxidising power of the halogens in the solid state reactions also shows the same order. This is because lattice energies of the ionic halides (Table 10.1) follow the same order as the hydration energy; fluorides having the highest and iodides the lowest lattice energy.

Another important factor which makes fluorine the strongest oxidising agent is the high element-fluorine covalent bond energy as shown in Table 10.3.

Table 10.3 : Halogen-element bond energy, kJ mol^{-1}

Element	B	C	N	O	F	Si	P	S	Cl	H
F	644	489	286	213	158	598	498	285	251	565
Cl	433	326	192	205	251	402	331	272	244	431
Br	368	272		201	251	331	268	213	209	364
I	272	238			243	234	184		209	299

You will notice that the values in the first row representing fluorine-element bond energy are highest except in the case of fluorine-fluorine bond energy; the reasons for which you have studied earlier in Section 10.3. Thus fluorine forms a very strong bond with almost all other elements. A consequence of this is that fluorine is able to form compounds with other elements in their higher oxidation states. The order of the ability of the halogens to combine with elements in higher oxidation states is F > Cl > Br > I.

A comparison of the reduction potential of halogens with that of oxygen can indicate which of them would oxidise water to oxygen. The standard electrode potential for reduction of oxygen to water in acid solution in 1.23 volts:

$$^1/_2 O_2 + 2H^+ + 2e \longrightarrow H_2O$$

The standard reduction potential of the halogen half cell reaction,

$$^1/_2 X_2(g) + e \longrightarrow X^-(aq)$$

is +2.87 volts in the case of fluorine and +1.36 volts in the case of chlorine (Table 10.1). These are more positive than that for reduction of oxygen to water. These two halogens can, therefore, oxidise water to oxygen. Fluorine does so readily but chlorine reacts rather slowly, at first giving HClO which later decomposes to oxygen and HCl. The electrode potentials of bromine and iodine are less than that of oxygen, therefore, they are not able to oxidise water to oxygen.

To sum up, the main thermodynamic factors responsible for making fluorine so uniquely highly oxidising and reactive are:

- high hydration energy of the fluoride ion
- high lattice energy of ionic fluorides
- low F–F bond energy and
- high element fluorine bond energy.

SAQ 3

Table 10.1 lists the standard reduction potential for the half cell reaction

$$^1/_2\,X_2\,(g) + e \longrightarrow X^-(aq)$$

and the standard potential for the reaction

$$^1/_2\,O_2\,(g) + 2H^+\,(aq) + 2e \longrightarrow H_2O\,(l)$$

is 1.23V. What reaction do you predict between bromine and water and iodine and water on this basis?

....

....

....

....

10.3.4 Chemical Properties

All the halogens are very reactive. Fluorine is the most reactive of all the halogens, combining directly with every other element except oxygen and some of the noble gases. Therefore, it is also called a **super halogen.** You have also seen that the reactivity decreases from F_2 to I_2. In displacement reactions we find that fluorine displaces all the remaining three halogens from their salts, chlorine displaces bromine and iodine and bromine displaces only iodine. Halogens react with each other to form **interhalogen compounds**; brief description of these is given in Section 10.4.4. Halogens, in general, react with most metals, though bromine and iodine do not react with some noble metals like Ag, Au. Halogens also react with many non-metals to form halides.

Halogens react with hydrogen to form hydrides which are called hydrogen halides. Fluorine and chlorine react with hydrogen with explosive violence, fluorine-hydrogen mixture explodes even in the dark. Chlorine-hydrogen mixture does so only in presence of light. This is called a **photochemical reaction.** It has been shown that this reaction starts with the formation of halogen free radicals. It is not surprising in view of the lower X–X bond energy as compared to H–H bond energy. Reactions of bromine and iodine with hydrogen are slow, the latter being reversible.

$Cl{-}Cl \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot}$ initiation .... step I

$Cl^{\cdot} + H{-}H \longrightarrow HCl + H^{\cdot}$ propagation .... step II

$H^{\cdot} + Cl{-}Cl \longrightarrow HCl + Cl$ propagation .... step III

$Cl^{\cdot} + H^{\cdot} \longrightarrow HCl$ termination .... step IV

Such reactions are called **Chain Reactions** since after the initiation of the reaction, the propagation steps II and III are repeated in sequence till the reactants are consumed. The reaction gets terminated when free radicals start combining with each other as in step IV.

Fluorine reacts vigorously with water to form hydrofluoric acid and oxygen :

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

The other halogens are sparingly soluble in water ($Br_2 > Cl_2 > I_2$) and react partly to give a mixture of hydrohalic and hypohalous acids :

$$X_2 + H_2O \rightleftharpoons HX + HOX$$

Halogens react with aqueous alkali, the reactivity decreasing from fluorine to iodine. Fluorine behaves differently from other halogens. It reacts with alkalies violently forming fluorides and fluorine oxides or oxygen as shown below :

$$2F_2 + 2NaOH \xrightarrow{\text{in cold}} 2NaF + OF_2 + H_2O$$

$$2F_2 + 4NaOH \xrightarrow{\text{in hot}} 4NaF + O_2 + H_2O$$

Other halogens react with alkalies in cold to give hypohalites (XO^-) and in hot to form halates (XO_3^-) :

$$2NaOH + X_2 \xrightarrow{\text{in cold}} NaOX + NaX + H_2O$$

$$6NaOH + 3X_2 \xrightarrow{\text{in hot}} NaOXO_2 + 5NaX + 5H_2O$$

(where X = Cl, Br or I)

- Hypohalites are oxidising agents. Bleaching powder CaCl (OCl) owes its bleaching action to its oxidising properties.

All halogens react with hydrocarbons but reactivity decreases with the increase in atomic number. Fluorine is the most reactive and brings about decomposition of the hydrocarbons:

$$CH_4 + 2F_2 \longrightarrow C + 4HF$$

Chlorine and bromine substitute hydrogen atoms, reaction with bromine being slower. Iodine has little or no reaction :

$$CH_4 + 4X_2 \longrightarrow CX_4 + 4HX, \quad \text{where X = Cl or Br}$$

Some more reactions of halogens are summarised in Table 10.4.

Table 10.4: Some reactions of halogens

General Reaction	Remarks
$nX_2 + 2M \longrightarrow 2MX_n$	F_2, Cl_2 with practically all metals; Br_2, I_2 with all except noble metals.
$X_2 + H_2 \longrightarrow 2HX$	Reaction with iodine reversible.
$3X_2 + 2P \longrightarrow 2PX_3$	Similar reactions with As, Sb, Bi.
$5X_2 + 2P \longrightarrow 2PX_5$	With excess X_2, but not with I_2; SbF_5, $SbCl_5$, AsF_5, $AsCl_5$ and BiF_5 may be prepared similarly.
$X_2 + 2S \longrightarrow S_2X_2$	With Cl_2, Br_2.
$X_2 + H_2O \longrightarrow H^+ + X^- + HOX$	Not with F_2.
$2X_2 + 2H_2O \longrightarrow 4H^+ + 4X^- + O_2$	F_2 rapidly, Cl_2 and Br_2 slowly in sunlight.
$X_2 + H_2S \longrightarrow 2HX + S$	
$X_2 + CO \longrightarrow COX_2$	$X_2 = Cl_2, Br_2$.
$X_2 + SO_2 \longrightarrow SO_2X_2$	$X_2 = F_2, Cl_2$.
$X_2 + Y_2 \longrightarrow 2XY$	Formation of interhalogen compounds (all except IF).
[X and Y are two different halogens]	

10.3.5 Basic Properties of Halogens

In general, the basic or metallic nature of elements increases as we descend down a group. Thus, you have seen in preceding units that the last member of each of the Groups 14, 15 and 16, i.e., Pb, Bi and Po, respectively, is definitely metallic in character. But, this trend is not so well marked in the elements of Group 17 because very little is known about the last member of the group, astatine. There is, however, definite evidence to show the existence of halogen cations in media which are weakly nucleophilic.

Fluorine is the most electronegative element and has no basic properties. Chlorine shows a slight tendency to form cations. For example, ClF ionises to form Cl^+ and F^- due to the higher electronegativity of fluorine. Bromine cation, Br^+, exists in complexes such as $[Br\,(pyridine)]^+ NO_3^-$. Electrolysis of ICN in pyridine solution gives iodine at the cathode. This indicates that ICN ionises to I^+ and CN^-. Many pyridine complexes, e.g., $[I\,(pyridine)]^+ NO_3^-$, $[I\,(pyridine)_2]^+ ClO_4^-$ and $I\,(pyridine)^+CH_3COO^-$ containing I^+ are known.

Iodine dissolves in oleum giving a bright blue solution which has been shown to have I_2^+ and I_3^+ :

$$2I_2 + 6H_2S_2O_7 \longrightarrow 2I_2^+ + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

$$3I_2 + 6H_2S_2O_7 \longrightarrow 2I_3^+ + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

Electrical conductivity of molten iodine is due to the presence of $I_3^+ + I_3^-$ species produced by the self ionisation of iodine:

$$3I_2 \rightleftharpoons I_3^+ \text{ and } I_3^-$$

The cations, Cl_3^+ and Br_3^+ are formed in the following reactions:

$$ClF + Cl_2 + AsF_5 \longrightarrow Cl_3^+{\cdot}AsF_6^-$$

$$O_2^+{\cdot}\,AsF_6^- + {}^3\!/_2Br_2 \longrightarrow Br_3^+{\cdot}AsF_6^- + O_2.$$

SAQ 4

Complete the following reactions:

i) $I_2 + IF_3 \longrightarrow$ ....

ii) $Cl_2 + H_2O \longrightarrow$ .... + ...

iii) $Cl + 2NaOH \longrightarrow$ .... + ... + ...

iv) $Cl_2 + H_2S \longrightarrow$ .... + ...

v) $CH_4 + 4Br_2 \longrightarrow$ .... + ...

10.4 COMPOUNDS OF HALOGENS

In the preceding section you have learnt that the halogens form a variety of compounds with other elements. In this section, you will study the salient features of the chemistry of some of these compounds, viz., hydrogen halides, halogen oxides, oxoacids of halogens and the interhalogen compounds.

10.4.1 Hydrogen Halides

You have studied in the preceding section that all the halogens combine with hydrogen and form volatile hydrides of the type HX, which are also known as hydrogen halides. The reaction of fluorine with hydrogen is very violent whereas bromine and iodine react with hydrogen only at elevated temperatures and in the case of iodine the reaction does not proceed to completion:

$$H_2 + X_2 \longrightarrow 2HX, \text{ where } X = Cl, Br \ \& \ I$$

Hydrogen fluoride and hydrogen chloride are obtained by the action of concentrated sulphuric acid on fluorides and chlorides :

$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4$$

$$NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$$

Since concentrated sulphuric acid partially oxidises HBr and HI to Br_2 and I_2, these are prepared by the action of concentrated orthophosphoric acid on bromides and iodides:

$$NaBr + H_3PO_4 \xrightarrow{\hspace{3cm}} HBr + NaH_2PO_4$$

$$NaI + H_3PO_4 \xrightarrow{\hspace{3cm}} HI + NaH_2PO_4$$

Hydrogen bromide and hydrogen iodide are usually prepared in the laboratory by the hydrolysis of PBr_3 and PI_3:

$$PBr_3 + 3H_2O \xrightarrow{\hspace{3cm}} 3HBr + H_3PO_3$$

$$PI_3 + 3H_2O \xrightarrow{\hspace{3cm}} 3HI + H_3PO_3$$

Under ordinary conditions HCl, HBr and HI are gases while HF is a liquid, due to strong hydrogen bonding. Their melting and boiling points show a gradual increase in the order HCl < HBr < HI, but H–F does not follow the trend and has unexpectedly higher values. This is because of strong hydrogen bonding in H–F molecules about which you have studied in Unit 3. Due to hydrogen bonding HF_2^- ion is stable and gives salts like KHF_2.

Hydrogen halides are covalent compounds with varying degree of polarity of the H–X bond depending upon the electronegativity of the halogen atom. Thus, H–F bond is most polar and the decreasing order of polarity is H–F > H–Cl > H–Br > H–I as shown by the per cent ionic character in these bonds.

Some physical properties of the hydrogen halides are listed in the Table 10.5.

Table 10.5: Physical properties of hydrogen halides

	Physical state	Colour	B.P. (K)	M.P. (K)	% dissociation at 373 K	Per cent ionic character
HF	liquid	Colourless	293	190	Very slight	44
HCl	gas	"	188	159	0.0014	17
HBr	gas	"	208	186	0.5	11
HI	gas	"	237	222	33	5

The thermal stability of hydrogen halides decreases from HF to HI. Thus hydrogen fluoride is the most stable whereas hydrogen iodide is the least stable. This can be seen from their percentage dissociation data (Table 10.5). For example, while HF and HCl are not appreciably dissociated even at 1473 K, HBr is dissociated to the extent of 0.5% and HI is dissociated to the extent of 33% at 373 K.

A constant boiling point mixture is a mixture of two or more substances with a definite composition, which boils at a specific temperature at a specific pressure. HCl, for example forms a constant boiling point mixture containing 20.24% HCl with a boiling point 383 K.

Hydrohalic Acids

Aqueous solutions of hydrogen halides are called hydrohalic acids, viz., hydrofluoric, hydrochloric, hydrobromic and hydriodic acid. Hydrohalic acids form constant boiling point mixtures with water. The aqueous solutions of acids ionise as follows :

$$HX(aq) + H_2O \xrightarrow{\hspace{3cm}} H_3O^+(aq) + X^-(aq)$$

Their acid strength follows the order HI > HBr > HCl > HF. Acid strength is in general the tendency of $HX(aq)$ to give $H_3O^+(aq)$ and $X^-(aq)$. The enthalpy changes associated with the dissociation of hydrohalic acids can be represented with the help of Born–Haber cycle in its simplest form as given below:

$$\begin{tikzcd}
HX(g) \arrow[r, "\Delta H_d"] & H(g) \arrow[d, "I"] & + & X(g) \arrow[d, "E_A"] \\
 & H^+(g) \arrow[d, "\Delta H_{hyd}"] & & X^-(g) \arrow[d, "\Delta H_{hyd}"] \\
HX(aq) \arrow[uu, "\Delta H_{dehyd}"] \arrow[r] & H^+(aq) & + & X^-(aq)
\end{tikzcd}$$

The acid strength depends upon the sum of all enthalpy terms for various stages indicated in the Born Haber cycle. Of these the most marked change is in the enthalpy of dissociation of H–X bond, which decreases in the order HF > HCl > HBr > HI and the enthalpy of hydration of X^-, which decreases from $F^- > Cl^- > Br^- > I^-$. The total enthalpy change becomes more negative, i.e., the reaction,

$$HX(aq) \longrightarrow H^+(aq) + X^-(aq)$$

becomes more exothermic from HF to HI. As expected, acid strength varies in the reverse order, HI being the strongest acid and HF the weakest acid.

SAQ 5

Explain briefly in the space given below, why HF is the weakest acid.

....

....

....

10.4.2 Halogen Oxides

All halogens form oxides. Numerous halogen oxides have been reported although many of them are unstable. These are listed in Table 10.6. Halogen-oxygen bonds are largely covalent because of the similarities in electronegativity of halogens and oxygen. Fluorine is more electronegative than oxygen, hence compounds of fluorine with oxygen are considered as fluorides of oxygen rather than oxides of fluorine.

I_2O_5 is the only halogen oxide which is stable with respect to dissociation into elements. Chlorine oxides decompose violently while the bromine oxides are the least stable among the halogen oxides. Of these only Cl_2O and ClO_2 find some practical importance as bleaching agents in paper pulp and flour industries; I_2O_5 is used in the estimation of CO.

Table 10.6 : Oxides of halogens

Fluorides		Oxides					
Compound	**Oxidation number (O.N.)**	**Chlorine Compound**	**O.N**	**Bromine Compound**	**O.N**	**Iodine Compound**	**O.N**
OF_2	–1	Cl_2O	+1	Br_2O	+1		
O_2F_2	–1	ClO_2	+4	BrO_2	+4	I_2O_5	+5
		Cl_2O_6	+6	BrO_3	+6		
		Cl_2O_7	+7				

Preparation of Halogen Oxides

Oxygen difluoride is prepared by passing fluorine into a 2% NaOH solution:

$$2F_2 + 2NaOH \longrightarrow 2NaF + H_2O + OF_2$$

It is a stable colourless gas. It reacts vigorously with metals, sulphur, phosphorus and halogens and gives fluorides and oxides. It reacts with bases to give F^- ion and free oxygen.

Cl_2O and Br_2O are prepared by heating freshly precipitated mercuric oxide with the halogen gas :

$$2X_2 + 2HgO \xrightarrow{573\ K} HgX_2.\ HgO + X_2O, \text{ where } X = Cl \text{ or } Br$$

Chlorine dioxide (ClO_2) is also prepared by the following reactions :

$$2NaClO_3 + SO_2 + H_2SO_4 \longrightarrow 2ClO_2 + 2NaHSO_4$$

It is also obtained by treating silver chlorate with dry chlorine at 363 K :

$$2AgClO_3 + Cl_2 \longrightarrow 2AgCl + 2ClO_2 + O_2$$

Chlorine dioxide is a gas at normal temperature, b.p. 284 K. It is a powerful oxidising and chlorinating agent. It reacts with alkalies to form chlorites and chlorates :

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

Iodine pentoxide (I_2O_5) is prepared by dehydration of iodic acid at 513 K :

$$2HIO_3 \xrightarrow[H_2O]{513\text{ K}} I_2O_5 + H_2O$$

It is a white solid which decomposes to iodine and oxygen above 573 K. I_2O_5 is a good oxidising agent, it oxidises H_2S to sulphur and HCl to chlorine.

Properties of Halogen Oxides

All oxides of halogens have positive free energies of formation except F_2O and are thus unstable with respect to dissociation into elements. F_2O is stable upto 475 K. A combination of kinetic and thermodynamic factors leads to the generally decreasing order of stability I > Cl > Br. The higher oxides tend to be more stable than the lower. Except for that of iodine all oxides tend to be explosive. Iodine pentoxide, I_2O_5, is white solid stable upto 575 K. Because of their oxidising properties, chlorine oxides, Cl_2O and ClO_2 are used as bleaching agents and as **germicides.** I_2O_5 quantitatively oxidises CO into CO_2 and therefore, is used in the estimation of CO.

Structure of Oxides of Halogens

Structures of only OF_2, Cl_2O, Br_2O, Cl_2O_7 and I_2O_5 are definitely known. Structures of the monoxides can be explained on the basis of VSEPR theory about which you have already studied in Unit 3 of the course, **Atoms and Molecules.** These oxides have tetrahedral structure with two lone pairs on oxygen. Thus, the molecule is V shaped or angular in shape. The bond angle EOE varies in the order FOF < ClOCl < BrOBr. This is because electrons in the case of OF_2 are nearer to fluorine due to high electronegativity of F compared to Cl or Br. The bonded electron pairs in Cl_2O and Br_2O are closer to oxygen making the repulsion between them more and thereby reducing the lone pair - lone pair repulsion on oxygen to some extent. Also due to the bulkiness of Cl and Br, the angles ClOCl and BrOBr increase to such an extent that they are greater than 109°28′, the tetrahedral angle. Fig. 10.1 shows some of the structures of halogen oxides.

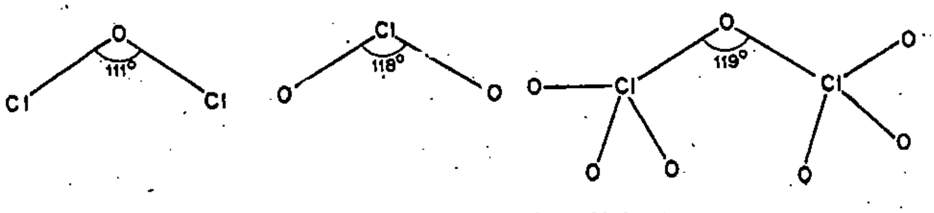


Fig. 10.1: Structures of some oxides of halogens

10.4.3 Oxoacids of Halogens

Oxoacids of halogens have oxygen attached to the halogen atom. They have the general formula $HOX(O)_n$ where n = 0, 1, 2 or 3. The oxoacids are named as hypohalous acid (HOX), halous acid (HOXO), halic acid ($HOXO_2$) and perhalic acid ($HOXO_3$), in which the oxidation state of the halogen is +1, +3, +5 and +7, respectively. Most of the oxoacids are known only in solution or as salts. Fluorine being more electronegative than oxygen, does not form oxoacids except the unstable HOF. Some important oxoacids of halogens are given in Table 10.[illegible]

Table 10.7 : Important oxoacids of halogens

Names of the acid and their salts	Oxidation state of halogen in the acid	Oxoacids of			Structure
		Cl	Br	I	
Hypohalous, Hypohalites	+1	* HOCl Hypochlorous acid	* HOBr Hypobromous acid	* HOI Hypoiodous acid	H–O–X
Halous, Halites	+3	* HOClO Chlorous acid	* HOBrO Bromous acid		H–O–X→O
Halic, Halates	+5	* $HOClO_2$ Chloric acid	* $HOBrO_2$ Bromic acid	$HOIO_2$ Iodic acid	O ↑ H–O–X→O
Perhalic, Perhalates	+7	$HOClO_3$ Perchloric acid	* $HOBrO_3$ Perbromic acid	$HOBrO_3$ Periodic acid	O ↑ HO–X→O ↓ O

* Stable only in solution

The oxoacids containing higher number of oxygen atoms, i.e., having halogens in higher oxidation state are thermally more stable and are known in pure state. You may compare this with the increased stability in case of higher oxides of halogens. However, the thermal stability decreases with increase in the atomic number of the halogen. Thus, HOCl is the most stable and HOI the least stable among the hypohalous acids.

Acid strength of oxoacids increases with increase in the oxidation number of the halogen. This can be explained as follows. Because oxygen is more electronegative than halogens (consider only Cl, Br and I), the terminal oxygen atom pulls the electrons of O–X bond towards itself, leaving a slight positive charge on the halogen atom. The halogen atom then draws the electrons of X–OH bond towards itself. This oxygen atom in turn pulls the electrons of O–H bond towards itself, leaving hydrogen atom slightly positively charged and making the O–H bond more easily ionisable. This makes the compound more acidic.

$$H \rightarrow O \rightarrow Cl \rightarrow\rightarrow O$$

It is obvious from the above that higher the oxidation number of the halogen,

- higher is the number of oxygen atoms attached to the halogen,
- more effective is the displacement of shared electrons towards the terminal oxygen atoms and
- more acidic is the oxoacid.

Acid strength of oxoacids with halogen in the same oxidation state, decreases as we go down the group. Thus HOCl is the strongest and HOI is the weakest amongst these acids. Hypoiodic acid is amphoteric and may be regarded as iodine hydroxide, $\dot{I}\breve{O}H$, in many reactions. Decrease in acid strength of corresponding oxoacids down the group may be explained on the basis of decreasing electronegativities of the halogens.

NaOCl is one of the important salts of hypochlorous acid and is used in bleaching cotton fabrics, wood pulp and also as a disinfectant.

Anhydrous perchloric acid, $HClO_4$, is an extremely powerful oxidising agent which explodes when in contact with organic matter and sometimes on its own. Periodic acid, HIO_4, is extensively used in organic chemistry for oxidation of alkenes to glycols.

SAQ 6

Arrange the following in the order of increasing acid strength : HOCl, $HOClO_2$, $HOClO_3$ and HOClO.

....

....

10.4.4 Interhalogen Compounds

Compounds formed by the interaction of one halogen with other halogens are called **interhalogen compounds.** Such compounds are either binary, formed by a combination of two halogens or ternary, formed by a combination of three halogens. The binary compounds are of four types, viz., XY, XY_3, XY_5 and XY_7 where X and Y are the two halogens and Y is more electronegative than X. Interhalogen compounds are named as the halides of less electronegative halogen. Thus ClF is called chlorine monofluoride and not fluorine monochloride. Ternary interhalogen compounds were unknown until recently except as polyhalide anions or polyhalonium cations, but now some compounds, e.g., $IFCl_2$ and IF_2Cl have been prepared. The interhalogen compounds with fluorine are more common.

The stability of interhalogen compounds depends on the electronegativity difference of the two halogens. Greater the difference, more polar is the bond and therefore, greater is the thermal stability and higher their melting and boiling points.

The interhalogen compounds can be prepared by direct combination of the halogens or by action of the halogen on a lower interhalogen compound. A few examples are given below :

- $Cl_2 + F_2 \xrightarrow{498\text{ K}} 2ClF$
- $Cl_2 + 3F_2 \longrightarrow 2ClF_3$
- $I_2 + 3Cl_2 \longrightarrow 2ICl_3$
- $Br_2 + 5F_2 \longrightarrow 2BrF_5$
- $\underset{}{ClF_3} + \underset{\text{(excess)}}{F_2} \xrightarrow{523\text{ K}} ClF_5$
- $IF_5 + F_2 \longrightarrow IF_7$

Mono-and penta-fluorides of iodine are prepared by the action of AgF on I_2:

$$I_2 + AgF \xrightarrow{273\text{ K}} IF + AgI$$

$$3I_2 + 5AgF \longrightarrow IF_5 + 5AgI$$

Properties

Some physical properties of the interhalogen compounds like colour are intermediate between those of the constituent elements but their melting and boiling points are higher than expected from interpolation of the melting and boiling points of the constituent halogens. Some properties of interhalogen compounds are given in Table 10.8.

Interhalogen compounds are generally more reactive than the halogens (except F) since X—Y bond is more polar than the X—X bond. They are hydrolysed by water or alkali to the halide ion of the lighter halogen (Y^-) and the hypohalite ion of the heavier halogen (OX^-). The interhalogen compounds react with alkenes and add across the double bond (C = C). They are strong oxidising agents and are used to prepare metal halides. They convert metals into mixed halides :

$$XY + 2M \longrightarrow MX + MY$$

Their most important use is as fluorinating agents. They are also used as non-aqueous solvents. Iodine trichloride and bromine trifluoride autoionise like water and ammonia to give polyhalide ions, e.g.,

$$2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Thus, the substances which furnish ICl_2^- and BrF_2^+ behave as acids and those furnishing ICl_4^- and BrF_4^- behave as bases in ICl_3 and BrF_3 solvent systems, respectively.

Table 10.8 : Some interhalogen compounds

Type of interhalogen compound	Formulae and names of compounds	Physical state and colour at ordinary temperatures	Melting point (K)	Boiling point (K)
XY	ClF Chlorine fluoride	Gas, Colourless.	119	163
	BrF Bromine fluoride	Liquid below 293K, pale-brown gas above 293K	240	293
	BrCl Bromine chloride	Liquid, reddish yellow	207	283
	ICl Iodine chloride	Solid, ruby red	–	310
	IBr Iodine bromide	Solid, brown like iodine	232	
XY_3	ClF_3 Chlorine trifluoride	Liquid below 261K, colourless gas above 261 K	197	261
	BrF_3 Bromine trifluoride	Liquid, Colourless	282	400
	$BrCl_3$ Bromine trichloride	Solid, Orange	374 (decomposes)	–
XY_5	ClF_5 Chlorine pentafluoride	Gas, Colourless	170	259
	BrF_5 Bromine pentafluoride	Liquid, Colourless	213	314
	IF_5 Iodine pentafluoride	Liquid, Colourless	283	314
XY_7	IF_7 Iodine heptafluoride	Gas, Colourless	279.5	–

Structure of Interhalogen Compounds

The interhalogen compounds are generally covalent in which the larger atom lies in the centre. Their shapes can be predicted by VSEPR theory about which you have already studied in Unit 3 of the "**Atoms and Molecules**" course. Shapes of some of the interhalogen compounds are given in Table 10.9.

Table 10.9 : Shapes of molecules of interhalogens predicted by VSEPR theory

Molecule	Total number of electron pairs around X	Bond pairs	Lone pairs	Shape
XY	4	1	3	Linear
XY_3	5	3	2	T-shaped
XY_5	6	5	1	Square pyramidal
XY_7	7	7	0	Pentagonal bipyramidal

X—Y

Fig. 10.2: Linear structure of interhalogen molecule of the type XY.

Structures of interhalogens can be explained with the help of Valence Bond Theory also in the following manner :

i) Type XY : As expected, the compounds of the type XY are linear (Fig.10.2). Thus ClF, BrF, BrCl, IBr and ICl all have a linear structure. In these compounds both the halogen atoms have an unpaired electron in the p_z orbital. Axial overlap of the p_z orbitals of the two halogen atoms results in a linear interhalogen molecule.

ii) Type XY_3 : Structure of the interhalogens of this type can be explained on the basis of sp^3d hybridisation of the central halogen atom X. Three of the hybrid orbitals having an electron each are used in making three covalent bonds with three atoms of the other halogen atom. The remaining two orbitals accommodate the two lone pairs of the central atom. In order to minimise lone pair-lone pair and lone pair-bond pair repulsions, the lone pairs occupy the two equatorial sites around the central halogen atom, thereby giving a T-shape to the molecule (Fig. 10.3). Thus ClF_3, BrF_3 and ICl_3 have a T–shaped structure.

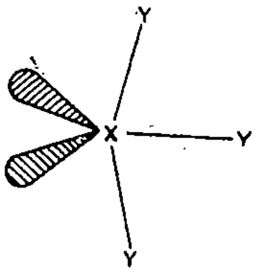


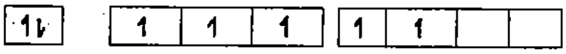
Fig. 10.3: T-shaped structure of interhalogen molecules of the type XY_3.

X atom in excited state

sp^3d hybridisation – trigonal bipyramidal structure with two equatorial sites occupied by lone pairs.

iii) Type XY_5 : This type of compounds have a square pyramidal structure (Fig.10.4). The central atom X uses five of its seven valence electrons in forming five bonds with Y and two electrons remain as a lone pair. Thus X–atom in XY_5 molecule is sp^3d^2 hybridised. The lone pair occupies the axial hybrid orbital.

X atom in excited state



sp^3d^2 hybridisation – octahedral structure with one of the axial sites occupied by lone pair.

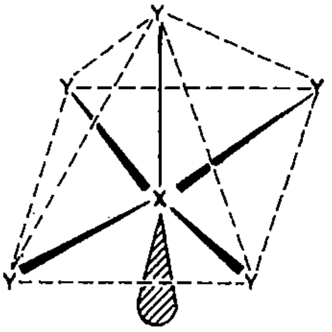
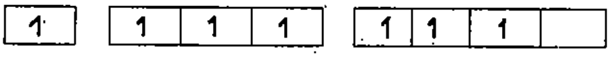


Fig 10.4: Square pyramidal structure of interhalogen molecules of the type XY_5.

iv) Type XY_7 : In these molecules, the central X atom uses all its seven valence electrons in forming seven X–Y bonds. Formation of this type of compounds can be explained on the basis of sp^3d^3 hybridisation of the X atom. These compounds have a pentagonal bipyramidal structure with two axial X—Y bonds and five equatorial X—Y bonds (Fig. 10.5).

X atom in excited state



sp^3d^3 hybridisation – pentagonal bipyramidal structure.

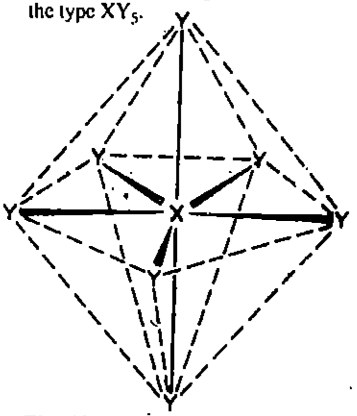


Fig. 10.5 : Pentagonal bipyramidal structure of interhalogen molecules of the type XY_7.

10.4.5 Polyhalides and Polyhalonium Ions

Halide ions often associate with molecules of halogens or with interhalogen compounds to form polyhalide ions. For example, on addition of potassium iodide, the solubility of iodine in water is greatly enhanced due to the formation of the triiodide ion, I_3^-:

$$KI + I_2 \longrightarrow KI_3$$

More complex ions of iodine, such as penta-iodide, I_5^-, heptaiodide, I_7^- and nona-iodide, I_9^- are also known.

These are generally found in the form of salts of large metal ions, e.g., $Rb^+ I_9^- \cdot 2C_6H_6$ or large complex cations, e.g., $NH_4^+ I_5^-$, $(C_2H_5)_4 N^+ I_7^-$). A number of mixed polyhalide ions containing two or three different halogens are also known, e.g., ICl_2^-, ICl_4^- and $IBrF^-$ and $IBrCl^-$.

All the polyhalides are hydrolysed to some extent in aqueous solution. The ease of hydrolysis increases with the introduction of the more electronegative halogen, into the ion. Thus, the triiodide being the most stable and Cl_3^- the least. In non-aqueous solutions, polyhalides behave as mild halogenating agents.

You have learnt in Section 10.4.4 that polyhalonium cations, e.g., ICl_2^+ and BrF_2^+ are formed as a result of autoionisation of ICl_3 and BrF_3. Other cations like Br_2^+, I_2^+, I_3^+, ClF_2^+, IF_2^+, IBr_2^+, $IBrCl^+$, ClF_4^+, BrF_4^+, IF_4^+, ClF_6^+, BrF_6^+, IF_6^+, etc. are also known. These are established by large anions like BF_4^-, PF_6^-, AsF_6^-, $AlCl_4^-$, $SbCl_6^-$, etc.

SAQ 7

Write 'T' for true and 'F' for false in the given boxes for the following statements about the interhalogen compounds.

i) Interhalogen compounds are strong oxidising agents ☐

ii) Interhalogen compounds are strong reducing agents ☐

iii) X–Y bond is more polar than X–X and Y–Y bonds ☐

iv) Interhalogen compounds are ionic ☐

v) XY_3 type of molecules have square pyramidal structure ☐

10.5 PSEUDOHALOGENS AND PSEUDOHALIDES

Some molecules like cyanogen, $(CN)_2$, thiocyanogen, $(SCN)_2$ and selenocyanogen, $(SeCN)_2$, have properties similar to those of the halogens. Therefore, these are called pseudohalogens. Pseudohalogens form hydro acids similar to the hydrohalic acids, e.g., H–CN. They also form anions such as cyanide, CN^-, cyanate, OCN^-, thiocyanate, SCN^-, selenocyanate, $SeCN^-$, tellurocyanate, $TeCN^-$ and azide, N_3^-, which resemble the halide ions to some extent.

The best known pseudohalide is the cyanide, CN^-, which resembles Cl^-, Br^- and I^- in the following respects :

- It can be oxidised to form a molecule, $(CN)_2$.
- It forms an acid HCN similar to HCl, HBr, etc.
- It forms insoluble salts with Ag^+, Pb^{2+} and Hg^+.
- Interpseudohalogen compounds ClCN, BrCN and ICN can also be formed.
- Like AgCl, AgCN is insoluble in water but soluble in liquor ammonia.
- It forms a large number of complexes similar to the halide complexes, e.g., $[Cu(CN)_4]^{2-}$ is similar to $[CuCl_4]^{2-}$ and $[Co(CN)_6]^{3-}$ is similar to $[CoCl_6]^{3-}$.

10.6 ANOMALOUS BEHAVIOUR OF FLUORINE

Fluorine differs from other elements of the group because of its exceptionally small atomic and ionic size and low fluorine—fluorine bond dissociation energy. The result of these differences is that fluorine is the most electronegative element in the periodic table and is a powerful oxidant. Some differences between fluorine and other halogens are :

- It is more reactive than other halogens because of low F–F bond energy, also due to its high electronegativity the bond between fluorine and other elements is very strong so its compounds are more stable. Some of them are inert, e.g., SF_6.
- Fluorine is almost invariably monocoordinate (coordination number = 1) and is never more than mono covalent.
- Fluorides are more ionic.
- Fluorine forms strong hydrogen bonds resulting in the properties of hydrogen fluoride being anomalous.
- Fluorine is the strongest oxidising agent and oxidises the elements to their highest oxidation state, for example in IF_7, iodine has oxidation number seven.
- The reactions of fluorine are also different from other halogens. Fluorine fumes in moist air and decomposes water to give oxygen, whereas other halogens are sparingly soluble in water and react partly to give hydrohalic and hypohalous acids.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$X_2 + H_2O \rightleftharpoons HOX + HX$$

- Fluorine reacts with alkalies to yield the oxide, F_2O :

$$2F_2 + 2NaOH \longrightarrow F_2O + 2NaF + H_2O$$

The other halogens react with alkalies to yield a solution of hypohalite ions, which may disproportionate. The oxoacid of fluorine, HOF, prepared recently is very unstable. The oxides of fluorine are not acidic.

10.7 SUMMARY

Let us now summarise what we have learnt in this unit.

- The halogens are only one electron short of the noble gas configuration.
- The elements form the anion X^- or a single covalent bond. Their chemistry is completely non-metallic though there is some evidence of their forming cations.
- Their chemical and the physical properties show variations according to the expected group trends.
- Because of the extremely small size of fluorine, it exhibits anomalous behaviour in the F–F bond energy and electron affinity.
- Fluorine is the strongest oxidising agent in the whole group. This is mainly because of very low F–F bond energy, very high F–element bond energy and the high hydration energy of the fluoride ion.
- Fluorine can oxidise all the other halide ions like Cl^-, Br^-, I^- to their respective elements. Because of its high oxidising power, fluorine forms compounds in which the other elements are in high oxidation states.
- The oxidation state of fluorine is –1 while the other halogens exhibit variable oxidation states due to the availability of vacant *d* orbitals.
- Halogens form a variety of compounds like, hydrohalic acids of the type HX, halogen oxides (OX_2 etc.), oxoacids like HOX, HOXO, $HOXO_2$ and $HOXO_3$ and interhalogen compounds of the type XY_n where X and Y are two different halogens. The bond in interhalogen compounds is polar with a positive charge on the heavier halogen. You have also learnt about the polyhalide ions, X_n^- and $XY_n^{\pm}$.

10.8 TERMINAL QUESTIONS

1 Fill the appropriate halogen in the following blanks :

i) ______________ displaces three halogens from their compounds.

ii) Cl^- can be oxidised by ______________

iii) Br_2 can be reduced by ______________

iv) Fluorine and ______________ can oxidise water to oxygen .

v) Oxidation of ______________ and ______________ by Cl_2 will give Br_2 and I_2, respectively.

2 We have listed the physical properties of all the halogens except astatine in Table 10.1. From your study of the periodicity in the properties of elements, predict the following for the astatine :

i) Atomic number

ii) Molecular formula

iii) M.P., B.P:

iv) Physical state

v) At-At bond energy

vi) Strength of aqueous hydroastatic acid.

3 Why does fluorine combine with other elements in their higher oxidation states.

4 Write the name of the following oxoacids and deduce the oxidation number of halogen atom in each.

(i) HOCl (ii) HOClO (iii) HOBr

(iv) $HOBrO_2$ (v) $HOIO_3$ (vi) $HOClO_3$

5 The bond dissociation energy increases from I_2 to Cl_2. Thus, bond dissociation energy of F_2 should be higher than that of Cl_2. But it is not so, why?

6 The solutions of the salts of hypohalous acids are alkaline, explain why?

10.9 ANSWERS

Self-Assessment Questions

1 Fluorine formed by the electrolysis of aqueous solution of NaF will react immediately with water so it cannot be obtained by this method.

2 i) Chlorine

ii) Iodine

iii) Fluorine

iv) Iodine

3 The standard reduction potentials of bromine and iodine are 1.07 and 0.54, respectively, which are less than that for reduction of oxygen to water. These elements, therefore, can not oxidise water to oxygen.

4 i) $I_2 + IF_3 \longrightarrow 3IF$

ii) $Cl_2 + H_2O \longrightarrow HCl + HOCl$

iii) $Cl_2 + 2NaOH \longrightarrow NaCl + NaOCl + H_2O$

iv) $Cl_2 + H_2S \longrightarrow 2HCl + S$

v) $CH_4 + 4\,Br_2 \longrightarrow CBr_4 + 4HBr$

5 HF has the highest bond dissociation enthalpy amongst all the halogen acids. The hydration enthalpy of the fluoride ion is also highest. However, the former outweighs making HF the weakest of the halogen acids.

6 $HOCl < HOClO < HOClO_2 < HOClO_3$

7 (i) T (ii) F (iii) T

(iv) F (v) F

Terminal Questions

1 i) Fluorine ii) Fluorine iii) I^-

iv) Chlorine v) Br^- and I^-

2 i) Atomic number should be 85.

ii) At_2

iii) Melting and boiling point should be higher than those of iodine.

iv) Solid.

v) At-At bond energy should be less than that of I-I bond.

vi) Strength of aqueous hydroastatic acid should be highest according to known trend

$HF < HCl < HBr < HI$

3 The highest oxidising power, high lattice energy of fluorides and high enthalpy of hydration of fluoride ion, lower F-F bond dissociation energy and a high fluorine element covalent bond energy are the factors contributing to this unique ability of fluorine to combine with other elements in their higher oxidation states. Chlorine, however, is a close second in this respect.

4 i) Hypochlorous acid : + 1

ii) Chlorous acid : +3

iii) Hypobromous acid : +1

iv) Bromic acid : +5

v) Periodic acid : +7

vi) Perchloric acid : +7

5 Fluorine has the smallest size of all the halogens. In the F-F bond, there is considerable repulsion in the nonbonding electrons which weakens the F-F bond. Therefore, the bond dissociation energy of F_2 is less than that of the Cl_2.

6 The salts of hypohalous acids undergo hydrolysis in water as shown below :

$$NaOX + H_2O \quad = \quad Na^+ + OH^- + HOX$$

The hypohalous acids are fairly weak acids and remain largely undissociated in solution. As the solution contains OH^-, it becomes alkaline in nature.

UNIT 11 ELEMENTS OF GROUP 18

Structure

11.1 Introduction
Objectives
11.2 Discovery of Noble Gases
Position of Noble Gases in the Periodic Table
11.3 Occurrence, Isolation and Uses of Noble Gases
11.4 General Characteristics
11.5 Compounds of Noble Gases
Compounds of Xenon
Clathrates of Noble Gases
Structure and Bonding in Xenon Compounds
Structure of Noble Gas Compounds and VSEPR Theory
11.6 Summary
11.7 Terminal Questions
11.8 Answers

11.1 INTRODUCTION

In the preceding unit, you have learnt about the chemistry of a group of highly reactive elements, viz., the halogens. This unit deals with the chemistry of a group of elements which were considered to be rather inert till recently. These elements are helium, neon, argon, krypton, Xenon and radon. These elements constitute Group 18 of the modern periodic table. If you compare Mendeleev's periodic table of 1871 with the modern periodic table, you will see that it is remarkably similar in its coverage to the modern periodic table, with the exception that the Group 18 is missing. Elements of Group 18 were not known at that time and have been discovered only about a hundered years back. Since these elements have very low reactivity, they were called inert. However, the term inert is no longer applicable to the group as a whole, as the heavier elements of this group form compounds and, thus, are not inert. These elements have also been called the rare gases, but as argon forms nearly 1% of the atmosphere, and the gases can be readily isolated by the fractional distillation of liquid air at low temperatures, this name is also not very appropriate. They are now called the noble gases by analogy with the noble metals, like gold and platinum which are not very reactive. The unique chemical inertness of the noble gases is well reflected in the history of their discovery which was followed by a long gap of a few decades before xenon could be made to combine with only the most electronegative elements, fluorine and oxygen. In this unit you will study the discovery, isolation, uses, general characteristics and the compounds of noble gases.

Objectives

After studying this unit you should be able to :

describe the discovery of noble gases.

discuss their electronic configuration and position in the periodic table.

enumerate the properties of the noble gases and their uses and

describe the important compounds of the noble gases, particularly xenon, espectally the bonding in these compounds.

11.2 DISCOVERY OF NOBLE GASES

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

Of all the noble gases, first came the **discovery of helium**, which is unique in being the first element to be discovered extra-terrestrially before being found on the earth. In 1868 the French astronomer Pierre Janssen came to India to study the total eclipse of the sun. Using a spectroscope he observed a new yellow line close to the sodium D lines in the spectrum of the sun's chromosphere. This led two Englishmen, chemist E. Frankland and astronomer Sir J. Norman Lockyer to suggest the existence of a new element, which, appropriately, they named helium, from the Greek word helios meaning the sun. The terrestrial existence of helium was established by Sir William Ramsay in 1895. He showed that a gas present in trace amounts in the uranium mineral, clevcite, 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 meaning new) by the fractional distillation of impure liquid oxygen. Shortly thereafter, they showed that the less volatile fractions of liquid air contain two other new elements, **krypton** (from the Greek word meaning hidden) and **xenon** (from the Greek word meaning stranger).

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

11.2.1 Position of Noble Gases in the Periodic Table

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

After studying the chemical nature of the noble gases, Ramsay introduced a new group in Mendeleev's periodic table to accommodate these elements. He placed this group after the halogens and before the alkali metals in the periodic table. As you have studied in Unit 1, in the long form of the periodic table, the noble gases occupy the last column of the table. The inclusion of the noble gases has actually improved the periodic table because it provides a bridge between the strongly electronegative halogens and the strongly electropositive alkali metals.

As you have studied in Unit 7 of the course, initially the group consisting of noble gases used to be termed as the Group zero or the Group VIII A. But according to the latest IUPAC convention, number 18 has been assigned to this group. However, the position of the group in the periodic table remains unchanged, that is, after the halogens at the end of each period.

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

SAQ 1

a) What were the reasons for late discovery of noble gases?

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b) What made Lord Rayleigh suspect that there may be an additional element in air?

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11.3 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 11.1. 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.

Composition of dry air

Gas	% by volume	B.P.(K)
N_2	78.03	77.2
O_2	20.99	90.1
Ar	0.93	87.2
CO_2	0.033	194.7
Ne	0.0018	27.2
H_2	0.0010	20.2
He	0.0005	4.2
Kr	0.0001	119.6
Xe	0.000008	165.1

The principal source of Ne, Ar, Kr and Xe is air. Due to the difference in their boiling points (Table 11.1), 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. The residual helium is purified by passing it over activated charcoal cooled with liquid air. The charcoal absorbs traces of heavier noble gases, leaving pure helium. Radon is obtained by allowing radium or any of its salts to decay for some weeks in a sealed vessel.

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

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

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.

11.4 GENERAL CHARACTERISTICS

All the noble gas elements are colourless, odourless and tasteless monoatomic gases. Indeed, they are the only elements that exist as uncombined gaseous atoms at room temperature and one atmosphere pressure. Each atom, behaves as if it is effectively isolated. Some properties of noble gases are summarised in Table 11.1

Table 11.1 : 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	$1s^2$	$[He]2s^2\,2p^6$	$[Ne]\,3s^23p^6$	$[Ar]3d^{10}\,4s^24p^6$	$[Kr]\,4d^{10}5s^25p^6$	$[Xe]4f^{14}\,5d^{10}6s^26p^6$
Atomic weight	4.0026	20.183	39.948	83.80	131.30	(222)
van der Waals radius (pm)	-	131	174	189	210	215
Boiling point (K)	4.2	27.2	87.2	119.6	165.1	211
Melting point (K)	1 at 26 atm	24	84	116	161	202
Density of liquid at.b.p. ($10^3 \times$ kg m^{-3})	0.126	1.20	1.40	2.6	3.06	4.4
Ionisation energy (kJ mol^{-1})	2372	2081	1520	1350	1170	1037
Electron affinity (kJ mol^{-1})	54	99	-			
Abundance in dry air (ppm by volume)	5.2	18.2	93.40	1.14	0.087	0
Abundance in igneous rocks (ppm by weight)	3×10^{-3}	7×10^{-5}	4×10^{-2}			1.7×10^{-10}

You can see from the Table that all the noble gases have eight electrons in their valence shell except helium which has only two electrons. Till 1962, the noble gases were considered to be inert as their compounds were not known. Lewis and Kossel in formulating their **electronic theory of Valence** in 1916 stipulated that a grouping of eight electrons or an **octet** in the valence shell represents a very stable configuration. Hence, they proposed the octet rule. According to this, the 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 in their periods. This reflects their reluctance for chemical reactivity. Analogously, the electron affinity of these elements is either zero or has a small positive value. Therefore, they are unable to accept electrons to form anions. As we go down the group, the ionisation energy of the noble gases decreases. Thus, there is an increase in chemical reactivity of the noble gases as we go down the group from helium to radon.

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

Helium has two isotopes, ^{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.

SAQ 2

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

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

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

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11.5 COMPOUNDS OF NOBLE GASES

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 1896, found that argon would not react with fluorine under any conditions. Secondly, attempts at reacting xenon with fluorine using electric discharge methods did not meet with success, although Pauling had predicted that some noble gas fluorides should be stable. Chemists were discouraged by these failures and also by the preconceived notion that the noble gases must be inert because of their stable configuration.

The first breakthrough in the noble gas compounds was achieved in 1960 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 picture of the red solid showed it to be the first known salt of dioxygenyl cation, i.e., $[O_2]^+[PtF_6]^-$. This showed that PtF_6 oxidises the oxygen molecule. Bartlett 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 diffluoride, 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 atleast one fluoride, but its formula has not yet been established because of the vigorous distintegration of the nucleus. Thus, the noble gas chemistry is effectively limited to the compounds of xenon.

11.5.1 Compounds of Xenon

The chemistry of xenon is the most extensive in this group and the known oxidation states of Xe range from +2 to +8. Structural details of some of the more important compounds of Xe are listed in Table 11.2

Xenon reacts directly with fluorine on heating the gases in a nickel vessel. The products depend upon the amount of fluorine present and the reaction conditions :

$$Xe + F_2 \xrightarrow[\text{700 K, sealed vessel}]{\text{2 : 1 mixture}} XeF_2$$

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

$$Xe + 3F_2 \xrightarrow[\text{500-600 K, 50-60 atmosphere}]{\text{1 : 20 mixture}} XeF_6$$

The compounds XeF_2, XeF_4 and XeF_6 are white solids which can be sublimed at room temperature. The lower fluorides react with fluorine on heating under pressure forming higher fluorides. The fluorides are extremely strong oxidising and fluorinating agents. They react quantitatively with hydrogen.

$$XeF_2 + H_2 \longrightarrow 2HF + Xe$$

$$XeF_4 + 2H_2 \longrightarrow 4HF + Xe$$

$$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$$

They oxidise chlorides to chlorine, iodides to iodine, cerium (III) to cerium (IV), Ag(I) to Ag(II), Cr(III) to Cr(VI) and Br(V) to Br(VII) :

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

$$XeF_4 + 4KI \longrightarrow Xe + 4KF + 2I_2$$

$$XeF_2 + BrO_3 + H_2O \longrightarrow Xe + BrO_4 + 2HF$$

They fluorinate many compounds as well as elements :

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

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

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

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

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

Reaction of XeF_4 with water is violent since xenon trioxide, XeO_3, formed is highly explosive :

$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + \frac{3}{2}O_2$$

XeF_6 also reacts violently with water and hydrolysis by atmospheric moisture gives the highly explosive solid XeO_3 :

$$2XeF_6 + 6H_2O \longrightarrow 2XeO_3 + 12HF$$

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

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

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

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

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

$$XeO_3 + NaOH \longrightarrow \underset{\text{sodium xenate}}{Na^+ HXeO_4^-}$$

Xenates slowly disproportionate in alkaline solution to form perxenates and Xe gas :

$$2HXeO_4^- + 2OH^- \longrightarrow \underset{\text{Perxenate ion}}{XeO_6^{4-}} + Xe + O_2 + 2H_2O$$

Alkaline hydrolysis of XeF_6 also forms perxenates :

$$2XeF_6 + 16OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 12F^- + 8H_2O$$

Perxenates are extremely powerful oxidising agents, and can oxidise HCl to Cl_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, NbF_5, TaF_5, RuF_5, RhF_5, IrF_5 and PtF_5 to form salts of the type $[XeF]^+[MF_6]^-$, $[XeF]^+[M_2F_{11}]^-$ 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 SAQ related to xenon compounds.

SAQ 3

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) $Xe + F_2 \xrightarrow[\text{Nickel crucible}]{\text{1:20 ratio of Xe:F}_2} \underline{\quad ? \quad}$

iii) $XeF_2 + H_2O \longrightarrow Xe + \underline{\quad ? \quad} + \underline{\quad ? \quad}$

11.5.2 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 cavities in the crystal lattice of certain other compounds such as quinol or water. The formation of clathrates seems to depend on relative molecular dimensions rather than on any particular chemical affinity. The atoms or molecules of any substance, which are of a suitable size to fit in the cavities in the host lattice, can form clathrates. Thus, O_2, SO_2, H_2S and MeOH are examples of other substances which form clathrates with quinol.

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

When quinol is crystallised from its aqueous solution in the presence of heavier noble gases like Ar, Kr or Xe under a pressure of 10-40 atmosphere, crystals of clathrates of the composition G.3Quinol are obtained. The crystals are quite stable and can persist for several years. However, when heated or dissolved in water, the gas escapes leaving behind quinol. Similarly, when water is allowed to freeze in the presence of Ar, Kr or Xe under pressure, atoms of noble gas get trapped in the crystal lattice of ice giving clathrates corresponding to the composition, $8G.46H_2O$. These clathrates are also known as the noble gas hydrates. You can see the hydrates may not be stoichiometric since the degree to which the cavities are filled depends on the partial pressure of the guest material.

The hydrates increase in thermal stability down the group as the noble gases become more polarisable. With xenon, at a partial pressure of one atmosphere, the hydrate is stable upto 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.

SAQ 4

Explain briefly :

i) Why no compounds of He and Ne are known ?

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ii) Why noble gas compounds are formed only with O_2 and F_2?

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iii) Why does the tendency to form clathrates increase down the group ?

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11.5.3 Structure and Bonding in Xenon Compounds

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

Xenon Difluoride

It is a linear molecule. Bonding in XeF_2 may be explained with the help of Valence Bond Theory (cf. Unit 4, Block 1, Atoms & Molecules course). An electron from the $5p$ level of Xe is promoted to the $5d$ level, followed by sp^3d hybridisation.

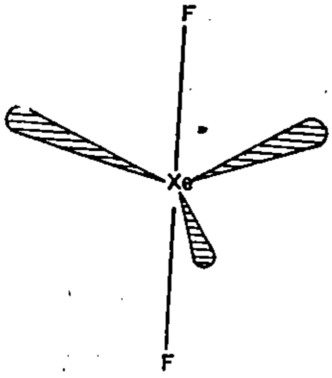
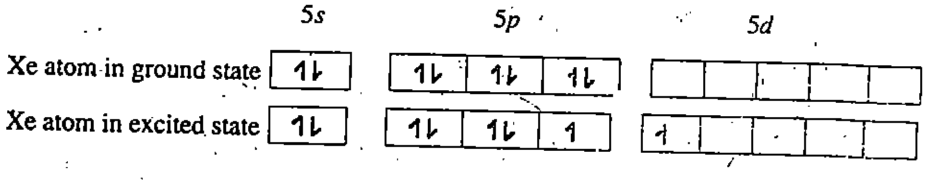


Fig. 11.1: Structure of XeF_2

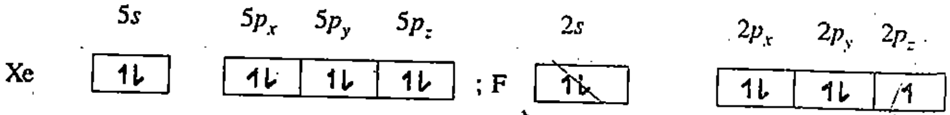


sp^3d–hybridisation

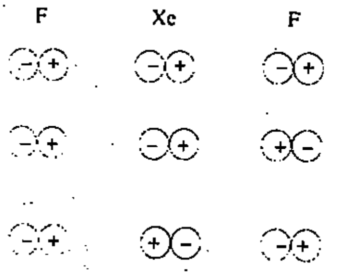
The two unpaired electrons in axial orbitals form bonds with two fluorine atoms and three lone pairs occupy the equatorial positions of the trigonal bipyramid giving rise to a linear molecule as shown in Fig. 11.1.

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 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 nonbonding and one antibonding which can be represented as shown in Fig. 11.2.



antibonding	(orbitals have wrong symmetry for overlap).
nonbonding	($5p_z$ orbital of Xe has no contribution, since the bonding effect in one half is cancelled by the antibonding effect in the other half).
bonding	(orbitals have correct symmetry for overlap).

Fig. 11.2 : 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. 11.3.

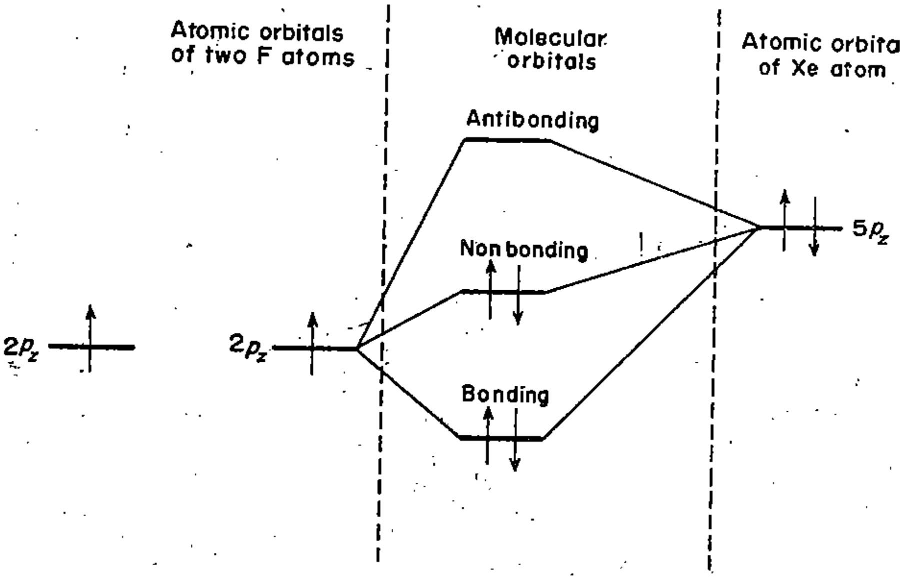


Fig . 11.3 : Molecular orbital energy level diagram for XeF_2 molecule.

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 Unit 6), except that in XeF_2 there are four electrons involved compared with two electrons in the boranes.

Xenon Tetrafluoride

The structure of XeF_4 is square planar (Fig. 11.4). 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.

	5s	5p			5d			
Xe atom in excited state	↑↓	↑↓	↑	↑	↑	↑		

sp^3d^2– hybridisation

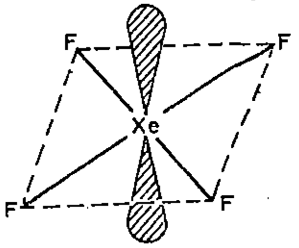


Fig 11.4 : Structure of XeF_4

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

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. 11.5.

	5s	5p			5d				
Xe atom in excited state	↑↓	↑	↑	↑	↑	↑	↑		

sp^3d^3– hybridisation

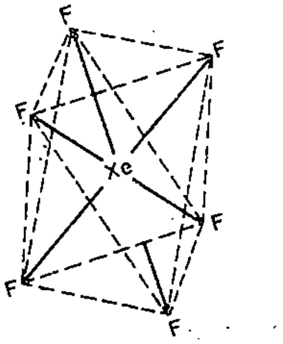


Fig. 11.5 : Structure of XeF_6

According to M.O. theory, the structure of XeF_6 can be explained by considering three three-centre molecular orbitals mutually at right angles and giving a regular octahedral shape. Thus, M.O. theory fails here to predict the correct structure. A more detailed discussion regarding this can be found in higher courses in the subject.

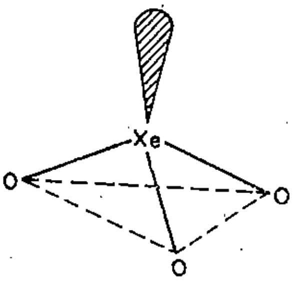


Fig. 11.6 : Structure of XeO_3

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

Thus, we have seen above that neither the Valence Bond approach nor the Molecular Orbital theory is able to explain the bonding in all the noble gas compounds. The approach which has given the most rational explanation about the stereochemistry of noble gas compounds and provided the most readily visualised description of their shapes is the Valence Shell Electron Pair Repulsion Theory (VSEPR) of Gillispie and Nyholm. You may have come across this in Unit 3 of **Atoms and Molecules** course. To recollect, this theory assumes that stereochemistry is determined by the repulsions between valence shell electron pairs, both bonding and nonbonding, and that the latter exert the stronger effect. Thus in XeF_2, the valence shell of Xe atom has ten electrons, eight from the Xe atom and one each from the two F atoms. These are distributed in five pairs, two bonding and three nonbonding, which are directed to the corners of a trigonal bipyramid. Because of their greater mutual repulsion, the three nonbonding pairs are situated in the equatorial plane at 120° to each other, leaving the two bonding pairs perpendicular to the plane and so producing a linear F–Xe–F molecule.

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

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

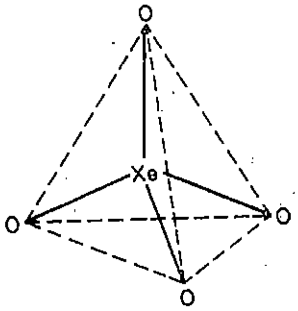


Fig. 11.7 : Structure of XeO_4

It will be interesting to devise similar rationalisations for the xenon oxides. Three electron pairs of the Xe atom can be used to complete the octet of three oxygen atoms, leaving one lone pair on xenon. This gives a trigonal pyramidal shape to XeO_3 molecule (Fig. 11.6). Similarly in xenon tetroxide, four electron pairs from xenon can coordinate with each of the four oxygens forming a tetrahedral molecule (Fig. 11.7). Such coordination, however, leaves a rather high positive charge on the central atom. The tetrahedral silicate, phosphate and sulphate ions, which are isoelectronic with XeO_4, are stabilised by $p\pi$–$d\pi$ back bonding in which lone-pair electrons on oxygen spend some time in *d* orbitals on the central atom. This helps to even out the charge distribution. But 5*d* orbitals of xenon are ill-matched with 2*p* orbitals of oxygen, thus weak Xe–O bond is consistent with rather little $p\pi$–$d\pi$ bonding and considerable polar character. Structural details of some xenon compounds based on VSEPR theory are given in Table 11.2. 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.

Table 11.2: Structures of some important 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.

SAQ 5

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

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

11.6 SUMMARY

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

- The atmosphere surrounding the earth is a mixture of gases consisting of nitrogen (78%), oxygen (21%), noble gases (1%), some other gases like CO_2 and air pollutants.
- Noble gases were discovered in the order : helium in 1868, then neon, argon, krypton and xenon in the 1890s and finally radon in 1902.

- The characteristic stable electronic configuration of noble gases is $1s^2$ or ns^2np^6. They have the highest ionisation energies and the lowest electron affinity, melting and boiling points and heat of vaporisation in their periods.
- Noble gases have various applications like as coolants and for providing inert atmosphere. Their chemistry is limited due to the exceptional stability of their closed valence shells. Only xenon reacts directly with fluorine forming fluorides. Oxides may be prepared by the reaction of water with fluorides.
- The shapes of xenon compounds can usually be explained with the help of Valence Shell Electron Pair Repulsion Theory.

11.7 TERMINAL QUESTIONS

1 How did the terrestrial helium originate?

2 What are the factors which led Bartlett to think that Xe can be oxidised by PtF_6.

3 Would you expect nitrogen to form a compound of the type $N_2^+[PtF_6]^-$? Give reason for your answer. (Ionisation energy of N_2 is 1403 kJ mol^{-1})

4 Would you expect radon to form more stable compounds than xenon? If so why ?

5 Work out the oxidation states of xenon in XeF_2, XeF_4 and XeF_6.

11.8 ANSWERS

Self-assessment Questions

1 a) Chemical inertness of lighter noble gases, i.e., He, Ne and Ar, and rare abundance of comparatively reactive noble gases, i.e, Kr, Xe and Rn were the reasons for the late discovery of noble gases.

b) Lord Raleigh found that the density of nitrogen isolated from air was consistently about 0.5% higher than that of the nitrogen obtained chemically from ammonia. This observation made Lord Raleigh suspect that there may be an additional gaseous element in air.

2 a) Boiling point is directly proportional to the van der Waals forces between the atoms/molecules. More is the force of attraction, higher is the temperature required to overcome these binding forces and higher will be the boiling point.

b) As we move down the group from He to Rn, the van der Waals force of attraction between the noble gas atoms increases giving rise to a steady increase in boiling points.

3 i) 2 : 1 ratio of Xe : F_2, nickel crucible

ii) XeF_6

iii) $2HF + 1/2O_2$

4 i) Valence shells of He and Ne are completely filled, so they have no tendency to lose, gain or share electrons. Because of these reasons, compounds of He and Ne are not known.

ii) Because the noble gases have extremely low reactivity, they need the strongest oxidising agents to form compounds.

iii) In clathrates, the noble gases are held by weak van der Waals forces which increase with the increase in the polarisability of the noble gas down the group. Therefore, the tendency to form clathrates increases down the group.

5 i) Square planar

ii) Square pyramidal

iii) Tetrahedral

iv) Distorted octahedral

Terminal Questions

1 Terrestrial helium originated from the decay of radioactive elements in rocks.

2 The very fact that the first ionisation energy of xenon is slightly less than that of oxygen, led Bartlett to think that like oxygen, xenon can also be oxidised by PtF_6.

3 Oxygen and xenon which have ionisation energies, 1180 kJ mol^{-1} and 1170 KJ mol^{-1}, respectively, can be oxidised by PtF_6 while nitrogen having comparatively much higher ionisation energy, 1403 kJ mol^{-1} cannot be oxidised, so a compound of the type $[N_2]^+[PtF_6]^-$ cannot be formed.

4 On the basis of comparatively high polarisability and low ionisation energy, radon is expected to form more stable compounds. But because of very short half-life, its compounds are highly unstable.

5 Oxidation state of xenon in XeF_2 is + 2.

Oxidation state of xenon in XeF_4 is + 4.

Oxidation state of xenon in XeF_6 is + 6.

FURTHER READING

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

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

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

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

Uttar Pradesh
Rajarshi Tandon Open University

UGCHE-03
Inorganic Chemistry

Block

4

d– AND *f*– BLOCK ELEMENTS

UNIT 12

Transition Elements 5

UNIT 13

Inner-Transition Elements 24

UNIT 14

Coordination Compounds 36

UNIT 15

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22

BLOCK 4 *d*-AND *f*-BLOCK ELEMENTS

In Blocks 1, 2 and 3 of this course you had studied the salient features of the chemistry of *s*– and *p*–block elements, wherein emphasis had been on the relationships between the periodic properties of the elements. You observed that the similarity of the elements within a gr the most striking feature of the chemistry of the *s*–block elements. All the *s*–block elen except hydrogen, are reactive metals exhibiting only one stable oxidation state and the occur in combined state in nature. The chemistry of *p*–block elements, on the other han very extensive and varied. The elements exhibit more than one oxidation state. On descending a group of *p*–block elements, the differences between the successive elements become more pronounced as compared to the *s*–block elements, and a change from non-metallic to metallic character is observed.

In this block you will study the general features of the chemistry of the *d*– and *f*–block elements. These elements are quite different from those of the *s*– and *p*–blocks. Thus after studying this course, you would get a brief glimpse of all the elements in the periodic table.

Unit 12 deals with the *d*–block elements which constitute three series of elements belonging to the fourth, fifth and sixth periods of the periodic table. The chemistry of *d*–block elements, which are also called transition elements, is very vast and varied and cannot be covered in one unit in a detailed manner. Therefore, we have discussed briefly the general trends in the chemistry of these elements in this unit.

In Unit 13, you will study, in brief, the chemistry of *f*–block elements comprising the lanthanide and the actinide elements, which are collectively known as inner-transition elements. The lanthanides and the actinides constitute two series of elements, each consisting of fourteen closely similar elements.

Metals, in general, and the transition and the inner-transition metals, in particular, have a strong tendency to form coordination compounds. These compounds play a very important role in various chemical and biochemical processes. In Unit 14 you will study the various aspects of the chemistry of coordination compounds.

Metals have acquired a unique importance in the modern world. You will get an idea of the importance of metals, their properties and uses from the audio, ''Metals'' which accompanies this unit. Metals usually occur in nature in combined state as ores. Every year several million tonnes of metals are extracted from their ores throughout the world. In Unit 15, you will study the various aspects of isolation and purification of metals.

We expect that after studying this block, you should be able to:

- discuss the periodic trends in the properties of the *d*– and *f*–block elements,
- compare the properties of *s*–, *p*–, *d*– and *f*–block elements,
- describe the nomenclature of and isomerism in the coordination compounds,
- explain the magnetic properties and structures of coordination compounds in the light of various theories of bonding,
- describe the various aspects of extraction and purification of metals.

UNIT 12 TRANSITION ELEMENTS

Structure

12.1 Introduction
  Objectives
12.2 Electronic Configuration
12.3 General Characteristics
12.4 Periodic Trends in Properties
  Atomic Radii, Atomic Volume and Density
  Melting and Boiling Points
  Ionisation Energy
  Electrode Potential
  Electronegativity
  General Reactivity
  Oxidation States
12.5 Formation of Complexes
12.6 Colour of Transition Metal Compounds
12.7 Magnetic Properties
12.8 Catalytic Properties
12.9 Interstitial Compounds
12.10 Summary
12.11 Terminal Questions
12.12 Answers

12.1 INTRODUCTION

As you already know, elements are classified on the basis of their electronic configuration, into *s*–block, *p*–block, *d*–block and *f*–block elements. The *s*– and *p*–block elements together represent one of the major groups of the elements and are called main group elements. The *d*–block and the *f*–block elements represent the transition and the inner-transition elements, respectively. Most of the discussion so far has centered around the chemistry of main group elements having valence electrons in *s* and/or *p* orbitals only. From this unit onwards, we will start the study of rest of the elements of the periodic table, namely, the *d*–block or transition elements and the *f*–block or inner-transition elements. The name transition is given to the elements on the basis of their position in the periodic table and their properties, that is, they occupy a position between the highly electropositive elements on the left and the electronegative elements on the right. Their properties are also intermediate of the *s*– and *p*–block elements. Thus, in this unit we will describe the general features of the transition elements with the emphasis on the 3*d* series and also the periodic trends in their properties.

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

Objectives

After studying this unit, you should be able to:

- describe the electronic configuration of transition elements and their ions,
- outline the general properties of transition elements,
- describe the periodic trends in the properties of transition elements,
- explain the colour, magnetic and catalytic properties of transition elements.

12.2 ELECTRONIC CONFIGURATION

Electronic configuration of the elements has been discussed in detail in Unit 1 of this course. Hence, we will concentrate here only on the features relevant to transition elements. You already know that the electronic configuration of the argon atom is $1s^2 2s^2 2p^6 3s^2 3p^6$. In atoms of the successive elements from potassium to zinc, electrons can enter either 3*d* or 4*s* levels. In potassium and calcium atoms the differentiating electrons enter the 4*s* level, so the electronic configuration of calcium can be written as $[Ar]4s^2$. At scandium the 3*d* level begins to fill instead of 4*p* and the resulting configuration of the atoms of transition elements is shown in Table 12.1. 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+} will have the configuration as $[Ar]3d^8$.

Table 12.1: Electronic configurations of the free atoms and dipositive ions of the first transition series

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

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

The radial dependence of the *d* orbitals is responsible for this order of filling of electrons in these elements. Fig. 12.1 shows the plot of radial probability functions introduced in Unit 2 of **Atoms and Molecules** course for a 3*d* and 4*s* electron in the hydrogen atom. Let us assume that the radial probability functions for 3*d* and 4*s* electron in a multi electron atom follow the same pattern as in the hydrogen atom.

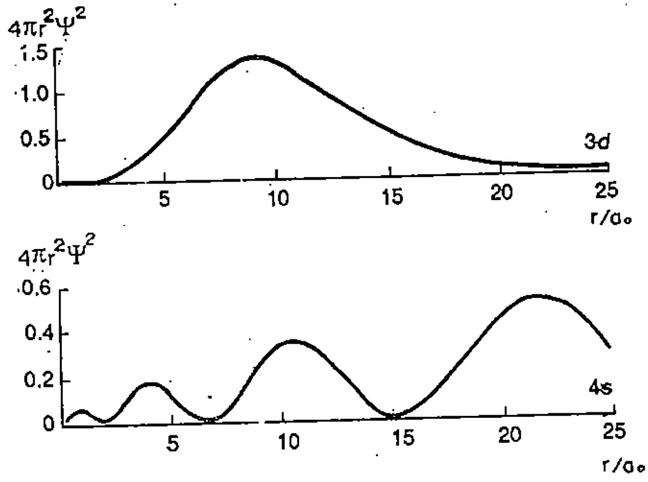


Fig. 12.1: Radial probability functions for 3*d* and 4*s* orbitals in hydrogen atom. a_0, the radius of first Bohr orbit is 52.9 pm.

You can see from Fig. 12.1 that significant humps in the 4*s* probability function occur close to the origin, and well inside the maximum of the 3*d* probability function. This suggests that the 4*s* 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 3*d* electron and thus after argon, in potassium and calcium the electrons enter the 4*s* orbital rather than the 3*d*. As these two electrons are added the nuclear charge is also increased by two units. As the 3*d* orbitals penetrate the 4*s* orbital more than the 4*p* orbitals can penetrate the 4*s* orbital, the net result is that the effective nuclear charge for the 3*d* orbitals increases abruptly and they now drop well below the 4*p* orbitals to about the level of the 4*s* orbital. Moreover, as the atomic number increases, the 3*d* probability maximum progressively moves closer to the core and they continue to drop in energy. The next electron, therefore, enters the 3*d* orbital prior to the 4*p* orbital. The variation of the energies of the orbitals with increasing atomic number is shown very clearly in Fig. 12.2.

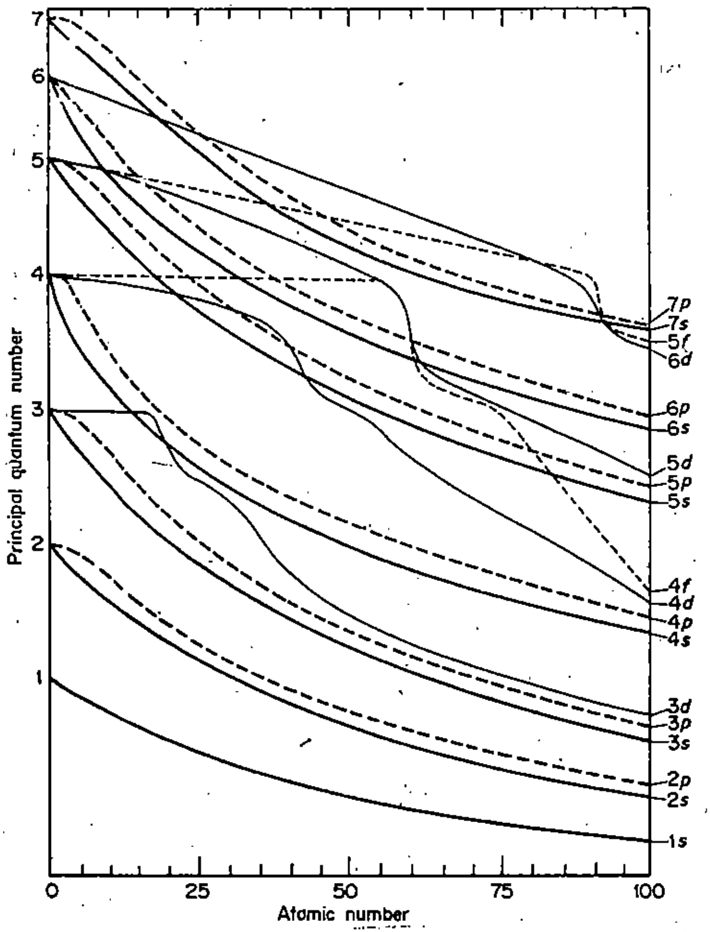


Fig. 12.2: The variation of the energies of atomic orbitals with increasing atomic number in neutral atoms

This process continues until the entire 3*d* 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 $[Kr]4d^{10}5s^2$. 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 6*s* 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. 12.2). 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 5*d* 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 6*s* and 4*f* shells full, the next lowest levels are the 5*d*'s. Hence from lutecium onwards, the electrons enter the 5*d* orbital. This continues till we reach mercury which has the configuration $[Xe]6s^2 4f^{14} 5d^{10}$. The electronic configurations of transition elements of 4*d* and 5*d* transition series are given in Table 12.2.

If the filling of the orbitals in transition elements takes place through the above scheme, then you may wonder why in the case of some elements e.g., Cr & Cu (belonging to the first transition series) and Mo & Ag (belonging to the second transition series) the electronic configuration is written as $[Ar]3d^5 4s^1$ & $[Ar]3d^{10}4s^1$ and $[Kr]4d^5 5s^1$ & $[Kr]4d^{10}5s^1$, respectively. This is because these configurations are considered to give more stability to the elements, rather than $[Ar]3d^4 4s^2$ & $[Ar]3d^9 4s^2$ and $[Kr]4d^4 5s^2$ & $[Kr]4d^9 5s^2$, 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 12.2: Electronic configurations of elements of the second and third transition series

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]$4f^{14} 5d^{10} 6s^2$

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., $E_{ex} = K \times P$, where K is a constant and P is the number of possible pairs of electrons with parallel spin. If n is the number of electrons with parallel spin for any configuration, P will be equal to $^nC_2$. Accordingly values of P for different values of n are given below :

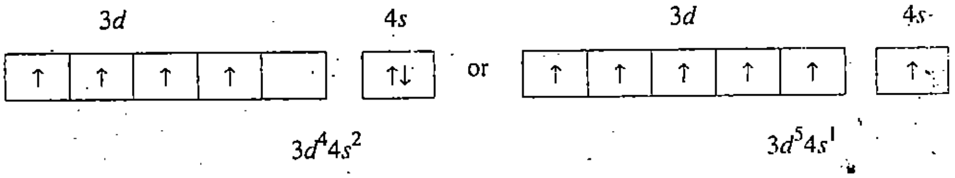
n	1	2	3	4	5	6	7
P	0	1	3	6	10	15	21

$^nC_2$ is the number of combinations that we can make out of the n objects taking 2 at a time

$$^nC_2 = \frac{n!}{2!(n-2)!}$$

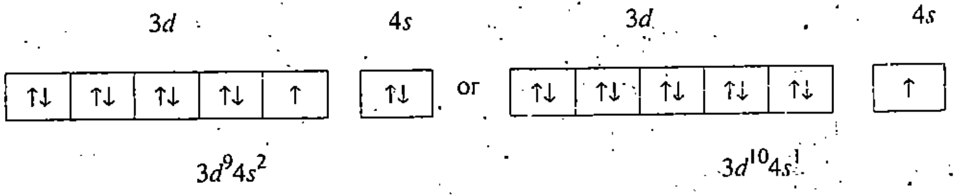
where n ! = 1, 2, 3, 4 . . . (n–1) . n
(n–2) ! = 1, 2, 3, 4 . . . (n–1) (n–2)
2 ! = 1, 2

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



Electrons present in 4s orbital in two configurations contribute nothing to exchange energy as they do not constitute any pair with parallel spin. Four unpaired d-electrons in first configuration can make six pairs of electrons with parallel spin and thus contribute 6K towards exchange energy whereas five unpaired d-electrons in second configuration contribute 10K towards exchange energy because they can constitute 10 combinations of pairs of electrons with parallel spin. This gain of 4K in exchange energy would favour the $3d^5 4s^1$ configuration for chromium. But, you should remember that in achieving this configuration, there would be loss of energy in promoting an electron from 4s to 3d orbital. In case of chromium the gain in exchange energy is more than the loss in energy and therefore, $3d^5 4s^1$ is the favoured configuration.

Similarly you can compare the exchange energies for two possible configurations $3d^9 4s^2$ 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 16*K* 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 3*d* orbital, which happens to be less than 4*K*, 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 4*s* orbitals are occupied before 3*d* orbitals, we cannot say that they are always more stable. In fact, the ionisation of the transition elements takes place by the loss of *ns* electrons first. What happens actually is that when the electron is ionised from any transition element, say the one from 3*d* series, the effective nuclear charge experienced by the 3*d* electrons is greatly enhanced over that of any 4*s* electron as a direct consequence of the greater stability attained by the 3*d* orbitals in the due course of filling (cf. Fig. 12.2). Consequently, the 3*d* 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.

SAQ 1

In the given space, explain :

a) Why a transition series contains ten elements.

....

....

....

....

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

....

....

....

....

12.3 GENERAL CHARACTERISTICS

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

- All are metals and form alloys with one another and with other metallic elements.
- They are hard, strong, ductile, malleable, high melting and high boiling. They are good conductors of heat and electricity.
- Many of them are sufficiently electropositive to dissolve in mineral acids although a few are noble — that is, they have such low electrode potentials that they are unaffected by simple acids.
- They usually exhibit multiple oxidation states.
- They form coordination compounds/ions. In fact, the chemistry of the transition elements is mainly associated with the use of *d* as well as *s* and *p* orbitals in forming coordination compounds.
- The transition metal complexes are usually coloured.
- Most of their compounds are paramagnetic.
- Many of these elements and their compounds act as catalysts for chemical reactions.

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

12.4 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 are listed in Table 12.3. If you study the data in the Table carefully, you will notice that along a period, these properties vary much less from one element to the other as compared to the main group elements. Although, the horizontal similarity amongst the *d*-block elements is well marked, yet the chemistry of the elements of first transition series differs considerably from that of the elements of the second and third transition series, which are incidentally more similar to each other. This difference in the trends in the properties of *d*-block elements from those of *s*–and *p*–block elements arises from a basic difference in their electronic configuration. While in the building up of elements from lithium to fluorine, the electrons are added to the outermost shell, in the case of transition metals, the electrons are added to inner $(n-1)d$ subshell. Let us see how this contributes to the variation in the properties of the elements.

Table 12.3: Some properties of *d*-block 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 energy (kJ mol^{-1}) 1st	633	659	650	653	717	762	759	736	745	906
2nd	1235	1309	1414	1591	1509	1561	1644	1751	1958	1732
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 parantheses refer to oxidation states of the metal, + (III) refers to couple M^{3+}/M, etc.

12.4.1 Atomic Radii, Atomic Volume and Density

From Table 12.3, 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 Unit 2 on Periodicity in Block 1, 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 $(n-1)d$ electron(s) is more efficient than the shielding of a *ns* electron by another *ns* electron (or that of a *np* electron by another *np* electron). This is why the decrease in atomic radius from sodium to chlorine is greater than that from scandium to copper. The elements which occur immediately after the transition elements are smaller than expected from simple extrapolation from the group elements. This is due to the cumulative effect of incomplete shielding provided by $(n-1)d^{10}$ electrons and therefore, the effective nuclear charge felt 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 $4f$ 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 12.4: 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. 12.3. You can see in Fig. 12.3 that as we move from alkali metals to alkaline earth metals and from alkaline earth metals to the transition elements, the radii decrease steeply but within transition elements this rate of decrease is less. However, the data in Table 12.4 and Fig. 12.3 show that the general trend of decreasing size is reversed towards the end of the series. This could be due to an increase in inter-electronic repulsion after the addition of sufficient number of electrons in the d orbitals leading to the gradual increase in size.

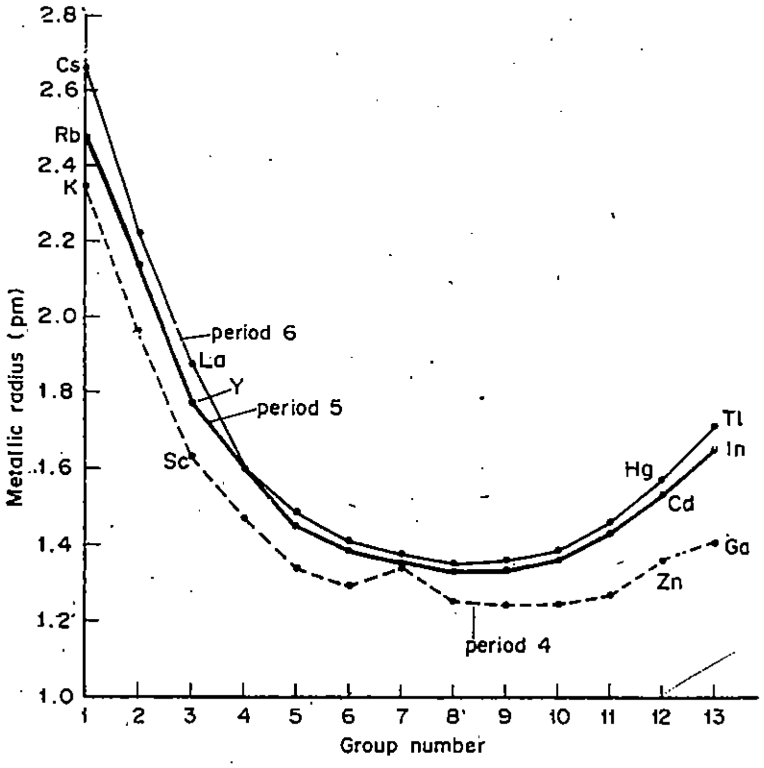


Fig. 12.3: Trends in metallic radii of alkali, alkaline earth and transition metals of fourth, fifth and sixth periods

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

Atomic volume of an element is directly related to its size and, therefore, atomic volumes follow the same trend as the atomic size. Similarly density is also related to the size of the element. The smaller the size, the higher is the density of the element. Thus there is a general trend of increasing density across the elements of a transition series. This is well represented in Fig 12.4 which gives the variation of the densities of alkali, alkaline earth and the transition metals of the fourth, fifth and sixth periods. For 4*d* and 5*d* elements, this increase is not that regular as the increase in densities for 3*d* elements. Along the group also, the density increases (Fig. 12.4). The increase in density within the *d* block groups is greater than that within the *s* and *p* block groups.

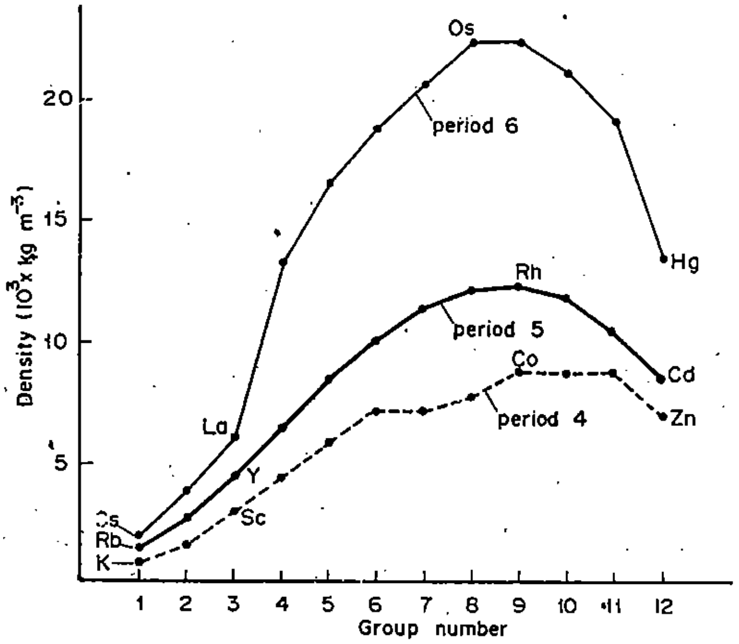


Fig. 12.4: Trend in densities of the alkali, alkaline earth and transition metals of the fourth, fifth and sixth periods.

SAQ 2

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

(i) Calcium or scandium

(ii) Vanadium or titanium

(iii) Chromium or molybdenum

(iv) Iron or osmium

12.4.2 Melting and Boiling Points

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

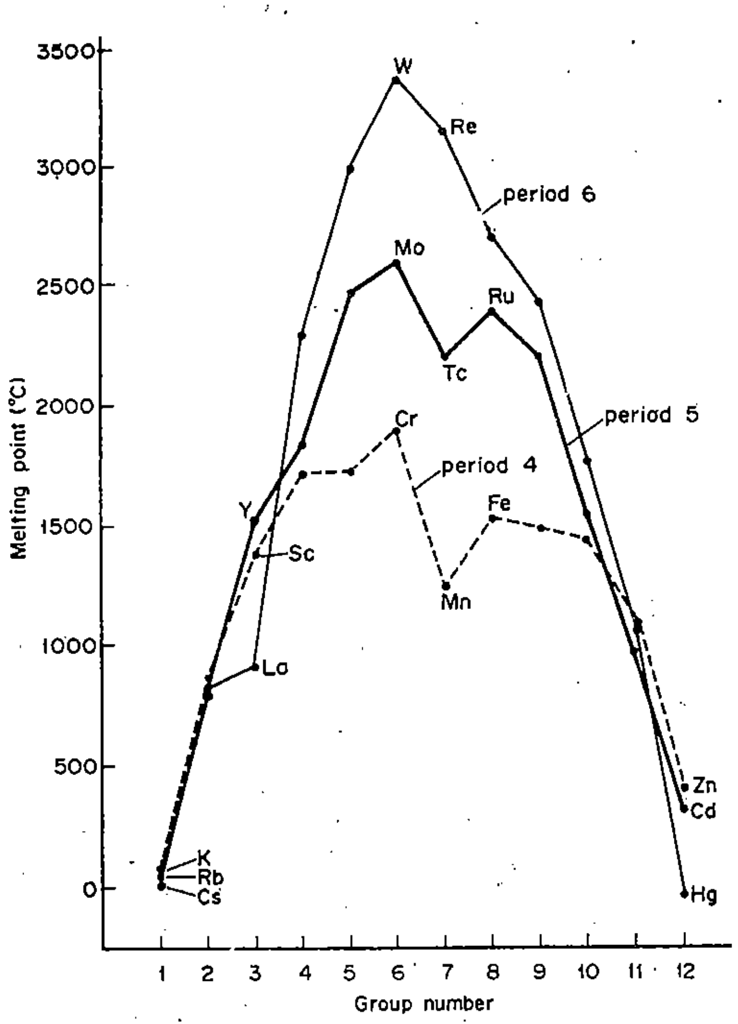


Fig. 12.5 : Trend in melting points of alkali, alkaline earth and transition metals of the fourth, fifth and sixth periods

there is a sharp decrease of melting point at manganese, which has five unpaired *d* electrons. However, the softness and low melting point of Zn, Cd and Hg (Hg is a liquid) in which all the electrons are paired up can tentatively be explained on the above basis. The melting points of the elements of the first transition series are comparatively lower than those of the elements of the second and third transition series. This trend is very well illustrated in the Fig. 12.5.

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

SAQ 3

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

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12.4.3 Ionisation Energy

You have already learnt about the concepts of ionisation energy and how it varies with the atomic size in Unit 2 on periodicity. In the case of transition metals also, the variation of ionisation energy across the periods and down the groups parallels quite closely the trend in atomic size. This is shown nicely in the Figure 12.6.

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 12.3. The second and the third ionisation energies follow the same pattern, except for the second ionisation energies of Cr and Cu which are 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. 12.6). Since *s* and the *d* electrons do not differ much in energy, the difference in the successive ionisation energies is relatively small.

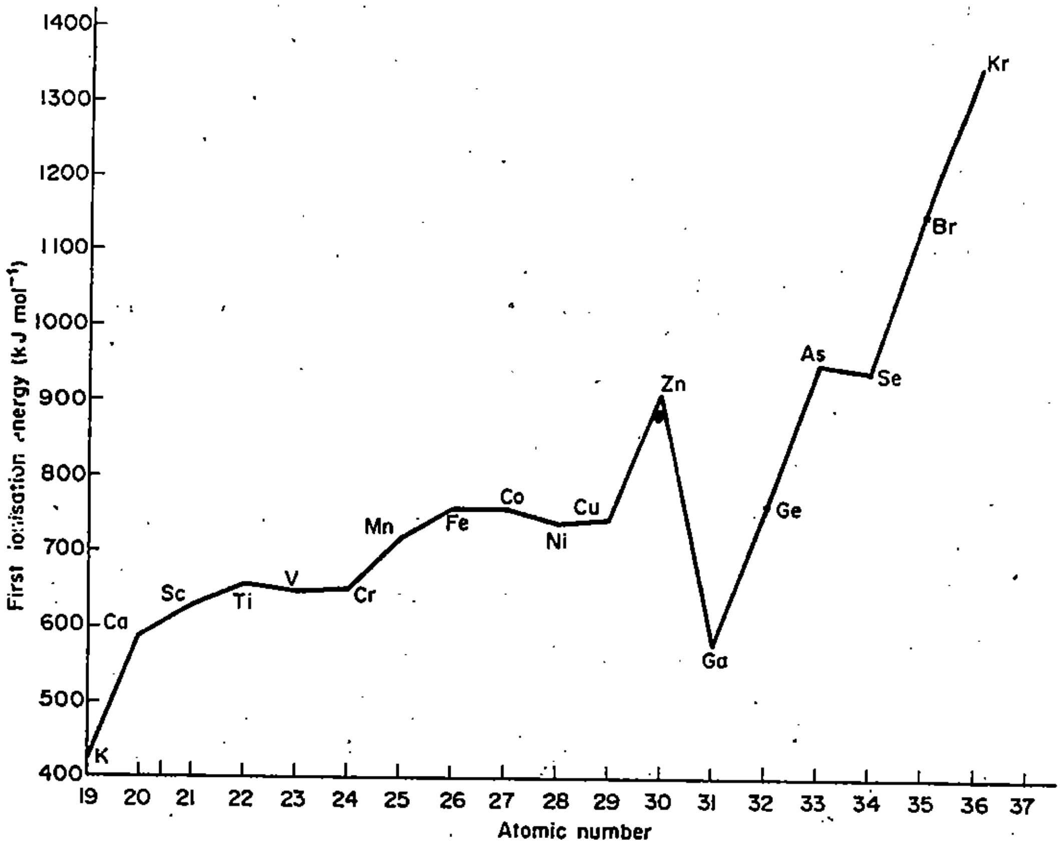

Fig. 12.6 : Variation in first ionisation energy of the elements of the fourth period

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.

12.4.4. Electronegativity

Transition elements have fairly low values of electronegativity. It increases from Sc to Cu with a fall at Mn and Zn. However, this increase in electronegativity is much slower because the additional electron is being added to an inner shell which provides relatively good shielding to the outer electrons from the nucleus. The increasing electronegativity from Sc to Cu means that the elements become slightly less metallic and this is reflected in the increasing positive electrode potentials of their ions M^{2+} and M^{3+} (Table 12.3).

12.4.5 Electrode Potential

Before going into the details of the variation in the electrode potential of the transition elements, let us discuss the concept of electrode potential first. When a metal is placed in a solution of its ions a potential difference is set up between the metal and the solution. There is a tendency for the metal ions to leave the metal lattice and go into the solution thus leaving an excess of electrons and hence a negative charge on the metal; there is also a reverse tendency for the metal ions from the solution to deposit on the metal leading to a positive charge on the metal. In practice one of these effects is greater than the other, bringing about a potential difference between the metal and the solution. The value of this potential difference for a particular metal depends upon the nature of metal, the concentration of the metal ions in solution and the temperature. By convention, the potential difference set up in a 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.

29A

In general, we can say that more negative the value of the electrode potential for the couple M^{n+}/M, more is the reducing power of the element. Similarly, more positive is the value of electrode potential for the couple M^{n+}/M, more is the oxidising power of the element. The values of some standard electrode potentials for the elements of first transition series are given in Table 12.3. 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 12.3, 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 3*d* series is shown in Fig. 12.7.

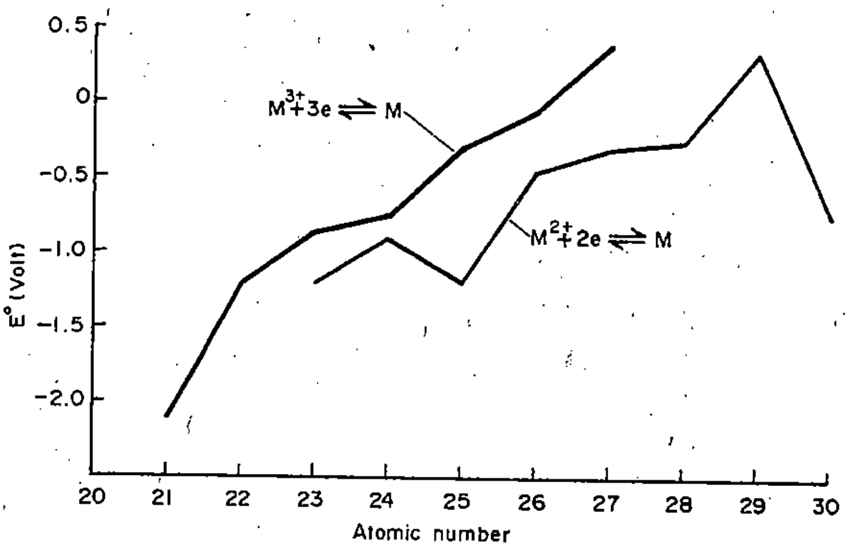

Fig. 12.7: Trends in electrode potentials of transition metals of 3*d* series

12.4.6 General Reactivity

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

12.4.7 Oxidation States

The concept of oxidation state has already been introduced in Unit 4 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 electrons in $(n-1)d$ orbitals are in an energy state comparable to ns electrons. From Table 12.5 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 12.5 : 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 12.5. 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 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, most stable oxidation state is +4. However Ti(II) and Ti(III) can be formed from Ti(IV) by the use of good reducing agents but lower oxidation states of Zr and Hf are extremely difficult to prepare. Table 12.6 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 12.6 : 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+}	–

SAQ 4

Explain, briefly in the space provided below, the existence of OsO_4 in terms of trends in oxidation states.

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12.5 FORMATION OF COMPLEXES

By now you must be familiar with the word 'complexes'. The chemistry of the transition metals is dominated by their tendency to form complex ions. This is because the transition elements form small, highly charged ions which have vacant orbitals of suitable energy to accept lone pairs of electrons donated by other groups or ligands. In case of transition metals in high oxidation states, highly charged ions can strongly bind electrostatically a wide variety of negative or polar ligands. In the case of transition metals in low oxidation states, the electrons in the *d* orbitals become involved in π bonding with ligands. The majority of transition metal ion complexes contain six ligands surrounding the central ion octahedrally. Some elements contain four ligands which are either arranged tetrahedrally or less frequently at the corners of a square. Besides these geometries, other geometries like trigonal bipyramid, pentagonal bipyramid, etc., are also present occasionally. The bonding between the ligand and the transition metal ion can either be predominantly electrostatic or covalent or in many cases intermediate between the two extremes. Some of the typical complexes of the transition metals are $[Fe(CN)_6]^{3-}$, $[Ni(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{3-}$, $[Cu(NH_3)_4]^{2+}$, etc. The nature of these complexes and the important theories of bonding related to them are discussed in Unit 14 of this block.

12.6 COLOUR OF TRANSITION METAL COMPOUNDS

Compounds of transition elements are usually markedly coloured, in contrast to compounds of *s*– and *p*– block elements which are mostly white or colourless unless the anion is coloured. As you know, substances appear coloured when they absorb light of a particular wavelength in the visible region of the spectrum and transmit light of other wavelengths. The colour which we see is the colour of the transmitted wavelengths. In other words, the colour of the compound observed by us is the complementary colour of the colour absorbed by the compound. You know that the transition metals as such or in the form of ions have partly filled *d*–orbitals which are degenerate, i.e., they are of equal energy. You will study in Unit 14 that in transition metal complexes the *d*– orbitals do not remain degenerate, but these split into sets of orbitals of different energies. By absorbing energy, electrons can move from a *d*–orbital of lower energy to that of higher energy. This transition of electron from one *d*–orbital to another corresponds to a fairly small energy difference, therefore, light is absorbed in the visible region of spectrum. For example, the aqua ion $Ti(H_2O)_6^{3+}$, 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 12.7 gives the relationship between the colour and the wavelength of light.

Table 12.7 : Relationship between the colour and wavelength

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

Whenever the *d*–orbitals are completely filled or empty, there is no possibility of electronic transitions within the *d*–orbitals. In such cases, the ions will not show any colour. For example, the compounds of Sc^{3+}, Ti^{4+}, Cu^+ and Zn^{2+} are white or colourless. Table 12.8 gives the colour and oxidation states of the metal ions present in some hydrated ions of transition elements.

Table 12.8 : Oxidation states and observed colours for some aqua species

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

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

SAQ 5

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

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12.7 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 μ_S.

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

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

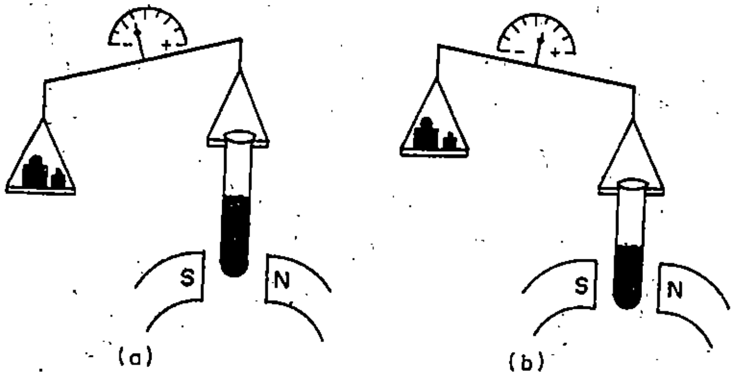
$$\text{Hence, } \mu_S = \sqrt{4S(S+1)} = \sqrt{4n/2\,(n/2+1)}$$

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

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

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

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. 12.8). Diamagnetic



(a) Loss in weight (diamagnetic)

(b) Increase in weight (paramagnetic)

Fig. 12.8: Measurement of molecular paramagnetism using a Gouy balance

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

In some cases (e.g., Mn^{2+}, or Fe^{3+}, in which all the *d* orbitals are occupied singly by electrons for which $m_l = 2, 1, 0, -1$ and -2, giving $L = 0$) the observed magnetic moment values agree very well with the spin-only value as given in Table 12.10. But generally, experimental values differ from the spin-only values. This is because the orbital motion of the electron also makes some contribution to the moment. More details on the magnetic properties of the transition elements can be studied in higher courses on the subject.

Table 12.9 : 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
$[Cr(H_2O)_6]^{2+}$	$3d^4$ ↑ ↑ ↑ ↑	4	4.90	4.80
$[Mn(H_2O)_6]^{2+}$	$3d^5$ ↑ ↑ ↑ ↑ ↑	5	5.92	5.96
$[Fe(H_2O)_6]^{2+}$	$3d^6$ ↑↓ ↑ ↑ ↑ ↑	4	4.90	5.00
$[Co(H_2O)_6]^{2+}$	$3d^7$ ↑↓ ↑↓ ↑ ↑ ↑	3	3.87	4.40
$[Ni(H_2O)_6]^{2+}$	$3d^8$ ↑↓ ↑↓ ↑↓ ↑ ↑	2	2.84	2.90
$[Cu(H_2O)_6]^{2+}$	$3d^9$ ↑↓ ↑↓ ↑↓ ↑↓ ↑	1	1.73	1.80

SAQ 6

In $[Co(H_2O)_6]^{2+}$ the observed magnetic moment is higher than the spin-only value. Explain the reason for this in the space provided below.

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12.8 CATALYTIC PROPERTIES

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

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

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

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

d. Pt/PtO as Adians catalyst for reductions

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

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

g. Ni (Raney nickel) in reduction processes

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

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

An enzyme is a biological catalyst which can bring about specific chemical reactions. It is known that several transition metal ions, e.g., iron, manganese, cobalt, zinc and molybdenum ions are involved in various processes.

12.9 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.

12.10 SUMMARY

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

12.11 TERMINAL QUESTIONS

1. How do the following properties vary in the transition elements?
    a) Atomic size
    b) Ionisation energy
    c) Stability of various oxidation states.
2. Why gold and silver are used for making ornaments?
3. Explain the following
    a) Mercury is a liquid.
    b) TiO_2 is white but $TiCl_3$ is violet.
4. Predict the spin-only magnetic moment for :
    a) Fe^{2+}
    b) Mn^{7+}
    c) Cu^{+}
    d) Ti^{3+}

5. Arrange each of the following groups of elements in order of increasing atomic size : (a) iron, osmium, ruthenium (b) molybdenum, strontium, zirconium (c) scandium, lanthanum, yttrium.

6. Which one of the following pairs is more stable?

   a) CrO_3, WO_3

   b) MnO_4^-, ReO_4^-

   c) Cr^{2+}, Cr^{3+}

   d) Mn^{2+}, MnO_4^-

   e) CrO_4^{2-}, MoO_4^{2-}

   f) Mn_2O_7, Re_2O_7

   g) V^{2+}, VO_4^{3-}

7. Which of the following tend to be an oxidising agent or a reducing agent?

   a) Ti^{2+}

   b) CrO_4^{2-}

   c) Cu^+

   d) MnO_4^-

8. Yttrium with chlorine does not form YCl or YCl_2 but only YCl_3. How does this agree with the trends in stability of oxidation states?

9. Write a balanced equation for the reaction of each of the following elements with oxygen:
   a. Scandium b. Titanium c. Vanadium d. Chromium e. Manganese f. Nickel g. Copper

12.12 ANSWERS

Answers to Self Assessment Questions

1. a) In transition series, the electrons enter the *d* orbitals which can accommodate ten electrons and therefore, there are ten elements in one transition series.
   b) 3*d* is at higher energy than 4*s* at potassium, that is why the electron enters the 4*s* orbital instead of 3*d* orbital.

2. (i) Calcium
   (ii) Titanium
   (iii) Molybdenum
   (iv) Iron

3. Zn and Cd have electronic configuration $[Ar]3d^{10}4s^2$ and $[Kr]4d^{10}5s^2$, respectively. Therefore, there is no unpaired electron for metallic bonding. Thus, these metals are soft.

4. The oxidation number of osmium in OsO_4 is +8. The stability of higher oxidation states increases as we go down the group of the transition metals. Osmium being in third transition series is, therefore, stable in oxidation state +8 and exists as OsO_4.

5. Cu^{2+} in $CuSO_4$ has $[Ar]3d^9 4s^0$ configuration and its electron can be promoted to the half filled *d* orbital. Thus it can undergo *d–d* transition which absorbs mainly in the red region of the visible light and $CuSO_4$ appears blue in colour (blue is complementary colour of red). Because Zn^{2+} in $ZnSO_4$ has the configuration $[Ar]3d^{10}4s^0$, the transition of electron from one *d* orbital to another is not possible and no light is absorbed in the visible region of spectrum by $ZnSO_4$ and therefore, it appears white.

6. The observed magnetic moment at times differs from that of the calculated spin-only

magnetic moment due to the contribution of orbital motion of the electrons. The observed magnetic moment for $[Co(H_2O)_6]^{2+}$ has contribution from the spin as well as orbital angular momentum and thus the observed magnetic moment is higher than the calculated spin-only magnetic moment.

Answers to Terminal Questions

1. See the trends in properties.
2. Because of their noble nature gold and silver are used for making ornaments.
3. a) No metallic bond formation

   b) Ti(IV) has d^0 configuration
4.

	Ion	Electronic configuration	Number of unpaired electrons	Magnetic moment
a)	Fe^{2+}	$[Ar]3d^6 4s^0$	4	4.90 BM
b)	Mn^{7+}	$[Ar]3d^0 4s^0$	0	0 BM
c)	Cu^+	$[Ar]3d^{10} 4s^0$	0	0 BM
d)	Ti^{3+}	$[Ar]3d^1 4s^0$	1	1.73 BM

5. a) $Fe < Ru < Os$

   b) $Mo < Zr < Sr$

   c) $Sc < Y < La$
6. (a) WO_3 (b) ReO_4^- (c) Cr^{3+} (d) Mn^{2+}

   (e) MoO_4^{2-} (f) Re_2O_7 (g) VO_4^{3-}
7. a) Reducing agent

   b) Oxidising agent

   c) Reducing agent

   d) Oxidising agent
8. Stability of high oxidation state as we go down a group.
9. a) $4Sc(s) + 3O_2(g) \longrightarrow 2Sc_2O_3(s)$

   b) $Ti(s) + O_2(g) \longrightarrow TiO_2(s)$

   c) $4(V)(s) + 5O_2(g) \longrightarrow 2V_2O_5(s)$

   d) $4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s)$

   e) $Mn(s) + O_2(g) \longrightarrow MnO_2(s)$

   f) $2Ni(s) + O_2(g) \longrightarrow 2NiO(s)$

   g) $2Cu(s) + O_2(g) \longrightarrow 2CuO(s)$

UNIT 13 INNER-TRANSITION ELEMENTS

Structure

13.1 Introduction
  Objectives
13.2 General Characteristics
  Electronic Configuration and Position in Periodic Table
  Atomic Radius
  Oxidation States
  Colour of Ions
  Electrode Potentials
  Complexation Behaviour
  Magnetic Properties
  Chemical Properties
13.3 Occurrence, Extraction and Uses
  Occurrence
  Extraction
  Uses
13.4 Summary
13.5 Terminal Questions
13.6 Answers

13.1 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 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.

Objectives

After studying this unit you should be able to :

- distinguish between transition and inner-transition elements,
- define the terms lanthanides and actinides,
- compute the electronic configurations of lanthanide and actinide ions from the electronic configurations of free atoms,
- discuss the ways in which actinide elements resemble their lanthanide congeners,
- discuss the ways in which the actinides resemble more closely *d*–block transition elements,
- explain lanthanide and actinide contraction,
- describe general characteristics of lanthanide and actinide elements and bring out periodicity in their properties.

13.2 GENERAL CHARACTERISTICS

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

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

13.2.1 Electronic Configuration and Position in Periodic Table

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

You know that lanthanum, the element preceding the lanthanides in the periodic table, has the electronic configuration $[Xe]5d^1 6s^2$. Like lanthanum, the lanthanides also exhibit the stable oxidation state of +3. It is, therefore, expected that in these elements the successive electrons will be filled in the 4*f* orbitals; thereby the elements may have the electronic configuration from $[Xe]4f^1 5d^1 6s^2$ to $[Xe]4f^{14} 5d^1 6s^2$. The actual ground state electronic configurations of lanthanide elements have been determined by atomic spectroscopy and are given in Table 13.1. You can see from the Table that there is an electron in 5*d* 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 5*d* orbitals. Whether there is an electron in 5*d* orbital or not, is of little importance because the lanthanides mostly form ionic compounds in +3 oxidation state and the electronic configuration of M^{3+} ions varies in a regular manner from $[Xe]4f^1$ for Ce^{3+} to $[Xe]4f^{14}$ for Lu^{3+}, as shown in Table 13.1.

Table 13.1 : Some properties of lanthanum and the lanthanides

Z	Name	Symbol	Electronic configuration outside the [Xe] core		Metallic radius pm	Ionic radius M^{3+} pm	E° (V) M^{3+}/M	Colour of Ln^{3+}
			Ln	Ln^{3+}				
57	Lanthanum	La	$5d^1 6s^2$	–	187	106	–2.52	Colourless
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^1$	183	103	–2.48	Colourless
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^2$	182	101	–2.46	Green
60	Neodymium	Nd	$4f^4 6s^2$	$4f^3$	181	100	–2.43	Lilac
61	Promethium	Pm	$4f^5 6s^2$	$4f^4$	–	98	–2.42	Yellow
62	Samarium	Sm	$4f^6 6s^2$	$4f^5$	179	96	–2.41	Yellow
63	Europium	Eu	$4f^7 6s^2$	$4f^6$	204	95	–2.41	Pale pink
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$	180	94	–2.40	Colourless
65	Terbium	Tb	$4f^9 6s^2$	$4f^8$	178	92	–2.39	Pale 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	Rose pink
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$	174	87	–2.28	Pale green
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$	194	86	–2.27	Colourless
71	Lutecium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$	174	85	–2.26	Colourless

The ground state electronic configuration of actinium, $[Rn]6d^1 7s^2$ is similar to that of lanthanum and indeed the two elements possess similar chemical properties. The electronic configurations of the elements that follow actinum are not known precisely; these are less certain than those of the lanthanide elements. The difference in energy between 5*f* and 6*d* orbitals in the beginning of the actinide series is less than that between the 4*f* and 5*d* 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 13.2) 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 6*d* orbitals, and so the electrons preferably fill the former.

Table 13.2 : Some properties of actinium and the actinides

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

SAQ 1

Explain briefly :

(a) What are inner-transition elements ?

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

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

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13.2.2 Atomic Radius

You have studied in Unit 2 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 3*d* 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 13.1) and also along the actinide series (Table 13.2) is even less than that in the transition series, since the difference in the electronic configurations of these elements is in the number of electrons in the ante-penultimate (last but two) shell of electrons. But the additive effect of decrease in atomic radius across the fourteen elements of lanthanide series is quite substantial. This decrease in atomic radius across the lanthanide series is known as lanthanide contraction. Similarly, there is an actinide contraction across the actinide series. As a result of lanthanide contraction, the normal increase in size from Sc→Y→La disappears after the lanthanides, and pairs of elements such as Zr and Hf, Nb and Ta, Mo and W, etc., possess nearly similar sizes (Table 13.3). The properties of these elements, therefore, are very similar. The similarities in properties within these pairs make their separation very difficult. Thus, due to lanthanide contraction, the elements of 5*d* and 4*d* transition series resemble each other much more closely than do the elements of 4*d* and 3*d* series.

Table 13.3: Atomic (covalent) radii of the elements preceding and following the lanthanides in pm

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

SAQ 2

Explain the term lanthanide contraction and its consequences.

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13.2.3 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+} ($4f^{13}$), etc. with non-f^0, non-f^7 and non-f^{14} electronic configurations also exist. This reminds us that there may be other factors also such as ionisation energies and sublimation energies of the metals and lattice energies, etc., which are responsible for the stability of these oxidation states. The known oxidation states of actinium and the actinides are given in Table 13.4 in which numbers in bold indicate the most stable oxidation state in aqueous solution. You can see from the Table that nearly all the actinides exhibit at least two stable oxidation states and oxidation states higher than +3 are easily accessible in the early actinides. For thorium, protactinium and uranium the highest accessible oxidation state is the most stable one also in aqueous solution. This may be because 5*f* orbitals extend further from the nucleus than the 4*f* orbitals and 5*f* electrons are more effectively shielded from the nuclear charge than are the 4*f* electrons of the corresponding lanthanides. Because the 5*f* electrons are less firmly held, they are all available for bonding in the early actinides. However, as the later actinides are approached, the build-up of nuclear charge causes contraction of the 5*f* orbitals so that the metal-ligand 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 13.4: Oxidation states of actinium and the actinides. The more stable states are in bold type; unstable states are enclosed in parentheses.

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

SAQ 3

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

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13.2.4 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 13.1 and 13.2, respectively.

13.2.5 Electrode Potentials

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

$$Ln^{3+}(aq) + 3e \longrightarrow Ln\,(s)$$

are given in Table 13.1. 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 13.2). Therefore, the actinides also are highly electropositive and reactive metals.

13.2.6 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 $[Th(acac)_4]$, $[Ce(NO_3)_4 \cdot (OPPh_3)_2]$ 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.

13.2.7 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 type (e.g.,

La^{3+}, Ce^{4+}, Ac^{3+}, Th^{4+}, Pa^{5+}, U^{6+}) and f^{14} type (e.g., Yb^{2+}, Lu^{3+}, Lr^{3+}), are all paramagnetic, because each of the seven *f* orbitals characterising inner-transition metal species (lanthanide and actinide) must contain a single electron before any pairing can take place (Hund's rule).

You have also studied that in case of transition elements, the contribution of orbital motion of electrons to paramagnetism is negligible and can be ignored. The magnetic moments of transition metal ions can be explained in terms of unpaired electrons present in *d*–orbitals. But the magnetic moments of only those lanthanide ions, which have f^0, f^7 and f^{14} configuration agree with the spin only value. In all other cases, the magnetic moment values are higher than those calculated on the basis of spin only formula. However, these can be explained by taking orbital contribution to magnetic moment also into account. In lanthanide ions, the 4*f* orbitals are comparatively better shielded from the surroundings by the overlying 5*s* and 5*p* 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 6*d* electrons as compared with 4*f* and 5*d* 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.

13.2.8 Chemical Properties

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

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

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

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

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

The metals tranish readily in air forming an oxide coating. On heating in oxygen, they burn easily to give M_2O_3, except for cerium which forms CeO_2. The oxides are ionic and basic, the base strength decreases as the ionic radius decreases.

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

When heated in halogens, the lanthanides burn 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 :

$$Ce + 2Fe_2 \longrightarrow CeF_4$$

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 MH3. 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.

SAQ 4

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

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13.3 OCCURRENCE, EXTRACTION AND USES

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

13.3.1 Occurrence

Apart from promethium which is unstable and is found in traces in uranium ores, all the lanthanides generally occur together. Although a large number of minerals are known to contain lanthanides, only three of them, viz., monazite, bastnaesite and xenotime are of commercial importance. Monazite and xenotime are a mixture of phosphates of thorium, lanthanum and lanthanides. Monazite is widely but sparsely distributed in many rocks, but because of its high density and inertness, it is concentrated by weathering into sands on beaches and river beds. Deposits of monazite occur in Southern India, South Africa and Brazil. Bastnaesite is a mixture of fluoride carbonates, $LnFCO_3$, of lanthanum and the lanthanides. Both monazite and bastnaesite are richer in the lighter lanthanides, i.e., the cerium earths, but with the difference that monazite also contains upto 30% ThO_2, which is absent in bastnaesite. On the other hand xenotime is a valuable source of the heavier rare earths.

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

13.3.2 Extraction

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

Earlier the lanthanides used to 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 $2Ln(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ and $Ln_2(SO_4)_3 \cdot Na_2SO_4 \cdot xH_2O$ 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$_3$H or –OH. In these resins, hydrogen ions are mobile and can be exchanged with other cations. Thus, the lanthanide ions replace the H$^+$ ions and get bound to the resin :

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

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

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

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

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

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

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

$$Ln_2O_3 + 2La \longrightarrow La_2O_3 + 2Ln, Ln = Sm \text{ and } Eu$$

Other lanthanides are obtained by the reaction of LnCl$_3$ or LnF$_3$ with Ca metal at 1300 K. LnCl$_3$ or LnF$_3$ are prepared by heating Ln$_2$O$_3$ with appropriate ammonium halide :

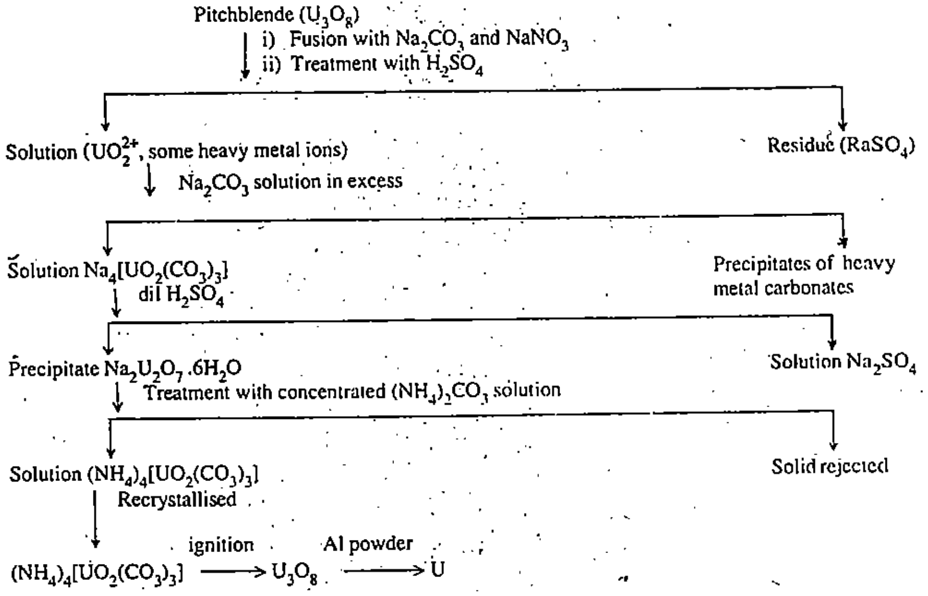
$$Ln_2O_3 + 6NH_4X \longrightarrow LnX_3 + 6NH_3 + 3H_2O$$

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

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

$$ThX_4 + 2Ca \longrightarrow Th + 2CaX_2$$

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



Flow sheet for extraction of uranium from pitchblende

13.3.3 Uses

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

SAQ 5

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

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13.4 SUMMARY

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

- The lanthanide and actinide elements are characterised by filling of 4*f* and 5*f* subshells, respectively.
- For the lanthanides, actinium and transamericium elements, the tripositive oxidation state is the most stable in every case. However, the oxidation states higher than +3 are quite common for the early actinide elements.
- The lanthanides exhibit greater similarities in their properties in their most prominent oxidation state, +3. Cerium and europium are the only lanthanides to be stable as Ce^{4+} and Eu^{2+} in aqueous solution.
- All the lanthanide and actinide ions which have unpaired electrons are paramagnetic. Paramagnetism of lanthanide and actinide ions depends on both spin and angular momentum of the unpaired electrons.
- All the lanthanides and actinides are highly electropositive and reactive metals. They react with oxygen, halogens, hydrogen, water and acids. Their hydrides are non-stoichiometric compounds.
- Cerium is the most abundant of all the lanthanides. Its main ores are monazite and bästnaesite.
- 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.

13.5 TERMINAL QUESTIONS

1. What are *f*–block elements ?
2. What are rare earth elements ? Why are they so called ?
3. Discuss the ways in which the actinide elements resemble their lanthanide congeners.
4. Discuss the ways in which the early actinide elements more closely resemble normal transition elements.
5. Discuss the position of lanthanide and actinide elements in the periodic table.
6. Why most of the lanthanide and actinide compounds are paramagnetic ?
7. Why the range of oxidation states is much more restricted in the lanthanide series as compared to the early actinides ?

13.6 ANSWERS

Answers to Self Assessment Questions

1. (a) Two series of elements from cerium (atomic number 58) to lutecium (atomic number 71) and thorium (atomic number 90) to lawrencium (atomic number 103) are known as inner-transition elements. The term transition is used because they exhibit transition behaviour by exhibiting variable oxidation states, forming coloured ions and exhibiting paramagnetism. The prefix inner is used because in the building up process of their atoms the differentiating electron enters the *f* orbitals of an inner shell.

   (b) The 14 elements from cerium (atomic number 58) to lutecium (atomic number 71) which follow lanthanium (atomic number 57) in the periodic table are called lanthanides. Similarly, 14 elements from thorium (atomic number 90) to lawrencium (atomic number 103) which follow actinium (atomic number 89) in the periodic table are called actinides.

(c) The electronic configuration of the elements of atomic number 61 and 95 is $[Xe]4f^5 6s^2$ and $[Rn]5f^7 7s^2$, respectively.

2. The gradual decrease in atomic size of the lanthanide elements starting from cerium to lutecium is known as lanthanide contraction. Because of lanthanide contraction, the elements from hafnium to mercury that follow the lanthanides have unusually small sizes.

3. The most common oxidation state of lanthanides is +3. This oxidation state of the lanthanide ions arises due to the loss of two 6*s* electrons and the lone 5*d* electron, if present, from the atom of the elements. If no electron is present in the 5*d* orbital, then one of the electrons from the 4*f* shell is lost. The lanthanide ions in this oxidation state have the general configuration $[Xe]4f^{1-14}$.

4. i) $2Ln + 6H_2O \longrightarrow 2Ln(OH)_3 + 3H_2$

   ii) $2Ln + 6H^+ \longrightarrow 2Ln^{3+} + 3H_2$

   iii) $4Ln + 3O_2 \longrightarrow 2Ln_2O_3$

   $Ce + O_2 \longrightarrow CeO_2$

   iv) $2Ln + 3X_2 \longrightarrow 2LnX_3$

   $Ce + 2F_2 \longrightarrow CeF_4$

5. The most stable oxidation state of the lanthanide elements is +3. The ionic radius of Ln^{3+} ions is quite comparable and varies very little from one element to another. Therefore, the chemical properties of the lanthanides are almost similar due to which the separation of lathanides is very difficult — almost as difficult as the separation of isotopes. The three most important methods which can be used for the separation of lanthanides are fractional crystallisation, solvent extraction and ion exchange chromatography.

Answers to Terminal Questions

1. Those elements, in the building up process of whose atoms the differentiating electron enters the *f* orbitals of an inner shell, are called *f*–block elements. There are two series of *f*–block elements containing 14 elements each. The lanthanide series contains elements from cerium to lutecium and the actinide series contains elements from thorium to lawrencium.

2. A group of elements, which includes the lanthanides, lanthanum and yttrium, is known as rare earth elements or simply rare earths. The word earth is used because these elements occur as oxides which in early usage meant earth, and the word rare was used because of great difficulty in their separation from each other.

3. Actinide elements resemble their lanthanide congeners in the following ways :
   - They have the similar electronic configurations,
   - They exhibit a common oxidation state of +3,
   - They form complexes,
   - Most of them form coloured ions and exhibit paramagnetism.

4. The early actinide elements exhibit a large number of oxidation states. In this respect they resemble normal transition elements.

5. There is no separate place for lanthanide and actinide elements in the periodic table. Therefore, the lanthanides are placed along with lanthanum and actinides along with actinium in the periodic table. Customarily, they are listed separately in two series at the bottom of the periodic table.

6. Most compounds of lanthanides and actinides are paramagnetic because they contain lanthanide and actinide ions which possess unpaired electrons. Presence of unpaired electrons gives rise to paramagnetism in the compound.

7. The range of oxidation states is much more restricted in the members of lanthanide series as compared to those of the actinide series. This is a result of stabilising effects

exerted on 4*f* orbitals by increasing ionic charge. By the time an ionic charge of +3 is developed on a lanthanide ion, the 4*f* orbitals are so stabilised that they become part of the inner core of the electrons. It becomes increasingly difficult to remove further electrons to give rise to higher oxidation states. On the other hand, in the beginning of the actinide series, the difference in energy of the 5*f* and 6*d* orbitals is much less. Therefore, 5*f* electrons along with 6*d* and 7*s* electrons participate in bonding, resulting in a wider range of oxidation states. However, later the 5*f* orbitals also become more stable and show reluctance to involve themselves in bonding.

UNIT 14 COORDINATION COMPOUNDS

Structure

14.1 Introduction
  Objectives
14.2 Some Basic Definitions
  Complex
  Ligands
  Oxidation State
14.3 Classification of Coordination Compounds
14.4 Nomenclature
14.5 Isomerism in Coordination Compounds
  Structural Isomerism
  Stereoisomerism
14.6 Theories of Bonding as Applied to Complexes
  Werner's Theory
  Valence Bond Theory
  Crystal Field Theory
14.7 Applications
14.8 Summary
14.9 Terminal Questions
14.10 Answers

14.1 INTRODUCTION

In Unit 12 of this block you have learnt about transition metals and their tendency to form coordination compounds or complexes. In this unit we shall study such complexes in more detail in view of their interesting chemistry and growing importance in chemical and biochemical processes. The complexes show a wide variety of physical and chemical properties which are quite different from normal salts. These differences arise due to the differences in their structures. In view of a special mode of bonding called 'coordination' being involved in their formation, they are also termed as coordination compounds. In this unit we shall briefly look at some of the basic definitions related to coordination compounds, familiarise you with different types of isomerism possible in them as well as the basic rules for naming these compounds. We shall then explain the formation of complexes in terms of different prevalent theories. However, we shall not deal with some other aspects, such as their thermodynamic and kinetic stability and reaction mechanism. These cannot be dealt with satisfactorily in such a short course. Finally, we shall consider a few applications of complexes in different fields.

Objectives

After studying this unit you should be able to:

- define the terms coordination compounds, coordination number, ligand and oxidation state,
- describe IUPAC rules for naming coordination compounds,
- name the coordination compounds according to IUPAC rules,
- write the formulae of coordination compounds if the systematic names are provided,
- describe the types of isomerism in coordination compounds,
- compare and contrast the different theories of bonding as applied to coordination compounds,
- explain geometries, magnetic and spectral properties of coordination compounds in terms of different bonding theories, and
- discuss the applications of coordination compounds in analytical chemistry, living systems and industry.

14.2 SOME BASIC DEFINITIONS

Some of the terms which we use in connection with coordination compounds carry specific meaning and thus form a kind of language for coordination chemistry. It is, therefore, desirable that we define these terms right in the beginning. Let us start with the definition of a coordination compound which is more commonly called a complex compound or simply a complex.

Complex: A very general definition of complex is, 'A compound that results from the combination of a central atom or ion and a group of atoms/ions/molecules surrounding it'. As you can see this definition is so broad in nature that practically all the known compounds of organic as well as inorganic chemistry will fall under this category. Hence, we will arbitrarily define complexes in such a way that it would refer to a group of compounds which have similar physical and chemical properties and can be treated by one or the other known theories of bonding. For our purpose we shall define a complex as:

We have used atom in a general sense which could equally mean an ion.

"A compound that results when a central metal atom or ion is chemically bonded to a group of ions or/and molecules such that the normal valency of the central atom is exceeded".

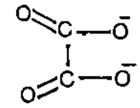
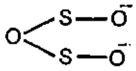
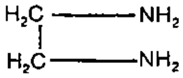
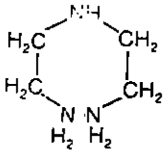
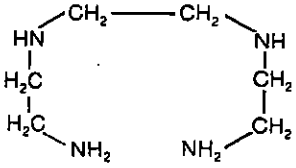
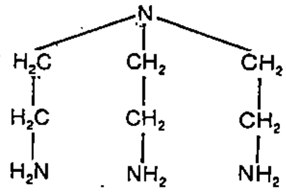
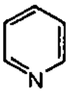
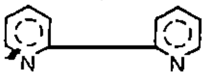
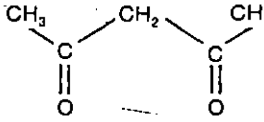
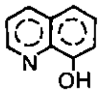
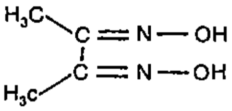
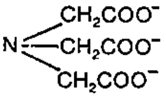
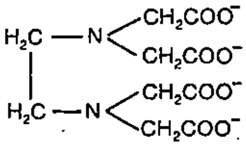
These compounds are usually formed by the donation of pair of electrons to the central metal ion by the group of ions or molecules. The bond so formed is called a coordinate bond and hence the name coordination compound. However, such a simple donor-acceptor bond approach does not seem to apply to all types of coordination compounds. In the following discussion we shall not only restrict ourselves to those complexes where the central atom or ion is a metal or more specifically a transition metal, but also exclude a class of compounds known as double salts, addition products and organometallic compounds. It will be useful to briefly define these compounds to avoid any future confusion. Double salts, as you know, are compounds such as alums where two salts crystallise together as one solid but when dissolved in water they dissociate into their constituent ions. For example, a compound like potash alum, $K_2Al_2(SO_4)_4 \cdot 24H_2O$ or $KAl(SO_4)_2 \cdot 12H_2O$, when dissolved in water dissociates to give K^+, Al^{3+}, SO_4^{2-} ions. A complex shows different properties from the original constituents and generally does not dissociate into component ions. In case of addition products, two apparently stable compounds such as NH_3 and BF_3 when brought together result in the formation of a compound called addition product or simply adduct with the formulation $NH_3 . BF_3$. The formation of such a compound is no doubt due to donation of a pair of electrons from nitrogen atom of NH_3 molecule to the boron atom of BF_3; but we cannot assign the role of a central atom to any particular atom on the resultant molecule. Organometallic compounds are those compounds where the central metal atom or ion is directly attached to atleast one carbon atom of a molecule. A complex compound could be neutral, cationic or anionic depending upon the total charge carried by the complex species.

$KAl(SO_4)_2 . 12H_2O$ is a mixture of K_2SO_4 and $Al_2(SO_4)_3$ which have crystallised together with water of crystallisation.

Ligands: The ions and/or molecules which are directly attached to the central atom/ion are called ligands. A ligand could be an ion, an atom or a neutral molecule but should contain at least one atom which can donate a pair of electrons to the metal ion for the bond formation. Since the ligands are directly attached to the metal ion, they are said to be in the first coordination sphere of the central atom. In writing the formula of a complex, the metal ion and all the ligands are put in square brackets. The sum total of all the ligands so attached to the metal ion, is called the **coordination number** of the metal. For example, in a compound like $[Ag(NH_3)_2]Cl$, there are two ammonia molecules acting as ligands and are said to be in the first coordination sphere of the Ag^+ ion. The coordination number of Ag^+ ion in the complex is 2.

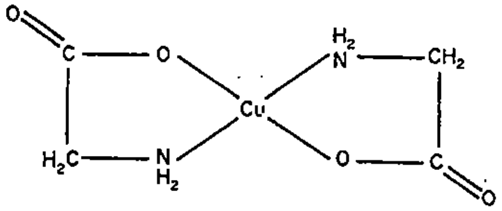
Ligands which contain one donor atom are called monodentate; the donor atom may contain one or more than one lone pairs of electrons. The ligands that contain two, three, four and so on donor atoms are called bidentate, tridentate, tetradentate etc., respectively. For example, NH_3, H_2O, F^- are all monodentate ligands; CO_3^{2-}, SO_4^{2-}, H_2NCH_2COOH (glycine) are all bidentate ligands. Table 14.1 gives a list of anions/molecules commonly used as ligands.

Table 14.1 : List of anions/molecules commonly used as ligands

Name	Abbreviation	Structure
Oxalate anion	ox	
Thiosulphate anion	$S_2O_3^{2-}$	
Thiocyanate anion	—	SCN^-
Cyanate anion	—	OCN^-
Ethylenediamine	en	
Diethylenetriamine	dien	
Triethylenetetraamine	trien	
tris(2-aminoethyl) amine	tren	
Pyridine	py	
2,2′-Bipyridine	bipy	
1,10-Phenanthroline	phen	
1,2-Phenylenebis (diarsine)	diars	
Acetylacetone	acacH	
8-Hydroxyquinoline	oxineH	
Dimethylglyoxime	dmgH	
Glycinate anion	gly	$H_2NCH_2COO^-$
Nitrilotriacetate anion	nta	
Ethylenediamine-tetraacetate anion	edta	

A bidentate ligand like ethylenediamine is a neutral molecule but a glycinate ion, $H_2NCH_2COO^-$, which is not neutral can also act as a bidentate ligand. The nitrogen atom and one of the oxygen atoms of glycinate ion can form chemical bonds with a metal ion. In order to differentiate a ligand like glycinate we call it a bidentatemononegative ligand.

Finally, a multidentate ligand which combines with a metal ion through two or more atoms on the ligand simultaneously, is called a chelating agent. The resulting complex is called a chelate compound. Consider the example of copper glycinate complex where two glycinates are combined with one copper ion as shown below:



Such glycinate ion is joined through N and O to the copper ion simultaneously. Hence, glycinate is acting as chelating agent.

Oxidation State : Oxidation state of an atom is defined as an apparent or formal charge on that particular atom in a molecule. In majority of the cases it is easily identified. For example, a complex $[Cu(NH_3)_4]Cl_2$ has the copper ion in the oxidation state of +2 since NH_3 molecules are neutral or do not carry any net charge. Note that the valency is not the same as oxidation state. We can say that in the above complex, copper shows a covalency of four and electrovalency of two. In some cases, however, it may not be easy to find out the oxidation state of the metal ion from the knowledge of the formula of the complex only. Suppose we consider a complex like $[Fe(H_2O)_5NO]^{2+}$. We also know that NO can exist as a neutral entity having no charge or as NO^- or NO^+. Now if in the above compound NO is acting as a neutral molecule, the oxidation state of Fe would be +2. If NO is present as NO^-, Fe would be in +3 oxidation state. Finally if it is present in the form of NO^+, Fe would have +1 oxidation state. Thus more information is required before the oxidation state of the metal ion can be decided.

$[Fe(H_2O)_5NO]^{2+}$ is responsible for the brown ring test for NO_3^- ion

You may try the following SAQ which is based on the above definitions.

SAQ 1

Determine the coordination number and the oxidation state of the transition metal ion in each of the following complexes:

(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Pt(NH_3)_2Cl_2]$ (d) $[CuF_4]^{2-}$

....

....

....

14.3 CLASSIFICATION OF COORDINATION COMPOUNDS

Since the number of known complexes is so large, we need to classify and categorise them in order to study their chemistry systematically.

The first and the most obvious choice is to classify them on the basis of the central metal ion. There are over eighty elements which can act as acceptor atoms in a complex. Most of these elements like transition metals can exist in several different oxidation states. Each of these states behaves as a different kind of acceptor and forms complexes having different formulas and properties. Hence, such a classification cannot be very useful.

A second way of classification is based on the coordination number of the metal ion. It is useful to the extent that the coordination number determines the geometry of the complex which can be correlated with properties like isomerism. However, majority of the complexes formed are either four coordinated or six-coordinated. Four-coordinated complexes commonly show square planner and less frequently tetrahedral geometry. On the other hand, all six coordinated complexes invariably exist in octahedral geometry. Thus, a further sub-classification would become necessary.

There is yet another useful way for the classification and that is on the basis of ligands. Ligands of one kind generally tend to give complexes with similar structure and properties. Most of the ligands are either simple anions like Cl^-, Br^-, NO_2^- etc. or are neutral molecules containing at least one donor atom. Let us look at the most commonly encountered elements whose atoms, either in simple ionic form or as a part of a molecule, can act as a ligand. These are :

N	O	F
P	S	Cl
As	Se	Br
		I

Halogens are always attached to the metal ion in a simple anionic form whereas all others commonly form a part of a molecule or ion. Examples are: NH_3, H_2O, SCN^-, $CH_3COCH_2COCH_3$ etc.

It is an observed fact that some metals form their most stable complexes with ligands having N, O and F as donor atoms. These have been grouped together and are called class 'a' elements or 'hard acids'. These include elements of Groups 1, 2 and 13 or transition elements with one, two or three *d*–electrons. Some metals form their most stable complexes with ligands where the coordinating atom is any element (P, S, Cl etc.) other than N, O, F in the above group. These metals are referred to as class 'b' elements or 'soft acids'. These include a few transition elements such as Pt, Pd, Hg etc. A large number of elements, however, cannot be clearly classified under either of the above two categories. These include elements from Mn to Cu amongst the first transition series, and Mo, Os, Cd etc. These differences in behaviour of the metal ions arise due to many factors such as charge, size, electronegativity, etc.

In the following section, we shall look at the rules for naming the complexes.

14.4 NOMENCLATURE

In the earlier days naming of complexes was based on the colour of the complex. For example:

Compound	Colour	Name
$CoCl_3 \cdot 4NH_3$	Green	Praseocobaltic chloride
$CoCl_3 \cdot 5NH_3$	Purple	Perpureocobaltic chloride
$CoCl_3 \cdot 5NH_3 \cdot H_2O$	Red	Roseocobaltic chloride
$CoCl_3 \cdot 6NH_3$	Orange-yellow	Luteocobaltic chloride

It is apparent that this system of naming cannot be useful when we are dealing with a large number of compounds. A summary of the rules of nomenclature as recommended by the International Union of Pure and Applied Chemistry (IUPAC) is given below:

- If the complex is a salt, the cation is named first followed by the name of the anion. For example, in naming $K_2[PtCl_6]$ we shall name potassium first followed by the name of the anion. In another example of $[Cu(NH_3)_4]Cl_2$, the name of the cation, $[Cu(NH_3)_4]^{2+}$, will be placed before chloride ion.

When writing the formula of a complex, the central atom is listed first. The coordinated groups (i.e., ligands) are listed in the order: formally anionic ligands, neutral ligands followed by cationic ligands. Within each group, the ligands are listed alphabetically according to the first symbol.

- For the complex entity, whether it is in cationic, anionic or neutral form, the name of the ligand(s) is put before the name of the metal atom. However, the reverse order is followed in writing the formula of the compound. For example in $[Cu(NH_3)_4]Cl_2$, we shall name the four ammonia molecules first followed by copper and finally the presence of chloride is mentioned; but in writing the formula copper is written before ammonia molecules.
- The names of all anionic ligands end in 'o' replacing the final 'e' in endings. Sometimes endings are also changed. Thus the given ligands acquire the following endings:

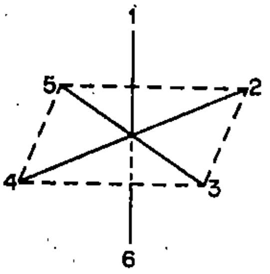
Ligands	Endings
F^- (fluoride)	fluoro
Cl^- (chloride)	chloro
O^{2-} (oxide)	oxo
OCN^- (cyanate)	cyanato

Cationic and neutral ligands have no special ending. There are a few exceptions like 'aqua' for H_2O, ammine for NH_3, carbonyl for CO, and nitrosyl for NO groups.

- The number of ligands is indicated by adding prefixes di–, tri–, tetra–, penta–, hexa–, etc. for two, three, four, five, six, etc. entities of the ligand. For example, $[Co(NH_3)_6]Cl_3$ will be called hexaamminecobalt chloride.
  If the ligands are big complicated groups, instead of di–, tri–, tetra–, penta– prefixes we use bis–, tris–, tetrakis–, pentakis– etc. For instance $Cu(CH_3COCHCOCH_3)_2$ is called bis(acetylacetonato) copper.
- In any complex species, the ligands are quoted in alphabetical order, without regard to charge, before the name of the central metal atom. Numerical prefixes indicating the number of ligands are not considered in determining that order. For example, a compound like $[CoCl\,(NO_2)\,(en)_2]Cl$ will be called chlorobis (ethylenediamine) nitrocobalt(III) chloride.
- The oxidation state of the metal ion in a complex is indicated by Roman (I), (II), (III) etc. or an Arabic (O) and placed in parenthesis immediately after the name of the metal. If, however, the complex species is an anion, the oxidation state of the metal is mentioned at the end of the name of the complex.
- The name of the complex anion always ends in 'ate' and the Latin name of the metal atom is used. No specific ending is used for neutral or cationic complex species. For example, $K_2[PtCl_6]$ is called potassium hexachloroplatinate(IV) and $K[Ag(CN)_2]$ is named as potassium dicyanoargentate(I).
- A little space is given between the name of the cation and the anion. No space or hypen is used anywhere else.
- Once the complex entity is completely identified according to the above rules, no mention of the number of cations or anions used for charge balancing is required. For example, $[Co(NH_3)_6]Cl_3$ is called hexaamminecobalt(III) chloride and not hexaamminecobalt(III) trichloride. Similarly, $K_2[PtCl_6]$ is named potassium hexachloroplatinate(IV) and not dipotassium hexachloroplatinate(IV).
- If a ligand has more than one donor atom, the actual atom involved in the bond formation with the metal ion is indicated by putting italicised symbol of the atom after the name of the ligand. For example, $[Ag(S_2O_3)_2]^{3-}$ is called dithiosulphato-*S*-argentate(I) ion. Some exceptions in this connection should be remembered. These are :

–SCN	thiocyanato
–NCS	isothiocyanato
$–NO_2$	nitro
–ONO	nitrito

- A bridging group is indicated by putting the Greek letter 'μ' immediately before its name and separated by hyphens from other ligands. For example, $[(H_2O)_4\,Fe\overset{OH}{\underset{OH}{<>}}Fe(H_2O)_4]^{4+}$ is called 'octaaqua-μ-dihydroxodiiron(III)' ion and the formula could be written as $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(H_2O)_4]^{4+}$ also.
- Structural information may be given names and formulas by prefixes such as cis–, trans– etc. $[Pt(NH_3)_2Cl_2]$ can be written as cis-dichlorodiammineplatinum(II) or trans-dichlorodiammineplatinum(II), respectively.
- In an octahedral compound with different ligands the positions of the ligands are specified as shown in margin.



The above rules are simple but you need practice. You should be able to answer the following SAQ.

SAQ 2

(a) Write down the names of the following complexes:

(i) $[Cr(NH_3)_3(NO_2)_3]$, ...

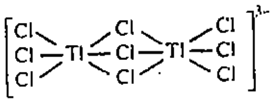
(ii) $[Co(NH_3)_5(H_2O)]Cl_3$. ....

(iii) $[Cr(NH_3)_6]\,[Cr(SCN)_6]$. ....

(iv) $[K_3Al\,(ox)_3]$. ....

(v) $[Pt(py)_4]\,[PbF_4]$ ....

(vi)



(b) Write down the formula for each of the following compounds:

(i) hexaamminecobalt(II) chloride ....

(ii) potassium trioxalatoferrate(III) ....

(iii) dichlorobis (triethylphosphine)-μ- dichlorodiplatinum(II) ....

14.5 ISOMERISM IN COORDINATION COMPOUNDS

You have already learnt about isomerism in your earlier studies. The phenomenon of isomerism is not restricted to organic compounds only but is quite frequently observed with coordination compounds. Whenever we come across compounds with the same chemical composition but different arrangement of atoms we call them isomers. Isomerism in complexes can be broadly classified into(a) structural and (b) stereo-isomerism. We shall discuss each of these categories separately.

14.5.1 Structural Isomerism

When two molecules have the same atoms but different bonds, they are called structural isomers. Thus, the variation of bond type or multiplicity of molecular arrangement gives rise to structural isomerism. The following different categories of isomerism can be all grouped together under the heading structural isomerisms:

(I) Hydrate Isomerism : In a compound, water molecules may be present in either coordinated form or as lattice water (water of crystallisation). In the former case water molecules are directly attached to the metal ion, or in the latter case they may occupy lattice sites in a crystal without getting attached to the metal ion. This type of isomerism is known as hydrate isomerism and the physical and chemical properties of hydrate isomers are quite different. As an example, we consider at least three well-established isomers of a complex $CrCl_3{\cdot}6H_2O$. These are:

(i) $[Cr(H_2O)_4Cl_2]\,Cl{\cdot}2H_2O$, a dark green compound where four molecules of water are coordinated to Cr(III) ion and the other two molecules occupy the lattice position.

(ii) $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ is blue green in colour and has five coordinated and one lattice molecules of water.

(iii) $[Cr(H_2O)_6]Cl_3$ is violet in colour and all the molecules of water are coordinated.

A few other examples are:

$[Co(NH_3)_4(H_2O)Cl]Br_2$, $[Co(NH_3)_4Br_2]Cl{\cdot}H_2O$

and $[Co(NH_3)_3(H_2O)_2Cl]Br_2$, $[Co(NH_3)_3Br_2\,(H_2O)]Br{\cdot}H_2O$

(II) Ionisation Isomerism : When coordinated ions exchange positions with ions present in the lattice position, we get ionisation isomers. Thus compounds having the same chemical composition give different ions in solution. For example, a compound $[Co(NH_3)_5Br]SO_4$ which is violet in colour yields $[Co(NH_3)_5Br]^{2+}$ and SO_4^{2-} ions in solution, whereas a red isomer of the compound $[Co(NH_3)_5SO_4]Br$ produces $[Co(NH_3)_5SO_4]^+$ and Br^- ions in solution. Other examples are:

$[Co(en)_2(NO_2)Cl]NO_2$ and $[Co(en)_2(NO_2)_2]Cl$

$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ etc.

(III) Linkage Isomerism : Some ligands can coordinate to the metal through different donor atoms present in the ligand. They are called ambidentate ligands and they can produce linkage isomers with a metal ion. Isomerism of this kind is shown by the isomeric pair : $[(NH_3)_5CoNO_2]^{2+}$ yellow brown known as nitro compound and $[(NH_3)_5CoONO]^{2+}$ red coloured isomer known as nitrito-complex. Other example are: Compounds with ligands like SCN^- which can bind through S or N donor atom, or sulphoxides, R_2SO, which may combine through S or O.

(IV) Coordination Isomerism : If the complex is a salt having both cation and anion as complex ions then the ligands can exchange position between the cation and the anion. This will result in the formation of coordination isomers. Let us consider one such series:

$[Co(en)_3][Cr(C_2O_4)_3]$, $[Co(en)_2(C_2O_4)][Cr(en)(C_2O_4)_2]$,

$[Cr(en)_2(C_2O_4)][Co(en)(C_2O_4)_2]$ and $[Cr(en)_3][Co(C_2O_4)_3]$

It is possible to have the same metal ion present in both cationic and anionic species as shown by the following example :

$[Cr(en)_3][Cr(C_2O_4)_3]$ and $[Cr(en)_2(C_2O_4)][Cr(en)(C_2O_4)_2]$

Notice that since (en) is neutral and $C_2O_4^{2-}$ carries two negative charges, the third and the fourth isomers contain Cr in the cationic species rather than Co.

Note that in the above example both the oxidation state of the metal ion and its coordination number are same in the cation and anion. Let us consider yet another example where the above condition may be different:

$[Pt^{II}(NH_3)_4][Pt^{IV}Cl_6]$ and $[Pt^{IV}(NH_3)_4Cl_2][Pt^{II}Cl_4]$

(V) Coordination Position Isomerism : If in a multinuclear complex the distribution of ligands around the metal centres changes it will result in a different isomer. Such an isomerism is called coordination position isomerism. Some typical examples are :

$[(NH_3)_4Co{<}^{NH_2}_{O_2}{>}Co(NH_3)_2Cl_2]Cl_2$ and $[Cl(NH_3)_3Co{<}^{NH_2}_{O_2}{>}Co(NH_3)_3Cl]Cl_2$

$[(R_3P)_2Pt{<}^{Cl}_{Cl}{>}PtCl_2]$ and $[Cl(R_3P)Pt{<}^{Cl}_{Cl}{>}Pt(R_3P)Cl]$

(VI) Electronic Isomerism: The complex $[Co(NH_3)_5NO]Cl_2$ exists in two forms. One is black paramagnetic while the other is pink and diamagnetic. Thorough structural studies show that the black isomer is a Co(II) complex containing neutral NO group whereas the pink one is a Co(III) complex where NO^- ion is present. This kind of isomerism is known as electronic isomerism.

(VII) Polymerisation Isomerism : This term is used to describe compounds having same empirical formula but different molecular compositions. The difference from normal polymerisation is that here we have differences in arrangements of group as well as multiplication of molecular weight. This is exemplified by $[Co(NH_3)_3(NO_2)_3]$ which gives the following isomers:

Formula	**Molecular weight**
$[Co(NH_3)_6][Co(NO_2)_6]$	double
$[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$	double
$[Co(NH_3)_5(NO_2)][Co(NH_3)_2(NO_2)_4]_2$	triple
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	quadruple
$[Co(NH_3)_4(NO_2)_2]_3[Co(NO_2)_6]$	quadruple
$[Co(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2$	quintuple

14.5.2 Stereoisomerism

Stereoisomers have the same bonds but the arrangement of atoms in space is different. Stereoisomerism can be divided into two kinds: geometrical and optical.

(I) **Geometrical isomerism** occurs when ligands can assume different positions around rigid bonds with the metal ion. For example, the compound $Pt(NH_3)_2Cl_2$ has a square planar structure. The two possible arrangements are shown in Fig. 14.1.

In the cis–isomer the two ammonia molecules are next (cis) or adjacent to each other whereas in the trans-isomer the two ammonia molecules are across (trans) to each other.

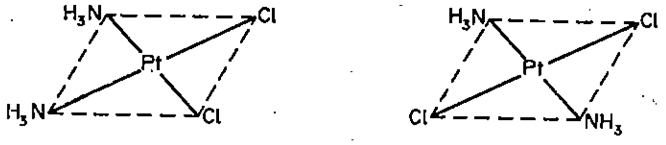
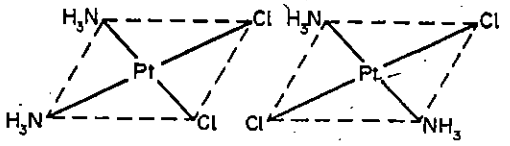
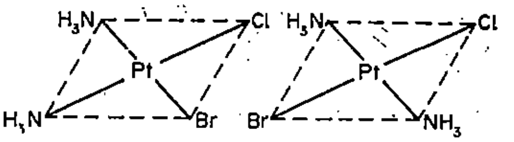
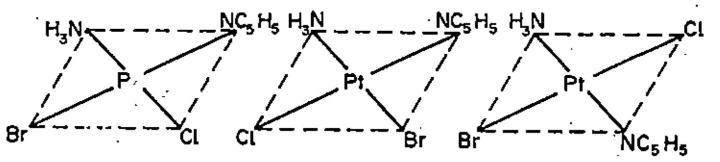


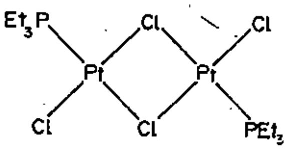
Fig. 14.1 Cis– and trans– isomers of dichlorodiammineplatinum(II)

This type of isomerism is not possible for complexes with coordination number 2 (linear molecule), 3 (trigonal planar) and 4 (tetrahedral geometry).

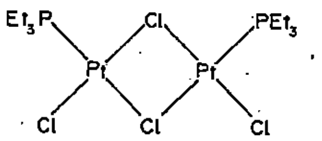
For square planar complexes Ma_4, Ma_3b or Mab_3 where a and b etc., are monodentate ligands, again the geometrical isomerism is not possible. However, square planar complexes of the type Ma_2b_2, Ma_2bc, Mabcd and $M(AA)_2$, $M(AB)_2$—where AA and AB represent symmetrical and unsymmetrical chelating agents – do give geometrical isomers. A few examples are given below:

Type	**Compound**	**Isomers**
Ma_2b_2	$Pt(NH_3)_2Cl_2$	
Ma_2bc	$Pt(NH_3)_2ClBr$	
Mabcd	$Pt(NH_3)(C_5H_5N)(Cl)(Br)$	

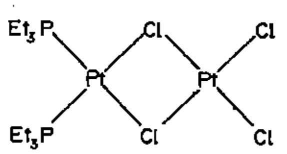
Bridged binuclear planar complexes like $[Pt(PEt_3)Cl_2]_2$ may exist in three isomeric forms:



trans–

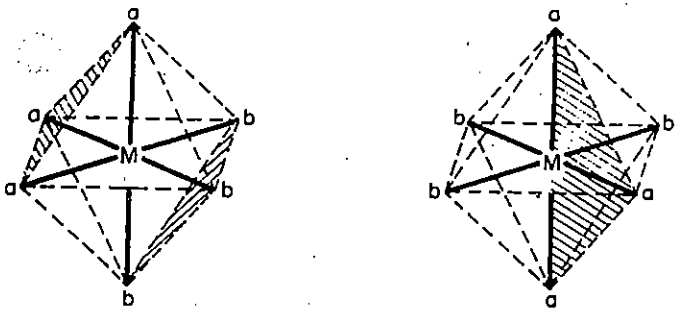


cis–



unsymmetrical

Six coordinated octahedral complexes of the type Ma_4b_2, Ma_3b_3, Ma_3b_2c, Ma_3bcd, Ma_2b_2cd, Ma_2bcde, Mabcdef would all give geometrical isomers. Systems with one or two bidentate ligands and rest monodentate would also give geometrical isomers. Thus we see that with this geometry a large number of isomers are possible whether they can be isolated or separated is a different question which depends on so many factors. As we increase the number of different ligands, the possible number of isomers increases. For example, Ma_4b_2 type of complex would give only two isomers cis– and trans–. Similarly for Ma_3b_3 type of complex we again get two isomers facial (fac–) and meridional (mer–) isomers. In the former (fac–) three ligands of one type form one triangular face of the octahedron and the other three on the opposite face, Fig. 14.2(a). In the latter (mer–), one set of these ligands are arranged around an edge of the octahedron whereas the other set occupies the opposite edge as shown in Fig. 14.2(b).



(a) (b)

Fig. 14.2: (a) facial and (b) meridional isomers of Ma_3b_3 complex.

Let us take one final example of Ma_2b_2cd where the following five isomers are possible as shown in Fig. 14.3.

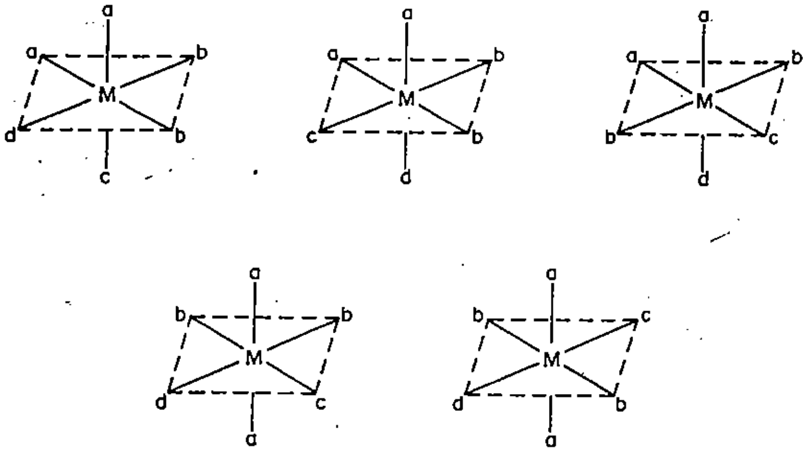


Fig. 14.3 : Geometrical isomers of Ma_2b_2cd complex

When writing the geometrical isomers you must make sure that the relative positions of the ligands must be different in each configuration and it is not just a rotation of the molecule as a whole. The trick in writing these configurations is that if you fix the position of some ligands initially and rotate the other ligands, then write configuration with the changed positions of the ligands which were fixed earlier. For example, in the above case we have fixed the cis position for the two ligands 'a' and wrote all possible configurations I, II & III. Once that is over then we put the two 'a' ligands in trans-positions and again rotate other ligands in all possible ways to get a different configuration. Finally, you must remember that there is no formula available which can predict the number of possible isomers for any particular compound and hence, you have to try writing down all possible configurations in each and every case (which of course, requires a lot of patience and practice).

(II) Optical Isomerism : Two isomers which have almost identical physical and chemical properties like mp, bp, density, colour etc., but differ in the way they rotate the plane-polarised light are called optical isomers. Such optically active compounds exist in pairs and are known as stereoisomers or enantiomers. These isomers are non-superimposable mirror images of each other. Hence, any molecule which contains either a centre of symmetry or a plane of symmetry will not show optical isomerism.

Optical isomerism is rarely observed in square planar complexes. Tetrahedral complexes of the type $[M(AB)_2]$ do give optical isomers as shown in Fig. 14.4, especially where M = Be, B etc.

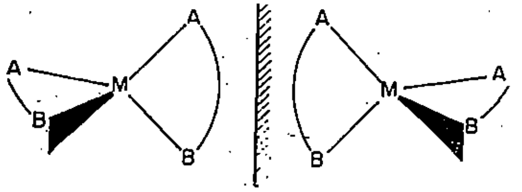


Fig. 14.4 : Optical isomers of $M(AB)_2$ complex

However, optical iomerism is very common with octahedral complexes of the type $M(AA)_3$, $M(AA)_2ab$, $M(AA)a_2b_2$, $M(AA)(BB)a_2$ etc. A few typical examples are shown in Fig. 14.5.

It is customary to symbolise a chelating agent as a curved line with the abbrevation for the ligand in the middle. Thus en could be used to represent $NH_2CH_2-CH_2NH_2$

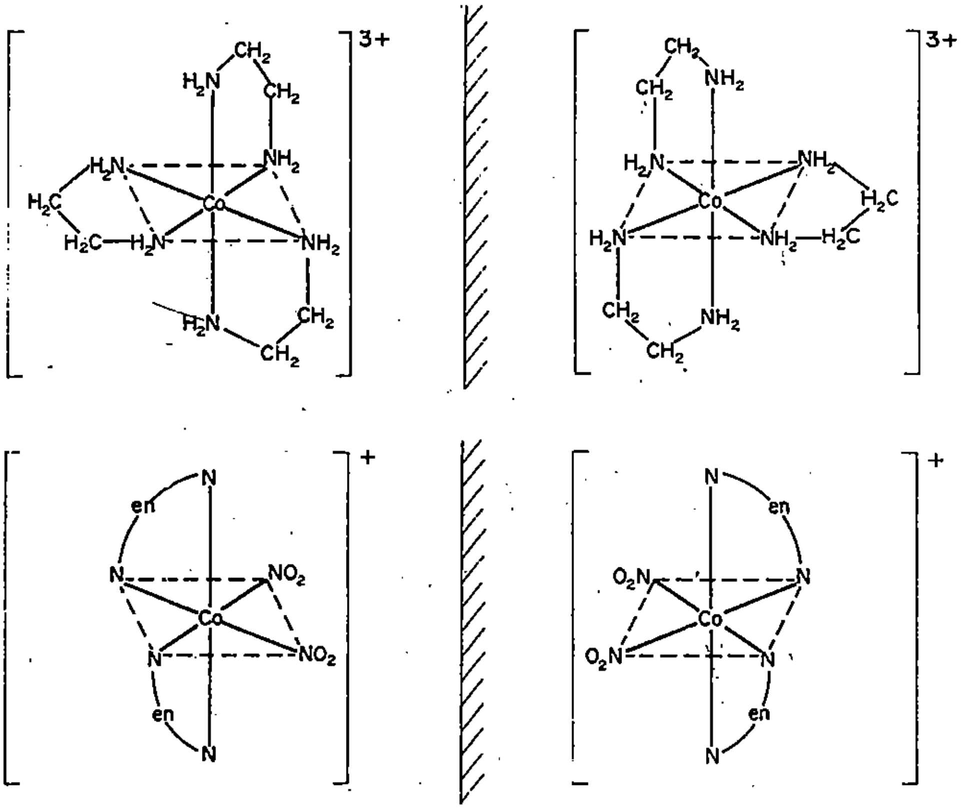


Fig.14.5: Optical isomers of $[Co(en)_3]^{3+}$ and $[Co(en)_2(NO_2)_2]^+$

In the next section we shall study the nature of chemical bond in complexes. However, after reading this section you should be able to solve the following SAQ.

SAQ 3

Write down all possible isomers of $[Co(en)_2Cl_2](NO_2)$ and give their names.

14.6 THEORIES OF BONDING AS APPLIED TO COMPLEXES

In the early period of development of the chemistry of complexes, a number of theories were put forward in order to explain in a simple manner the formation of a new compound by the combination of two or more stable and apparently saturated compounds. Though these early theories were not fully successful in many ways, yet they served their purpose of encouraging the workers in the field to perform new experiments in order to prove or disprove the theory. The slow accumulation of experimental data helped to understand the nature of chemical bond by the latter workers. However, the real credit goes to Werner who in 1893 introduced bold new ideas which explained a number of experimental facts. Though the modern theories are more encompassing in nature yet the basic postulates introduced by Werner are still valid to this day. In the next four subsections we shall discuss four different approaches including Werner's to explain three main properties namely, geometry, colour and the magnetic properties of the complexes.

14.6.1 Werner's Theory

Based on the study of a large number of compounds, Werner gave the following postulates:

- Metal atoms in complexes possess two types of valencies namely, principal or primary and auxiliary or secondary.
- Primary valencies are always satisfied by anions but the secondary valencies can be satisfied either by anions and/or neutral molecules.
- Every metal atom has a fixed number of auxiliary valencies.
- The secondary valencies show directional properties. In other words secondary valencies are directed in space around the central ion.

Werner showed that his postulates are consistent with experimental observations. He made use of basically three kind of experiments to justify his conclusions. Let us look at some of these experiments.

1. It is well known fact that weaker base in a compound is replaced on reacting with a stronger base. For example, ammonia is released from ammonium salts by reaction with a strong base like NaOH. However, when a complex containing ammonia molecules like $[Co(NH_3)_6]^{3+}$ is treated with NaOH, no ammonia is released. It is not released even on treatment with strong acids under mild conditions. A reasonable conclusion would be that the ammonia molecules are bound in a different manner to the metal ion.

2. The qualitative and quantitative presence of halogen in ionic form can be established by treating the compound with silver nitrate, which would give a precipitate of silver chloride. For example, a compound with a composition $CoCl_3 \cdot 5NH_3$ on treatment with $AgNO_3$ gives two mole AgCl precipitate per mole of the compound. From this observation the obvious conclusion is that one chlorine is bound to metal in a different way from the other two.

3. Measurement of molar conductance of a salt solution of approximately 10^{-3} M concentration can tell us the number of ions present in solution. For instance a molar conductance value of around 520 ohm^{-1} mol^{-1} cm^2 indicates the presence of five ions in solution whereas values around 400, 230 and 100 ohm^{-1} mol^{-1} cm^2 indicate 4, 3 and 2 ions respectively. Werner analysed a series of platinum ammine complexes and arrived at correct formulation in each case on the basis of molar conductance measurements. These are given in Table 14.2.

Table 14.2 : Molar conductance values of platinum complexes

Formula of the compound on the basis of analysis	Molar conductance (ohm^{-1} mol^{-1} cm^2)	Number of ions indicated	Werner's formulation of the compound
$PtCl_4 \cdot 6NH_3$	523	5	$[Pt(NH_3)_6]Cl_4$
$PtCl_4 \cdot 4NH_3$	229	3	$[Pt(NH_3)_4Cl_2]Cl_2$
$PtCl_4 \cdot 3NH_3$	97	2	$[Pt(NH_3)_3Cl_3]Cl$
$PtCl_4 \cdot 2NH_3$	0	0	$[Pt(NH_3)_2Cl_4]$
$PtCl_4 \cdot NH_3 \cdot KCl$	109	2	$K[Pt(NH_3) Cl_5]$
$PtCl_4 \cdot 2KCl$	257	3	$K_2[PtCl_6]$

4. Werner argued that since the secondary valencies have a definite orientation in space, complexes should show stereoisomerism. In the case of a six coordinated complex three geometrical shapes are possible namely, planar, prismatic or octahedral.

   Werner argued that a disubstituted complex of the type Ma_4b_2 would give three isomers if its structure is either planar or prismatic but only two if it is octahedral as shown in Fig. 14.6.

In all the compounds with the formula Ma4b2 synthesised by Werner, he could isolate only two isomers. This indicated that the structure was probably octahedral. For example, he could isolate only two geometrical isomers for the complex [Co(NH3)4Cl2]Cl clearly indicating an octahedral geometry, the cis– and trans– forms of which are illustrated in Fig. 14.7.

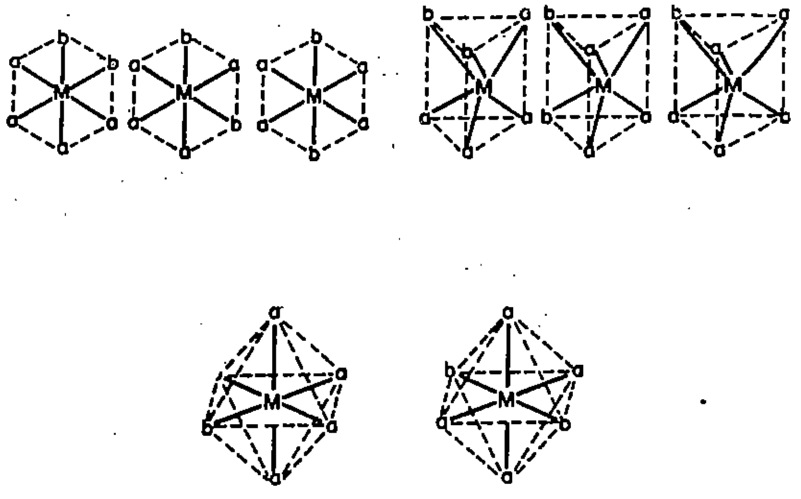


Fig. 14.6 : Three possible geometries of a 6-coordinated Ma_4b_2 complex

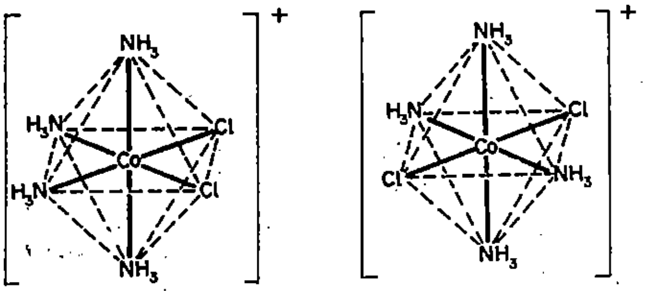


Fig. 14.7 : Possible number of isomers for the octahedral complex ion $[Co(NH_3)_4Cl_2]^+$

The final confirmation of the directional properties of auxiliary valencies and of the predicted geometry of a molecule came in the form of isolation of optical isomers for a number of complexes. Two such examples are shown in Fig. 14.5.

One of the main objections raised at the time when Werner introduced these ideas was that there was no theoretical justification for arbitrarily introducing two types of valency — primary and secondary. However, this was soon overcome when Lewis introduced his ideas on covalency and electrovalency. It was thus realised that Werner's primary and secondary valencies were just alternative names for electrovalent and covalent bonds, respectively. Thus, the properties assigned to primary and secondary valencies become a natural consequence of bond properties given by Lewis.

However, there were inherent limitations with such a simple approach. For example, the following experimental facts cannot be explained on the basis of such a simple model :

- certain metal ions show stronger tendency to form complexes compared to others;
- certain elements can form complexes with different coordination numbers as well as in different oxidation states;
- some metal ion complexes are very reactive and exchange ligands in typical substitution reactions whereas others do not.
- a particular geometrical shape appears to be preferred by some ions;
- most of the transition element complexes show typical sharp colours.

Those complexes which exchange their ligands within a short time of mixing the reactants are known as labile complexes while others are referred to as inert complexes.

The above developments can also be cited as a typical example of the manner in which scientific theories grow and are refined in any particular field. Although Werner's theory could explain most of the observations and facts known at that time, yet many other observations made by him and later workers indicated the need for further improvements in the theory of complex compounds.

The next major step in understanding the nature of bond in complexes was the application of the well known concepts of valence bond theory developed by Pauling. Valence bond theory places main emphasis on the atomic orbitals of the metal ion which are involved in the bond formation. Once these were identified, the stereochemistry, geometry and the magnetic properties could be better interpreted in terms of suitable combinations of these orbitals.

14.6.2 Valence Bond Theory

This concept starts with the assumption that the bond between the metal ion and the ligand is basically covalent in nature. In order to form a chemical bond the central metal ion must have enough of vacant orbitals to accept the lone pairs of electrons from the ligands. The number of bonds formed is thus directly related to the number of vacant orbitals on the metal ion. At this stage, Pauling introduced the concept of hybridised atomic orbitals. Accordingly, the vacant atomic orbitals on the metal ion combine to give a set of hybridised orbitals. For hybridisation only those orbitals are used which have the correct orientation in space and whose energy values are very near to each other. These hybridised orbitals overlap with the ligand orbitals to share the lone pairs of electrons from the ligands. Since these hybridised orbitals show a definite orientation in space, the geometry of the molecule is determined by the kind of hybridisation involved. The correct combinations of the atomic orbitals have been worked out as shown in table 14.3.

Table 14.3 Suitable atomic orbitals for hybridisation

Coordination number	Vacant atomic orbitals on the metal ion	hybridised orbitals	Geometry of the molecule	Example
2	s, p	sp	linear	$[Ag(NH_3)_2]^+$
3	s, $(2)p$	sp^2	planar triangular	$[HgI_3]^-$
	s, $(3)p$	sp^3	tetrahedral	$[Zn(NH_3)_4]^{2+}$
	or			
4	d_{xy}, d_{yz}, d_{xz} and s	d^3s	tetrahedral	$[MnO_4]^-$
	$d_{x^2-y^2}$, s, $(2)p$	dsp^2	square planar	$[Ni(CN)_4]^{2-}$
5	d_{z^2}, s, $(3)p$	dsp^3	trigonal bipyramid	$[CuCl_5]^{3-}$
	or			
	$d_{x^2-y^2}$, s, $(3)p$	dsp^3	square pyramid	$[Ni(CN)_5]^{3-}$
	or			
	$(4)d$, s	d^4s	square pyramid	
6	$d_{x^2-y^2}$, d_{z^2}, s, $(3)p$	d^2sp^3	octahedral	$[Co(NH_3)_6]^{3+}$
	or s, $(3)p$, $d_{x^2-y^2}$, d_{z^2}	sp^3d^2	octahedral	$[CoF_6]^{3-}$

Once the geometry of the molecule is known, the suitable combination of atomic orbitals can be found but the reverse process is not always possible.

In Table 14.3, the numbers shown in paranthesis represent the number of specific orbitals involved in hybridisation. They do not indicate either the principal quantum number or the number of electrons in a particular orbital.

Pauling showed that there is a direct correlation between the type of hybridisation and the magnetic properties of the complex. In order to understand this relationship, you should recapitulate the basic concepts of magnetism. The orbital motion and the spinning of the electron gives rise to a certain angular momentum to an atom. This angular momentum causes the atom to acquire magnetic moment. The magnetic moment due to spin angular momentum is much greater in comparison to magnetic moment arising out of orbital angular momentum. Further, if there are two electrons in an orbital having opposite spins, the magnetic moment due to spin angular momentum will be zero. However, if there are unpaired electrons in an atom its magnetic moment is given by the expression:

$\mu_s = \sqrt{n(n+2)}$ BM where n is the number of unpaired electrons and BM is the unit of magnetic moment. It is called Bohr Magneton and abbreviated as BM The formula is known as spin-only formula for the calculation of magnetic moment since in its derivation we have omitted the contribution due to orbital angular momentum.

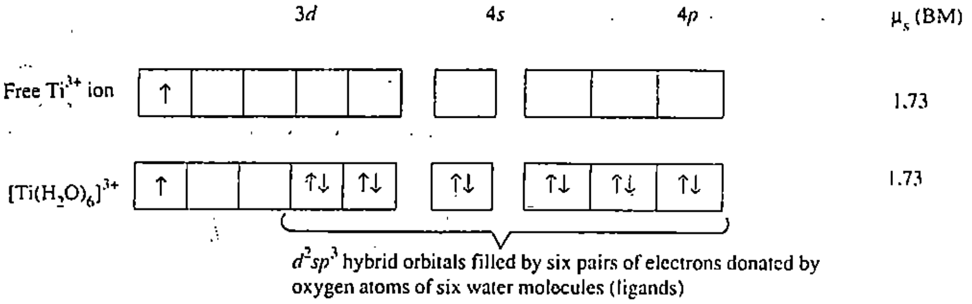
In cases where paramagnetic ions are very close together they interact with each other and result in more intense form of magnetism known as ferromagnetism and antiferromagnetism. However, we shall not be concerned with these types of magnetism in our discussions since in complexes the paramagnetic metal ions are never too close

If all the electrons in an atom/ion have paired spins they will not give rise to any magnetic moment. Such substances are called diamagnetic and when put in an external magnetic field they are slightly repelled by the field. On the other hand an atom/ion having unpaired electrons gives rise to magnetic moment. Such substances are called paramagnetic and when placed in an external magnetic field are pulled towards the field. Table 14.4 gives the number of unpaired electrons and the associated magnetic moment.

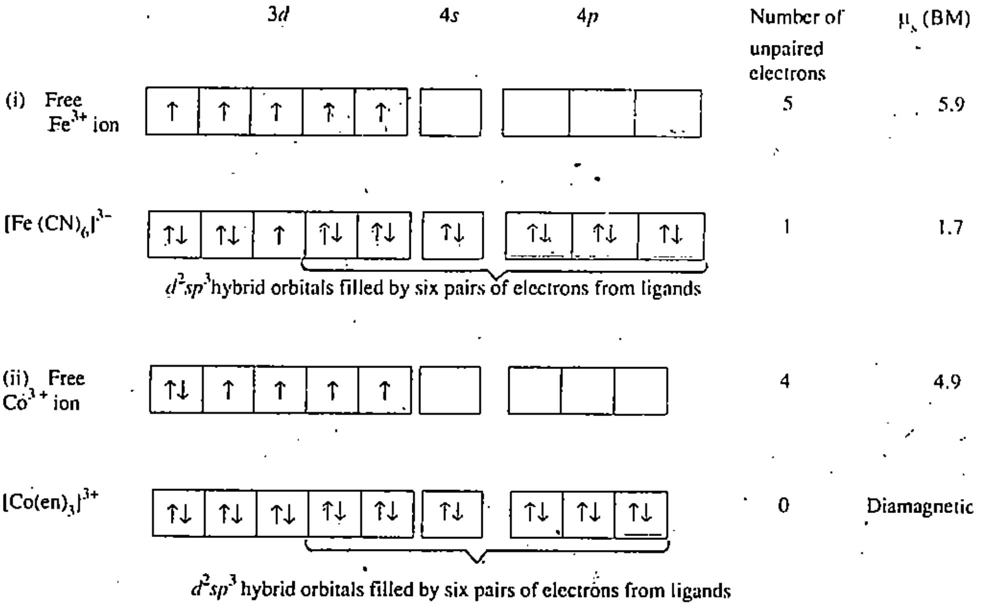
Table 14.4 : Corelation between number of unpaired electrons and expected magnetic moment

Number of unpaired electrons, n	Magnetic moment (BM.) $\mu_s = n(n+2)$
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

Let us now turn our attention to the complexes having transition metal ion with d^1, d^2 or d^3 electrons. With these configurations, there are enough of vacant orbitals available to accept the pairs of electrons from four or six ligands to form tetrahedral, square planar or octahedral compound. The magnetic moment of the complex will be the same as free ion value as shown in the diagram given below:



When the number of *d* electrons is greater than three and up to six as in d^4, d^5, d^6 systems, there is still a possibility of forming octahedral complexes using d^2sp^3 hybridised orbitals by forcing some of the electrons to pair up. Following two examples should make the point clear.

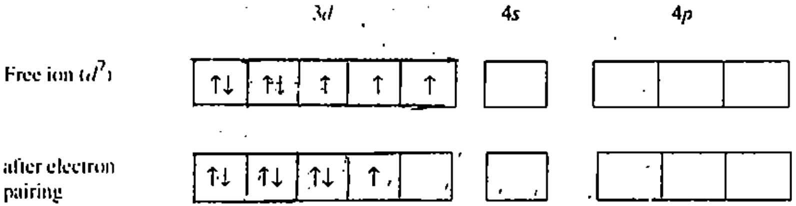


In majority of the cases the decrease in the number of unpaired electrons agrees well with the magnetic moment values obtained experimentally. However, it does not hold true for a number of complexes. For example a complex ion like $[FeF_6]^{3-}$ gives a magnetic moment value equal to five unpaired electrons indicating thereby that the electronic distribution on the Fe^{3+} ion remains the same as in free ion state. Pauling suggested that instead of using the inner orbitals (3*d*, 4*s*, 4*p*), iron can use outer orbitals (4*s*, 4*p*, & 4*d*) for d^2sp^3 hybridisation leaving the electronic distribution the same as in free ion state. Different authors call the two types of complexes with different names as listed below.

Author	Upper level	Lower level
Pauling	hypoligated	hyperligated
Orgel	high spin	low spin
Taube	outer orbital	inner orbital
Nyholm	spin free	spin paired

Craig showed that highly electronegative ligands tend to form spin-free complexes. Although the valence bond theory suggests two correct alternatives in low spin and high spin, yet it does not help in making the choice. However, it indirectly suggests that the low spin complexes should be relatively less reactive. It has also been shown that a d^6 high spin octahedral complexes will be more stable than four coordinated complexes which do not require outer d-orbitals for hybridisation.

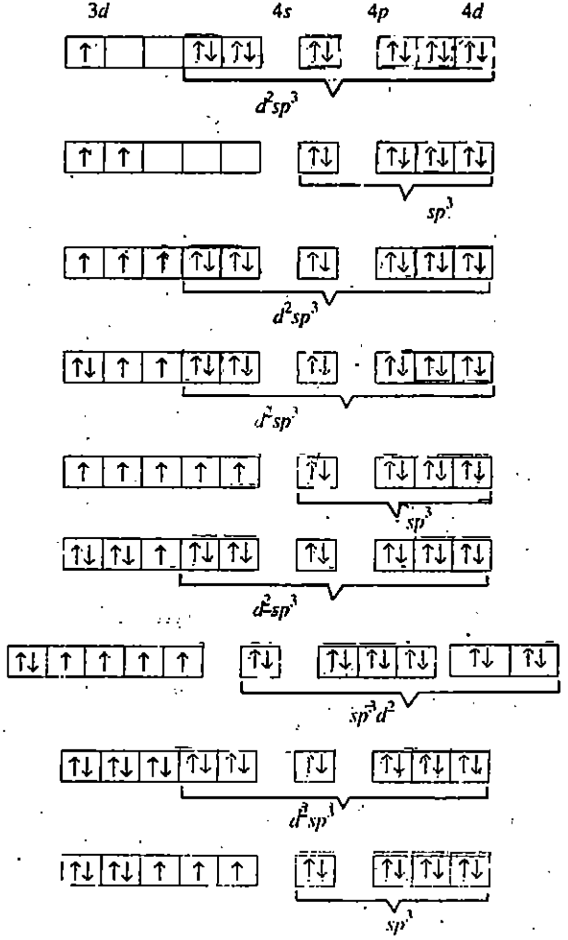
Turning our attention to systems having d^7 to d^{10} electronic configuration, we find that even forcing all the d electrons to pair up in the inner orbitals it still does not leave two vacant d-orbitals for hybridisation: hence d^2sp^3 hybridisation is not possible in such cases as shown below:

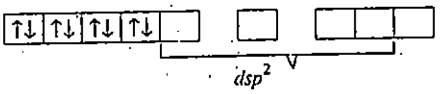
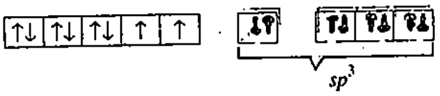
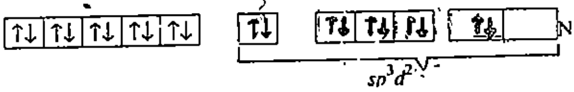


In complexes of this type, we are left with just one choice of forming high spin octahedral complex or else metal ion should form complexes with lower coordination number. Table 14.5 gives examples of a number of compounds having different geometrics and different number of unpaired electrons.

Table 14.5 : Hybridised orbitals and the corresponding geometries of some complexes

No. of d electron in ion	Complex	Hybrid orbitals and electronic distribution	Number of unpaired electrons	Geometry



No. of *d* electron in ion	Complex	Hybrid orbitals and electronic distribution	Number of unpaired electrons	Geometry
d^7	$[Co(NH_3)_6]^{2+}$		Three	Octahedral
d^8	$[Ni(CN)_4]^{2-}$		Nil	Square planar
	$[NiCl_4]^{2-}$		Two	Tetrahedral
d^9	$[Cu(NH_3)_4]^{2+}$		One	Square planar
d^{10}	$[Zn(NH_3)_6]^{2+}$		Nil	Octahedral
d^{10}	$[Ag(CN)_2]^-$		Nil	Linear

*Hybrid orbitals are always occupied by lone pairs of electrons from ligands.

As you can see this theory is not only easy to apply but it also gives more information about the complexes and became more acceptable initially. However, its limitations also became obvious very soon. Let us consider a few of these in detail:

- It gives no idea whether a particular metal ion would prefer to have any particular geometry say, an octahedral or tetrahedral with a given ligand.
- Even if we know that a complex formed is four coordinated we cannot decide whether it would be tetrahedral or square planar. It is only after measuring the magnetic moment that we can decide the correct geometry. For example, in the case of two parallel compounds, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ the former is a square planar compound the other is tetrahedral. This example leads to the next weakness.
- The important role ligands play in deciding the geometry of the resultant complex is not taken into account by this theory.
- It gives only an approximate magnetic moment value which in some cases may differ considerably.
- Besides magnetic property, it does not throw any light on other physico-chemical properties of complexes like—spectral, stability, reactivity etc.

Thus we see the need for a more comprehensive theory which could explain the observed properties and if possible, predict the formation of new compounds. Even if such a theory may not be all comprehensive, it should at least be able to recognise the factors responsible for the typical properties of complexes. Crystal field theory is such an attempt and in the next sub-section we shall deal with this new theory. However, before proceeding any further, you may try to solve the following SAQ based on valence bond theory.

SAQ 4

Classify each of the following complexes as either high or low spin. Explain you answers.

$[Co(H_2O)_6]^{2+}$, $\mu = 4.6$ BM; $[Co(CN)_6]^{4-}$, $\mu = 1.9$ BM;

$[Fe(NO_2)_6]^{4-}$, $\mu = 0.0$ BM; $[Fe(H_2O)_6]^{3+}$, $\mu = 5.94$ BM.

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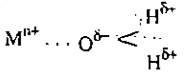
14.6.3 Crystal Field Theory

This theory is based on two main assumptions. First, all the ligands are considered as point (negative) charges. It means that the size and shape of ligands are not taken into account. Second, the bonds between the metal ion and the ligands are purely electrovalent in nature. With these assumptions, the theory sets on to find the effect of these point charges (ligands) on the energy levels (s, p, d, f) of the metal ion. This effect is also evaluated in terms of force of repulsion only and does not concern itself with the force of attraction.

The point charges of CFT (ligands) create an electric field, which is responsible for the changes in the energy levels of the metal ion. The electric field is usually referred to as crystal field or ligand field.

Let us start with s-orbitals which are spherically symmetrical. Any effect due to mutual repulsions between the s–electrons and the negatively charged ligands will be equal in all the three directions. The net result of such an interaction would be to raise the total energy of the system — metal and ligand combined. In the case of p-orbitals, when they are completely filled as in a transition metal ion, once again the interaction will raise the total energy of the system.

Even a neutral molecule can be considered as a source of negative charges. Negative end of the dipole points towards the metal ion as in



$$M^{n+} \cdots O^{\delta-} \begin{matrix} H^{\delta+} \\ \\ H^{\delta+} \end{matrix}$$

The real differences arise in case of d–orbitals. They will all be raised in energy compared to free ion state. However, due to the differences in their orientation, all the five d–orbitals are not effected equally by the presence of ligands. Three orbitals, d_{xy}, d_{yz}, d_{xz} have their electron density concentrated between the three Cartesian axes whereas in the other two orbitals $d_{x^2-y^2}$, d_{z^2} the electron density is concentrated along the axes as shown in Fig. 14.8.

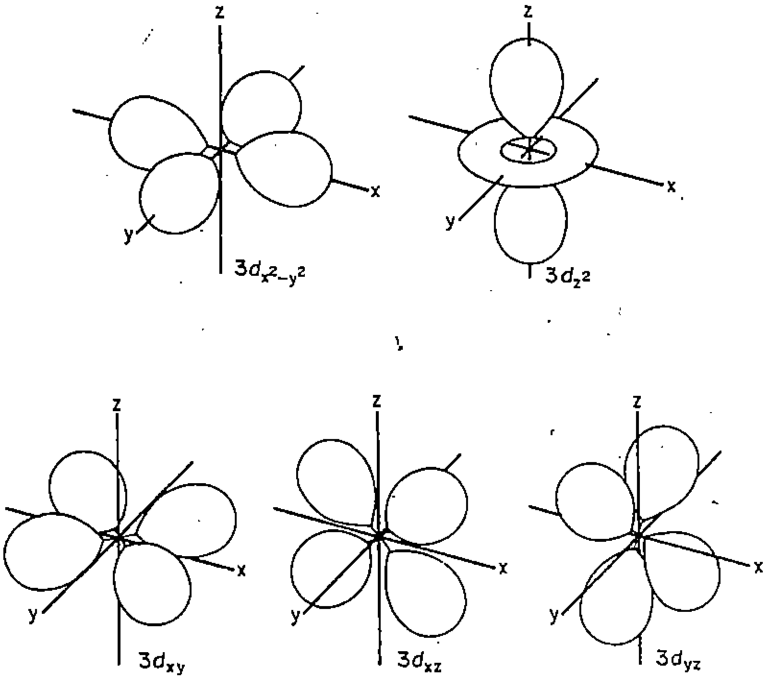


Fig. 14.8 : Orientation of d–orbitals in space

Thus, depending upon the position of the ligands the interaction between the d–electrons will not be uniform and the five d–orbitals will no more be equal in energy. When all the orbitals are equal in energy we call them degenerate but when they are no more equal as in case of complexes we say that the degeneracy of the orbitals has been removed due to the presence of ligands. Crystal field theory accounts for the properties of complexes in terms of splitting of the d–orbitals into different energy levels. We shall consider the complexes with three most common geometries namely octahedral, tetrahedral and square planar and see how the splitting of the orbitals takes place in each case.

Crystal Field Splitting in Octahedral Complexes

Let us consider an octahedral complex, ML_6, where M is a metal ion and L stands for a ligand. The total charge on the complex and the oxidation state of the metal ion are omitted since they would not make any difference in our results. This complex can be represented as shown in Fig. 14.9.

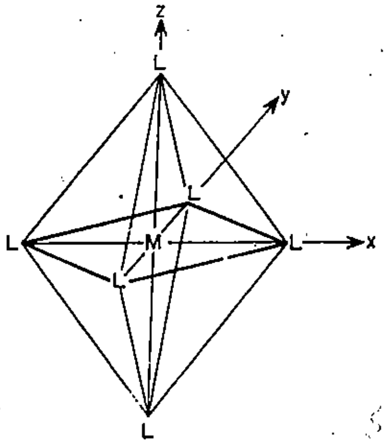


Fig. 14.9 : An Octahedral complex where the positions of the ligands are shown by negative charges

Here four ligands lie in one plane and the other two in a plane perpendicular to the first plane. Six ligands are at the corners of a regular octahedron and they all lie along the three perpendicular axes, x, y and z. Thus we see that all those orbitals which lie in the direction of these axes will experience a stronger force of repulsion as compared to the orbitals which lie between the axes (Fig. 14.10).

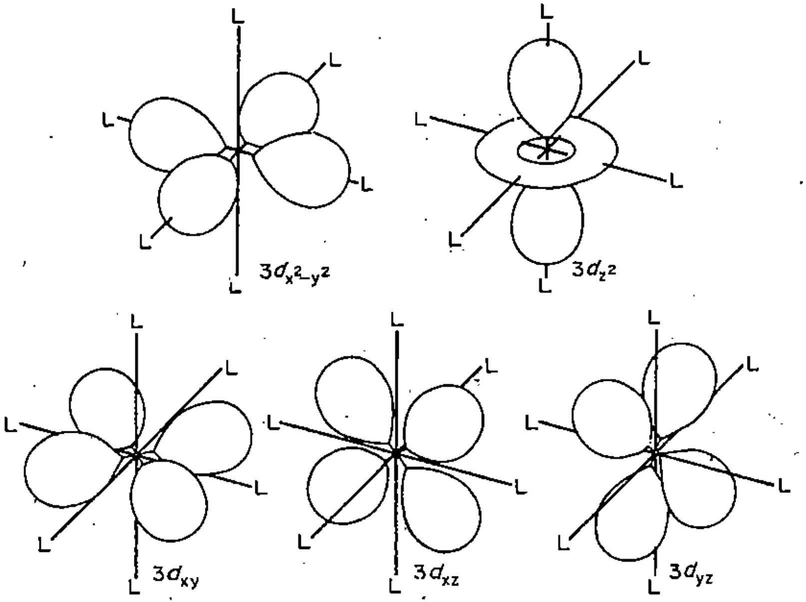


Fig. 14.10 : Orientation of d–orbitals in relation to six ligands in an octahedral compound

The $d_{x^2-y^2}$ and d_{z^2} orbitals which lie along the axes will be repelled more by the ligands and will be higher in energy than d_{xy}, d_{yz} and d_{xz} set of orbitals. These results are shown diagrammatically in Fig. 14.11.

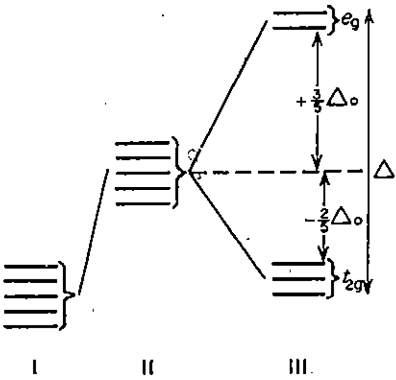
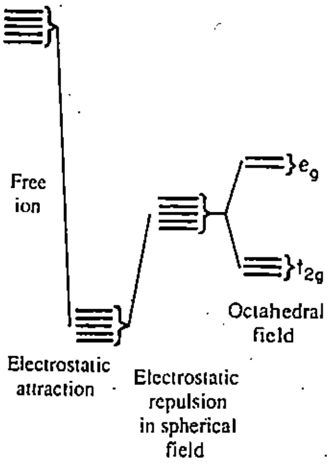


Fig. 14.11 : d–orbital energy level in degenerate state(I), in an uniform field of six negative charges(II) and in an octahedral crystal field (III).

Initially in a free ion state (I) all the orbitals are in degenerate state. In state (II), all the five orbitals are raised in energy when surrounded uniformly by negative charges. State (III) shows how the degeneracy is removed in an octahedral field. The set of lower three orbitals equal in energy in an octahedral field is given a symbol t_{2g} while the upper two equal-energy levels are denoted by e_g. The difference in energy between t_{2g} and e_g sets is given by a symbol Δ_o (delta octahedral). Comparing states (II) and (III), we find that the only difference between them is that instead of uniformly distributing the six negative charges (as shown in state II), we have put the six charges at the corners of a regular octahedron. Just by the redistribution of charges the total energy of the system should not change. However, at the same time we say that in state (III), the t_{2g} set of orbitals will be lower in energy and the e_g set will be higher. The two facts can be reconciled if the total lowering of t_{2g} set is equal to the total raise in energy of e_g orbitals which would give no resultant change in energy as compared to state (II): Of the five orbitals, three are lowered in energy and two are raised in energy. Thus each orbitals is lowered in energy by $2/5\ \Delta_o$ causing a total lowering of $6/5\ \Delta_o$ the other two orbitals are each raised in energy by $3/5\Delta_o$ causing a total raise of $6/5\ \Delta_o$. The sum total of lowering and raise, being equal and opposite, turns out to be zero or no change. The Δ_o values are generally in the range of 100-250 kJ mol^{-1}.

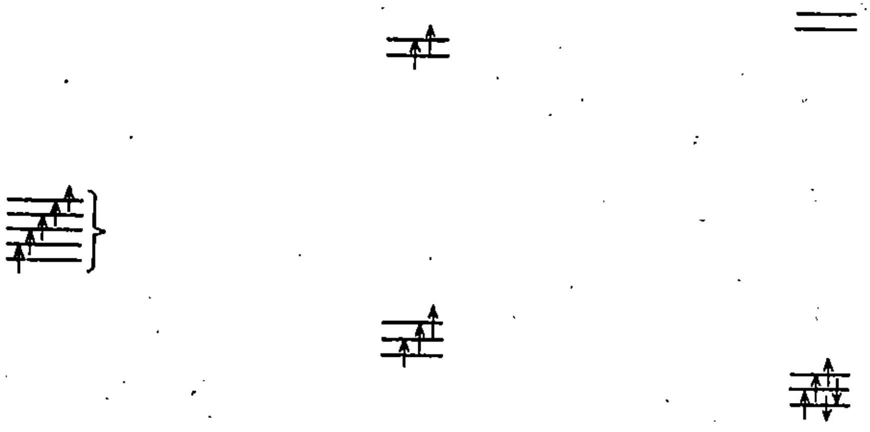
Fig. 14.11 may given an erroneous impression that the d-orbitals in degenerate state are lower in energy than in the complex. This arises since we are considering only the repulsive forces between the d-orbitals and the ligands. The real state of affairs may be depicted by the following diagram.



Let us consider one of the consequences of the d–orbital energy level splittings. $[Ti(H_2O)_6]^{3+}$ is a d^1 system meaning that the central metal ion, Ti^{3+}, has one electron in d–orbital. In a free ion this one electron could be found in any one of the d–orbitals since all the d–orbitals are equal in energy. However, in the complex $(Ti(H_2O)_6]^{3+}$ the electron would prefer to go into any one of the t_{2g} set of orbitals since they are lower in energy. By doing so it will lower the energy of the system by $2/5\ \Delta_o$ as compared to the energy of the Ti^{3+} ion in a uniform field. This difference in energy between the ion in a uniform field and the complex is called Crystal Field Stabilisation Energy (CFSE). If there are two electrons present in t_{2g} set of orbitals, the CFSE would be equal to $2 \times (-2/5\Delta_o)$ or $-4/5\Delta_o$. Hence, we can calculate the CFSE for any complex provided we know the electronic distribution.

Raise in energy is given a positive sign and hence, the lowering is given a negative sign.

Consider a complex, $Fe^{(III)}L6$, which belongs to the d^5 system. In a Fe^{3+} ion in a spherically uniform field the five d-electrons will go into five different orbitals with parallel spins according to Hund's rules, as shown in Fig. 14.12(a). However, when it is surrounded by six ligands, the five d-electrons will distribute themselves in either of the following two ways, Fig. 14.12 (b) and (c) :


Fe^{3+} ion in a uniform field (a)

Weak ligand field, high spin complex (b)

Strong ligand field, low spin complex (c)

Fig. 14.12 : Possible configurations of a d^5 system in an octahedral field

Fig. 14.12(b) represents the complex in high spin state with five unpaired electrons while Fig. 14.12(c) shows the low spin configuration. These conclusions are the same as obtained by valence bond theory with a slight difference. The present theory gives the reason for the existence of the two types of complexes and can also predict which of the two configurations will be more stable in a particular case provided certain parameters are known. These parameters are Δ_o, crystal field splitting energy and P, the pairing energy. Whenever we put an electron in e_g set of orbitals, the system gets destabilised by energy equal to $3/5\Delta_o$. On the other hand, by putting two electrons in the same orbital, the system again gets destabilised by an amount equal to pairing energy P. The decision as to which of the two configurations, i.e., high spin or low spin is more stable is rather easy to make. If the pairing energy is greater than Δ_o, then the two electrons will prefer to go in different orbitals with parallel spins giving a high spin complex. The reverse will be true for a low spin complexes. Thus, we can write

if $P > \Delta_o$ ------ high spin complex

$P < \Delta_o$ ------ low spin complex

$P = \Delta_o$ ------ the two states are in equilibrium.

Pairing energy, P, depends mainly on the electronic distribution of the central metal ion and its value can be obtained from the atomic spectra of the element. The Δ_o is obtained from the molecular spectra of the complex. It depends on the metal ion, ligand and the geometry of the complex. Once these two values are known for any complex, you will know whether it will be high spin or low spin and you will also be able to calculate the CFSE. Table 14.6 gives the pairing energy values for d^4 to d^7 ions of first row transition elements as well as Δ_o values for a few complexes. In d^1, d^2, d^3, d^8, d^9 and d^{10} systems only one configuration each is possible.

Table 14.6 : P and Δ_0 values for octahedral complexes of some first row transition elements

d^n	Ion	Pairing energy (cm^{-1}) P	Complex	Δ_o (cm^{-1})
d^4	Cr^{2+}	20,425	$[Cr(H_2O)_6]^{2+}$	13,900
	Mn^{3+}	25,215	$[Mn(H_2O)_6]^{3+}$	21,000
d^5	Mn^{2+}	23,825	$[Mn(H_2O)_6]^{2+}$	7,800
	Fe^{3+}	29,875	$[Fe(H_2O)_6]^{3+}$	13,700
d^6	Fe^{2+}	19,150	$[Fe(H_2O)_6]^{2+}$	10,400
			$[Fe(CN)_6]^{4-}$	33,000
	Co^{3+}	23,625	$[Co(H_2O)_6]^{3+}$	18,200
			$[Co(NH_3)_6]^{3+}$	22,900
			$[Co(CN)_6]^{3-}$	33,500
d^7	Co^{2+}	20,800	$[Co(H_2O)_6]^{2+}$	9,300

As you can see from Table 14.6 there is a large variation in Δ_o values as you change the ligand. It is possible to list most common ligands in order of increasing field strength, Δ_o. Such an arrangement, known as spectrochemical series, is given below:

$I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < H_2O < NCS < NH_3 < en > bipy < phen < NO_2^- < CN^-$

Spectrochemical series helps us in relationalising the differences in the spectral properties of complexes. As the strength of the crystal field created by the ligands Δ_o increases, the frequency of absorption of light by the complex would also increase. Absorption of high frequency radiations means that light of lower frequency will be transmitted and will be responsible for the particular colour of the complex. It thus explains as to why the colours of a series of complexes of one particular metal ion, in the same oxidation state having the same geometry, could be different. For example, the following four octahedral compounds of Co^{3+} ion show different colours which are in accordance with spectrochemical series.

Complex	Δ_o (cm^{-1})	Colour
$[Co(C_2O_4)_3]^{3-}$	18,000	Dark green
$[Co(H_2O)_6]^{3+}$	18,200	Blue
$[Co(NH_3)_6]^{3+}$	22,900	Golden-brown
$[Co(CN)_6]^{3-}$	33,500	Yellow

The spectrochemical series can sometimes be helpful in making certain prediction about the complex. For instance, if we know that a particular metal ion gives a low spin complex with ammonia ligands, then it is certain that its analogus compound with CN^- ligands would also be low spin, since CN^- creates much stronger crystal field than NH_3. However, these predictions are pure qualitative in nature and many a times the order may be reversed for adjacent ligands in the spectrochemical series.

Once again let us consider one final consequence of the splitting of d-orbital energy levels. Except for d^{10} configuration, all other configurations in an octahedral field would have e_g

set of orbitals incompletely filled. Under the circumstances, electrons from t_{2g} orbitals can jump to e_g orbitals, if the correct amount of energy is supplied to the complex. In the case of transition metal complexes the energy required for the electronic transition from ground state to the excited state generally falls in the visible part of the electromagnetic radiation. A plot of absorbance versus the wavelength of light for the compound is known as absorption spectrum of the complex. If the complex absorbs the red portion of the white light, the blue part will pass through the compound and the compound will appear blue to our eyes. As an example, we take $[Ti(H_2O)_6]^{3+}$ where in the ground state one electron of Ti^{3+} ion is present in t_{2g} set of orbitals as shown in Fig. 14.13.

When light associated with energy hν, such that $\Delta_o = h\nu$, is passed through a solution of $[Ti(H_2O)_6]^{3+}$, absorption of light takes place and the lone electron from ground state is raised to the excited state. Experimentally, it is found that the energy for this absorption is around 20,400 cm^{-1}. Hence, we can write $\Delta_o = 20{,}400\ cm^{-1}$ and CFSE = $-2/5 \times 20{,}400$ or $-8{,}160\ cm^{-1}$ or approximately 98 kJ mol^{-1}.

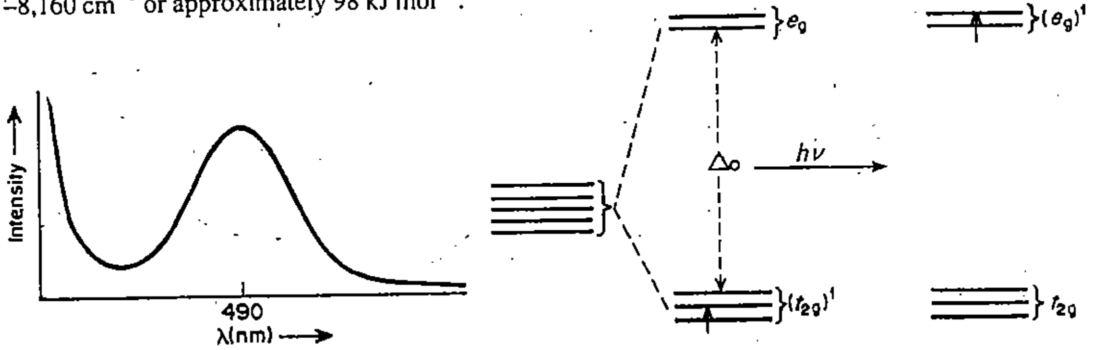


Fig. 14.13 : (a) Absorption spectra of $[Ti(H_2O)_6]^{3+}$ corresponding to (b) the electronic transition $(t_{2g})^1 \rightarrow (e_g)^1$

In the next subsection, we shall consider the tetrahedral geometry and how the splitting of the d-levels takes place. You should try the following SAQ first.

SAQ 5

If pairing energy P for Fe^{3+} ion is 29,875 cm^{-1} and Δ_o for $[Fe(H_2O)_6]^{3+}$ is 13,700 cm^{-1}, find out

(i) whether the complex is high spin or low spin

....

....

....

....

(ii) the number of unpaired electrons

....

....

....

....

(iii) whether the complex is coloured or not ?

....

....

....

....

Crystal Field Splitting in Tetrahedral Field

A tetrahedron can be viewed as a part of cube where the metal ion occupies the centre of the cube and the four ligands are placed at four alternate corners of the cube (Fig. 14.14).

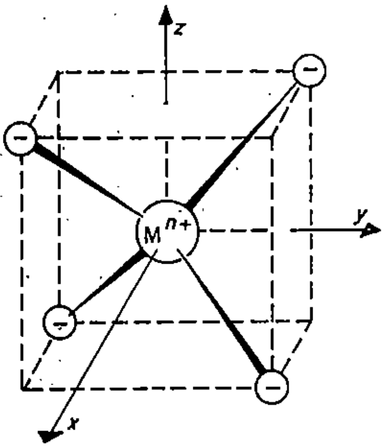


Fig. 14.14 : Tetrahedron as a part of a cube

It is obvious from the figure that none of the orbitals d_{xy}, d_{yz}, d_{xz} or $d_{x^2-y^2}$ and d_{z^2} point directly at the ligands but the first set of three orbitals are nearer to the ligands as compared to the last two orbitals. Hence, in this case the *d* orbital splitting will be as shown in Fig. 14.15.

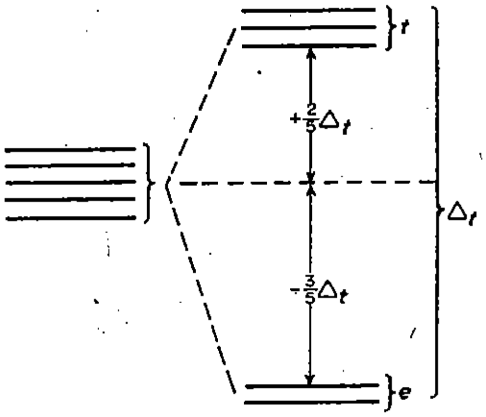


Fig. 14.15 : Splitting of *d*–orbitals in a tetrahedral crystal field.

Note that the lower set of orbitals is denoted by a symbol '*e*' while the upper is designated as '*t*' which are different from those used in case of octahedral complexes. This is so because a tetrahedral molecule does not possess a centre of symmetry. The difference in energy between the two sets of orbitals is denoted by Δ_t. It is found that if the metal ion and the ligands remain same and the distances between metal and ligands are also same in octahedral and tetrahedral compounds then,

$$\Delta_t = \frac{4}{9}\Delta_o,$$

Following the arguments parallel to those used in case of octahedral complexes we find the each orbital of e set is lowered by $-3/5\Delta_t$ and each orbital belonging to the 't' set is raised in energy by $+2/5\Delta_t$.

In a d^1 or d^2 system the electrons will always go in the '*e*' set of orbitals with the release of corresponding amount of energy (CFSE). For d^1 it will be $-3/5\Delta_t$ and for d^2 it will be $2(-3/5\Delta_t)$ or $-6/5\Delta_t$. These values can be converted in terms of Δ_o for comparison. Again for systems from d^3 to d^6 there are two different configurations possible in each case as shown in Fig. 14.16.

From Table 14.5, you can see that the pairing energies (*P*) and Δ_o for common ligands are of comparable order of magnitude. It is also true that Δ_t is almost one-half the value of Δ_o. Hence, we can say that pairing energy, *P*, is almost double the value of Δ_t or in other words $P >> \Delta_t$. Under the circumstances all the electrons in any system in tetrahedral field will spread out in *e* and *t* sets of orbitals rather than pair up in *e*–orbitals. To put it in other terms it is said that the low spin tetrahedral complexes of the first row transition elements are not known.

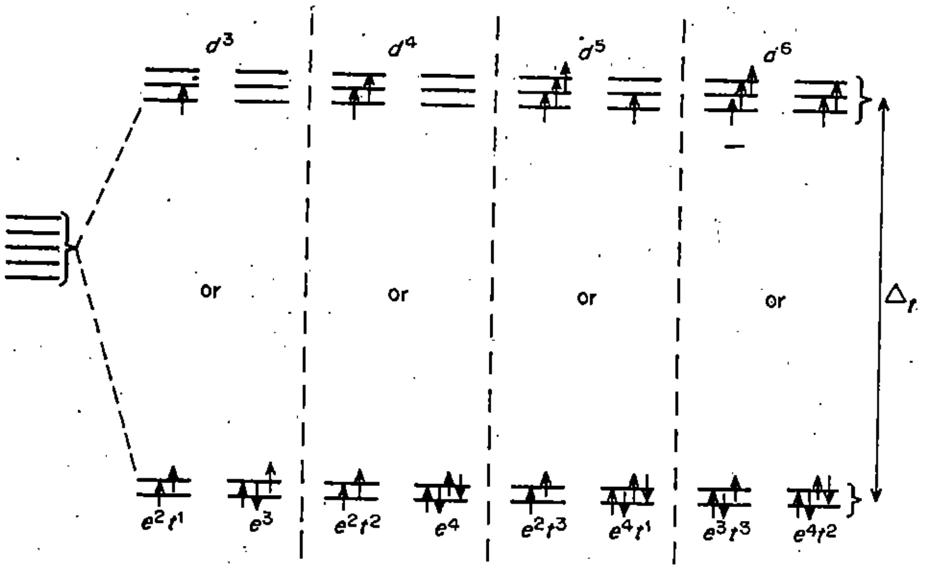


Fig. 14.16 : Possible electronic configurations for d^3 to d^6 systems in a tetrahedral crystal field.

Crystal Field Splitting in Square Planar Complexes

In order to find the d–orbital splitting in a square planar complex, it is easier to start with an octahedral compound where splitting patterns are known and then imagine slowly moving two trans ligands away from the metal. This would at first distort the molecule which is known as tetragonally distorted octahedron. Moving the ligands further to such an extent that the interaction between the metal ion and the ligands is practically nil would result in a square planar compound. This situation is best described as square planar complex because the other two ligands are so far off that they can be considered to be unattached to the metal ion and are thus unable to form a true chemical bond. These situations are depicted in pictorial form in Fig. 14.17.

Let us see what happens to the energy values of d- orbitals under these stages. We start with the energy level diagram of a lower triplet (t_{2g}) and upper doublet (e_g) in an octahedral field. Fig. 14.17(I). When the two trans ligands placed along say, z-axis, are moved away the most affected orbital would be d_{z^2}. The repulsion between the orbital and the ligand will decrease, thus making it more stable compared to others. At the same time all other orbitals containing z–axis namely d_{xz}, d_{yz} will also be affected by the movement of the two ligands along the z-axis. However, these will experience less effect than the d_{z^2} orbital. These two orbitals will become lower in energy by equal amount but less than d_{z^2} as indicated by different slopes in Fig. 14.17

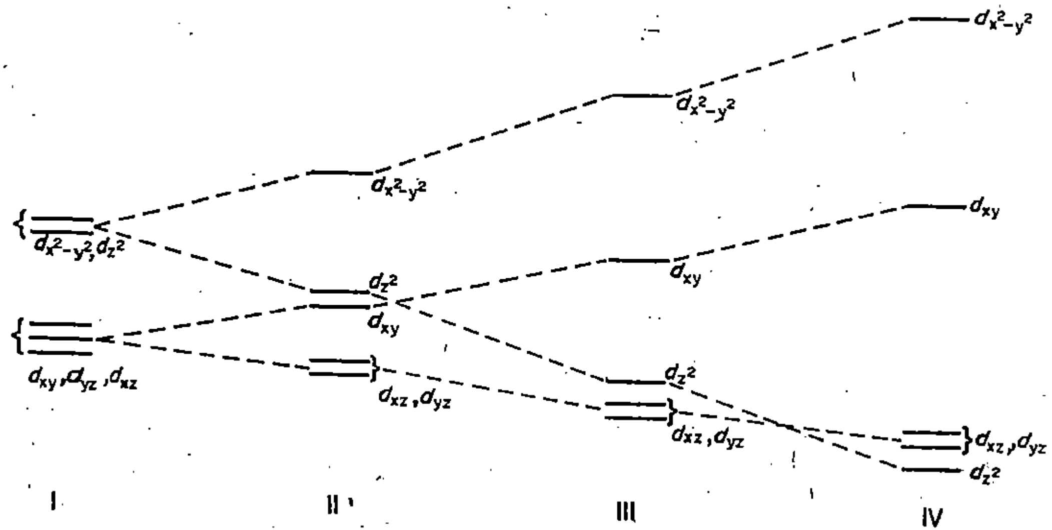


Fig. 14.17 : Crystal field splitting of d–orbitals in a tetragonally distorted octahedral field

For e_g set of orbitals, if d_{z^2} orbital is lowered in energy due to distortion, then $d_{x^2-y^2}$ must go up in energy by an equal amount so that the net result is no change. Similarly, d_{xz} and d_{yz} are lowered whereas d_{xy} is raised in energy by such an amount that the net resultant is zero. Thus in a distorted octahedral molecule the orbitals in order of increasing energy or decreasing stability are : d_{xz}, d_{yz} (degenerate), d_{xy}, d_{z^2}, $d_{x^2-y^2}$ as shown in Fig. 14.17 (II). A further distortion results in the formation of a square planar complex. Here, d_{z^2} is lowered so much so that it is almost equal to d_{xz}, d_{yz} orbitals Fig. 14.17 (III). Much higher will be d_{xy} and the least stable or the highest in energy would be $d_{x^2-y^2}$. In a few rare instances d_{z^2} falls even below d_{xz} and d_{yz} orbitals Fig. 14.17 (IV). We realise that in case of a square planar complex we shall not be able to calculate quantitatively the energy values of the orbitals in terms of crystal field splitting parameter (Δ_0). The actual values have, however, been calculated; based on these values we can calculate CFSE as well as the magnetic moment for any particular complex. It has been observed that at least the first row transition elements show greater tendency to form square planar rather than tetrahedral complexes. These observations are in line with the CFSE calculations for the two geometries.

We have thus come to the stage where we can appreciate that a simple electrostatic approach can lead to many useful results and these results are pretty close to the experimental values. We do not expect to get perfect results since our assumptions so far are imperfect. We are, thus, left with two choices either to discard the theory completely and look for a new approach or to modify it in such way so as to account for the observed discrepancies.

Molecular orbital theory is a completely different approach. It starts with identifying the metal orbitals and the ligand orbitals (hybridised) which have the correct symmetry and energies for combination to yield molecular orbitals. The total electrons from the ligands and metal ion are placed into these molecular orbitals and the bond order, which is a measure of the covalency, is determined. Once the energy sequence of molecular orbitals in a complex is known, the properties of the complex can be all explained. It does not start with any assumption regarding the type of bond involved in the complex; rather it comes out as a natural consequence of the theory. Further, it is much more comprehensive yet the theory has not become very popular. The reason for this is that the quantum mechanical calculations involved are too tedious and many a time cannot be solved. We shall not go into the details of this theory but would like to emphasise that this is the best and comprehensive approach; in all those cases where precise calculations have been possible, the results are in almost perfect agreement with the experimental observations.

The second approach, though not as perfect, is more useful. Here we do all the calculations based on crystal field theory. The differences between the calculated values and the experimental results are accounted for on the basis of covalency. This is known as **adjusted crystal field theory** or sometimes referred to as 'ligand field theory'. Some authors prefer to call the molecular orbital theory as ligand field theory.

In the next section we shall discuss very briefly a few applications of complexes. Try the following SAQ before proceeding to the next section.

SAQ 6

The complex $[NiCl_4]^{2-}$ contains two unpaired electrons while $[Ni(CN)_4]^{2-}$ is diamagnetic. Propose structures for these two complex ions on the basis of CFT.

14.7 APPLICATIONS

Innumerable applications of coordination compounds in fields as divergent as biology, industry, agriculture, analytical chemistry make it impossible to cite them all at one place. A few selected examples are given below to indicate their application to different fields. Let us first consider the role which the complexes play in gravimetric, volumetric, colorimetric analysis.

A selective precipitation of Fe(III), Al(III) or Cr(III) with amonia takes place keeping Ag(I), Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) in solution as soluble ammine complexes.

From a mixture of Fe(III), Cu(II), Pb(II), Bi(III) and Ag(I), only Ag(I) ion can be precipitated as iodide, all other ions can be made to remain in solution by previous addition of EDTA (ethylenediamine tetraacetate ion) to the solution.

The EDTA complexes of some metal ions are stable even to hydrogen sulphide. For example, in the presence of EDTA, Pb(II) is not precipitated as sulphide from weakly acidic solutions; Ni(II), Co(II), Mn(II) and Zn(II) which are normally precipitated as sulphides in ammonical solution would also not give any precipitate.

The EDTA is one of the most important reagents now used in volumetric analysis. Since the estimation of various cations using EDTA is largely pH dependent, EDTA is also used as masking or demasking agent in titration of mixture of cations.

Yet another effective masking agent is the cyanide ion. It forms stable cyano complexes with the cations of zinc(II), cadmium(II), mercury(II), cobalt(II), nickel(II), copper(II) etc., but not with alkaline earths. Therefore, it is possible to estimate calcium(II), magnesium(II), in the presence of above mentioned metal ions with an excess of cyanide ion.

Quantitative determination of a number of ions like Cu, Ag, Zn, Fe, Ni, Co, Cd etc. has been done by using 1,2,3-benztriazole as precipitating agent under different experimental conditions. This is just one such reagent out of many known ligands. Specific reagents like dimethylglyoxime are used to isolate red Ni(II) complex and cupferron is used for the estimation of Fe, Ti etc.

Colorimetric analysis depends on the variation of the colour with the change in concentration of the compound. Usually, absorption of light is measured at different known concentrations of a compound and a graph is plotted between the absorption and concentration. Absorption of an unknown concentration of the compound is then measured and its concentration evaluated from the graph. Thus, 1,10-phenanthroline or 2,2′-bipyridyl which forms coloured complexes with iron, are often used for its determination in fruits, wines, leather and other biological materials. There are many such reagents which are fruitfully employed for the quantitative determination of various metal ions.

Bioinorganic chemistry or the study of the role of metal ions in biological cycles is mainly the study of some typical metal complexes of biological importance. These complexes act as oxygen carriers, electron transfer agents, catalyst and as drugs. Out of all the first row transition elements, perhaps iron plays the most important role. The source of energy in human body comes from the oxidation of carbohydrates, proteins and fats. Transfer of electrons from these nutrients to the oxygen molecule is not direct but through a complex chain of molecules. One main electron transfer molecules in the chain is called cytochrome. It consists of two parts: an iron complex heme (Fig. 14.18) and a protein. The iron ion can be either Fe^{2+} or Fe^{3+}. The ligand is called by a general name porphyrin. Porphyrin is a name given to a large number of compounds having the same central ring structure as shown in Fig. 14.19 but having different substituent groups.

A magnesium complex of porphyrin (with different substituents from the one shown in Fig.14.18) is called chlorophyll, the green colouring material in plants and which is essential for photosynthesis.

Hemoglobin, plays the role of oxygen carrier in mammalian blood. In hemoglobin Fe^{2+} ion is not only surrounded by four nitrogens of porphyrin but the fifth position is occupied by a nitrogen of the protein as shown in Fig. 14.20.

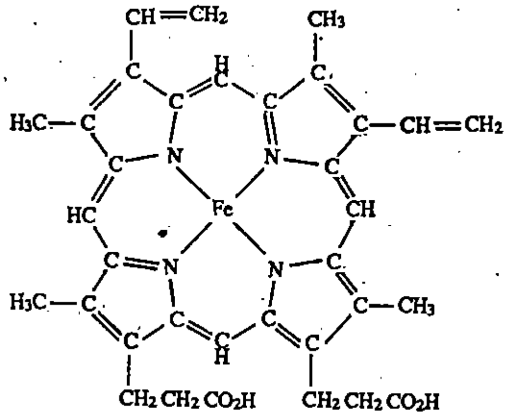


Fig. 14.18: Structure of heme

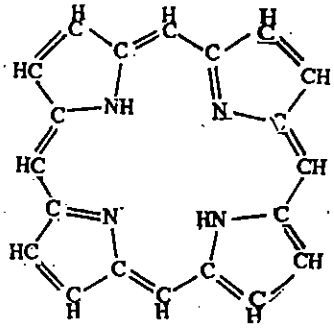


Fig. 14.19 : The structure of porphine

The sixth position marked by X is either occupied by H_2O or O_2 molecule. Important thing to note is that Fe^{2+} in hemoglobin does not get oxidised to Fe^{3+}. On the other hand if gaseous O_2 is bubbled into an aqueous solution containing heme, the Fe^{2+} gets oxidised to Fe^{3+}. It is believed that the oxidation of Fe^{2+} to Fe^{3+} is prevented by the bulky protein in the hemoglobin. Each hemoglobin can bind four O_2 molecules to give a bright red complex. When oxygen molecules are replaced by water molecules it gives a bluish coloured complex which is characteristic of venous blood. Both CO and CN^- can form more stable complexes with Fe^{2+} ion than molecular oxygen. Thus they can destroy the normal functioning of blood as in oxygen carrier.

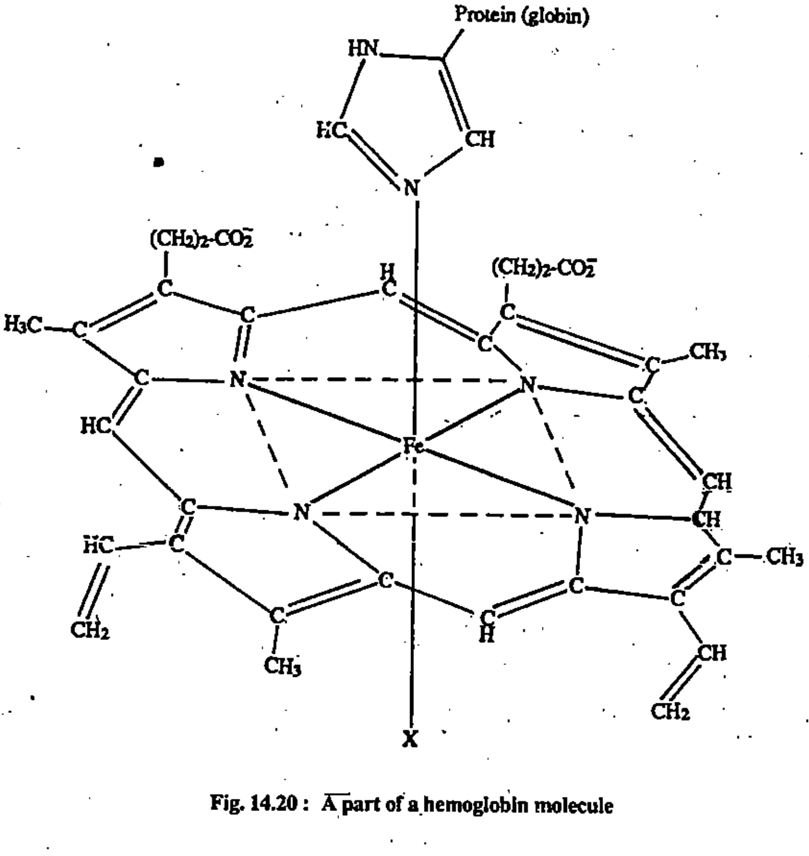


Fig. 14.20 : A part of a hemoglobin molecule

Catalytic activity of metalloenzymes depends on the complex forming ability of a particular metal ion. One specific example is carbonic anhydrase which is a Zn^{2+} activated metalloenzyme. Carbonic anhydrase is an important enzyme of respiration. It catalyses dehydration of carbonic acid and the release of CO_2.

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

Carbonic anhydrase consists of a zinc ion which is tetrahedrally coordinated by three imidazole nitrogen atoms and a water molecule (Fig. 14.21). The active site of the enzyme is the one where water molecule is attached to the zinc ion.

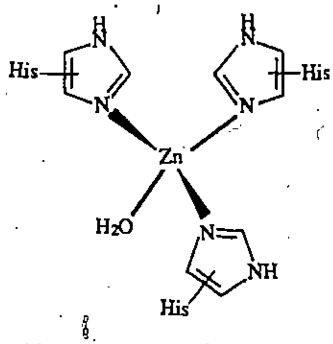


Fig. 14.21 : Skeleton of carbonic anhydrase

Finally we shall consider a few examples of the application of complex formation in industrial processes. It is quite an arbitrary selection.

Extraction of metals is very often done by complex formation. For example, the cyanide process for the extraction of silver and gold is well known. Purification of metals is often accomplished by solvent extraction of neutral complexes. Commonly encountered ligands for such purposes are oxine, acac, dmg, salicylaldoxime or salicyldineimines. The role of complexes as catalysts in the production of organic chemicals is yet another field of importance. For example various complexes of copper, silver, mercury, ruthenium, cobalt etc. are known to be good catalysts for hydrogenation process [RhCl $(PPh_3)_3$], tris(triphenylphoshine) chlororhodium(I) is one of the best known and thoroughly investigated compounds. Similarly, oxidation, polymerisation, hydroformylation of olefins all involve the formation of complexes as intermediates. However, quite often they are not simple complexes rather they are organometallic compounds.

14.8 SUMMARY

This unit represents an introduction to the coordination chemistry with special emphasis on the first row transition metal complexes. In this unit we have learnt about the basic definitions of the terms used in the study of coordination compounds. Next we learnt the rules for naming of these compounds according to IUPAC system of nomenclature. An important aspect of coordination compounds, isomerism, has been explained in detail. It is to show convincingly that the phenomenon of isomerism is more common and varied in coordination compounds than even in organic chemistry.

We have learnt three main theories of bonding as applied to coordination compounds. Molecular orbital theory which is perhaps the best theory has been left out from discussion at this stage because of its complexity.

In the last section of the unit we learnt about a few of the applications of coordination compounds in analytical chemistry, biology and industry.

14.9 TERMINAL QUESTIONS

1. Give formulas of the following complexes:
   (a) nitritopentaamminecobalt(III) chloride
   (b) dichlorobis(ethylenediamine) rhodium(III) ion
   (c) dicarbonatodiamminecobaltate(III) ion
   (d) potassium tetracyanonickelate(II)

2. Write down the names of the following species
   (a) $K[CrOF_5]$; (b) $[Cr(en)_2(H_2O)(NCS)]^+$
   (c) $[Co(en)_3][Fe(CN)_6]$; (d) $[Cr(C_5H_5N)_2(H_2O)Cl_3]\cdot H_2O$

3. How do you account for the indicated molecular geometry for the following compounds in terms of valence bond theory:

   $[AuCl_4]^-$ – Square planar; $[Fe(CN)_6]^{3-}$ – Octahedral;

   $[GaCl_4]^-$ – Tetrahedral; $[NiCl_4]^{2-}$ – Tetrahedral

4. The complex $[PdCl_2(PPh_3)_2]$ gives geometrical isomers and is found to be diamagnetic whereas an analogous compound $[NiCl_2(PPh_3)_2]$ does not give any geometrical isomers and is found to be paramagnetic. Can you explain these observations?

5. An aqueous solution of $CoCl_3 \cdot 6NH_3$ is found to be a better conductor of electricity than an aqueous solution of $CoCl_3.4NH_3$. No ammonium ions are detected by the addition of H_2SO_4 to the solutions of either of these compounds. Can you explain the difference in the conductivities of two solutions?

6. For which of the following complexes are optical isomers possible? Give reasons for your answer.

   (a) $[Fe(CN)]_6^{3-}$ (b) $[Co(en)_2(NH_3)_2]^{3+}$ and

   (c) $[Cr(C_2O_4)_3]^{3-}$

14.10 ANSWERS

Answers to Self-Assessment Questions

1. The coordination number and oxidation state of the metal ion in (a) to (d) are given below:

   (a) 6, +2, (b) 6, +3, (c) 4, +2, (d) 4, +2

2. (a) i) Trinitrotriamminechromium(III)

   ii) Pentaammineaquacobalt(III) chloride

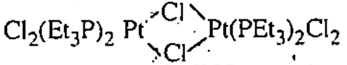
   iii) Hexaamminechromium(III) hexathiocyanatochromate(III)

   iv) Potassium trioxalatoaluminate(III)

   v) Tetrapyridineplatinum(II) tetrafluoroplumbate(II)

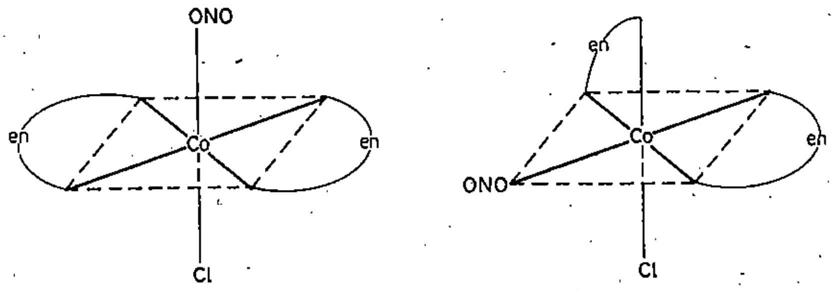
   vi) Hexachloro-µ-trichlorodithallate(III) ion

   (b) i) $[Co(NH_3)_6]Cl_3$ ii) $K_3[Fe(ox)_3]$

   iii) 

   $$Cl_2(Et_3P)_2Pt\begin{matrix}\diagup Cl \diagdown \\ \diagdown Cl \diagup\end{matrix}Pt(PEt_3)_2Cl_2$$

3. The compound $[Co(en)_2Cl_2]NO_2$ may have $[Co(en)_2(NO_2)Cl]Cl$ as an ionisation isomer. This ionisation isomer in turn may give a linkage isomer, $[Co(en)_2(ONO)Cl]Cl$. These three isomers would thus constitute what are known structural isomers. All three structural isomers can exist as cis- and trans- isomers, one such pair is given below:



The cis- form of each of the above three compounds would have an optical isomer an enantiomer. This would make a total of nine possible isomers for the given compound.

4. Consider the two compounds $[Co(H_2O)_6]^{2+}$ and $[Co(CN)_6]^{4-}$ each of which contain Co^{2+} ion in an octahedral field. Obviously the compound $[Co(H_2O)_6]^{2+}$ is high spin

having a magnetic moment value of 4.6 BM whereas $[Co(CN)_6]^{4-}$ is low spin with a magnetic moment value of 1.9 BM. The complex $[Fe(NO_2)_6]^{4-}$ contains Fe^{2+} which belongs to a d^6 system. As the magnetic moment of the complex is zero, it indicates that all the six *d*–electrons are paired up. Hence the compound is low spin. On the otherhand, the magnetic moment of 5.94 BM for the complex $[Fe(H_2O)_6]^{3+}$ corresponds to five unpaired electrons in Fe^{3+}. It indicates that there is no pairing of *d*–electrons of Fe^{3+} ion, hence the complex is high spin.

5. i) Since $P >> \Delta_0$, the complex should be high spin.

   ii) Fe^{3+} in high spin state in $[Fe(H_2O)_6]^{3+}$ will have the following electronic configuration:

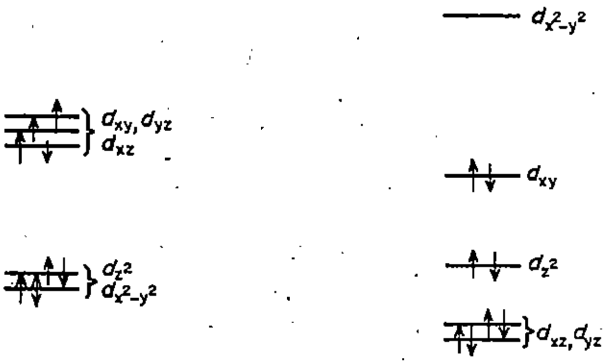
   ↑ ↑ e_g^2

   ↑ ↑ ↑ t_{2g}^3

   Hence, the number of unpaired electrons is 5.

   iii) Yes, it should be coloured. Since the e_g orbitals are not completely filled, the electrons from t_{2g} set of orbitals can be excited to e_g orbitals. Such a transition would absorb light in the visible region and hence the compound would appear coloured.

6. Since both the compounds given are tetra-coordinated, but show different magnetic properties, they must differ in their geometries. The two possible geometries for tetra-coordinated compounds are tetrahedral or square planar. According to crystal field theory, the *d*-orbital splitting in the two cases can be shown as given below:



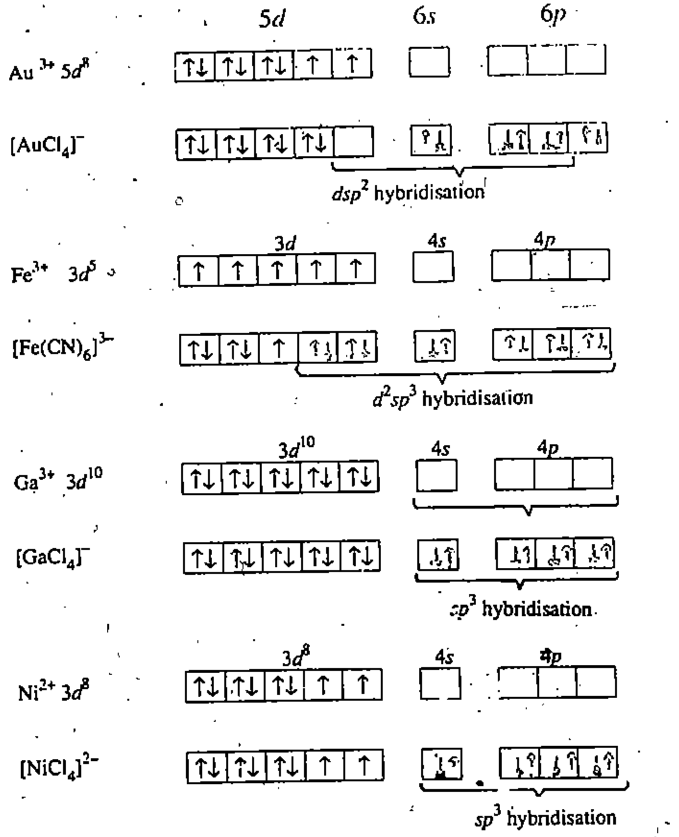
(a) (b)

Electronic distribution in (a) tetrahedral field (b) square planar field.

As you can see, if the configuration is tetrahedral the compound would be paramagnetic and would have a magnetic moment corresponding to two unpaired electrons. However, if the geometry is square planar, all the eight electrons would pair up in low energy orbitals rather than any electron occupying $d_{x^2-y^2}$ orbital. Hence, the compound $[NiCl_4]^{2-}$ is tetrahedral and $[Ni(CN)_4]^{2-}$ is square planar.

Answers to Terminal Questions

1. (a) $[Co(NH_3)_5(ONO)]Cl_2$
   (b) $[Rh(en)_2Cl_2]^+$
   (c) $[Co(NH_3)_2(CO_3)_2]^-$
   (d) $K_2[Ni(CN)_4]$
2. (a) Potassium pentafluorooxochromate(VI)
   (b) Isothiocyanatoaquabis(ethylenediamine) chromium(II) ion
   (c) Tris(ethylenediamine) cobalt(III) hexacyanoferrate(III)
   (d) Trichloroaquadipyridinechromium(III) monohydrate.
3. According to valence bond theory, the geometry of any species is guided by the hybrid orbitals available on the central metal ion for bond formation. Electronic configuration and type of hybrid orbitals used for different anions are given below:



4. Since [$PdCl_2(PPh_3)_2$] is a four coordinated complex and gives geometrical isomers, it must have square planar geometry. It will also be diamagnetic as explained in answer to SAQ 6. Though [$NiCl_2(PPh_3)_2$] is also four coordinated and belongs to a d^8 system just like the first compound, yet it does not give geometrical isomers. This indicates a tetrahedral geometry for the compound which will also be paramagnetic.

5. As no ammonium ions are detected in the solutions of these compounds, it indicates that ammonia molecules are in the first coordination sphere of the metal ion in both the cases. The compound $CoCl_3.6NH_3$ can, therefore, be formulated as [$Co(NH_3)_6$]Cl_3 which may give four ions per mole in solution as indicated by the conductivity of the solution. Since, the solution of $CoCl_3.4NH_3$ is less conducting than that of $CoCl_3.6NH_3$, it means it gives less than four ions per mole in solution. It will be possible only if two of the chlorines are also present in the first coordination sphere and the compound has the formula [$Co(NH_3)_4Cl_2$]Cl.

6. Since, compound (a) is a completely symmetrical molecule, it will not give optical isomers. Trans-isomers of (b) and (c) will also be symmetrical and, therefore, will not give optical isomers. Only the cis forms of (b) and (c) which do not have any plane or centre of symmetry will give optical isomers.

UNIT 15 ISOLATION AND PURIFICATION OF METALS

Structure

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  Oxide Minerals
  Oxosalts
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15.8 Summary
15.9 Terminal Questions
15.10 Answers

15.1 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.

After studying this unit, you should be able to:

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

- use Ellingham diagrams for selecting suitable reducing agents for extraction of metals,
- describe various methods of purification of metals, and
- discuss the importance and uses of alloys.

15.2 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 15.1. You may note that about 75% of the earth's crust is composed of nonmetals, oxygen and silicon. The relative abundance of only three industrially important metals, i.e., aluminium, iron and magnesium is more than 2%. The abundance of most other useful metals in the earth's crust is very low. Therefore, if the metals had been uniformly distributed in earth's crust, it would have not been possible to extract them. But luckily, the metals generally in the form of their minerals, are unevenly distributed and are accumulated 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 overburden. The thickness of overburden may vary from a few metres as in case of iron ore to thousands of metres as in case of deposits of gold. The mineral deposit is brought to the surface by mining.

Table 15.1: 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

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:

15.2.1 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.

15.2.2 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.

15.2.3 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 ($Al_2O_3 \cdot 2H_2O$), cassiterite (SnO_2), cuprite (Cu_2O), zincite (ZnO), rutile (TiO_2), pyrolusite (MnO_2), chromite ($FeO \cdot Cr_2O_3$), uraninite or pitchblende ($2UO_3 \cdot UO_2$), etc.

15.2.4 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 ($MgCO_3 \cdot CaCO_3$), cerussite ($PbCO_3$), malachite ($CuCO_3 \cdot Cu(OH)_2$), calamine ($ZnCO_3$), barytes ($BaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), anglesite ($PbSO_4$), soda nitre ($NaNO_3$), monazite ($LaPO_4 \cdot CePO_4 \cdot NdPO_4 \cdot PrPO_4 \cdot Th_3(PO_4)_4$), 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.

15.2.5 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 (KCl), horn silver ($AgCl$), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), fluorspar ($CaF_2$) and cryolite ($AlF_3 \cdot 3NaF$).

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

As said earlier, in addition to the earth's crust, oceans also provide a huge storehouse of minerals in which the metals occur primarily as soluble sulphates and halides. It is estimated that one cubic kilometre of sea water contains 1 million tonnes of magnesium, 1,500 tonnes of strontium and 5 tonnes each of gold, copper, manganese, zinc and lead. Magnesium is already being extracted from sea water. In future, greater attention will be paid to sea as a source of raw materials when supplies of ore deposits on land are depleted. In addition to sea water, nodules or lumps about the size of an orange have been found on sea bed at depths of 4,000-5,000 metres. The nodules are relatively rich in manganese (25%) and iron (15%). Recently technology for deep sea mining of these nodules has been developed.

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

SAQ 1

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

....

....

....

....

15.3 BENEFICIATION OF ORES

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

The methods used for beneficiation of ores are based on differences in such properties of ores and gangue as colour, lustre, size, density, and wettability by water or oil. The simplest method of ore beneficiation consists of hand picking of ore particles, which is based on difference in colour, lustre or shape and size of ore particles and gangue. Hand picking can be adopted in areas where labour is cheap. However, this method is outdated and is practised only in very specific cases when other methods are not possible, e.g., hand picking of diamonds from gravel and clay. Important methods of beneficiation of ores are gravity separation, magnetic separation and froth flotation, which we will now discuss in brief.

15.3.1 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.

15.3.2 Magnetic Separation

This technique is based on the difference in magnetic properties of minerals. If the ore but not the gangue is attracted by a magnetic field, it can be concentrated to yield a sample which is rich in the metal. The pulverised mineral is passed over a rubber belt which moves on a pully in a magnetic field (Fig. 15.1). The non-magnetic gangue particles fall off in a verticle position when the belt passes over the pully, but the magnetic ore clings to the belt. When the belt passes out of the influence of the magnetic field, the ore drops off. Magnetite (Fe_3O_4), haematite (Fe_2O_3), wulframite ($FeWO_4$), chromite ($FeO{\cdot}Cr_2O_3$) and ilmenite ($FeO{\cdot}TiO_2$) are some of the minerals which are separated from non- magnetic impurities by this method.

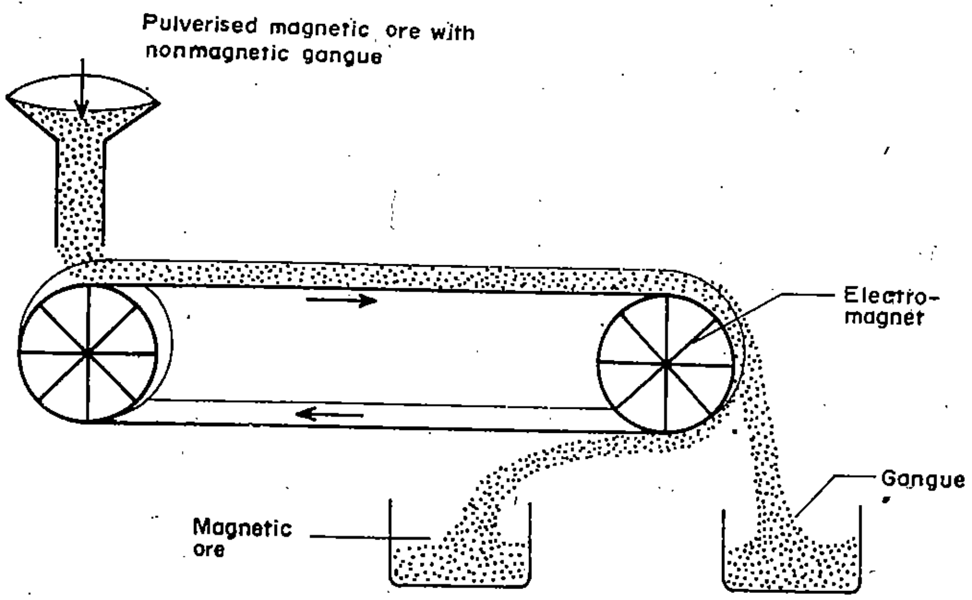

Fig. 15.1 : Magnetic separation of ores

15.3.3 Froth Flotation Process

Froth flotation process is the most important method for beneficiation of ores. This process has made possible the beneficiation of low grade ores which could not be processed earlier. The process of froth flotation is widely employed to concentrate sulphide ores. However, many oxide ores can also be concentrated by this process. It is based on the difference in wettability of different minerals. In this process, the ore is finely ground to give a thick pulp containing 30-40% solids. A small amount of pine oil, oleic acid or cresylic acid, which cause frothing, is added to the pulp. A substance, which is capable of repelling water from the surface of mineral and thus promotes attachment of mineral particles to 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. 15.2).

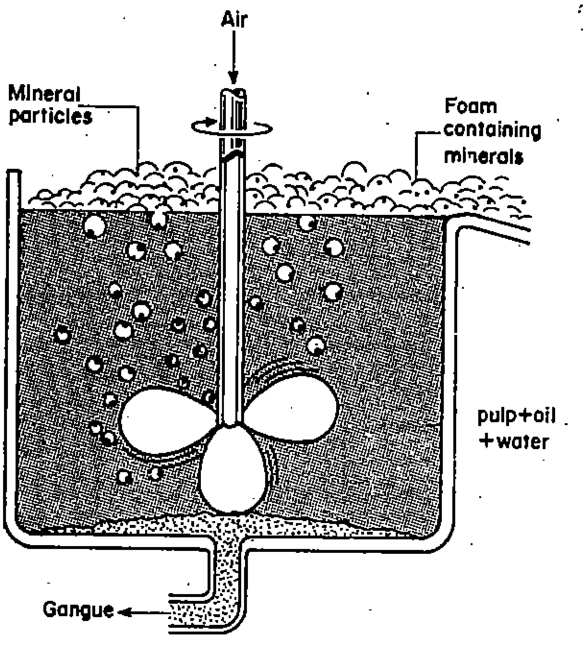

Fig. 15.2 : Froth flotation process for concentration of sulphide ores

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

SAQ 2

What method can be used for beneficiation of the following?

(i) Haematite ....

(ii) Casseterite ....

(iii) Chromite ....

(iv) Copper pyrites ....

15.4 REDUCTION TO METALS

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

15.4.1 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.

Calcination

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

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

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

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,

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

$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

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

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

When cuprous sulphide is roasted in a limited supply of air, it is partially oxidised to Cu_2O, which 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 :

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

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

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:

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$

However, the reactions that occur in a high temperature carbon reduction process are not as simple as represented above. In most cases, the effective reducing agent is carbon monoxide, not carbon. This is because both the metal oxide and coke are solids, therefore, contact between them is poor and direct reaction is slow :

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

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

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

$$MO(s) + CO(g) \longrightarrow M(l) + CO_2(g)$$

This aspect will be discussed further when we describe extraction of iron later in this unit.

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

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

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

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

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's aluminothermic process.**

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(l) + Al_2O_3(l)$$

$$3MnO_2(s) + 4Al(s) \longrightarrow 3Mn(l) + 2Al_2O_3(l)$$

$$3BaO(s) + 2Al(s) \longrightarrow 3Ba(l) + Al_2O_3(l)$$

The reactions are highly exothermic producing metals in the molten state. You have already studied in Unit 6 that the reaction of Fe_2O_3 with Al is used in spot welding of iron pieces. Other oxides commercially reduced by metals include UO_3 (by Al or Ca), V_2O_5, MoO_3 and WO_3 (by Al); Sc_2O_3, La_2O_3, ThO_2 (by Ca) and Ta_2O_5 (by Na).

Some metals can be more conveniently produced by reduction of their halides such as $TiCl_4$, $ZrCl_4$, $HfCl_4$, $LaCl_3$, 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 are too reactive to be liberated by electrolysis of an aqueous solution. We will discuss electrometallurgy later in this section.

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

SAQ 3

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

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

15.4.2 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 ΔG° 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, ΔG°, is related to the standard enthalpy change, ΔH°, and the standard entropy change, ΔS°, according to the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

In other words, the sign and magnitudes of ΔH° and ΔS° control the sign and magnitude of ΔG°. 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 ΔS° will be positive. Enthalpy of decomposition, ΔH°_d, is simply the negative of the enthalpy of formation of the oxide, ΔH°_f. Since ΔH°_f is generally negative for metal oxides, enthalpy of decomposition will be positive. As a result, the sign of ΔG° is determined by the difference between two positive quantities ΔH° and $T\Delta S^\circ$, T the absolute temperature being always positive.

From the above, we can deduce that if the enthalpy of formation of the metal oxide is small as in case of HgO, Ag_2O, CuO and Au_2O_3, then the enthalpy of decomposition will be a small positive quantity and ΔG°, which is given by the difference of ΔH° and $T\Delta S^\circ$, 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 ΔG° will become negative at a very high temperature where $T\Delta S^\circ$ becomes larger than ΔH°. 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, a knowledge of how the standard free energy change, ΔG°, for the reduction reaction varies with temperature is very important.

Ellingham Diagrams

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

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

Fig. 15.3 shows the Ellingham diagrams for the formation of metal oxides from free elements. By examining the Ellingham diagram for the formation of an oxide, we can find out the temperature at which the standard free energy change for the reaction will become positive. For example, consider the $\Delta G^\circ/T$ graph (Fig.15.3) for the reaction of zinc with oxygen:

$$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$$

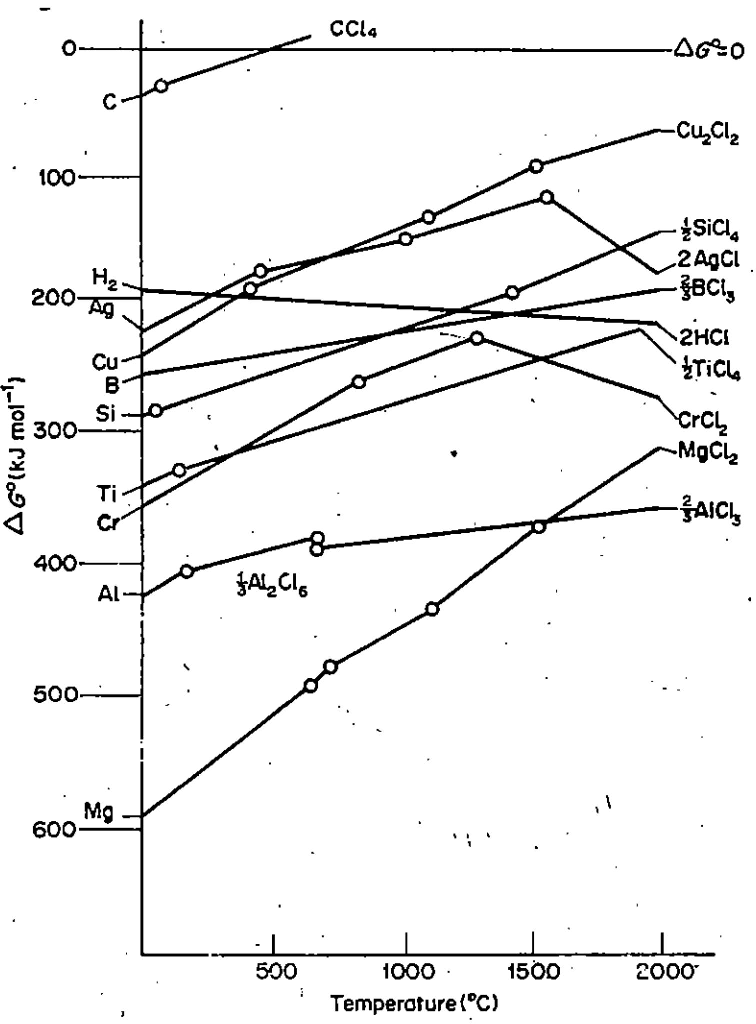

Fig. 15.3 : Ellingham diagram showing the variation of the free energy of formation of metal oxides with temperature

At 273 K, the value of standard free energy change for this reaction is –600 kJ, which becomes less negative as temperature rises and eventually at 2173 K, it becomes zero. Above this temperature, 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, we can find out the standard free energy changes for a large number of reactions. For example, we can read off from the diagram the standard free energy changes for the following two reactions at 298 K:

$$2C(s) + O_2(g) \longrightarrow 2CO(g);\ \Delta G^\circ = -275\ \text{kJ} \quad \ldots\ldots \quad (15.1)$$

$$2ZnO(s) \longrightarrow 2Zn(s) + O_2(g);\ \Delta G^\circ = +640\ \text{kJ} \quad \ldots\ldots \quad (15.2)$$

You may note that the standard free energy change in Eq. 15.2 is positive because it represents the decomposition of zinc oxide. On adding above two equations and respective ΔG° values we get,

$$2ZnO(s) + 2C(s) \longrightarrow 2Zn(s) + 2CO(g);\ \Delta G^\circ = +365\ \text{kJ} \quad \ldots\ldots \quad (15.3)$$

Because the standard free energy change for the above reaction is positive, the reaction has little tendency to occur at 298 K. Since, two moles of gaseous product, i.e., CO, are produced during the reaction, ΔS° is positive. Therefore, ΔG° decreases with increase in temperature and will become zero at some temperature. In this particular case, ΔG° becomes zero at 1173 K as can be seen from Fig. 15.3. This temperature corresponds to the point of intersection of the two graphs for C/CO and Zn/ZnO systems. Above this temperature, ΔG° will become negative. Therefore, carbon will reduce zinc oxide above 1173 K – a temperature 1000 K lower than the temperature of thermal decomposition of zinc oxide. Similarly, with the help of Ellingham diagrams for Zn/ZnO and H_2/H_2O systems, we can find out that H_2 will reduce ZnO at a temperature, of 1400 K. Since reduction of ZnO with carbon, which is also much cheaper than hydrogen, can be carried at a lower temperature, it is clear that reduction using carbon is much more economical than reduction using hydrogen.

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

Figure 15.4 shows the Ellingham diagram for sulphides of various elements. You can see from the diagram that carbon and hydrogen are not effective reducing agents for metal sulphides. Therefore, sulphides are first roasted in air to convert them to oxides, which are then reduced.

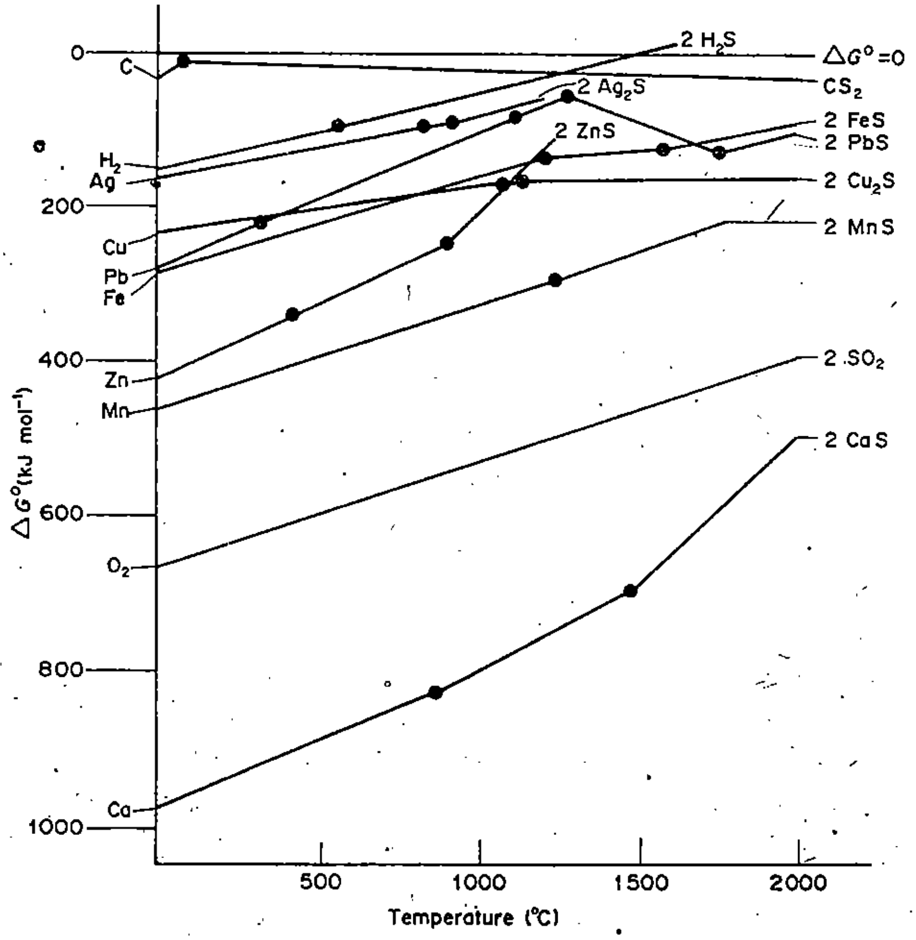

Fig. 15.4 : Ellingham diagram showing the variation of the free energy of formation of metal sulphides with temperature

The Ellingham diagram for chlorides is shown in Fig. 15.5. It can be concluded from the diagram that carbon is useless as a reductant for chlorides, but hydrogen can be used for this purpose, specially at higher temperatures.

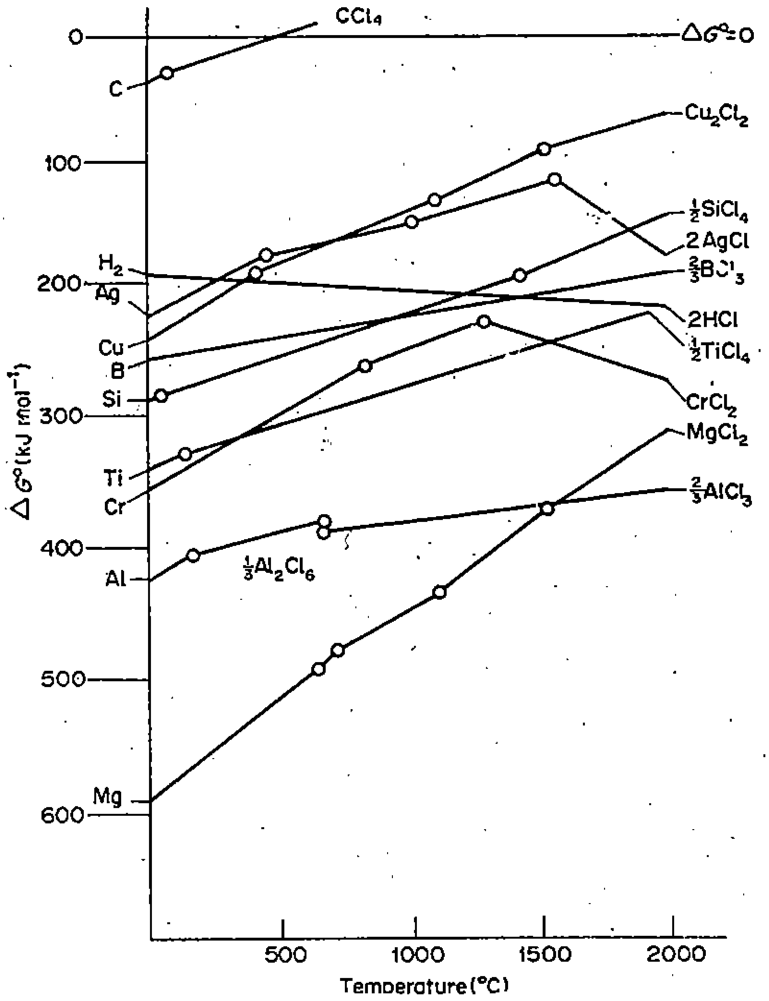

Fig. 15.5 : Ellingham diagram showing the variation of the free energy of formation of metal halides with temperature

SAQ 4

Explain briefly why carbon is theoretically capable of reducing almost all metal oxides at high temperatures. From the Ellingham diagrams shown in Fig. 15.3, compute the temperature of reduction of MgO, CaO, TiO_2 and Al_2O_3 by carbon.

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15.4.3 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:

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

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

$$Cu_2S + 2H_2SO_4 + 2O_2 \longrightarrow 2CuSO_4 + SO_2 + 2H_2O$$

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:

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

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

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

15.4.4 Electrometallurgy

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

- where the metal is highly reactive, e.g., Na, Li, etc. There are not any chemical-reducing agents strong enough to prepare these metals
- where the oxide gets reduced only at very high temperatures at which formation of carbides also takes place, e.g., Al, Mg, etc.

In these cases, metals can be extracted by electrolysis of their salts in molten state. Thus, sodium and magnesium are prepared by electrolysis of fused chlorides, where the metals are liberated at the cathode and chlorine gas is evolved at the anode (Fig. 15.6). Following reactions take place during electrolysis:

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

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

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

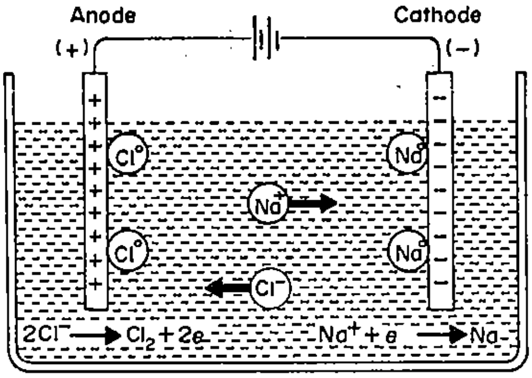

Fig. 15.6 : Electrolysis of molten sodium chloride

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:

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

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

$$\text{Cathode : } Al^{3+} + 3e \longrightarrow Al(s)$$

Before we discuss the various methods for purification of metals, try the following SAQ.

SAQ 5

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

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15.5 PURIFICATION OF METALS

The metals obtained by metallurgical processes still contain some impurities which persist from the ore or are derived from the flux or the fuel used. In order to get pure metal, further purification or refining is necessary. There 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:

15.5.1 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.

15.5.2 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.

15.5.3 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:

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

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

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 strip the cathode and copper sulphate solution the electrolyte (Fig. 15.7). The following electrode reactions take place:

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

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

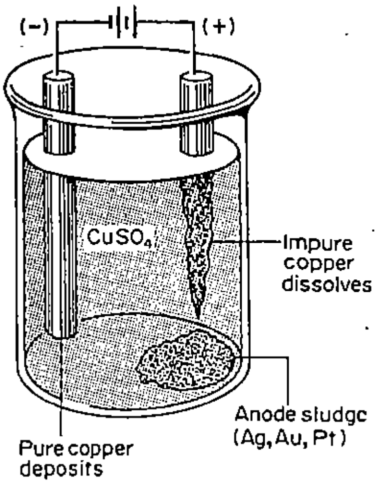

Fig. 15.7 : Purification of copper by electrolysis

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.

15.5.4 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. 15.8).

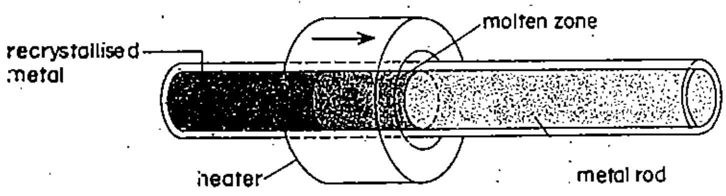

Fig. 15.8 : Diagram for zone refining

15.5.5 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 which 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.

15.5.6 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
s. As we

1300-1000 K. The metal iodide decomposes to yield the pure metal, as in the case of zirconium.

$$Zr(s) + 2I_2(g) \xrightarrow{473\text{-}673\ K} ZrI_4(g) \xrightarrow[\text{Tungsten filament}]{1300-1800\ K} Zr(s) + 2I_2(g)$$

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.

15.5.7 Mond Process

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

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

SAQ 6

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

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15.6 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.

15.6.1 Titanium

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

The two most important ores of titanium are rutile, TiO_2 and ilmenite, $FeO{\cdot}TiO_2$. India possesses large reserves of ilmenite in beach sands of south and south-west coasts while deposits of rutile are limited. Titanium is extracted from these ores by Kroll process. In this process, rutile or ilmenite ore is first heated with carbon at 1200 K in a current of chlorine gas:

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

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

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:

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

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

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 used as a reducing agent in this process.

15.6.2 Chromium

Chromite, $FeO \cdot Cr_2O_3$, is the only commercially important ore of chromium. In order to isolate chromium, the ore is finely powdered and concentrated by gravity process. The concentrated ore is mixed with an excess of sodium carbonate and roasted in the presence of air so that Cr_2O_3 present in the ore is converted into sodium chromate:

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

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 by aluminothermic process or by heating with a calculated quantity of silicon in the presence of calcium oxide which forms a slag of calcium silicate with silica:

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

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

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

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

$$Fe_2O_3 \cdot 3H_2O \longrightarrow Fe_2O_3 + 3H_2O$$

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

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

In the iron ore, the chief impurities are of silica and alumina. To remove these, lime stone is used as a flux. The calcined or roasted ore is then **smelted**, i.e., reduced with carbon, in the presence of lime stone flux. Smelting is done in a **blast furnace** shown in Fig. 15.9. A modern blast furnace is a tall vertical furnace about 30 metre high and 9-10 metres in diameter at its widest part. It is designed to take care of volume changes, to allow sufficient time for the chemical reactions to be completed and to facilitate separation of slag from the molten metal. The outer structure of the furnace is made from thick steel plates which are lined with fireclay refractories. The furnace at its base is provided with (i) small pipes called **tuyeres** through which hot air is blown, (ii) a **tapping hole** through which molten metal can be withdrawn and (iii) a **slag hole** through which slag flows out. At the top, the furnace is provided with a **cup and cone** arrangement for introducing **charge**, i.e., starting materials in the furnace.

The 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 burns in the bottom of the furnace to form CO_2 liberating large amount of heat, which raises the temperature to 2200 K:

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

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

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

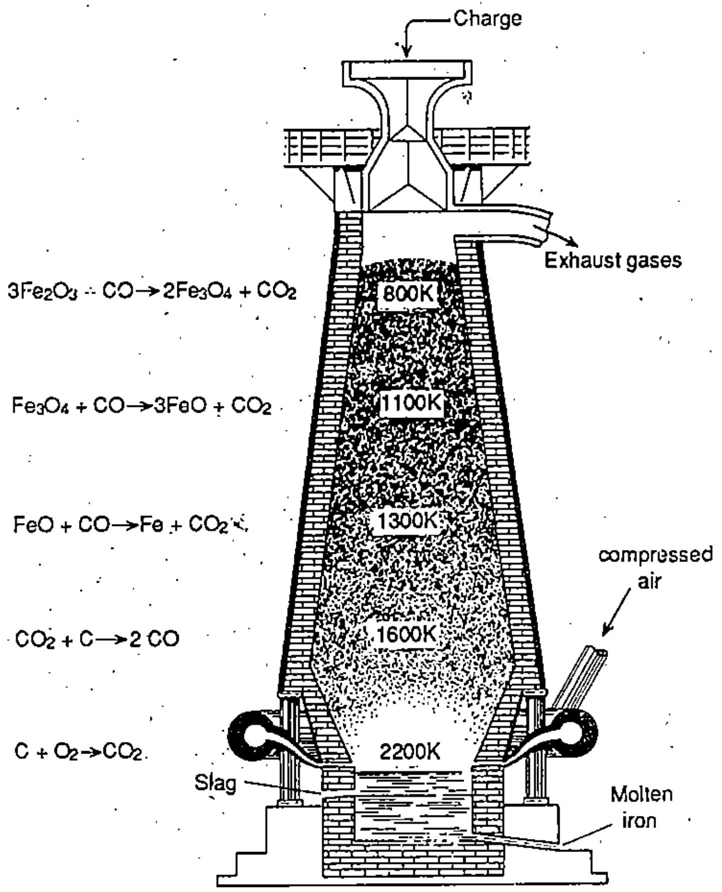

Fig. 15.9 : A blast furnace

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_2. 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 furnace, where temperature is around 1600 K, it melts, absorbs some carbon, phosphorus, sulphur, silicon and manganese, and collects at the bottom of the furnace. Slag being lighter floats on top of the molten iron. The molten iron withdrawn from the furnace is known as **pig iron.** The molten pig iron can be poured into moulds to produce **cast iron.**

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

Wrought iron is the purest form of iron containing 0.10–0.25% carbon and impurities of Si, P, S and Mn not more than 0.3%. It is prepared by heating pig iron in a reverberatory furnace lined with haematite. Haematite oxidises C, Si, P, S and Mn to CO, SiO_2, P_2O_5, SO_2 and MnO, respectively. Thus MnO combines with SiO_2 to form a slag of $MnSiO_3$ and so does Fe_2O_3 with P_2O_5 to give a slag of $FePO_4$. 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, bolts, chains and agricultural implements. Owing to its high cost it has been replaced by steel.

15.6.4 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, $(Ni,Mg)_6Si_4O_{10}(OH)_8$ containing upto 8% nickel.
- Pyrrhotite — an iron mineral, Fe_nS_{n+1}, also contains 3–5% nickel.
- Kupfer nickel, NiAs.
- Nickel glance, NiAsS.

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

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

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

$$S + O_2 \longrightarrow SO_2$$

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

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

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

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

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

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.

15.6.5 Copper

Copper is found in both the native as well as the combined state. 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 Bihar.

For extraction of copper, the sulphide ore is concentrated by froth flotation process and is then roasted in air when some sulphur is removed as SO_2:

$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$

The mixture of 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 $FeSiO_3$:

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

$FeO + SiO_2 \longrightarrow FeSiO_3$

The molten mixture of Cu_2S and remaining FeS is known as matte. It is transferred to a Bessemer converter (Fig. 15.10) 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:

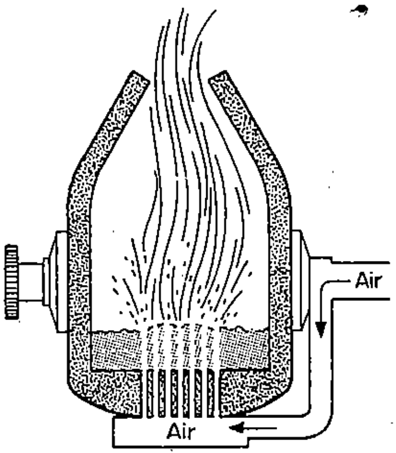

Fig. 15.10 : A Bessemer converter

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

$FeO + SiO_2 \longrightarrow FeSiO_3$

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

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

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.

SAQ 7

Write the chemical equations for :

a) reduction of Fe_2O_3 in blast furnace

....

....

....

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

....

c) reduction of Cr_2O_3 by aluminothermic process

....

d) reduction of NiO by watergas

....

....

15.7 ALLOYS

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

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

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 15.2.

Table 15.2 : 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

15.8 SUMMARY

Let us summarise what we have learnt in this unit.

- The earth's crust is the biggest source of metals. Only those metals which are relatively inactive occur in the free or native state. Metals which are reactive are found in the form of their compounds like oxides, chlorides, sulphides, carbonates, etc. mixed with impurities.
- Before the extraction of a metal, the ore is concentrated by mechanical washing, magnetic or froth flotation process depending upon nature of the ore and impurities.
- Different ores of metals require different treatment based on the reactivity of the metal, i.e., pyrometallurgy, hydrometallurgy or electrometallurgy.
- In pyrometallurgy, the concentrated ore is converted into the metal oxide, by calcination or roasting, which can be easily reduced to metal by smelting.
- In hydrometallurgy, the ore is heated with aqueous solvents containing a chemical reagent with a view to extracting the metal in the form of a suitable compound by leaching action.
- Metals, oxides of which cannot be reduced by carbon, hydrogen or even other metals can be obtained by electrolysis. The metal is liberated at the cathode.
- The metals obtained by the above metallurgical processes can be further purified by liquation, electrolysis, distillation, zone refining, Parke process, Van Arkel de Boer process and Mond process.
- Titanium, chromium, iron, nickel and copper can be isolated from ilmenite, chromite, haematite, pentlandite and copper pyrites, respectively.
- Metals have the special property of combining with other metals to form alloys. Alloys can be given desired properties.

15.9 TERMINAL QUESTIONS

1. What is the difference between gangue and slag? Write balanced chemical equations to show how the flux forms the slag in an iron blast furnace.
2. Why is it necessary to concentrate the ores before extracting metals from them?
3. Why must metal compounds always be reduced to extract metals from them?
4. Describe the froth flotation process for the concentration of ores.
5. Why is carbon a preferred reducing agent in commercial metallurgy?

6. Why are halide salts often used for preparing metals by electrolysis in molten state?
7. How is the impurity of iron sulphide removed from copper ores?
8. Write balanced equation for the reduction of each of the following to the metal:
   a) Fe_3O_4 with Al
   b) UF_6 with Ca
   c) VCl_4 with Mg and
   d) MoO_3 with H_2.

15.10 ANSWERS

Answers to Self Assessment Questions

1. Metals occur in nature in the form of minerals either in the native state or in the combined state. Earth's crust is the biggest source of metals. Some metals in the form of their compounds are also present in sea water and some others in the form of nodules are lying at sea-bed.
2. i) Magnetic separation
   ii) Gravity method
   iii) Magnetic separation or Gravity method
   iv) Froth flotation process
3. a) A good reducing agent for extraction of metals should possess the following properties:
      i) It should be cheaper than the metal being produced.
      ii) It should be able to reduce the metal compounds to free metal in a pure form at an experimentally manageable temperature.
      iii) It should not combine with the metal being produced.
   b) Carbon reduction is not used to obtain certain metals from their ores because it can combine with them to produce metal carbides.
4. In the reduction of a solid metal oxide with solid carbon, gaseous carbon monoxide is produced and in most of the cases metal is also produced in the liquid or in the gaseous state. Therefore, the reduction occurs with sizeable increase in entropy i.e., ΔS° is positive. Although the standard enthalpy of decomposition, ΔH°, of metal oxide is also a positive quantity, the difference $\Delta H^\circ - T\Delta S^\circ$ will become negative at a certain temperature, thereby the standard free energy change ΔG° will become negative. Thus, theoretically, the metal oxide should be reduced to metal. But practically, if the temperature of reduction is too high and the metal is fairly reactive, then the metal may combine with carbon to form metal carbide.
   For computing the temperature of reduction of MgO,CaO, TiO_2, and Al_2O_3 by carbon, draw perpendiculars from the point of intersections of C/CO and M/MO graphs to the X axis and read the temperature. You will find that the temperatures of reduction are 1935, 2445, 1865 and 2570 K, respectively.
5. The ease with which a metal can be reduced at cathode depends on its reduction potential. The metals which have a higher reduction potential than hydrogen can be commercially produced by electrolysis of their salts in aqueous solution. For example, copper and zinc. On the other hand, metals like Na, Mg, Al, etc., i.e., the metals which have a lower reduction potential than that of hydrogen are produced by electrolysis of their salts in fused state. Because if aqueous solutions of salts of these metals are electrolysed, hydrogen is liberated at the cathode instead of the metal.
6. Various methods used for the refining of crude metals are:
   i) Liquation
   ii) Distillation
   iii) Electrolysis

iv) Zone refining
v) Parke process
vi) Van Arkel de Boer process
vii) Mond process

7. a) $3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$
$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2$
$FeO + CO \longrightarrow Fe + CO_2$
b) $TiCl_4 + 2Mg \longrightarrow Ti + 2MgCl_2$ or
$TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$
c) $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$
d) $2NiO + H_2 + CO \longrightarrow 2Ni + H_2O + CO_2$

Answers to Terminal Questions

1. Gangue is an unwanted impurity like rock and sand, which is present in the ore. Flux, on the other hand, is a chemical substance which is added to remove the gangue during reduction of the metal compounds to metal. Gangue and flux combine to form slag, which is low melting, immiscible with molten metal and can be skimmed off.
Silica, alumina and phosphorus pentoxide are present as gangue in iron ore. Therefore, to remove them, limestone is added as a flux in an iron blast furnace. Limestone decomposes to give CaO which forms slag with impurities:

$CaCO_3 \longrightarrow CaO + CO_2$
$CaO + SiO_2 \longrightarrow CaSiO_3$
$CaO + Al_2O_3 \longrightarrow Ca(AlO_2)_2$
$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$

2. Ores often contain unwanted impurities in them. Therefore, to save in the cost of transportation, fuel and chemicals and also to get the metal in a reasonably pure state, ores are concentrated before extracting metals from them.

3. In their compounds, metals are present in the oxidised state. Therefore, to extract metals from them, the metal compounds must always be reduced.

4. See Section 15.3.3.

5. Carbon is a preferred reducing agent in commercial metallurgy because it is cheap and also because it reduces most metal oxides to metals at moderately high temperatures.

6. Most metal halides in molten state are conductors of electricity. Therefore, they are used for extracting metals by electrolysis in molten state.

7. Impurity of iron sulphide present in copper ores is removed by roasting the ore and then smelting it with SiO_2 flux in a blast furnace. On roasting FeS is converted to FeO. FeO on smelting forms a slag of $FeSiO_3$ which is tapped off:

$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$
$FeO + SiO_2 \longrightarrow FeSiO_3$

8. a) $3Fe_3O_4 + 8Al \longrightarrow 9Fe + 4Al_2O_3$
b) $UF_6 + 3Ca \longrightarrow U + 3CaF_2$
c) $VCl_4 + 2Mg \longrightarrow V + 2MgCl_2$
d) $MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$

FURTHER READING

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