Unit 7

The *p*-Block Elements

Diversity in chemistry is the hallmark of p–block elements manifested in their ability to react with the elements of s–, d– and f–blocks as well as with their own.

Objectives

After studying this Unit, you will be able to

- appreciate general trends in the chemistry of elements of groups 15,16,17 and 18;
- learn the preparation, properties and uses of dinitrogen and phosphorus and some of their important compounds;
- describe the preparation, properties and uses of dioxygen and ozone and chemistry of some simple oxides;
- know allotropic forms of sulphur, chemistry of its important compounds and the structures of its oxoacids;
- describe the preparation, properties and uses of chlorine and hydrochloric acid;
- know the chemistry of interhalogens and structures of oxoacids of halogens;
- enumerate the uses of noble gases;
- appreciate the importance of these elements and their compounds in our day to day life.

In Class XI, you have learnt that the *p*-block elements are placed in groups 13 to 18 of the periodic table. Their valence shell electronic configuration is ns^2np^{1-6} (except He which has $1s^2$ configuration). The properties of *p*-block elements like that of others are greatly influenced by atomic sizes, ionisation enthalpy, electron gain enthalpy and electronegativity. The absence of *d*-orbitals in second period and presence of *d* or *d* and *f* orbitals in heavier elements (starting from third period onwards) have significant effects on the properties of elements. In addition, the presence of all the three types of elements; metals, metalloids and non-metals bring diversification in chemistry of these elements.

Having learnt the chemistry of elements of Groups 13 and 14 of the *p*-block of periodic table in Class XI, you will learn the chemistry of the elements of subsequent groups in this Unit.

7.1 Group 15 Elements

Group 15 includes nitrogen, phosphorus, arsenic, antimony, bismuth and moscovium. As we go down the group, there is a shift from non-metallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids, bismuth and moscovium are typical metals.

7.1.1 Occurrence

Molecular nitrogen comprises 78% by volume of the atmosphere. In the earth's crust, it occurs as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate (Indian saltpetre). It is found in the form of proteins in plants and animals. Phosphorus occurs in minerals of the apatite family, $Ca_9(PO_4)_6 \cdot CaX_2$ (X = F, Cl or OH) (e.g., fluorapatite $Ca_9(PO_4)_6 \cdot CaF_2$) which are the main components of phosphate rocks. Phosphorus is an essential constituent of animal and plant matter. It is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. Arsenic, antimony and bismuth are found mainly as sulphide minerals. Moscovium is a synthetic radioactive element. Its symbol is Mc, atomic number 115, atomic mass 289 and electronic configuration [Rn] $5f^{14}6d^{10}7s^27p^3$. Due to very short half life and availability in very little amount, its chemistry is yet to be established.

Here, except for moscovium, important atomic and physical properties of other elements of this group along with their electronic configurations are given in Table 7.1.

Table 7.1: Atomic and Physical Properties of Group 15 Elements

Property		N	P	As	Sb	Bi
Atomic number		7	15	33	51	83
Atomic mass/g mol^{-1}		14.01	30.97	74.92	121.75	208.98
Electronic configuration		[He]$2s^22p^3$	[Ne]$3s^23p^3$	[Ar]$3d^{10}4s^24p^3$	[Kr]$4d^{10}5s^25p^3$	[Xe]$4f^{14}5d^{10}6s^26p^3$
Ionisation enthalpy	I	1402	1012	947	834	703
(Δ_iH/(kJ mol^{-1})	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9
Covalent radius/pm^a		70	110	121	141	148
Ionic radius/pm		171^b	212^b	222^b	76^c	103^c
Melting point/K		63*	317^d	1089^e	904	544
Boiling point/K		77.2*	554^d	888^f	1860	1837
Density/[g cm^{-3}(298 K)]		0.879^g	1.823	5.778^h	6.697	9.808

*[a] E^{III} single bond (E = element); [b] E^{3-}; [c] E^{3+}; [d] White phosphorus; [e] Grey α-form at 38.6 atm; [f] Sublimation temperature; [g] At 63 K; [h] Grey α-form; * Molecular N_2.*

Trends of some of the atomic, physical and chemical properties of the group are discussed below.

7.1.2 Electronic Configuration

The valence shell electronic configuration of these elements is ns^2np^3. The *s* orbital in these elements is completely filled and *p* orbitals are half-filled, making their electronic configuration extra stable.

7.1.3 Atomic and Ionic Radii

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled *d* and/or *f* orbitals in heavier members.

7.1.4 Ionisation Enthalpy

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled *p* orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$ (Table 7.1).

7.1.5 Electronegativity

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

7.1.6 Physical Properties

All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen, all the elements show allotropy.

7.1.7 Chemical Properties

Oxidation states and trends in chemical reactivity

The common oxidation states of these elements are –3, +3 and +5. The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. In fact last member of the group, bismuth hardly forms any compound in –3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF_5. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group. Besides +5 oxidation state, nitrogen exhibits + 1, + 2, + 4 oxidation states also when it reacts with oxygen. However, it does not form compounds in +5 oxidation state with halogens as nitrogen does not have *d*-orbitals to accommodate electrons from other elements to form bonds. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid. However +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.

Nitrogen is restricted to a maximum covalency of 4 since only four (one *s* and three *p*) orbitals are available for bonding. The heavier elements have vacant *d* orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalence as in PF_6^-.

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of this group due to its small size, high electronegativity, high ionisation enthalpy and non-availability of *d* orbitals. Nitrogen has unique ability to form ***pπ-pπ* multiple** bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group do not form *pπ-pπ* bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one *s* and two *p*) between the two atoms. Consequently, its bond enthalpy (941.4 kJ mol^{-1}) is very high. On the contrary, phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state. However, the single

N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of *d* orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form **$d\pi$–$p\pi$ bond** as the heavier elements can e.g., $R_3P = O$ or $R_3P = CH_2$ (R = alkyl group). Phosphorus and arsenic can form **$d\pi$–$d\pi$ bond** also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

(i) *Reactivity towards hydrogen*: All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table 7.2. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$. Due to high electronegativity and small size of nitrogen, NH_3 exhibits hydrogen bonding in solid as well as liquid state. Because of this, it has higher melting and boiling points than that of PH_3.

Table 7.2: Properties of Hydrides of Group 15 Elements

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	–
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) Distance/pm	101.7	141.9	151.9	170.7	–
HEH angle (°)	107.8	93.6	91.8	91.3	–
$\Delta_f H^{\ominus}$/kJ mol^{-1}	–46.1	13.4	66.4	145.1	278
$\Delta_{diss}H^{\ominus}$(E–H)/kJ mol^{-1}	389	322	297	255	–

(ii) *Reactivity towards oxygen*: All these elements form two types of oxides: E_2O_3 and E_2O_5. The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

(iii) *Reactivity towards halogens*: These elements react to form two series of halides: EX_3 and EX_5. Nitrogen does not form pentahalide due to non-availability of the *d* orbitals in its valence shell. Pentahalides are more covalent than trihalides. This is due to the fact that in pentahalides +5 oxidation state exists while in the case of trihalides +3 oxidation state exists. Since elements in +5 oxidation state will have more polarising power than in +3 oxidation state, the covalent character of bonds is more in pentahalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

(iv) *Reactivity towards metals*: All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Example 7.1

Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

Solution

Nitrogen with n = 2, has *s* and *p* orbitals only. It does not have *d* orbitals to expand its covalence beyond four. That is why it does not form pentahalide.

Example 7.2

PH_3 has lower boiling point than NH_3. Why?

Solution

Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

Intext Questions

7.1 Why are pentahalides of P, As, Sb and Bi more covalent than their trihalides?

7.2 Why is BiH_3 the strongest reducing agent amongst all the hydrides of Group 15 elements ?

7.2 Dinitrogen

Preparation

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl\ (aq)$$

Small amounts of NO and HNO_3 are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate. It can also be obtained by the thermal decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \rightarrow Ba + 3N_2$$

Properties

Dinitrogen is a colourless, odourless, tasteless and non-toxic gas. Nitrogen atom has two stable isotopes: ^{14}N and ^{15}N. It has a very low solubility in water (23.2 cm^3 per litre of water at 273 K and 1 bar pressure) and low freezing and boiling points (Table 7.1).

Dinitrogen is rather inert at room temperature because of the high bond enthalpy of N≡N bond. Reactivity, however, increases rapidly with rise in temperature. At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

$$N_2(g) + 3H_2(g) \xrightleftharpoons{773\text{ k}} 2NH_3(g); \qquad \Delta_f H^\ominus = -46.1 \text{ kJmol}^{-1}$$

Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

$$N_2 + O_2(g) \xrightleftharpoons{\text{Heat}} 2NO(g)$$

Uses: The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide). It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals). Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Example 7.3 Write the reaction of thermal decomposition of sodium azide.

Solution Thermal decomposition of sodium azide gives dinitrogen gas.

$$2NaN_3 \rightarrow 2Na + 3N_2$$

Intext Question

7.3 Why is N_2 less reactive at room temperature?

7.3 Ammonia

Preparation

Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

On a small scale ammonia is obtained from ammonium salts which decompose when treated with caustic soda or calcium hydroxide.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

$$(NH_4)_2 SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

On a large scale, ammonia is manufactured by Haber's process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta_f H^\ominus = -46.1 \text{ kJ mol}^{-1}$$

In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium. The flow chart for the production of ammonia is shown in Fig. 7.1. Earlier, iron was used as a catalyst with molybdenum as a promoter.

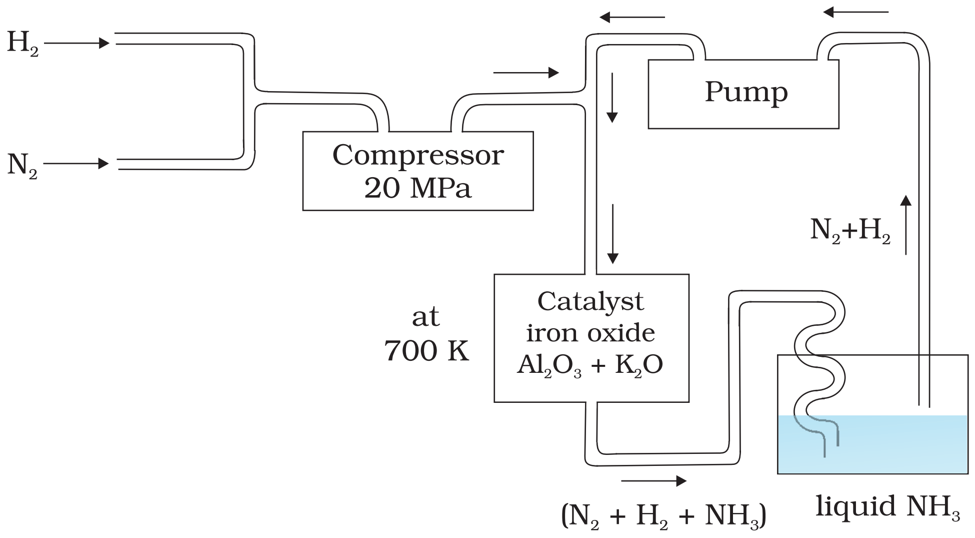
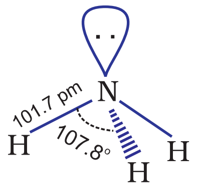


Fig. 7.1
Flow chart for the manufacture of ammonia



Properties

Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 198.4 and 239.7 K respectively. In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass. The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons as shown in the structure.

Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH^- ions.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+ (aq) + OH^- (aq)$$

It forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2SO_4$, etc. As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions. For example,

$$\underset{}{ZnSO_4 (aq) + 2NH_4OH (aq) \rightarrow} \underset{\text{(white ppt)}}{Zn(OH)_2 (s)} + (NH_4)_2 SO_4 (aq)$$

$$FeCl_3 (aq) + NH_4OH (aq) \rightarrow \underset{\text{(brown ppt)}}{Fe_2O_3.x\,H_2O (s)} + NH_4Cl (aq)$$

The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as Cu^{2+}, Ag^{+}:

$$\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4\,NH_3(aq) \rightleftharpoons \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$$

$$\underset{\text{(colourless)}}{Ag^{+}(aq)} + Cl^{-}(aq) \rightarrow \underset{\text{(white ppt)}}{AgCl(s)}$$

$$\underset{\text{(white ppt)}}{AgCl(s)} + 2NH_3(aq) \rightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl(aq)}$$

Uses: Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

Example 7.4 Why does NH_3 act as a Lewis base ?

Solution Nitrogen atom in NH_3 has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

Intext Questions

7.4 Mention the conditions required to maximise the yield of ammonia.

7.5 How does ammonia react with a solution of Cu^{2+}?

7.4 Oxides of Nitrogen

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table 7.3.

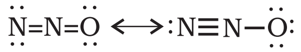
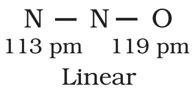
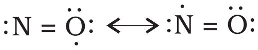
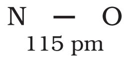
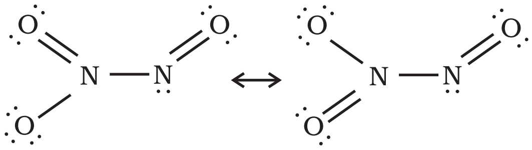
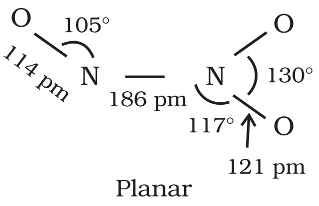
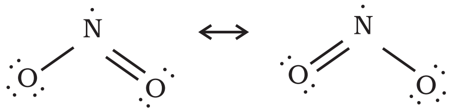
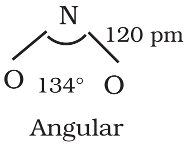
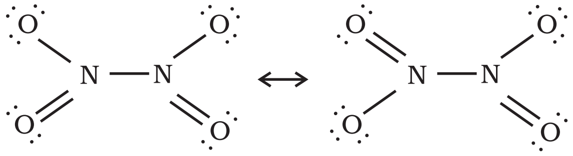
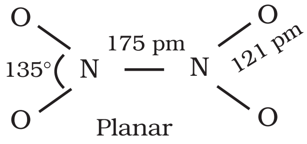
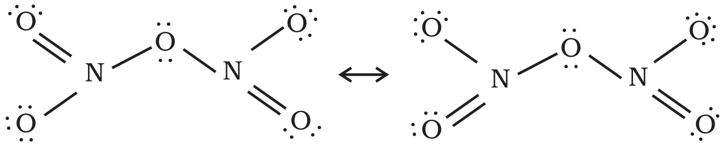
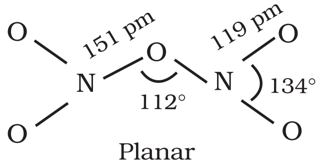
Table 7.3: Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas, neutral

Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\,K} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

Lewis dot main resonance structures and bond parameters of oxides are given in Table 7.4.

Table 7.4: Structures of Oxides of Nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O		
NO		
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		

Example 7.5

Why does NO_2 dimerise ?

Solution

NO_2 contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

Intext Question

7.6 What is the covalence of nitrogen in N_2O_5 ?

7.5 Nitric Acid

Nitrogen forms oxoacids such as $H_2N_2O_2$ (hyponitrous acid), HNO_2 (nitrous acid) and HNO_3 (nitric acid). Amongst them HNO_3 is the most important.

Preparation

In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

On a large scale it is prepared mainly by Ostwald's process. This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

$$4NH_3(g) + \underset{\text{(from air)}}{5O_2(g)} \xrightarrow[\text{500 K, 9 bar}]{\text{Pt / Rh gauge catalyst}} 4NO(g) + 6H_2O(g)$$

Nitric oxide thus formed combines with oxygen giving NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Nitrogen dioxide so formed, dissolves in water to give HNO_3.

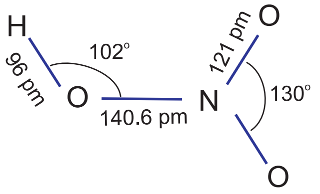
$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

Properties

It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K). Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown.



In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

$$3Cu + 8\,HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Zinc reacts with dilute nitric acid to give N_2O and with concentrated acid to give NO_2.

$$4Zn + 10HNO_3(dilute) \rightarrow 4\,Zn\,(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3(conc.) \rightarrow Zn\,(NO_3)_2 + 2H_2O + 2NO_2$$

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidises non–metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to H_2SO_4, and phosphorus to phosphoric acid.

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48HNO_3 \rightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Brown Ring Test: The familiar brown ring test for nitrates depends on the ability of Fe^{2+} to reduce nitrates to nitric oxide, which reacts with Fe^{2+} to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.

$$NO_3^{-} + 3Fe^{2+} + 4H^{+} \rightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe\,(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(brown)}}{[Fe\,(H_2O)_5\,(NO)]^{2+}} + H_2O$$

Uses: The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the *pickling of stainless steel*, etching of metals and as an oxidiser in rocket fuels.

7.6 Phosphorus — Allotropic Forms

Phosphorus is found in many allotropic forms, the important ones being white, red and black.

White phosphorus is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$

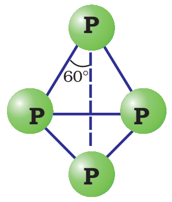


Fig. 7.2
White phosphorus

White phosphorus is less stable and therefore, more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60°. It readily catches fire in air to give dense white fumes of P_4O_{10}.

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

It consists of discrete tetrahedral P_4 molecule as shown in Fig. 7.2.

Red phosphorus is obtained by heating white phosphorus at 573K in an inert atmosphere for several days. When red phosphorus is heated under high pressure, a series of phases of black phosphorus is formed. Red phosphorus possesses iron grey lustre. It is odourless, non-poisonous and insoluble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark.

It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner as shown in Fig. 7.3.

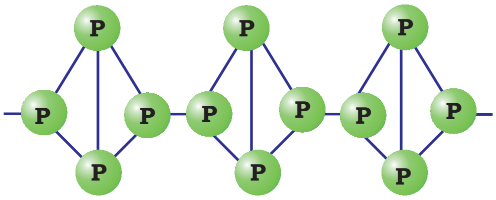


Fig.7.3: Red phosphorus

Black phosphorus has two forms α-black phosphorus and β-black phosphorus. α-Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air. β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

7.7 Phosphine

Preparation

Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$

When pure, it is non inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

Properties

It is a colourless gas with rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2. When absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$$

Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,

$$PH_3 + HBr \rightarrow PH_4Br$$

Uses: The spontaneous combustion of phosphine is technically used in *Holme's signals*. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal. It is also used in **smoke screens**.

Example 7.6

In what way can it be proved that PH_3 is basic in nature?

Solution

PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature.

$$PH_3 + HI \rightarrow PH_4I$$

Due to lone pair on phosphorus atom, PH_3 is acting as a Lewis base in the above reaction.

Intext Questions

7.7 (a) Bond angle in PH_4^+ is higher than that in PH_3. Why?

(b) What is formed when PH_3 reacts with an acid?

7.8 What happens when white phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2 ?

7.8 Phosphorus Halides

Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

7.8.1 Phosphorus Trichloride

Preparation

It is obtained by passing dry chlorine over heated white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

It is also obtained by the action of thionyl chloride with white phosphorus.

$$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties

It is a colourless oily liquid and hydrolyses in the presence of moisture.

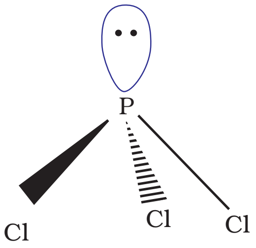
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

It has a pyramidal shape as shown, in which phosphorus is sp^3 hybridised.



7.8.2 Phosphorus Pentachloride

Preparation

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

It can also be prepared by the action of SO_2Cl_2 on phosphorus.

$$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$$

Properties

PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

When heated, it sublimes but decomposes on stronger heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

It reacts with organic compounds containing –OH group converting them to chloro derivatives.

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

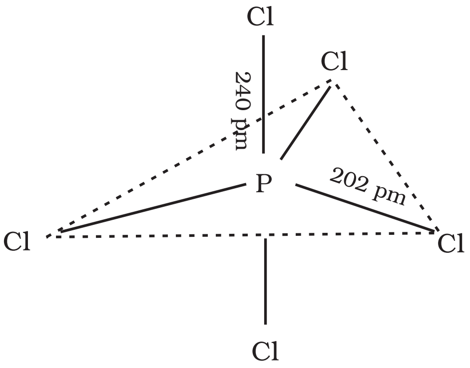
Finely divided metals on heating with PCl_5 give corresponding chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

$$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$$

It is used in the synthesis of some organic compounds, e.g., C_2H_5Cl, CH_3COCl.

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



Example 7.7 Why does PCl_3 fume in moisture ?

Solution PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Example 7.8 Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Solution PCl_5 has a trigonal bipyramidal structure and the three equatorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equatorial bonds.

Intext Questions

7.9 What happens when PCl_5 is heated?

7.10 Write a balanced equation for the reaction of PCl_5 with water.

7.9 Oxoacids of Phosphorus

Phosphorus forms a number of oxoacids. The important oxoacids of phosphorus with their formulas, methods of preparation and the presence of some characteristic bonds in their structures are given in Table 7.5.

Table 7.5: Oxoacids of Phosphorus

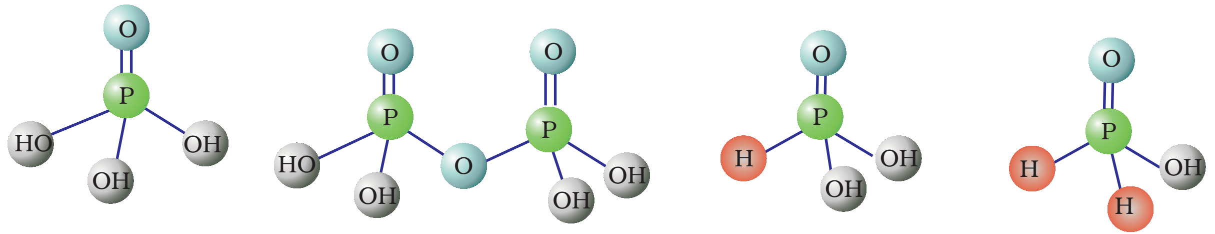
Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	$P_4O_{10}+H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2, heat in a sealed tube

* *Exists in polymeric forms only. Characteristic bonds of $(HPO_3)_3$ have been given in the Table.*

The compositions of the oxoacids are interrelated in terms of loss or gain of H_2O molecule or O-atom. The structures of some important oxoacids are given next.

In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain at least one P=O bond and one P–OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain, in addition to P=O and P–OH bonds, either P–P (e.g., in $H_4P_2O_6$) or P–H (e.g., in H_3PO_2) bonds but not both. These acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, orthophophorous acid (or phosphorous acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

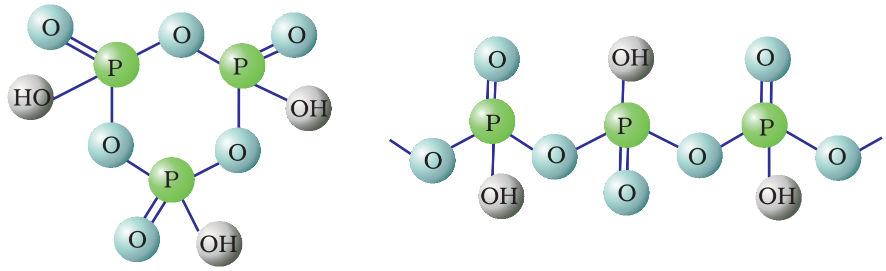


H_3PO_4 Orthophosphoric acid

$H_4P_2O_7$ Pyrophosphoric acid

H_3PO_3 Orthophosphorous acid

H_3PO_2 Hypophosphorous acid



Cyclotrimetaphosphoric acid, $(HPO_3)_3$

Polymetaphosphoric acid, $(HPO_3)_n$

Fig. 7.4 *Structures of some important oxoacids of phosphorus*

The acids which contain P–H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P–H bonds and reduces, for example, $AgNO_3$ to metallic silver.

$$4\ AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$$

These P–H bonds are not ionisable to give H^+ and do not play any role in basicity. Only those H atoms which are attached with oxygen in P–OH form are ionisable and cause the basicity. Thus, H_3PO_3 and H_3PO_4 are dibasic and tribasic, respectively as the structure of H_3PO_3 has two P–OH bonds and H_3PO_4 three.

Example 7.9 How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure ?

Solution In H_3PO_2, two H atoms are bonded directly to P atom which imparts reducing character to the acid.

Intext Questions

7.11 What is the basicity of H_3PO_4?

7.12 What happens when H_3PO_3 is heated?

7.10 Group 16 Elements

Oxygen, sulphur, selenium, tellurium, polonium and livermorium constitute Group 16 of the periodic table. This is sometimes known as group of *chalcogens*. The name is derived from the Greek word for brass and points to the association of sulphur and its congeners with copper. Most copper minerals contain either oxygen or sulphur and frequently the other members of the group.

7.10.1 Occurrence

Oxygen is the most abundant of all the elements on earth. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume.

However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as *gypsum* $CaSO_4.2H_2O$, *epsom salt* $MgSO_4.7H_2O$, *baryte* $BaSO_4$ and sulphides such as *galena* PbS, *zinc blende* ZnS, *copper pyrites* $CuFeS_2$. Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur.

Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals. Livermorium is a synthetic radioactive element. Its symbol is Lv, atomic number 116, atomic mass 292 and electronic configuration [Rn] $5f^{14}6d^{10}7s^27p^4$. It has been produced only in a very small amount and has very short half-life (only a small fraction of one second). This limits the study of properlies of Lv.

Here, except for livermorium, important atomic and physical properties of other elements of Group16 along with their electronic configurations are given in Table 7.6. Some of the atomic, physical and chemical properties and their trends are discussed below.

Table 7.6: Some Physical Properties of Group 16 Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass/g mol^{-1}	16.00	32.06	78.96	127.60	210.00
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)[a]	66	104	117	137	146
Ionic radius, E^{2-}/pm	140	184	198	221	230[b]
Electron gain enthalpy, $/\Delta_{eg}H$ kJ mol^{-1}	–141	–200	–195	–190	–174
Ionisation enthalpy (Δ_iH_1) /kJ mol^{-1}	1314	1000	941	869	813
Electronegativity	3.50	2.58	2.55	2.01	1.76
Density /g cm^{-3} (298 K)	1.32[c]	2.06[d]	4.19[e]	6.25	–
Melting point/K	55	393[f]	490	725	520
Boiling point/K	90	718	958	1260	1235
Oxidation states*	–2,–1,1,2	–2,2,4,6	–2,2,4,6	–2,2,4,6	2,4

[a] *Single bond;* [b] *Approximate value;* [c] *At the melting point;* [d] *Rhombic sulphur;* [e] *Hexagonal grey;* [f] *Monoclinic form, 673 K.*

* *Oxygen shows oxidation states of +2 and +1 in oxygen fluorides* OF_2 *and* O_2F_2 *respectively.*

7.10.2 Electronic Configuration

The elements of Group16 have six electrons in the outermost shell and have ns^2np^4 general electronic configuration.

7.10.3 Atomic and Ionic Radii

Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group. The size of oxygen atom is, however, exceptionally small.

7.10.4 Ionisation Enthalpy

Ionisation enthalpy decreases down the group. It is due to increase in size. However, the elements of this group have lower ionisation enthalpy values compared to those of Group15 in the corresponding periods. This is due to the fact that Group 15 elements have extra stable half-filled *p* orbitals electronic configurations.

7.10.5 Electron Gain Enthalpy

Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards the value again becomes less negative upto polonium.

7.10.6 Electronegativity

Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decreases with an increase in atomic number. This implies that the metallic character increases from oxygen to polonium.

Example 7.10

Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why?

Solution

Due to extra stable half-filled *p* orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

7.10.7 Physical Properties

Some of the physical properties of Group 16 elements are given in Table 7.6. Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). All these elements exhibit allotropy. The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecule (S_8).

7.10.8 Chemical Properties

Oxidation states and trends in chemical reactivity

The elements of Group 16 exhibit a number of oxidation states (Table 7.6). The stability of -2 oxidation state decreases down the group. Polonium hardly shows –2 oxidation state. Since electronegativity of oxygen is very high, it shows only negative oxidation state as –2 except in the case of OF_2 where its oxidation state is + 2. Other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation state in their compounds with oxygen and + 6 with fluorine. The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in +4 and +6 oxidation states is primarily covalent.

Anomalous behaviour of oxygen

The anomalous behaviour of oxygen, like other members of *p*-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S.

The absence of *d* orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shells can be expanded and covalence exceeds four.

(i) *Reactivity with hydrogen*: All the elements of Group 16 form hydrides of the type H_2E (E = O, S, Se, Te, Po). Some properties of hydrides are given in Table 7.7. Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of H–E bond down the group. Owing to the decrease in enthalpy for the dissociation of H–E bond down the group, the thermal stability of hydrides also decreases from H_2O to H_2Po. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

Table 7.7: Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p/K	273	188	208	222
b.p/K	373	213	232	269
H–E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H/\text{kJ mol}^{-1}$	–286	–20	73	100
$\Delta_{diss} H$ (H–E)/kJ mol^{-1}	463	347	276	238
Dissociation constant[a]	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

[a] *Aqueous solution, 298 K*

(ii) *Reactivity with oxygen*: All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type, sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

(iii) *Reactivity towards the halogens*: Elements of Group 16 form a large number of halides of the type, EX_6, EX_4 and EX_2 where E is an element of the group and X is a halogen. The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as *see-saw* geometry.

All elements except oxygen form dichlorides and dibromides. These dihalides are formed by sp^3 hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below:

$$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$$

H₂S is less acidic than H₂Te. Why?

Example 7.11

H_2S is less acidic than H_2Te. Why?

Solution

Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

Intext Questions

7.13 List the important sources of sulphur.

7.14 Write the order of thermal stability of the hydrides of Group 16 elements.

7.15 Why is H_2O a liquid and H_2S a gas ?

7.11 Dioxygen

Preparation

Dioxygen can be obtained in the laboratory by the following ways:

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O_2$$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g); \qquad 2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$
$$2HgO(s) \rightarrow 2Hg(l) + O_2(g)\ ; \qquad 2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$$

(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(1) + O_2(g)$$

On large scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

Industrially, dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

Properties

Dioxygen is a colourless and odourless gas. Its solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K which is just sufficient for the vital support of marine and aquatic life. It liquefies at 90 K and freezes at 55 K. Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. Molecular oxygen, O_2 is unique in being paramagnetic inspite of having even number of electrons (see Class XI Chemistry Book, Unit 4).

Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxgyen-oxygen double bond is high (493.4 kJ mol^{-1}).

Some of the reactions of dioxygen with metals, non-metals and other compounds are given below:

$$2Ca + O_2 \rightarrow 2CaO$$

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

$$C + O_2 \rightarrow CO_2$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Some compounds are catalytically oxidised. For example,

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

Uses: In addition to its importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel. Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering. The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

Intext Questions

7.16 Which of the following does not react with oxygen directly?
Zn, Ti, Pt, Fe

7.17 Complete the following reactions:
(i) $C_2H_4 + O_2 \rightarrow$
(ii) $4Al + 3 O_2 \rightarrow$

7.12 Simple Oxides

A binary compound of oxygen with another element is called oxide. As already stated, oxygen reacts with most of the elements of the periodic table to form oxides. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties.

Oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4). Simple oxides can be classified on the basis of their acidic, basic or amphoteric character. An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO_2, Cl_2O_7, CO_2, N_2O_5). For example, SO_2 combines with water to give H_2SO_3, an acid.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn_2O_7, CrO_3, V_2O_5). The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). For example, CaO combines with water to give $Ca(OH)_2$, a base.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

In general, metallic oxides are basic.

Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. For example, Al_2O_3 reacts with acids as well as alkalies.

$$Al_2O_3\,(s) + 6HCl\,(aq) + 9H_2O\,(l) \rightarrow 2\left[Al(H_2O)_6\right]^{3+}(aq) + 6Cl^-\,(aq)$$

$$Al_2O_3\,(s) + 6NaOH\,(aq) + 3H_2O\,(l) \rightarrow 2Na_3\left[Al\,(OH)_6\right](aq)$$

There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N_2O.

7.13 Ozone

Ozone is an allotropic form of oxygen. It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

Preparation

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.

$$3O_2 \rightarrow 2O_3 \quad \Delta H^{\ominus}\,(298\ K) = +142\ kJ\ mol^{-1}$$

Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition.

If concentrations of ozone greater than 10 per cent are required, a battery of ozonisers can be used, and pure ozone (b.p. 101.1K) can be condensed in a vessel surrounded by liquid oxygen.

Properties

Pure ozone is a pale blue gas, dark blue liquid and violet-black solid. Ozone has a characteristic smell and in small concentrations it is harmless. However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen. It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive.

Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$

$$2I^-(aq) + H_2O(l) + O_3(g) \rightarrow 2OH^-(aq) + I_2(s) + O_2(g)$$

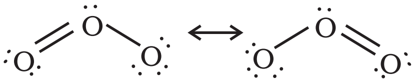
When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Experiments have shown that nitrogen oxides (particularly nitrogen monoxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

The two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117°. It is a resonance hybrid of two main forms:



Uses: It is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oils, ivory, flour, starch, etc. It acts as an oxidising agent in the manufacture of potassium permanganate.

Intext Questions

7.18 Why does O_3 act as a powerful oxidising agent?

7.19 How is O_3 estimated quantitatively?

7.14 Sulphur — Allotropic Forms

Sulphur forms numerous allotropes of which the **yellow rhombic** (α-sulphur) and **monoclinic** (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

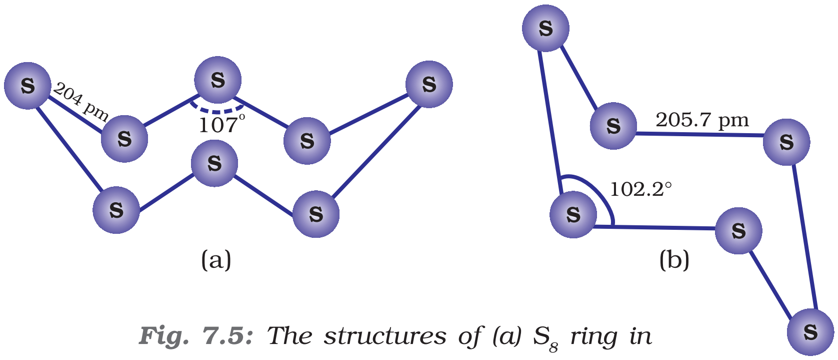
Rhombic sulphur (α-sulphur)

This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2. It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS_2.

Monoclinic sulphur (β-sulphur)

Its m.p. is 393 K and specific gravity 1.98. It is soluble in CS_2. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling, till crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β-sulphur are formed. It is stable above 369 K and transforms into α-sulphur below it. Conversely, α-sulphur is stable below 369 K and transforms into β-sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in Fig. 7.5(a).



(a) (b)

Fig. 7.5: The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo-S_6, the ring adopts the chair form and the molecular dimensions are as shown in Fig. 7.5 (b). At elevated temperatures (~1000 K), S_2 is the dominant species and is paramagnetic like O_2.

Example 7.12

Which form of sulphur shows paramagnetic behaviour ?

Solution

In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and, hence, exhibits paramagnetism.

7.15 Sulphur Dioxide

Preparation

Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$$S(s) + O_2(g) \rightarrow SO_2\ (g)$$

In the laboratory it is readily generated by treating a sulphite with dilute sulphuric acid.

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

Industrially, it is produced as a by-product of the roasting of sulphide ores.

$$4FeS_2\,(s) + 11O_2\,(g) \rightarrow 2Fe_2O_3\,(s) + 8SO_2\,(g)$$

The gas after drying is liquefied under pressure and stored in steel cylinders.

Properties

Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water. It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.

Sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

$$SO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2SO_3\,(aq)$$

It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

In its reaction with water and alkalies, the behaviour of sulphur dioxide is very similar to that of carbon dioxide.

Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride, SO_2Cl_2. It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.

$$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$$

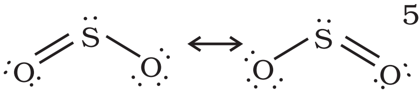
$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution; the latter reaction is a convenient test for the gas.

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:



Uses: Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

Intext Questions

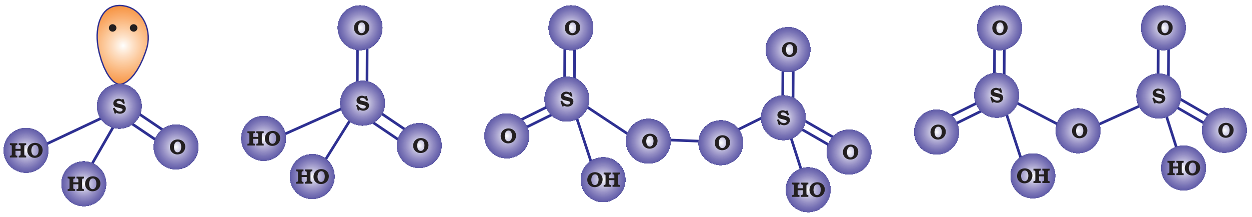
7.20 What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?

7.21 Comment on the nature of two S–O bonds formed in SO_2 molecule. Are the two S–O bonds in this molecule equal ?

7.22 How is the presence of SO_2 detected ?

7.16 Oxoacids of Sulphur

Sulphur forms a number of oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in Fig. 7.6.



Sulphurous acid (H_2SO_3)

Sulphuric acid (H_2SO_4)

Peroxodisulphuric acid ($H_2S_2O_8$)

Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Fig. 7.6: *Structures of some important oxoacids of sulphur*

7.17 Sulphuric Acid

Manufacture

Sulphuric acid is one of the most important industrial chemicals worldwide.

Sulphuric acid is manufactured by the **Contact Process** which involves three steps:

(i) burning of sulphur or sulphide ores in air to generate SO_2.

(ii) conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and

(iii) absorption of SO_3 in H_2SO_4 to give *Oleum* ($H_2S_2O_7$).

A flow diagram for the manufacture of sulphuric acid is shown in (Fig. 7.7). The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \quad \Delta_r H^\ominus = -196.6\,\text{kJmol}^{-1}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow.

In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce *oleum*. Dilution of oleum with water gives H_2SO_4 of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$$\underset{}{SO_3 + H_2SO_4 \rightarrow} \underset{\text{(Oleum)}}{H_2S_2O_7}$$

The sulphuric acid obtained by Contact process is 96-98% pure.

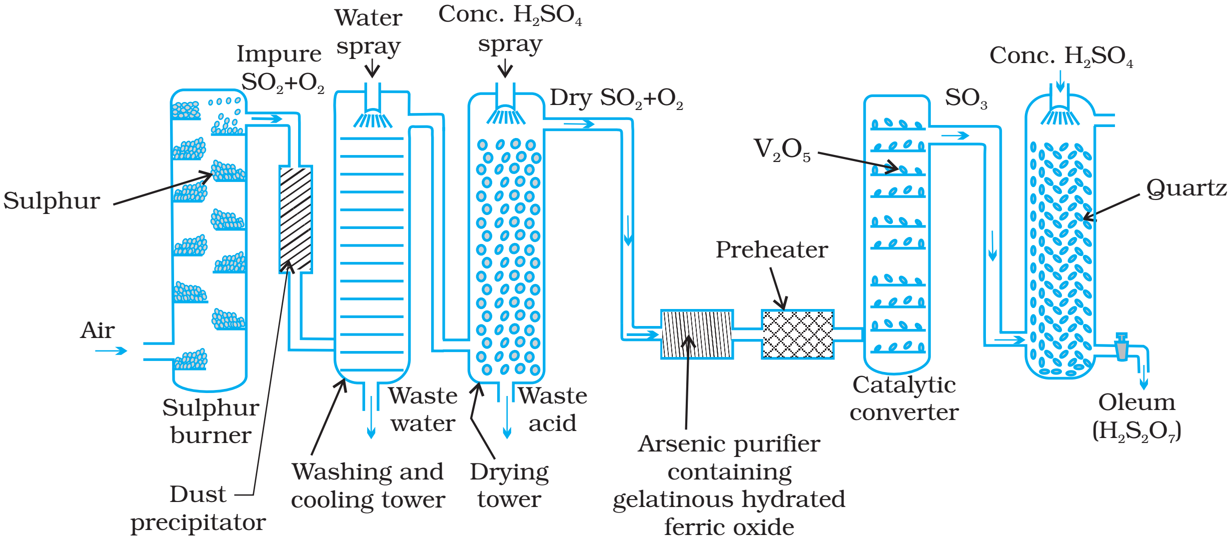


Fig. 7.7: Flow diagram for the manufacture of sulphuric acid

Properties

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

The chemical reactions of sulphuric acid are as a result of the following characteristics: (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent. In aqueous solution, sulphuric acid ionises in two steps.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq); K_{a_1} = \text{very large } (K_{a_1} > 10)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq) ; K_{a_2} = 1.2 \times 10^{-2}$$

The larger value of K_{a_1} (K_{a_1} >10) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-. Greater the value of dissociation constant (K_a), the stronger is the acid.

The acid forms two series of salts: normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium hydrogen sulphate).

Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.

$$2\ MX + H_2SO_4 \rightarrow 2\ HX + M_2SO_4\ (X = F, Cl, NO_3)$$

(M = Metal)

Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$$Cu + 2\ H_2SO_4(conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$S + 2H_2SO_4(conc.) \rightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2\ SO_2 + 2\ H_2O$$

Uses: Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in: (a) petroleum refining (b) manufacture of pigments, paints and dyestuff intermediates (c) detergent industry (d) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising (e) storage batteries (f) in the manufacture of nitrocellulose products and (g) as a laboratory reagent.

Example 7.13

What happens when

(i) Concentrated H_2SO_4 is added to calcium fluoride

(ii) SO_3 is passed through water?

Solution

(i) It forms hydrogen fluoride

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

(ii) It dissolves SO_3 to give H_2SO_4 .

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Intext Questions

7.23 Mention three areas in which H_2SO_4 plays an important role.

7.24 Write the conditions to maximise the yield of H_2SO_4 by Contact process.

7.25 Why is $K_{a_2} \ll K_{a_1}$ for H_2SO_4 in water ?

7.18 Group 17 Elements

Fluorine, chlorine, bromine, iodine, astatine and tennessine are members of Group 17. These are collectively known as the **halogens** (Greek *halo* means salt and *genes* means born i.e., salt producers). The halogens are highly reactive non-metallic elements. Like Groups 1 and 2, the elements of Group 17 show great similarity amongst themselves. That much similarity is not found in the elements of other groups of the periodic table. Also, there is a regular gradation in their physical and chemical properties. Astatine and tennessine are radioactive elements.

7.18.1 Occurrence

Fluorine and chlorine are fairly abundant while bromine and iodine less so. Fluorine is present mainly as insoluble fluorides (fluorspar CaF_2, cryolite Na_3AlF_6 and fluoroapatite $3Ca_3(PO_4)_2.CaF_2$) and small quantities are present in soil, river water plants and bones and teeth of animals. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass). The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite, $KCl.MgCl_2.6H_2O$. Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

Here important atomic and physical properties of Group 17 elements other than tennessine are given along with their electronic configurations [Table 7.8, page 198]. Tennessine is a synthetic radioactive element. Its symbol is Ts, atomic number 117, atomic mass 294 and electronic configuration [Rn] $5f^{14}6d^{10}7s^27p^5$. Only very small amount of the element could be prepared. Also its half life is in milliseconds only. That is why its chemistry could not be established.

Table 7.8: Atomic and Physical Properties of Halogens

Property	**F**	**Cl**	**Br**	**I**	**At**[a]
Atomic number	9	17	35	53	85
Atomic mass/g mol^{-1}	19.00	35.45	79.90	126.90	210
Electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$	$[Xe]4f^{14}5d^{10}6s^26p^5$
Covalent radius/pm	64	99	114	133	–
Ionic radius X^-/pm	133	184	196	220	–
Ionisation enthalpy/kJ mol^{-1}	1680	1256	1142	1008	–
Electron gain enthalpy/kJ mol^{-1}	–333	–349	–325	–296	–
Electronegativity[b]	4	3.2	3.0	2.7	2.2
$\Delta_{Hyd}H(X^-)$/kJ mol^{-1}	515	381	347	305	–
	$\mathbf{F_2}$	$\mathbf{Cl_2}$	$\mathbf{Br_2}$	$\mathbf{I_2}$	**–**
Melting point/K	54.4	172.0	265.8	386.6	–
Boiling point/K	84.9	239.0	332.5	458.2	–
Density/g cm^{-3}	1.5 (85)[c]	1.66 (203)[c]	3.19(273)[c]	4.94(293)[d]	–
Distance X – X/pm	143	199	228	266	–
Bond dissociation enthalpy /(kJ mol^{-1})	158.8	242.6	192.8	151.1	–
$E^\ominus/V^e$	2.87	1.36	1.09	0.54	–

[a] Radioactive; [b] Pauling scale; [c] For the liquid at temperatures (K) given in the parentheses; [d] solid; [e] The half-cell reaction is $X_2(g) + 2e^- \rightarrow 2X^-(aq)$.

The trends of some of the atomic, physical and chemical properties are discussed below.

7.18.2 Electronic Configuration

All these elements have seven electrons in their outermost shell (ns^2np^5) which is one electron short of the next noble gas.

7.18.3 Atomic and Ionic Radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. The atomic radius of fluorine like the other elements of second period is extremely small. Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

7.18.4 Ionisation Enthalpy

They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy decreases down the group.

7.18.5 Electron Gain Enthalpy

Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small $2p$ orbitals of fluorine and thus, the incoming electron does not experience much attraction.

7.18.6 Electronegativity

They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table.

Example 7.14

Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Solution

Halogens have the smallest size in their respective periods and therefore high effective nuclear charge. As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

7.18.7 Physical Properties

Halogens display smooth variations in their physical properties. Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F_2, has yellow, Cl_2 , greenish yellow, Br_2, red and I_2, violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

One curious anomaly we notice from Table 7.8 is the smaller enthalpy of dissociation of F_2 compared to that of Cl_2 whereas X-X bond dissociation enthalpies from chlorine onwards show the expected trend: Cl – Cl > Br – Br > I – I. A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

Example 7.15

Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

Solution

It is due to

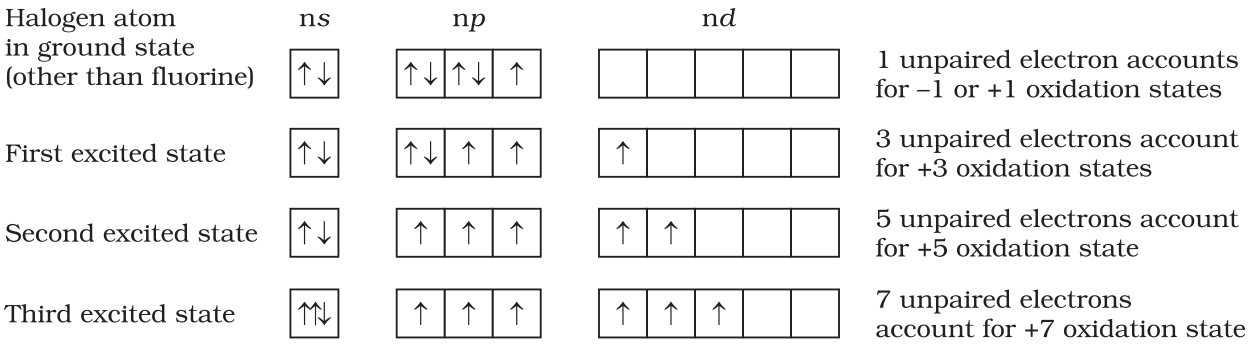
(i) low enthalpy of dissociation of F-F bond (Table 7.8).

(ii) high hydration enthalpy of F^- (Table 7.8).

7.18.8 Chemical Properties

Oxidation states and trends in chemical reactivity

All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also as explained below:



The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids. The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine. The fluorine atom has no *d* orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \text{ (X = Cl, Br or I)}$$

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \text{ (X = Br or I)}$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials (Table 7.8) which are dependent on the parameters indicated below:

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\ \Delta_{diss}H^\ominus} X(g) \xrightarrow{\Delta_{eg}H^\ominus} X^-(g) \xrightarrow{\Delta_{hyd}H^\ominus} X^-(aq)$$

The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is non-spontaneous. In fact, I^- can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$2F_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$$

$$(\text{where X = Cl or Br})$$

$$4I^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(l)$$

Anomalous behaviour of fluorine

Like other elements of *p*-block present in second period of the periodic table, fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected. The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of *d* orbitals in valence shell.

Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Hydrogen bond is formed in HF due to small size and high electronegativity of fluorine. Other hydrogen halides which have bigger size and less electronegativity are gases.

(i) *Reactivity towards hydrogen*: They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids. Some of the properties of hydrogen halides are given in Table 7.9. The acidic strength of these acids varies in the order: HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond (H–X) dissociation enthalpy in the order: H–F > H–Cl > H–Br > H–I.

Table 7.9: Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting point/K	190	159	185	222
Boiling point/K	293	189	206	238
Bond length (H – X)/pm	91.7	127.4	141.4	160.9
$\Delta_{diss}H^\ominus$/kJ mol^{-1}	574	432	363	295
pK_a	3.2	–7.0	–9.5	–10.0

(ii) *Reactivity towards oxygen*: Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. Higher stability of oxides of iodine is due to greater polarisability of bond between iodine and oxygen. In the case of chlorine, multiple bond formation between chlorine and oxygen takes place due to availability of *d*–orbitals. This leads to increase in stability. Bromine lacks both the characteristics hence stability of oxides of bromine is least. The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

The bromine oxides, Br_2O, BrO_2 , BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents.

The iodine oxides, I_2O_4 , I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

(iii) *Reactivity towards metals*: Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.

$$Mg(s) + Br_2(l) \rightarrow MgBr_2(s)$$

The ionic character of the halides decreases in the order MF > MCl > MBr > MI where M is a monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. For example, $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

(iv) *Reactivity of halogens towards other halogens*: Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX', XX_3', XX_5' and XX_7' where X is a larger size halogen and X' is smaller size halogen.

Example 7.16 Fluorine exhibits only –1 oxidation state whereas other halogens exhibit + 1, + 3, + 5 and + 7 oxidation states also. Explain.

Solution Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d* orbitals and therefore, can expand their octets and show + 1, + 3, + 5 and + 7 oxidation states also.

Intext Questions

7.26 Considering the parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy, compare the oxidising power of F_2 and Cl_2.

7.27 Give two examples to show the anomalous behaviour of fluorine.

7.28 Sea is the greatest source of some halogens. Comment.

7.19 Chlorine

Chlorine was discovered in 1774 by Scheele by the action of HCl on MnO_2. In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, *chloros* = greenish yellow).

Preparation

It can be prepared by any one of the following methods:

(i) By heating manganese dioxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

(ii) By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture of chlorine

(i) *Deacon's process*: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

(ii) *Electrolytic process*: Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as a by–product in many chemical industries.

Properties

It is a greenish yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It can be liquefied easily into greenish yellow liquid which boils at 239 K. It is soluble in water.

Chlorine reacts with a number of metals and non-metals to form chlorides.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$; $P_4 + 6Cl_2 \rightarrow 4PCl_3$

$2Na + Cl_2 \rightarrow 2NaCl$; $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$;

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$H_2S + Cl_2 \rightarrow 2HCl + S$$

$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$$

With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$

(cold and dilute)

$$6\ NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

(hot and conc.)

With dry slaked lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

The composition of bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$.

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{UV} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethene}}{C_2H_4} + Cl_2 \xrightarrow{\text{Room temp.}} \underset{\text{1,2-Dichloroethane}}{C_2H_4Cl_2}$$

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

Chlorine oxidises ferrous to ferric and sulphite to sulphate. Chlorine oxidises sulphur dioxide to sulphur trioxide and iodine to iodate. In the presence of water they form sulphuric acid and iodic acid respectively.

$$2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$$

Chlorine is a powerful bleaching agent; bleaching action is due to oxidation.

It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

$$Cl_2 + H_2O \rightarrow 2HCl + O$$

Coloured substance + O → Colourless substance

Uses: It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Example 7.17 Write the balanced chemical equation for the reaction of Cl_2 with hot and concentrated NaOH. Is this reaction a disproportionation reaction? Justify.

Solution $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Yes, chlorine from zero oxidation state is changed to –1 and +5 oxidation states.

Intext Questions

7.29 Give the reason for bleaching action of Cl_2.

7.30 Name two poisonous gases which can be prepared from chlorine gas.

7.20 Hydrogen Chloride

Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid. Davy in 1810 showed that it is a compound of hydrogen and chlorine.

Preparation

In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420\,K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\,K} Na_2SO_4 + HCl$$

HCl gas can be dried by passing through concentrated sulphuric acid.

Properties

It is a colourless and pungent smelling gas. It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p. 159 K). It is extremely soluble in water and ionises as follows:

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \quad K_a = 10^7$$

Its aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water.

It reacts with NH_3 and gives white fumes of NH_4Cl.

$$NH_3 + HCl \rightarrow NH_4Cl$$

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, **aqua regia** is formed which is used for dissolving noble metals, e.g., gold, platinum.

$$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$
$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$$

Uses: It is used (i) in the manufacture of chlorine, NH_4Cl and glucose (from corn starch), (ii) for extracting glue from bones and purifying bone black, (iii) in medicine and as a laboratory reagent.

Example 7.18

When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

Solution

Its reaction with iron produces H_2.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

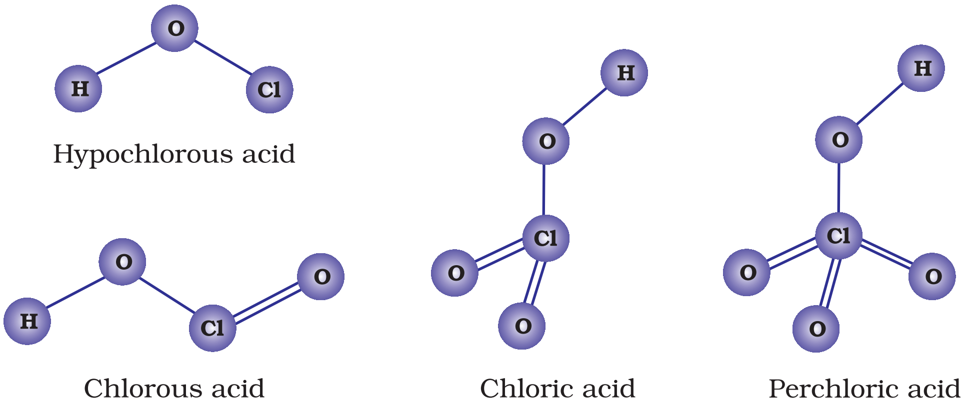
Liberation of hydrogen prevents the formation of ferric chloride.

7.21 Oxoacids of Halogens

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts. The oxoacids of halogens are given in Table 7.10 and their structures are given in Fig. 7.8.

Table 7.10: Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluorous acid)	**HOCl** (Hypochlorous acid)	**HOBr** (Hypobromous acid)	**HOI** (Hypoiodous acid)
Halic (III) acid (Halous acid)	– –	$HOClO$ (chlorous acid)	– –	– –
Halic (V) acid (Halic acid)	– –	$HOClO_2$ (chloric acid)	$HOBrO_2$ (bromic acid)	$HOIO_2$ (iodic acid)
Halic (VII) acid (Perhalic acid)	– –	$HOClO_3$ (perchloric acid)	$HOBrO_3$ (perbromic acid)	$HOIO_3$ (periodic acid)



Hypochlorous acid

Chlorous acid

Chloric acid

Perchloric acid

Fig. 7.8 *The structures of oxoacids of chlorine*

7.22 Interhalogen Compounds

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX' , XX'_3, XX'_5 and XX'_7 where X is halogen of larger size and X' of smaller size and X is more electropositive than X'. As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is IF_7 (having maximum number of atoms).

Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, For example,

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\,K} 2ClF; \qquad \underset{\text{(excess)}}{I_2 + 3Cl_2} \rightarrow 2ICl_3$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573\,K} 2ClF_3; \qquad \underset{\text{(diluted with water)}}{Br_2 + 3F_2} \rightarrow 2BrF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \rightarrow 2ICl; \qquad Br_2 + \underset{\text{(excess)}}{5F_2} \rightarrow 2BrF_5$$

Properties

Some properties of interhalogen compounds are given in Table 7.11.

Table 7.11: Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure
XX'_1	ClF	colourless gas	–
	BrF	pale brown gas	–
	IF^a	detected spectroscopically	–
	$BrCl^b$	gas	
	ICl	ruby red solid (α-form)	–
		brown red solid (β-form)	–
	IBr	black solid	–
XX'_3	ClF_3	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF_3	yellow powder	Bent T-shaped (?)
	$ICl_3{}^c$	orange solid	Bent T-shaped (?)
XX'_5	IF_5	colourless gas but solid below 77 K	Square pyramidal
	BrF_5	colourless liquid	Square pyramidal
	ClF_5	colourless liquid	Square pyramidal
XX'_7	IF_7	colourless gas	Pentagonal bipyramidal

[a] Very unstable; [b] The pure solid is known at room temperature; [c] Dimerises as Cl–bridged dimer (I_2Cl_6)

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids at 298 K except ClF which is a gas. Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

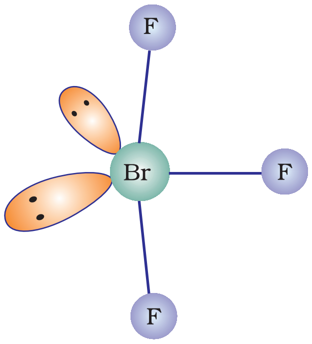
Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X–X′ bond in interhalogens is weaker than X–X bond in halogens except F–F bond. All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX′), halite (when XX'_3), halate (when XX'_5) and perhalate (when XX'_7) anion derived from the larger halogen.

$$XX' + H_2O \rightarrow HX' + HOX$$

Their molecular structures are very interesting which can be explained on the basis of VSEPR theory (Example 7.19). The XX_3 compounds have the bent 'T' shape, XX_5 compounds square pyramidal and IF_7 has pentagonal bipyramidal structures (Table 7.11).

Example 7.19 Discuss the molecular shape of BrF_3 on the basis of VSEPR theory.

Solution The central atom Br has seven electrons in the valence shell. Three of these will form electron-pair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid. The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.



Uses: These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$$

Intext Question

7.31 Why is ICl more reactive than I_2?

7.23 Group 18 Elements

Group 18 consists of elements: helium, neon, argon, krypton, xenon, radon and oganesson. All these are gases and chemically unreactive. They form very few compounds, because of this they are termed as **noble gases**.

7.23.1 Occurrence

All these gases except radon and oganesson occur in the atmosphere. Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of ^{226}Ra.

$$^{226}_{88}\text{Ra} \rightarrow \, ^{222}_{86}\text{Rn} + ^{4}_{2}\text{He}$$

Oganesson has been synthetically produced by collision of $^{249}_{98}Cf$ atoms and $^{48}_{20}Ca$ ions

$$^{249}_{98}\text{Cf} + ^{48}_{20}\text{Ca} \longrightarrow \, ^{294}_{118}\text{Og} + 3n$$

Example 7.20 Why are the elements of Group 18 known as noble gases ?

Solution The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

Oganesson has its symbol Og, atomic number 118, atomic mass 294 and electronic configuration [Rn] $5f^{14}6d^{10}7s^{2}7p^{6}$. Only very small amount of Og has been produced. Its half life is 0.7 milliseconds. Therefore, mainly predictions about its chemistry have been made.

Here, except for oganesson, important atomic and physical properties of other elements of Group 18 along with their electronic configurations are given in Table 7.12. The trends in some of the atomic, physical and chemical properties of the group are discussed here.

Table 7.12: Atomic and Physical Properties of Group 18 Elements

Propery	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/ g mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	[He]$2s^22p^6$	[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 radius/pm	120	160	190	200	220	–
Ionisation enthalpy /kJmol^{-1}	2372	2080	1520	1351	1170	1037
Electron gain enthalpy /kJmol^{-1}	48	116	96	96	77	68
Density (at STP)/gcm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	–	24.6	83.8	115.9	161.3	202
Boiling point/K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	–	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}

* *radioactive*

7.23.2 Electronic Configuration

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$ (Table 7.12). Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

7.23.3 Ionisation Enthalpy

Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increase in atomic size.

7.23.4 Atomic Radii

Atomic radii increase down the group with increase in atomic number.

7.23.5 Electron Gain Enthalpy

Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

Physical Properties

All the noble gases are monoatomic. They are colourless, odourless and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces. Helium has the lowest boiling point (4.2 K) of any known substance. It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Example 7.21

Noble gases have very low boiling points. Why?

Solution

Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

Chemical Properties

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

The reactivity of noble gases has been investigated occasionally, ever since their discovery, but all attempts to force them to react to form the compounds, were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJmol^{-1}) was almost identical with that of xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound $Xe^+PtF_6^-$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

(a) Xenon-fluorine compounds

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$Xe\,(g) + F_2\,(g) \xrightarrow{673\,K,\ 1\,bar} XeF_2(s)$$
(xenon in excess)

$$Xe\,(g) + 2F_2\,(g) \xrightarrow{873\,K,\ 7\,bar} XeF_4(s)$$
(1:5 ratio)

$$Xe\,(g) + 3F_2\,(g) \xrightarrow{573\,K,\ 60\text{–}70\,bar} XeF_6(s)$$
(1:20 ratio)

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

$$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$$

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2.

$$2XeF_2\,(s) + 2H_2O(l) \rightarrow 2Xe\,(g) + 4\,HF(aq) + O_2(g)$$

The structures of the three xenon fluorides can be deduced from VSEPR and these are shown in Fig. 7.9. XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase.

Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$$XeF_2 + PF_5 \rightarrow [XeF]^+\,[PF_6]^-;\quad XeF_4 + SbF_5 \rightarrow [XeF_3]^+\,[SbF_6]^-$$
$$XeF_6 + MF \rightarrow M^+\,[XeF_7]^-\ (M = Na,\ K,\ Rb\ or\ Cs)$$

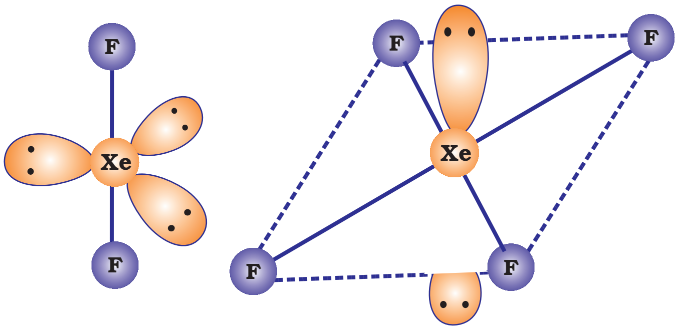
(b) Xenon-oxygen compounds

Hydrolysis of XeF_4 and XeF_6 with water gives $Xe0_3$.

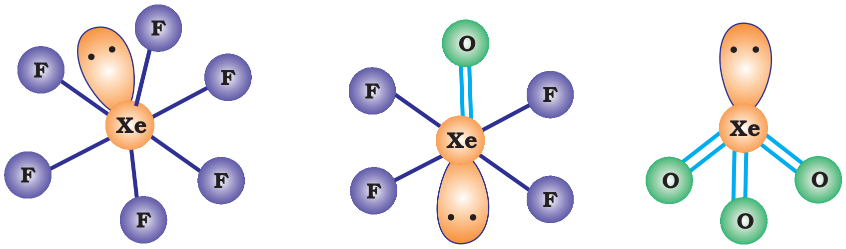
$$6XeF_4 + 12\,H_2O \rightarrow 4Xe + 2Xe0_3 + 24\,HF + 3\,O_2$$
$$XeF_6 + 3\,H_2O \rightarrow XeO_3 + 6\,HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\,HF$$
$$XeF_6 + 2\,H_2O \rightarrow XeO_2F_2 + 4HF$$



(a) Linear (b) Square planar



(c) Distorted octahedral (d) Square pyramidal (e) Pyramidal

Fig. 7.9
The structures of (a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_4$ and (e) XeO_3

XeO_3 is a colourless explosive solid and has a pyramidal molecular structure (Fig. 7.9). $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure (Fig.7.9).

Example 7.22

Does the hydrolysis of XeF_6 lead to a redox reaction?

Solution

No, the products of hydrolysis are $XeOF_4$ and XeO_2F_2 where the oxidation states of all the elements remain the same as it was in the reacting state.

Uses: Helium is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium (b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

Intext Questions

7.32 Why is helium used in diving apparatus?

7.33 Balance the following equation: $XeF_6 + H_2O \rightarrow XeO_2F_2 + HF$

7.34 Why has it been difficult to study the chemistry of radon?

Summary

Groups 13 to 18 of the periodic table consist of ***p*-block elements** with their valence shell electronic configuration ns^2np^{1-6}. Groups 13 and 14 were dealt with in Class XI. In this Unit remaining groups of the *p*-block have been discussed.

Group 15 consists of five elements namely, N, P, As, Sb and Bi which have general electronic configuration ns^2np^3. Nitrogen differs from other elements of this group due to small size, formation of **$p\pi$–$p\pi$ multiple bonds** with itself and with highly electronegative atom like O or C and **non-availability of *d* orbitals** to expand its valence shell. Elements of group 15 show gradation in properties. They react with oxygen, hydrogen and halogens. They exhibit two important oxidation states, + 3 and + 5 but +3 oxidation is favoured by heavier elements due to 'inert pair effect'.

Dinitrogen can be prepared in laboratory as well as on industrial scale. It forms oxides in various oxidation states as N_2O, NO, N_2O_3, NO_2, N_2O_4 and N_2O_5. These oxides have **resonating structures** and have multiple bonds. Ammonia can be prepared on large scale by **Haber's process**. HNO_3 is an important industrial chemical. It is a strong monobasic acid and is a powerful oxidising agent. Metals and non-metals react with HNO_3 under different conditions to give NO or NO_2.

Phosphorus exists as P_4 in elemental form. It exists in several **allotropic forms**. It forms hydride, PH_3 which is a highly poisonous gas. It forms two types of halides as PX_3 and PX_5. PCl_3 is prepared by the reaction of white phosphorus with dry chlorine while PCl_5 is prepared by the reaction of phosphorus with SO_2Cl_2. Phosphorus forms a number of oxoacids. Depending upon the number of P–OH groups, their basicity varies. The oxoacids which have P–H bonds are good reducing agents.

The Group 16 elements have general electronic configuration ns^2np^4. They show maximum oxidation state, +6. Gradation in physical and chemical properties is observed in the group 16 elements. In laboratory, dioxygen is prepared by heating $KClO_3$ in presence of MnO_2. It forms a number of oxides with metals. Allotropic form of oxygen is O_3 which is a highly oxidising agent. Sulphur forms a number of allotropes. Of these, α– and β– forms of sulphur are the most important. Sulphur combines with oxygen to give oxides such as SO_2 and SO_3. SO_2 is prepared by the direct union of sulphur with oxygen. SO_2 is used in the manufacture of H_2SO_4. Sulphur forms a number of oxoacids. Amongst them, the most important is H_2SO_4. It is prepared by **contact process**. It is a dehydrating and oxidising agent. It is used in the manufacture of several compounds.

Group 17 of the periodic table consists of the following elements F, Cl, Br, I and At.These elements are extremely reactive and as such they are found in the combined state only. The common oxidation state of these elements is –1. However, highest oxidation state can be +7. They show regular gradation in physical and chemical properties. They form oxides, hydrogen halides, interhalogen compounds and oxoacids. Chlorine is conveniently obtained by the reaction of HCl with $KMnO_4$. HCl is prepared by heating NaCl with concentrated H_2SO_4. Halogens combine with one another to form **interhalogen compounds** of the type $XX^1{}_n$ (n = 1, 3, 5, 7) where X^1 is lighter than X. A number of oxoacids of halogens are known. In the structures of these oxoacids, halogen is the central atom which is bonded in each case with one OH bond as X–OH. In some cases X = 0 bonds are also found.

Group 18 of the periodic table consists of **noble gases**. They have $ns^2\ np^6$ valence shell electronic configuration except He which has $1s^2$. All the gases except Rn occur in atmosphere. Rn is obtained as the decay product of ^{226}Ra.

Due to complete octet of outermost shell, they have less tendency to form compounds. The best characterised compounds are those of xenon with fluorine and oxygen only under certain conditions. These gases have several uses. Argon is used to provide inert atmosphere, helium is used in filling balloons for meteorological observations, neon is used in discharge tubes and fluorescent bulbs.

Exercises

7.1 Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.

7.2 Why does the reactivity of nitrogen differ from phosphorus?

7.3 Discuss the trends in chemical reactivity of group 15 elements.

7.4 Why does NH_3 form hydrogen bond but PH_3 does not?

7.5 How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

7.6 How is ammonia manufactured industrially?

7.7 Illustrate how copper metal can give different products on reaction with HNO_3.

7.8 Give the resonating structures of NO_2 and N_2O_5.

7.9 The HNH angle value is higher than HPH, HAsH and HSbH angles. Why? [**Hint:** Can be explained on the basis of sp^3 hybridisation in NH_3 and only *s–p* bonding between hydrogen and other elements of the group].

7.10 Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?

7.11 Explain why NH_3 is basic while BiH_3 is only feebly basic.

7.12 Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

7.13 Write main differences between the properties of white phosphorus and red phosphorus.

7.14 Why does nitrogen show catenation properties less than phosphorus?

7.15 Give the disproportionation reaction of H_3PO_3.

7.16 Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

7.17 Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

7.18 Why is dioxygen a gas but sulphur a solid?

7.19 Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-? (**Hint:** Consider lattice energy factor in the formation of compounds).

7.20 Which aerosols deplete ozone?

7.21 Describe the manufacture of H_2SO_4 by contact process?

7.22 How is SO_2 an air pollutant?

7.23 Why are halogens strong oxidising agents?

7.24 Explain why fluorine forms only one oxoacid, HOF.

7.25 Explain why inspite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.

7.26 Write two uses of ClO_2.

7.27 Why are halogens coloured?

7.28 Write the reactions of F_2 and Cl_2 with water.

7.29 How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only.

7.30 What inspired N. Bartlett for carrying out reaction between Xe and PtF_6?

7.31 What are the oxidation states of phosphorus in the following:
(i) H_3PO_3 (ii) PCl_3 (iii) Ca_3P_2 (iv) Na_3PO_4 (v) POF_3?

7.32 Write balanced equations for the following:
(i) NaCl is heated with sulphuric acid in the presence of MnO_2.
(ii) Chlorine gas is passed into a solution of NaI in water.

7.33 How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained?

7.34 With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

7.35 How are XeO_3 and $XeOF_4$ prepared?

7.36 Arrange the following in the order of property indicated for each set:
(i) F_2, Cl_2, Br_2, I_2 - increasing bond dissociation enthalpy.
(ii) HF, HCl, HBr, HI - increasing acid strength.
(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 – increasing base strength.

7.37 Which one of the following does not exist?
(i) $XeOF_4$ (ii) NeF_2 (iii) XeF_2 (iv) XeF_6

7.38 Give the formula and describe the structure of a noble gas species which is isostructural with:
(i) ICl_4^- (ii) IBr_2^- (iii) BrO_3^-

7.39 Why do noble gases have comparatively large atomic sizes?

7.40 List the uses of neon and argon gases.

Answers to Some Intext Questions

7.1 Higher the positive oxidation state of central atom, more will be its polarising power which, in turn, increases the covalent character of bond formed between the central atom and the other atom.

7.2 Because BiH_3 is the least stable among the hydrides of Group 15.

7.3 Because of strong pπ–pπ overlap resulting into the triple bond, $N\equiv N$.

7.6 From the structure of N_2O_5 it is evident that covalence of nitrogen is four.

7.7(a) Both are sp^3 hybridised. In PH_4^+ all the four orbitals are bonded whereas in PH_3 there is a lone pair of electrons on P, which is responsible for lone pair-bond pair repulsion in PH_3 reducing the bond angle to less than 109° 28′.

7.10 $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

7.11 Three P–OH groups are present in the molecule of H_3PO_4. Therefore, its basicity is three.

7.15 Because of small size and high electronegativity of oxygen, molecules of water are highly associated through hydrogen bonding resulting in its liquid state.

7.21 Both the S–O bonds are covalent and have equal strength due to resonating structures.

7.25 H_2SO_4 is a very strong acid in water largely because of its first ionisation to H_3O^+ and HSO_4^-. The ionisation of HSO_4^- to H_3O^+ and SO_4^{2-} is very very small. That is why $K_{a_2} << K_{a_1}$.

7.31 In general, interhalogen compounds are more reactive than halogens due to weaker X–X^1 bonding than X–X bond. Thus, ICl is more reactive than I_2.

7.34 Radon is radioactive with very short half-life which makes the study of chemistry of radon difficult.

Unit

8

The *d*- and *f*- Block Elements

Objectives

After studying this Unit, you will be able to

- learn the positions of the *d*– and *f*-block elements in the periodic table;
- know the electronic configurations of the transition (*d*-block) and the inner transition (*f*-block) elements;
- appreciate the relative stability of various oxidation states in terms of electrode potential values;
- describe the preparation, properties, structures and uses of some important compounds such as $K_2Cr_2O_7$ and $KMnO_4$;
- understand the general characteristics of the *d*– and *f*–block elements and the general horizontal and group trends in them;
- describe the properties of the *f*-block elements and give a comparative account of the lanthanoids and actinoids with respect to their electronic configurations, oxidation states and chemical behaviour.

Iron, copper, silver and gold are among the transition elements that have played important roles in the development of human civilisation. The inner transition elements such as Th, Pa and U are proving excellent sources of nuclear energy in modern times.

The *d*-block of the periodic table contains the elements of the groups 3-12 in which the *d* orbitals are progressively filled in each of the four long periods. The *f*-block consists of elements in which 4 *f* and 5 *f* orbitals are progressively filled. They are placed in a separate panel at the bottom of the periodic table. The names *transition metals* and *inner transition* metals are often used to refer to the elements of *d*-and *f*-blocks respectively.

There are mainly four series of the transition metals, 3*d* series (Sc to Zn), 4*d* series (Y to Cd), 5*d* series (La and Hf to Hg) and 6*d* series which has Ac and elements from Rf to Cn. The two series of the inner transition metals; 4*f* (Ce to Lu) and 5*f* (Th to Lr) are known as *lanthanoids* and *actinoids* respectively.

Originally the name transition metals was derived from the fact that their chemical properties were transitional between those of *s* and *p*-block elements. Now according to IUPAC, transition metals are defined as metals which have incomplete *d* subshell either in neutral atom or in their ions. Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the 3*d*, 4*d* and 5*d* transition series, respectively, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled *d* or *f* orbitals in their atoms makes transition elements different from that of the non-transition elements. Hence, transition elements and their compounds are studied separately. However, the usual theory of valence as applicable to the non-transition elements can be applied successfully to the transition elements also.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium belong to the transition metals series.

In this Unit, we shall first deal with the electronic configuration, occurrence and general characteristics of transition elements with special emphasis on the trends in the properties of the first row (3*d*) transition metals along with the preparation and properties of some important compounds. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the inner transition metals.

THE TRANSITION ELEMENTS (*d*-BLOCK)

8.1 Position in the Periodic Table

The *d*–block occupies the large middle section of the periodic table flanked between *s*– and *p*– blocks in the periodic table. The *d*–orbitals of the penultimate energy level of atoms receive electrons giving rise to four rows of the transition metals, i.e., 3*d*, 4*d*, 5*d* and 6*d*. All these series of transition elements are shown in Table 8.1.

8.2 Electronic Configurations of the d-Block Elements

In general the electronic configuration of outer orbitals of these elements is $(n\text{-}1)d^{1-10}ns^{1-2}$. The (n–1) stands for the inner *d* orbitals which may have one to ten electrons and the outermost n*s* orbital may have one or two electrons. However, this generalisation has several exceptions because of very little energy difference between (n-1)*d* and n*s* orbitals. Furthermore, half and completely filled sets of orbitals are relatively more stable. A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the 3*d* series. For example, consider the case of Cr, which has $3d^5\,4s^1$ configuration instead of $3d^4 4s^2$; the energy gap between the two sets (3*d* and 4*s*) of orbitals is small enough to prevent electron entering the 3*d* orbitals. Similarly in case of Cu, the configuration is $3d^{10}4s^1$ and not $3d^9 4s^2$. The ground state electronic configurations of the outer orbitals of transition elements are given in Table 8.1.

Table 8.1: Electronic Configurations of outer orbitals of the Transition Elements (ground state)

1st Series										
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
$5s$	2	2	1	1	1	1	1	0	1	2
$4d$	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
$6s$	2	2	2	2	2	2	2	1	1	2
$5d$	1	2	3	4	5	6	7	9	10	10

4th Series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
$7s$	2	2	2	2	2	2	2	2	1	2
$6d$	1	2	3	4	5	6	7	8	10	10

The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula $(n-1)d^{10}ns^2$. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. Therefore, they are not regarded as transition elements.

The *d* orbitals of the transition elements protrude to the periphery of an atom more than the other orbitals (i.e., *s* and *p*), hence, they are more influenced by the surroundings as well as affect the atoms or molecules surrounding them. In some respects, ions of a given d^n configuration ($n = 1 – 9$) have similar magnetic and electronic properties. With partly filled *d* orbitals these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands.

The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. All these characteristics have been discussed in detail later in this Unit.

There are greater similarities in the properties of the transition elements of a horizontal row in contrast to the non-transition elements. However, some group similarities also exist. We shall first study the general characteristics and their trends in the horizontal rows (particularly 3*d* row) and then consider some group similarities.

Example 8.1

On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not?

Solution

On the basis of incompletely filled 3*d* orbitals in case of scandium atom in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc atom has completely filled *d* orbitals ($3d^{10}$) in its ground state as well as in its oxidised state, hence it is not regarded as a transition element.

Intext Question

8.1 Silver atom has completely filled *d* orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

We will discuss the properties of elements of first transition series only in the following sections.

8.3 General Properties of the Transition Elements (d-Block)

8.3.1 Physical Properties

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

Lattice Structures of Transition Metals

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
hcp (bcc)	hcp (bcc)	bcc	bcc	X (bcc, ccp)	bcc (hcp)	ccp (hcp)	ccp	ccp	X (hcp)
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
hcp (bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X (hcp)
La	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
hcp (ccp,bcc)	hcp (bcc)	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

(bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = a typical metal structure).

The transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility. Their melting and boiling points are high. Fig. 8.1 depicts the melting points of transition metals belonging to 3*d*, 4*d* and 5*d* series. The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)*d* in addition to the *ns* electrons in the interatomic metallic bonding. In any row the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases. They have high enthalpies of atomisation which are shown in Fig. 8.2. The maxima at about the middle of each series indicate that one unpaired electron per *d* orbital is particularly

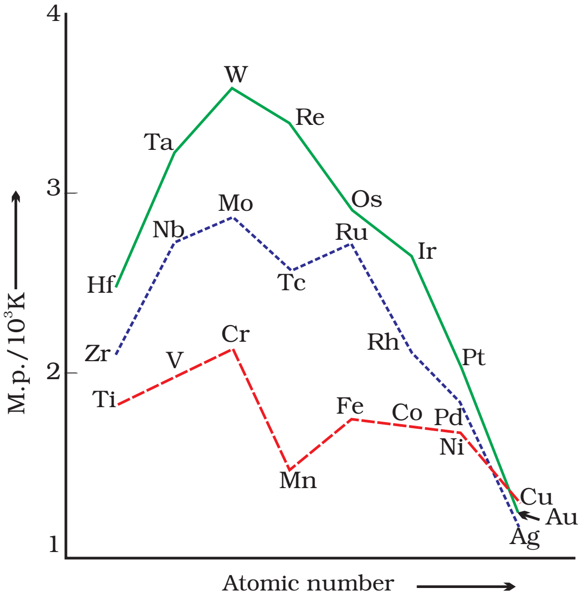


Fig. 8.1: Trends in melting points of transition elements

favourable for strong interatomic interaction. In general, greater the number of valence electrons, stronger is the resultant bonding. Since the enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal, metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions (see later for electrode potentials).

Another generalisation that may be drawn from Fig. 8.2 is that the metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series; this is an important factor in accounting for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition metals.

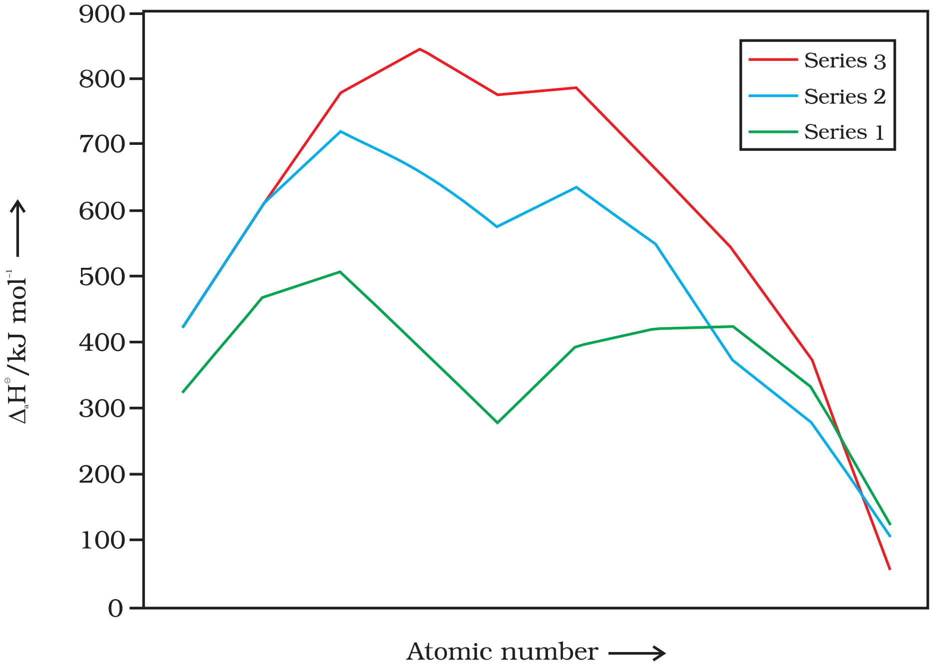


Fig. 8.2
Trends in enthalpies of atomisation of transition elements

8.3.2 Variation in Atomic and Ionic Sizes of Transition Metals

In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a *d* orbital each time the nuclear charge increases by unity. It may be recalled that the shielding effect of a *d* electron is not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases. The same trend is observed in the atomic radii of a given series. However, the variation within a series is quite small. An interesting point emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series. The curves in Fig. 8.3 show an increase from the first (3*d*) to the second (4*d*) series of the elements but the radii of the third (5*d*) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4*f* orbitals which must be filled before the 5*d* series of elements begin. The filling of 4*f* before 5*d* orbital results in a regular decrease in atomic radii called **Lanthanoid contraction** which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third *d* series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

The factor responsible for the lanthanoid contraction is somewhat similar to that observed in an ordinary transition series and is attributed to similar cause, i.e., the imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one 4*f* electron by another is less than that of one *d* electron by another, and as the nuclear charge increases along the series, there is fairly regular decrease in the size of the entire $4f^n$ orbitals.

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium (Z = 22) to copper (Z = 29) the significant increase in the density may be noted (Table 8.2).

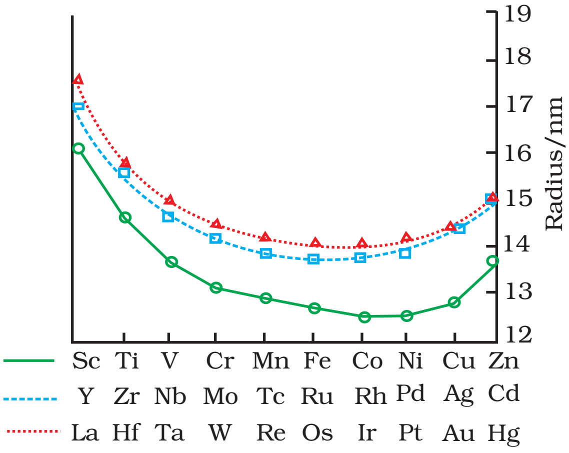


Fig. 8.3: *Trends in atomic radii of transition elements*

Table 8.2: Electronic Configurations and some other Properties of the First Series of Transition Elements

Element		**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Atomic number		21	22	23	24	25	26	27	28	29	30
Electronic configuration											
	M	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
	M^+	$3d^1 4s^1$	$3d^2 4s^1$	$3d^3 4s^1$	$3d^5$	$3d^5 4s^1$	$3d^6 4s^1$	$3d^7 4s^1$	$3d^8 4s^1$	$3d^{10}$	$3d^{10} 4s^1$
	M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
	M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
Enthalpy of atomisation, $\Delta_a H^\ominus$/kJ mol^{-1}											
		326	473	515	397	281	416	425	430	339	126
Ionisation enthalpy/$\Delta_i H^\ominus$/kJ mol^{-1}											
$\Delta_i H^\ominus$	I	631	656	650	653	717	762	758	736	745	906
$\Delta_i H^\ominus$	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
$\Delta_i H^\ominus$	III	2393	2657	2833	2990	3260	2962	3243	3402	3556	3837
Metallic/ionic	M	164	147	135	129	137	126	125	125	128	137
radii/pm	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
Standard											
electrode	M^{2+}/M	–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	-0.76
potential $E^\ominus$/V	M^{3+}/M^{2+}	–	–0.37	–0.26	–0.41	+1.57	+0.77	+1.97	–	–	–
Density/g cm^{-3}		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

Example 8.2

Why do the transition elements exhibit higher enthalpies of atomisation?

Solution

Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomisation.

Intext Question

8.2 In the series Sc ($Z = 21$) to Zn ($Z = 30$), the enthalpy of atomisation of zinc is the lowest, i.e., 126 kJ mol^{-1}. Why?

8.3.3 Ionisation Enthalpies

There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals. Table 8.2 gives the values of the first three ionisation enthalpies of the first series of transition elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the case of non-transition elements. The variation in ionisation enthalpy along a series of transition elements is much less in comparison to the variation along a period of non-transition elements. The first ionisation enthalpy, in general, increases, but the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, is much higher along a series.

The irregular trend in the first ionisation enthalpy of the metals of 3*d* series, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals. You have learnt that when *d*-block elements form ions, *ns* electrons are lost before $(n - 1)$ *d* electrons. As we move along the period in 3*d* series, we see that nuclear charge increases from scandium to zinc but electrons are added to the orbital of inner subshell, i.e., 3*d* orbitals. These 3*d* electrons shield the 4*s* electrons from the increasing nuclear charge somewhat more effectively than the outer shell electrons can shield one another. Therefore, the atomic radii decrease less rapidly. Thus, ionization energies increase only slightly along the 3*d* series. The doubly or more highly charged ions have d^n configurations with no 4*s* electrons. A general trend of increasing values of second ionisation enthalpy is expected as the effective nuclear charge increases because one *d* electron does not shield another electron from the influence of nuclear charge because *d*-orbitals differ in direction. However, the trend of steady increase in second and third ionisation enthalpy breaks for the formation of Mn^{2+} and Fe^{3+} respectively. In both the cases, ions have d^5 configuration. Similar breaks occur at corresponding elements in the later transition series.

The interpretation of variation in ionisation enthalpy for an electronic configuration d^n is as follows:

The three terms responsible for the value of ionisation enthalpy are attraction of each electron towards nucleus, repulsion between the electrons and the exchange energy. Exchange energy is responsible for the stabilisation of energy state. Exchange energy is approximately proportional to the total number of possible pairs of parallel spins in the degenerate orbitals. When several electrons occupy a set of degenerate orbitals, the lowest energy state corresponds to the maximum possible extent of single occupation of orbital and parallel spins (Hunds rule). The loss of exchange energy increases the stability. As the stability increases, the ionisation becomes more difficult. There is no loss of exchange energy at d^6 configuration. Mn^+ has $3d^5 4s^1$ configuration and configuration of Cr^+ is d^5, therefore, ionisation enthalpy of Mn^+ is lower than Cr^+. In the same way, Fe^{2+} has d^6 configuration and Mn^{2+} has $3d^5$ configuration. Hence, ionisation enthalpy of Fe^{2+} is lower than the Mn^{2+}. In other words, we can say that the third ionisation enthalpy of Fe is lower than that of Mn.

The lowest common oxidation state of these metals is +2. To form the M^{2+} ions from the gaseous atoms, the sum of the first and second ionisation enthalpy is required in addition to the enthalpy of atomisation. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where M^+ ions have the d^5 and d^{10} configurations respectively. The value for Zn is correspondingly low as the ionisation causes the removal of 1*s* electron which results in the formation of stable d^{10} configuration. The trend in the third ionisation enthalpies is not complicated by the 4*s* orbital factor and shows the greater difficulty of removing an electron from the d^5 (Mn^{2+}) and d^{10} (Zn^{2+}) ions. In general, the third ionisation enthalpies are quite high. Also the high values for third ionisation enthalpies of copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two for these elements.

Although ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is very complex and not amenable to ready generalisation.

8.3.4 Oxidation States

One of the notable features of a transition elements is the great variety of oxidation states these may show in their compounds. Table 8.3 lists the common oxidation states of the first row transition elements.

Table 8.3: Oxidation States of the first row Transition Metals (the most common ones are in bold types)

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

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many *d* electrons (hence fewer orbitals available in which to share electrons with others) for higher valence (Cu, Zn). Thus, early in the series scandium(II) is virtually unknown and titanium (IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no *d* electrons are involved). The maximum oxidation states of reasonable stability correspond in value to the sum of the *s* and *d* electrons upto manganese ($Ti^{IV}O_2$, $V^{V}O_2^{+}$, $Cr^{V1}O_4^{2-}$, $Mn^{VII}O_4^{-}$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II}, $Cu^{I,II}$, Zn^{II}.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d* orbitals in such a way that their oxidation states differ from each other by unity, e.g., V^{II}, V^{III}, V^{IV}, V^{V}. This is in contrast with the variability of oxidation states of non transition elements where oxidation states normally differ by a unit of two.

An interesting feature in the variability of oxidation states of the *d*–block elements is noticed among the groups (groups 4 through 10). Although in the *p*–block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of *d*-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

Example 8.3

Name a transition element which does not exhibit variable oxidation states.

Solution

Scandium ($Z = 21$) does not exhibit variable oxidation states.

Intext Question

8.3 Which of the 3*d* series of the transition metals exhibits the largest number of oxidation states and why?

8.3.5 Trends in the M^{2+}/M Standard Electrode Potentials

Table 8.4 contains the thermochemical parameters related to the transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials. The observed values of $E^\ominus$ and those calculated using the data of Table 8.4 are compared in Fig. 8.4.

The unique behaviour of Cu, having a positive $E^\ominus$, accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy. The general trend towards less negative $E^\ominus$ values across the series is related to the general increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the value of $E^\ominus$ for Mn, Ni and Zn are more negative than expected from the trend.

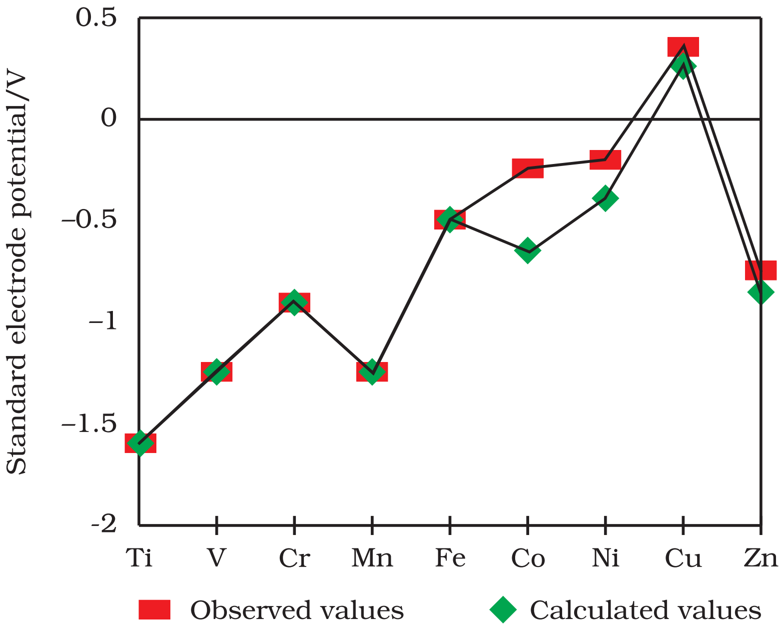


Fig. 8.4: *Observed and calculated values for the standard electrode potentials ($M^{2+} \rightarrow M^\circ$) of the elements Ti to Zn*

Example 8.4

Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration?

Solution

Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level (see Unit 9) . On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

Intext Question

8.4 The $E^\ominus(M^{2+}/M)$ value for copper is positive (+0.34V). What is possible reason for this? (Hint: consider its high $\Delta_a H^\ominus$ and low $\Delta_{hyd} H^\ominus$)

Table 8.4: Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M^{II} to M.

Element (M)	$\Delta_a H^\ominus$ (M)	$\Delta_i H_1^\ominus$	$\Delta_i H_2^\ominus$	$\Delta_{hyd} H^\ominus(M^{2+})$	$E^\ominus$/V
Ti	469	656	1309	-1866	-1.63
V	515	650	1414	-1895	-1.18
Cr	398	653	1592	-1925	-0.90
Mn	279	717	1509	-1862	-1.18
Fe	418	762	1561	-1998	-0.44
Co	427	758	1644	-2079	-0.28
Ni	431	736	1752	-2121	-0.25
Cu	339	745	1958	-2121	0.34
Zn	130	906	1734	-2059	-0.76

The stability of the half-filled *d* sub-shell in Mn^{2+} and the completely filled d^{10} configuration in Zn^{2+} are related to their $E^\ominus$ values, whereas $E^\ominus$ for Ni is related to the highest negative $\Delta_{hyd}H^\ominus$.

8.3.6 Trends in the M^{3+}/M^{2+} Standard Electrode Potentials

An examination of the $E^\ominus(M^{3+}/M^{2+})$ values (Table 8.2) shows the varying trends. The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+}. The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable, whereas comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5). The comparatively low value for V is related to the stability of V^{2+} (half-filled t_{2g} level, Unit 9).

8.3.7 Trends in Stability of Higher Oxidation States

Table 8.5 shows the stable halides of the 3*d* series of transition metals. The highest oxidation numbers are achieved in TiX_4 (tetrahalides), VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MnO_3F is known, and beyond Mn no metal has a trihalide except FeX_3 and CoF_3. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3, or higher bond enthalpy terms for the higher covalent compounds, e.g., VF_5 and CrF_6.

Although V^{+5} is represented only by VF_5, the other halides, however, undergo hydrolysis to give oxohalides, VOX_3. Another feature of fluorides is their instability in the low oxidation states e.g., VX_2 (X = CI, Br or I)

Table 8.5: Formulas of Halides of 3*d* Metals

Oxidation Number									
+ 6			CrF_6						
+ 5		VF_5	CrF_5						
+ 4	TiX_4	VX^I_4	CrX_4	MnF_4					
+ 3	TiX_3	VX_3	CrX_3	MnF_3	FeX^I_3	CoF_3			
+ 2	TiX_2^{III}	VX_2	CrX_2	MnX_2	FeX_2	CoX_2	NiX_2	CuX_2^{II}	ZnX_2
+ 1								CuX^{III}	

Key: X = F → I; X^I = F → Br; X^{II} = F, CI; X^{III} = CI → I and the same applies to CuX. On the other hand, all Cu^{II} halides are known except the iodide. In this case, Cu^{2+} oxidises I^- to I_2:

$$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2\,(s) + I_2$$

However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

$$2Cu^+ \rightarrow Cu^{2+} + Cu$$

The stability of Cu^{2+} (aq) rather than Cu^+(aq) is due to the much more negative $\Delta_{hyd}H^\ominus$ of Cu^{2+} (aq) than Cu^+, which more than compensates for the second ionisation enthalpy of Cu.

The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides. The highest oxidation number in the oxides (Table 8.6) coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7. Beyond Group 7, no higher oxides of Fe above Fe_2O_3, are known, although ferrates (VI)$(FeO_4)^{2-}$, are formed in alkaline media but they readily decompose to Fe_2O_3 and O_2. Besides the oxides, oxocations stabilise V^V as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}. The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7. The ability of oxygen to form multiple bonds to metals explains its superiority. In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by O's including a Mn–O–Mn bridge. The tetrahedral $[MO_4]^{n-}$ ions are known for V^V, Cr^{VI}, Mn^V, Mn^{VI} and Mn^{VII}.

Table 8.6: Oxides of 3d Metals

Oxidation Number	Groups									
	3	4	5	6	7	8	9	10	11	12
+ 7					Mn_2O_7					
+ 6				CrO_3						
+ 5			V_2O_5							
+ 4		TiO_2	V_2O_4	CrO_2	MnO_2					
+ 3	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3				
					$Mn_3O_4^*$	$Fe_3O_4^*$	$Co_3O_4^*$			
+ 2		TiO	VO	(CrO)	MnO	FeO	CoO	NiO	CuO	ZnO
+ 1									Cu_2O	

* *mixed oxides*

How would you account for the increasing oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?

Example 8.5

Solution

This is due to the increasing stability of the lower species to which they are reduced.

Intext Question

8.5 How would you account for the irregular variation of ionisation enthalpies (first and second) in the first series of the transition elements?

8.3.8 Chemical Reactivity and $E^{\ominus}$ Values

Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'—that is, they are unaffected by single acids.

The metals of the first series with the exception of copper are relatively more reactive and are oxidised by 1M H^+, though the actual rate at which these metals react with oxidising agents like hydrogen ion (H^+) is sometimes slow. For example, titanium and vanadium, in practice, are passive to dilute non oxidising acids at room temperature. The $E^{\ominus}$ values for M^{2+}/M (Table 8.2) indicate a decreasing tendency to form divalent cations across the series. This general trend towards less negative $E^{\ominus}$ values is related to the increase in the sum of the first and second ionisation enthalpies. It is interesting to note that the $E^{\ominus}$ values for Mn, Ni and Zn are more negative than expected from the general trend. Whereas the stabilities of half-filled *d* subshell (d^5) in Mn^{2+} and completely filled *d* subshell (d^{10}) in zinc are related to their E^{e} values; for nickel, $E^{\ominus}$ value is related to the highest negative enthalpy of hydration.

An examination of the $E^{\ominus}$ values for the redox couple M^{3+}/M^{2+} (Table 8.2) shows that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solutions. The ions Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from a dilute acid, e.g.,

$$2\ Cr^{2+}(aq) + 2\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + H_2(g)$$

Example 8.6 For the first row transition metals the E° values are:

E°	V	Cr	Mn	Fe	Co	Ni	Cu
(M^{2+}/M)	–1.18	– 0.91	–1.18	– 0.44	– 0.28	– 0.25	+0.34

Explain the irregularity in the above values.

Solution The $E^{\ominus}$ (M^{2+}/M) values are not regular which can be explained from the irregular variation of ionisation enthalpies $(\Delta_i H_1 + \Delta_i H_2)$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

Example 8.7 Why is the $E^{\ominus}$ value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}? Explain.

Solution Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

Intext Questions

8.6 Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

8.7 Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why ?

8.3.9 Magnetic Properties

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: *diamagnetism* and *paramagnetism* (Unit 1). Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted. Substances which are attracted very strongly are said to be **ferromagnetic**. In fact, ferromagnetism is an extreme form of paramagnetism. Many of the transition metal ions are paramagnetic.

Paramagnetism arises from the presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e.,

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

where n is the number of unpaired electrons and μ is the magnetic moment in units of **Bohr magneton (BM)**. A single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM).

The magnetic moment increases with the increasing number of unpaired electrons. Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion. The magnetic moments calculated from the 'spin-only' formula and those derived experimentally for some ions of the first row transition elements are given in Table 8.7. The experimental data are mainly for hydrated ions in solution or in the solid state.

Table 8.7: Calculated and Observed Magnetic Moments (BM)

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Tl^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

Example 8.8

Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Solution

With atomic number 25, the divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons). The magnetic moment, μ is

$$\mu = \sqrt{5(5+2)} = 5.92\,\text{BM}$$

Intext Question

8.8 Calculate the 'spin only' magnetic moment of $M^{2+}_{(aq)}$ ion ($Z = 27$).

8.3.10 Formation of Coloured Ions

When an electron from a lower energy *d* orbital is excited to a higher energy *d* orbital, the energy of excitation corresponds to the frequency of light absorbed (Unit 9). This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand. In aqueous solutions where water molecules are the ligands, the colours of the ions observed are listed in Table 8.8. A few coloured solutions of *d*–block elements are illustrated in Fig. 8.5.

Fig. 8.5: *Colours of some of the first row transition metal ions in aqueous solutions. From left to right:* V^{4+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} *and* Cu^{2+} .

Table 8.8: Colours of Some of the First Row (aquated) Transition Metal Ions

Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6 3d^7$	$Co^{3+} Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

8.3.11 Formation of Complex Compounds

Complex compounds are those in which the metal ions bind a number of anions or neutral molecules giving complex species with characteristic properties. A few examples are: $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$. (The chemistry of complex compounds is dealt with in detail in Unit 9). The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.

8.3.12 Catalytic Properties

The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in Catalytic Hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst (first row transition metals utilise 3*d* and 4*s* electrons for bonding). This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective as catalysts. For example, iron(III) catalyses the reaction between iodide and persulphate ions.

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$$

An explanation of this catalytic action can be given as:

$$2\ Fe^{3+} + 2\ I^- \rightarrow 2\ Fe^{2+} + I_2$$

$$2\ Fe^{2+} + S_2O_8^{2-} \rightarrow 2\ Fe^{3+} + 2SO_4^{2-}$$

8.3.13 Formation of Interstitial Compounds

Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc. The formulas quoted do not, of course, correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as *interstitial* compounds. The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

8.3.14 Alloy Formation

An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Such alloys are formed by atoms with metallic radii that are within about 15 percent of each other. Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel. Alloys of transition metals with non transition metals such as brass (copper-zinc) and bronze (copper-tin), are also of considerable industrial importance.

Example 8.9 What is meant by 'disproportionation' of an oxidation state? Give an example.

Solution When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese(VII) and manganese (IV) in acidic solution.

$$3\ Mn^{VI}O_4^{\ 2-} + 4\ H^+ \rightarrow 2\ Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$$

Intext Question

8.9 Explain why Cu^+ ion is not stable in aqueous solutions?

8.4 Some Important Compounds of Transition Elements

8.4.1 Oxides and Oxoanions of Metals

These oxides are generally formed by the reaction of metals with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic. The highest oxidation number in the oxides, coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7. Beyond group 7, no higher oxides of iron above Fe_2O_3 are known. Besides the oxides, the oxocations stabilise V^V as VO_2^+, V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+}.

As the oxidation number of a metal increases, ionic character decreases. In the case of Mn, Mn_2O_7 is a covalent green oil. Even CrO_3 and V_2O_5 have low melting points. In these higher oxides, the acidic character is predominant.

Thus, Mn_2O_7 gives $HMnO_4$ and CrO_3 gives H_2CrO_4 and $H_2Cr_2O_7$. V_2O_5 is, however, amphoteric though mainly acidic and it gives VO_4^{3-} as well as VO_2^+ salts. In vanadium there is gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5. V_2O_4 dissolves in acids to give VO^{2+} salts. Similarly, V_2O_5 reacts with alkalies as well as acids to give VO_4^{3-} and VO_4^+ respectively. The well characterised CrO is basic but Cr_2O_3 is amphoteric.

Potassium dichromate $K_2Cr_2O_7$

Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore ($FeCr_2O_4$) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$ can be crystallised.

$$2Na_2CrO_4 + 2\ H^+ \rightarrow Na_2Cr_2O_7 + 2\ Na^+ + H_2O$$

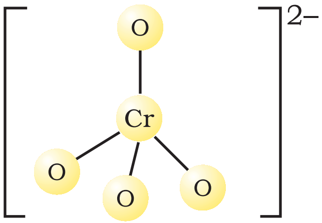
Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$

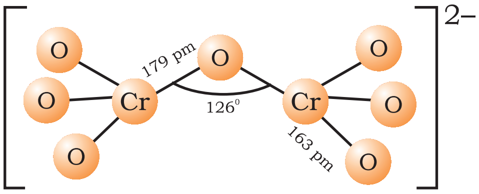
Orange crystals of potassium dichromate crystallise out. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

$$2\ CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$
$$Cr_2O_7^{2-} + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + H_2O$$

The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.



Chromate ion



Dichromate ion

Sodium and potassium dichromates are strong oxidising agents; the sodium salt has a greater solubility in water and is extensively used as an oxidising agent in organic chemistry. Potassium dichromate is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action can be represented as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \ (E^{\ominus} = 1.33V)$$

Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

$$6\ I^- \rightarrow 3I_2 + 6\ e^- ; \qquad 3\ Sn^{2+} \rightarrow 3Sn^{4+} + 6\ e^-$$
$$3\ H_2S \rightarrow 6H^+ + 3S + 6e^- ; \qquad 6\ Fe^{2+} \rightarrow 6Fe^{3+} + 6\ e^-$$

The full ionic equation may be obtained by adding the half-reaction for potassium dichromate to the half-reaction for the reducing agent, for e.g.,

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$

Potassium permanganate $KMnO_4$

Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercially it is prepared by the alkaline oxidative fusion of MnO_2 followed by the electrolytic oxidation of manganate (VI).

$$MnO_2 \xrightarrow{\substack{\text{Fused with KOH, oxidised} \\ \text{with air or } KNO_3}} \underset{\text{manganate ion}}{MnO_4^{2-}} \quad ; \quad \underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow{\substack{\text{Electrolytic oxidation in} \\ \text{alkaline solution}}} \underset{\text{permanganate ion}}{MnO_4^{-}}$$

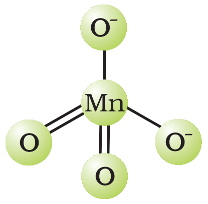
In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^{-} + 10SO_4^{2-} + 16H^{+}$$

Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.

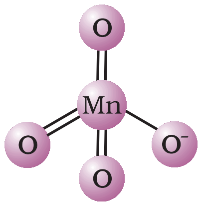
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

It has two physical properties of considerable interest: its intense colour and its diamagnetism along with temperature-dependent weak paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope.



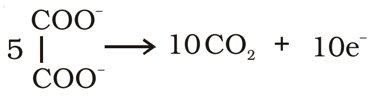
Tetrahedral manganate ion (green)

The manganate and permanganate ions are tetrahedral; the π-bonding takes place by overlap of *p* orbitals of oxygen with *d* orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.



Tetrahedral permanganate ion (purple)

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:



$$5\begin{array}{l}COO^{-}\\ |\\ COO^{-}\end{array} \longrightarrow 10CO_2 + 10e^{-}$$

$$5\,Fe^{2+} \rightarrow 5\,Fe^{3+} + 5e^{-}$$

$$5NO_2^{-} + 5H_2O \rightarrow 5NO_3^{-} + 10H^{+} + 10e^{-}$$

$$10I^{-} \rightarrow 5I_2 + 10e^{-}$$

The full reaction can be written by adding the half-reaction for $KMnO_4$ to the half-reaction of the reducing agent, balancing wherever necessary.

If we represent the reduction of permanganate to manganate, manganese dioxide and manganese(II) salt by half-reactions,

$$MnO_4^{-} + e^{-} \rightarrow MnO_4^{2-} \qquad (E^{\ominus} = +\,0.56\text{ V})$$

$$MnO_4^{-} + 4H^{+} + 3e^{-} \rightarrow MnO_2 + 2H_2O \qquad (E^{\ominus} = +\,1.69\text{ V})$$

$$MnO_4^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O \qquad (E^{\ominus} = +\,1.52\text{ V})$$

We can very well see that the hydrogen ion concentration of the solution plays an important part in influencing the reaction. Although many reactions can be understood by consideration of redox potential, kinetics of the reaction is also an important factor. Permanganate at $[H^{+}] = 1$ should oxidise water but in practice the reaction is extremely slow unless either manganese(ll) ions are present or the temperature is raised.

A few important oxidising reactions of $KMnO_4$ are given below:

1. In acid solutions:

(a) Iodine is liberated from potassium iodide :

$$10I^{-} + 2MnO_4^{-} + 16H^{+} \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

(b) Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):

$$5Fe^{2+} + MnO_4^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

(c) Oxalate ion or oxalic acid is oxidised at 333 K:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(d) Hydrogen sulphide is oxidised, sulphur being precipitated:

$$H_2S \longrightarrow 2H^+ + S^{2-}$$

$$5S^{2-} + 2MnO^-_4 + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

(e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

(f) Nitrite is oxidised to nitrate:

$$5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

2. In neutral or faintly alkaline solutions:

(a) A notable reaction is the oxidation of iodide to iodate:

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(c) Manganous salt is oxidised to MnO_2; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

Note: Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.

Uses: Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.

THE INNER TRANSITION ELEMENTS (*f*-BLOCK)

The *f*-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated. The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study; the two series will be considered separately here.

8.5 The Lanthanoids

The names, symbols, electronic configurations of atomic and some ionic states and atomic and ionic radii of lanthanum and lanthanoids (for which the general symbol Ln is used) are given in Table 8.9.

8.5.1 Electronic Configurations

It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of $4f$ level (Table 8.9). However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$ (n = 1 to 14 with increasing atomic number).

8.5.2 Atomic and Ionic Sizes

The overall decrease in atomic and ionic radii from lanthanum to lutetium (the **lanthanoid contraction**) is a unique feature in the chemistry of the lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in M^{3+} ions (Fig. 8.6). This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one $4f$ electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.

The cumulative effect of the contraction of the lanthanoid series, known as *lanthanoid contraction*, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

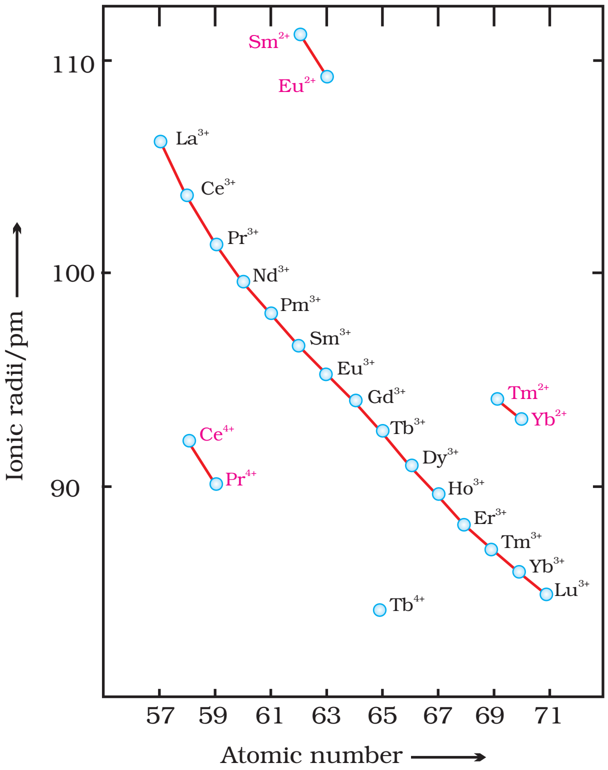


***Fig. 8.6:** Trends in ionic radii of lanthanoids*

8.5.3 Oxidation States

In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The $E^\ominus$ value for Ce^{4+}/Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2. Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f^{14} configuration is a reductant. Tb^{IV} has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

Table 8.9: Electronic Configurations and Radii of Lanthanum and Lanthanoids

Atomic Number	Name	Symbol	Electronic configurations*			Radii/pm		
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$	–	–	–

* *Only electrons outside [Xe] core are indicated*

8.5.4 General Characteristics

All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number, samarium being steel hard. Their melting points range between 1000 to 1200 K but samarium melts at 1623 K. They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.

Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of *f* electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so. However, absorption bands are narrow, probably because of the excitation within *f* level. The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3*d* orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals *f* level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.

In their chemical behaviour, in general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium. Values for $E^\ominus$ for the half-reaction:

$$Ln^{3+}(aq) + 3e^- \rightarrow Ln(s)$$

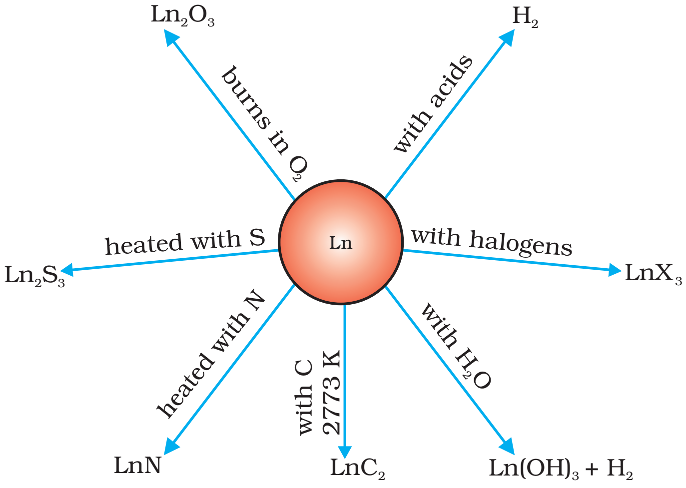


Fig 8.7: Chemical reactions of the lanthanoids.

are in the range of –2.2 to –2.4 V except for Eu for which the value is – 2.0 V. This is, of course, a small variation. The metals combine with hydrogen when gently heated in the gas. The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acids and burn in halogens to form halides. They form oxides M_2O_3 and hydroxides $M(OH)_3$. The hydroxides are definite compounds, not just hydrated oxides. They are basic like alkaline earth metal oxides and hydroxides. Their general reactions are depicted in Fig. 8.7.

The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well known alloy is *mischmetall* which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of **mischmetall** is used in Mg-based alloy to produce bullets, shell and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

8.6 The Actinoids

The actinoids include the fourteen elements from Th to Lr. The names, symbols and some properties of these elements are given in Table 8.10.

Table 8.10: Some Properties of Actinium and Actinoids

Atomic Number	Name	Symbol	Electronic conifigurations*			Radii/pm	
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einstenium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	–	–

The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z=103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

8.6.1 Electronic Configurations

All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to $5f$, though not in thorium (Z = 90) but from Pa onwards the $5f$ orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are $[\mathrm{Rn}]\ 5f^7 7s^2$ and $[\mathrm{Rn}]\ 5f^7 6d^1 7s^2$. Although the $5f$ orbitals resemble the $4f$ orbitals in their angular part of the wave-function, they are not as buried as $4f$ orbitals and hence $5f$ electrons can participate in bonding to a far greater extent.

8.6.2 Ionic Sizes

The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the **actinoid contraction** (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by $5f$ electrons.

8.6.3 Oxidation States

There is a greater range of oxidation states, which is in part attributed to the fact that the $5f$, $6d$ and $7s$ levels are of comparable energies. The known oxidation states of actinoids are listed in Table 8.11.

The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements (Table 8.11). The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

Table 8.11: Oxidation States of Actinium and Actinoids

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3		3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

8.6.4 General Characteristics and Comparison with Lanthanoids

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 *f* electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.

It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5*f* orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5*f* electrons, will therefore, be more effectively shielded from the nuclear charge than the 4*f* electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state. The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

Example 8.10 Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Solution Cerium ($Z = 58$)

Intext Question

8.10 Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

8.7 Some Applications of d- and f-Block Elements

Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells. The battery industry also requires Zn and Ni/Cd. The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au are restricted to collection items and the contemporary UK 'copper' coins are copper-coated steel. The 'silver' UK coins are a Cu/Ni alloy. Many of the metals and/or their compounds are essential catalysts in the chemical industry. V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid. $TiCl_4$ with $A1(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene). Iron catalysts are used in the Haber process for the production of ammonia from N_2/H_2 mixtures. Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene. The photographic industry relies on the special light-sensitive properties of AgBr.

Summary

The ***d*-block** consisting of **Groups 3-12** occupies the large middle section of the **periodic table**. In these elements the inner *d* orbitals are progressively filled. The ***f*-block** is placed **outside** at the **bottom** of the **periodic table** and in the elements of this block, 4*f* and 5*f* orbitals are progressively filled.

Corresponding to the filling of 3*d*, 4*d* and 5*d* orbitals, three series of transition elements are well recognised. All the transition elements exhibit typical metallic properties such as –high tensile strength, ductility, malleability, thermal and electrical conductivity and metallic character. Their melting and boiling points are high which are attributed to the involvement of $(n-1)\,d$ electrons resulting into **strong interatomic bonding**. In many of these properties, the maxima occur at about the middle of each series which indicates that one unpaired electron per *d* orbital is particularly a favourable configuration for strong interatomic interaction.

Successive ionisation enthalpies do not increase as steeply as in the main group elements with increasing atomic number. Hence, the loss of variable number of electrons from $(n-1)\,d$ orbitals is not energetically unfavourable. The involvement of **$(n-1)\,d$ electrons** in the behaviour of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions, interstitial compounds and complexes.

The **transition elements** vary widely in their chemical behaviour. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble'. Of the first series, with the exception of copper, all the metals are relatively reactive.

The transition metals react with a number of non-metals like oxygen, nitrogen, sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures. These oxides dissolve in acids and bases to form oxometallic salts. Potassium dichromate and potassium permanganate are common examples. Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore (MnO_2) is used for the preparation of potassium permanganate. Both the dichromate and the permanganate ions are strong oxidising agents.

The two series of **inner transition elements**, **lanthanoids** and **actinoids** constitute the ***f*-block** of the periodic table. With the successive filling of the inner orbitals, 4*f*, there is a gradual decrease in the atomic and ionic sizes of these metals along the series (**lanthanoid contraction**). This has far reaching consequences in the chemistry of the elements succeeding them. Lanthanum and all the lanthanoids are rather soft white metals. They react easily with water to give solutions giving +3 ions. The principal oxidation state is +3, although +4 and +2 oxidation states are also exhibited by some occasionally. The chemistry of the **actinoids** is more complex in view of their ability to exist in different oxidation states. Furthermore, many of the actinoid elements are radioactive which make the study of these elements rather difficult.

There are many useful applications of the *d*- and *f*-block elements and their compounds, notable among them being in varieties of steels, catalysts, complexes, organic syntheses, etc.

Exercises

8.1 Write down the electronic configuration of:
(i) Cr^{3+} (iii) Cu^{+} (v) $Co^{2}+$ (vii) Mn^{2+}
(ii) Pm^{3+} (iv) Ce^{4+} (vi) Lu^{2+} (viii) Th^{4+}

8.2 Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

8.3 Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

8.4 To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.

8.5 What may be the stable oxidation state of the transition element with the following *d* electron configurations in the ground state of their atoms : $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

8.6 Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

8.7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

8.8 What are the characteristics of the transition elements and why are they called transition elements? Which of the *d*-block elements may not be regarded as the transition elements?

8.9 In what way is the electronic configuration of the transition elements different from that of the non transition elements?

8.10 What are the different oxidation states exhibited by the lanthanoids?

8.11 Explain giving reasons:
(i) Transition metals and many of their compounds show paramagnetic behaviour.
(ii) The enthalpies of atomisation of the transition metals are high.
(iii) The transition metals generally form coloured compounds.
(iv) Transition metals and their many compounds act as good catalyst.

8.12 What are interstitial compounds? Why are such compounds well known for transition metals?

8.13 How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

8.14 Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

8.15 Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:
(i) iodide (ii) iron(II) solution and (iii) H_2S

8.16 Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO_2 and (iii) oxalic acid? Write the ionic equations for the reactions.

8.17 For M^{2+}/M and M^{3+}/M^{2+} systems the $E^{\ominus}$ values for some metals are as follows:

Cr^{2+}/Cr	-0.9V	Cr^{3}/Cr^{2+}	-0.4 V
Mn^{2+}/Mn	-1.2V	Mn^{3+}/Mn^{2+}	+1.5 V
Fe^{2+}/Fe	-0.4V	Fe^{3+}/Fe^{2+}	+0.8 V

Use this data to comment upon:

(i) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+} and

(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

8.18 Predict which of the following will be coloured in aqueous solution? Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each.

8.19 Compare the stability of +2 oxidation state for the elements of the first transition series.

8.20 Compare the chemistry of actinoids with that of the lanthanoids with special reference to:

(i) electronic configuration

(ii) atomic and ionic sizes and

(iii) oxidation state

(iv) chemical reactivity.

8.21 How would you account for the following:

(i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.

(ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(iii) The d^1 configuration is very unstable in ions.

8.22 What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

8.23 Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

8.24 Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+}, Cr^{3+}, V^{3+} and Ti^{3+}. Which one of these is the most stable in aqueous solution?

8.25 Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) The highest oxidation state is exhibited in oxoanions of a metal.

8.26 Indicate the steps in the preparation of:

(i) $K_2Cr_2O_7$ from chromite ore.

(ii) $KMnO_4$ from pyrolusite ore.

8.27 What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

8.28 What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.

8.29 The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

8.30 Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

8.31 Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

8.32 Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.

8.33 Compare the chemistry of the actinoids with that of lanthanoids with reference to:

(i) electronic configuration (ii) oxidation states and (iii) chemical reactivity.

8.34 Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.

8.35 Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

(i) electronic configurations (ii) oxidation states (iii) ionisation enthalpies and (iv) atomic sizes.

8.36 Write down the number of 3d electrons in each of the following ions: Ti^{2+}, V^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}. Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).

8.37 Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

8.38 What can be inferred from the magnetic moment values of the following complex species ?

Example	Magnetic Moment (BM)
$K_4[Mn(CN)_6]$	2.2
$[Fe(H_2O)_6]^{2+}$	5.3
$K_2[MnCl_4]$	5.9

Answers to Some Intext Questions

8.1 Silver (Z = 47) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element.

8.2 In the formation of metallic bonds, no eletrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds.

8.3 Manganese (Z = 25), as its atom has the maximum number of unpaired electrons.

8.5 Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d*-configurations (e.g., d^0, d^5, d^{10} are exceptionally stable).

8.6 Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.

8.7 Cr^{2+} is stronger reducing agent than Fe^{2+}

Reason: $d^4 \rightarrow d^3$ occurs in case of Cr^{2+} to Cr^{3+}

But $d^6 \rightarrow d^5$ occurs in case of Fe^{2+} to Fe^{3+}

In a medium (like water) d^3 is more stable as compared to d^5 *(see CFSE)*

8.9 Cu^+ in aqueous solution underoes disproportionation, i.e.,

$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

The E^0 value for this is favourable.

8.10 The 5*f* electrons are more effectively shielded from nuclear charge. In other words the 5*f* electrons themselves provide poor shielding from element to element in the series.

Unit

9

Coordination Compounds

Objectives

After studying this Unit, you will be able to

- appreciate the postulates of Werner's theory of coordination compounds;
- know the meaning of the terms: coordination entity, central atom/ ion, ligand, coordination number, coordination sphere, coordination polyhedron, oxidation number, homoleptic and heteroleptic;
- learn the rules of nomenclature of coordination compounds;
- write the formulas and names of mononuclear coordination compounds;
- define different types of isomerism in coordination compounds;
- understand the nature of bonding in coordination compounds in terms of the Valence Bond and Crystal Field theories;
- learn the stability of coordination compounds;
- appreciate the importance and applications of coordination compounds in our day to day life.

Coordination Compounds are the backbone of modern inorganic and bio–inorganic chemistry and chemical industry.

In the previous Unit we learnt that the transition metals form a large number of **complex compounds** in which the metal atoms are bound to a number of anions or neutral molecules by sharing of electrons. In modern terminology such compounds are called **coordination compounds**. The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. New concepts of chemical bonding and molecular structure have provided insights into the functioning of these compounds as vital components of biological systems. Chlorophyll, haemoglobin and vitamin B_{12} are coordination compounds of magnesium, iron and cobalt respectively. Variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

9.1 Werner's Theory of Coordination Compounds

Alfred Werner (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques. Werner proposed the concept of a **primary valence** and a **secondary valence** for a metal ion. Binary compounds such as $CrCl_3$, $CoCl_2$ or $PdCl_2$ have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol	$CoCl_3.6NH_3$ (Yellow)	gave	3 mol AgCl
1 mol	$CoCl_3.5NH_3$ (Purple)	gave	2 mol AgCl
1 mol	$CoCl_3.4NH_3$ (Green)	gave	1 mol AgCl
1 mol	$CoCl_3.4NH_3$ (Violet)	gave	1 mol AgCl

These observations, together with the results of conductivity measurements in solution can be explained if (i) six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown in Table 9.1, where the atoms within the square brackets form a single entity which does not dissociate under the reaction conditions. Werner proposed the term **secondary valence** for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

Table 9.1: Formulation of Cobalt(III) Chloride-Ammonia Complexes

Colour	Formula	Solution conductivity corresponds to
Yellow	$[Co(NH_3)_6]^{3+}3Cl^-$	1:3 electrolyte
Purple	$[CoCl(NH_3)_5]^{2+}2Cl^-$	1:2 electrolyte
Green	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte
Violet	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte

Note that the last two compounds in Table 9.1 have identical empirical formula, $CoCl_3.4NH_3$, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds. The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In modern formulations, such spatial arrangements are called coordination *polyhedra*. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions.

He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[CoCl_2(NH_3)_4]^+$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

Example 9.1

On the basis of the following observations made with aqueous solutions, assign secondary valences to metals in the following compounds:

Formula	Moles of AgCl precipitated per mole of the compounds with excess $AgNO_3$
(i) $PdCl_2.4NH_3$	2
(ii) $NiCl_2.6H_2O$	2
(iii) $PtCl_4.2HCl$	0
(iv) $CoCl_3.4NH_3$	1
(v) $PtCl_2.2NH_3$	0

Solution

(i) Secondary 4 (ii) Secondary 6

(iii) Secondary 6 (iv) Secondary 6 (v) Secondary 4

Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)_6]^{4-}$ of $K_4[Fe(CN)_6]$ do not dissociate into Fe^{2+} and CN^- ions.

(1866-1919)

Werner was born on December 12, 1866, in Mülhouse, a small community in the French province of Alsace. His study of chemistry began in Karlsruhe (Germany) and continued in Zurich (Switzerland), where in his doctoral thesis in 1890, he explained the difference in properties of certain nitrogen containing organic substances on the basis of isomerism. He extended vant Hoff's theory of tetrahedral carbon atom and modified it for nitrogen. Werner showed optical and electrical differences between complex compounds based on physical measurements. In fact, Werner was the first to discover optical activity in certain coordination compounds.

He, at the age of 29 years became a full professor at Technische Hochschule in Zurich in 1895. Alfred Werner was a chemist and educationist. His accomplishments included the development of the theory of coordination compounds. This theory, in which Werner proposed revolutionary ideas about how atoms and molecules are linked together, was formulated in a span of only three years, from 1890 to 1893. The remainder of his career was spent gathering the experimental support required to validate his new ideas. Werner became the first Swiss chemist to win the Nobel Prize in 1913 for his work on the linkage of atoms and the coordination theory.

9.2 Definitions of Some Important Terms Pertaining to Coordination Compounds

(a) ***Coordination entity***

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[CoCl_3(NH_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.

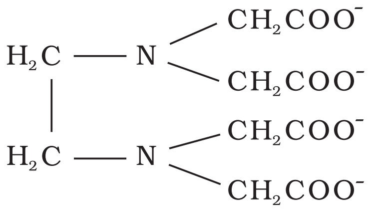
(b) ***Central atom/ion***

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively. These central atoms/ions are also referred to as **Lewis acids**.

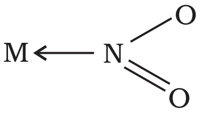
(c) ***Ligands***

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules, such as proteins.

When a ligand is bound to a metal ion through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be **unidentate.** When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be **didentate** and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.



When a di- or polydentate ligand uses its two or more donor atoms simultaneously to bind a single metal ion, it is said to be a **chelate** ligand. The number of such ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands (for reasons see Section 9.8). Ligand which has two different donor atoms and either of the two ligetes in the complex is called **ambidentate ligand**. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.



nitrito-N

$M \leftarrow O - N = O$

nitrito-O

$M \leftarrow SCN$

thiocyanato-S

$M \leftarrow NCS$

thiocyanato-N

(d) ***Coordination number***

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands.

It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

(e) Coordination sphere

The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the **coordination sphere**. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is K^+.

(f) Coordination polyhedron

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example, $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar. Fig. 9.1 shows the shapes of different coordination polyhedra.

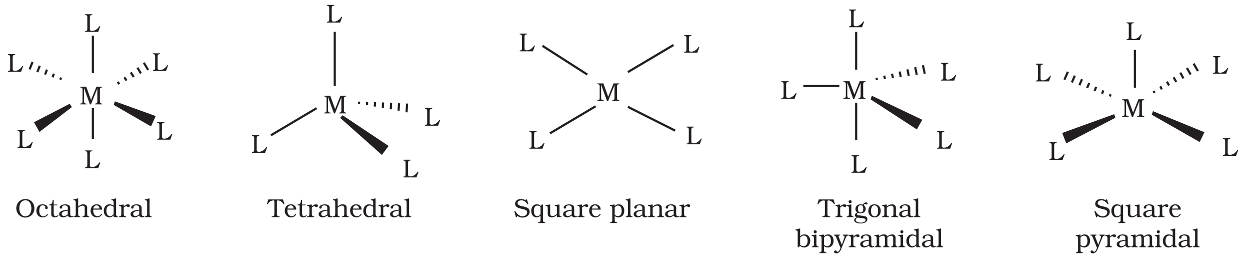


Fig. 9.1: *Shapes of different coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand.*

(g) Oxidation number of central atom

The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

(h) Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one kind of donor groups, *e.g.*, $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, *e.g.*, $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

9.3 Nomenclature of Coordination Compounds

Nomenclature is important in Coordination Chemistry because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers. The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

9.3.1 Formulas of Mononuclear Coordination Entities

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom. The following rules are applied while writing the formulas:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Note: *The 2004 IUPAC draft recommends that ligands will be sorted alphabetically, irrespective of charge.*

9.3.2 Naming of Mononuclear Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. While writing the formula of coordination entity, these are enclosed in brackets ( ).

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $\left[Co(SCN)_4\right]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, *e.g.*, ferrate for Fe.

Note*: The 2004 IUPAC draft recommends that anionic ligands will end with–ido so that chloro would become chlorido, etc.*

(vii) The neutral complex molecule is named similar to that of the complex cation.

The following examples illustrate the nomenclature for coordination compounds.

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as:

triamminetriaquachromium(III) chloride

Explanation: The complex ion is inside the square bracket, which is a cation. The amine ligands are named before the aqua ligands according to alphabetical order. Since there are three chloride ions in the compound, the charge on the complex ion must be +3 (since the compound is electrically neutral). From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

2. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ is named as:

tris(ethane-1,2–diamine)cobalt(III) sulphate

Explanation: The sulphate is the counter anion in this molecule. Since it takes 3 sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further, ethane-1,2–diamine is a neutral molecule, so the oxidation number of cobalt in the complex ion must be +3. *Remember that you never have to indicate the number of cations and anions in the name of an ionic compound.*

Notice how the name of the metal differs in cation and anion even though they contain the same metal ions.

3. $[Ag(NH_3)_2][Ag(CN)_2]$ is named as:

diamminesilver(I) dicyanidoargentate(I)

Example 9.2 Write the formulas for the following coordination compounds:

(a) Tetraammineaquachloridocobalt(III) chloride
(b) Potassium tetrahydroxidozincate(II)
(c) Potassium trioxalatoaluminate(III)
(d) Dichloridobis(ethane-1,2-diamine)cobalt(III)
(e) Tetracarbonylnickel(0)

Solution (a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (b) $K_2[Zn(OH)_4]$ (c) $K_3[Al(C_2O_4)_3]$
(d) $[CoCl_2(en)_2]^+$ (e) $[Ni(CO)_4]$

Example 9.3 Write the IUPAC names of the following coordination compounds:

(a) $[Pt(NH_3)_2Cl(NO_2)]$ (b) $K_3[Cr(C_2O_4)_3]$ (c) $[CoCl_2(en)_2]Cl$
(d) $[Co(NH_3)_5(CO_3)]Cl$ (e) $Hg[Co(SCN)_4]$

Solution
(a) Diamminechloridonitrito-N-platinum(II)
(b) Potassium trioxalatochromate(III)
(c) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
(d) Pentaamminecarbonatocobalt(III) chloride
(e) Mercury (I) tetrathiocyanato-S-cobaltate(III)

Intext Questions

9.1 Write the formulas for the following coordination compounds:

(i) Tetraamminediaquacobalt(III) chloride
(ii) Potassium tetracyanidonickelate(II)
(iii) Tris(ethane–1,2–diamine) chromium(III) chloride
(iv) Amminebromidochloridonitrito-N-platinate(II)
(v) Dichloridobis(ethane–1,2–diamine)platinum(IV) nitrate
(vi) Iron(III) hexacyanidoferrate(II)

9.2 Write the IUPAC names of the following coordination compounds:

(i) $[Co(NH_3)_6]Cl_3$
(ii) $[Co(NH_3)_5Cl]Cl_2$
(iii) $K_3[Fe(CN)_6]$
(iv) $K_3[Fe(C_2O_4)_3]$
(v) $K_2[PdCl_4]$
(vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

9.4 Isomerism in Coordination Compounds

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

(a) Stereoisomerism

(i) Geometrical isomerism
(ii) Optical isomerism

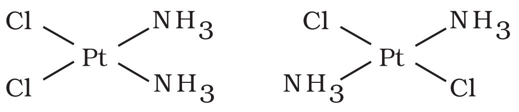
(b) Structural isomerism

(i) Linkage isomerism
(ii) Coordination isomerism
(iii) Ionisation isomerism
(iv) Solvate isomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A detailed account of these isomers are given below.

9.4.1 Geometric Isomerism

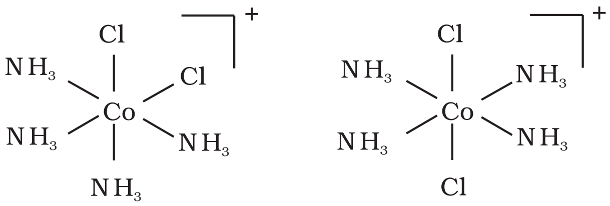
This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a ***cis*** isomer, or opposite to each other in a ***trans*** isomer as depicted in Fig. 9.2.



cis *trans*

Fig. 9.2: *Geometrical isomers (cis and trans) of Pt* $[NH_3)_2Cl_2]$

Other square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers-two *cis* and one *trans*. You may attempt to draw these structures. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented ***cis*** or ***trans*** to each other (Fig. 9.3).



cis *trans*

Fig. 9.3: *Geometrical isomers (cis and trans) of* $[Co(NH_3)_4Cl_2]^+$

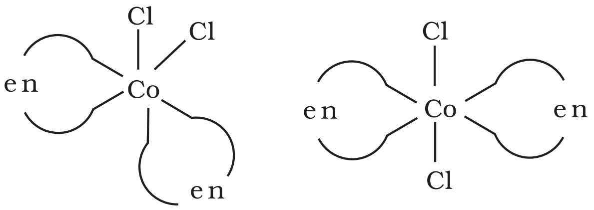
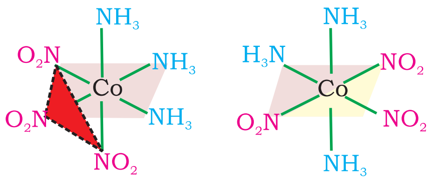


Fig. 9.4: *Geometrical isomers (cis and trans) of [CoCl$_2$(en)$_2$]*

This type of isomerism also arises when didentate ligands L–L [*e.g.*, $NH_2 CH_2 CH_2 NH_2$ (en)] are present in complexes of formula [$MX_2(L–L)_2$] (Fig. 9.4).

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma_3b_3] like [$Co(NH_3)_3(NO_2)_3$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. When the positions are around the meridian of the octahedron, we get the **meridional (mer) isomer** (Fig. 9.5).



fac– *mer–*

Fig. 9.5 *The facial (fac) and meridional (mer) isomers of [Co(NH$_3$)$_3$(NO$_2$)$_3$]*

Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Example 9.4

Solution

Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

9.4.2 Optical Isomerism

Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro (d)* and *laevo (l)* depending upon the direction they rotate the plane of polarised light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving didentate ligands (Fig. 9.6).

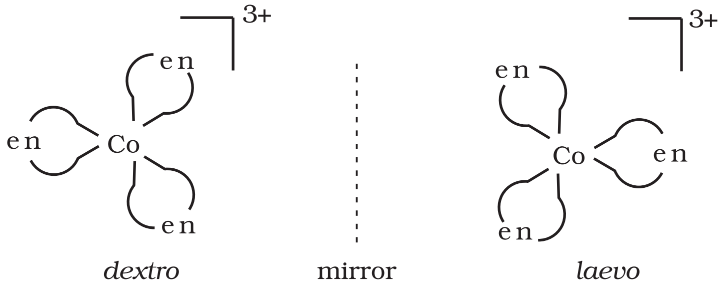


Fig.9.6: Optical isomers (d and l) of [Co(en)$_3$]$^{3+}$

In a coordination entity of the type [$PtCl_2(en)_2$]$^{2+}$, only the *cis*-isomer shows optical activity (Fig. 9.7).

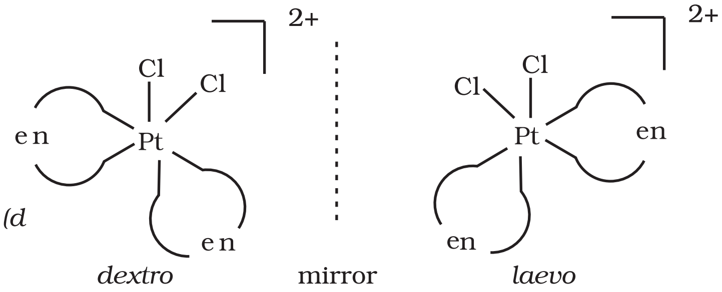
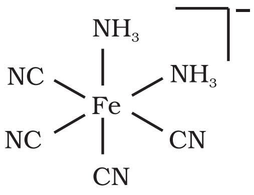


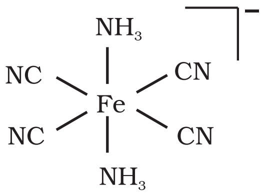
Fig.9.7 *Optical isomers (d and l) of cis-[PtCl$_2$(en)$_2$]$^{2+}$*

Example 9.5 Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

Solution



cis

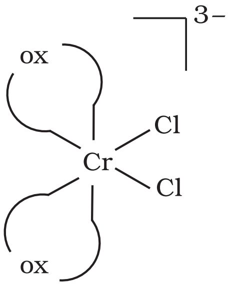


trans

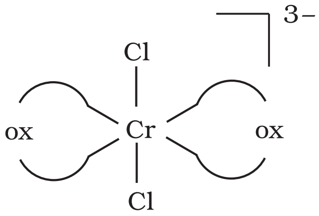
Example 9.6 Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

Solution The two entities are represented as



(a) *cis* – $[CrCl_2(ox)_2]^{3-}$



(b) *trans* – $[CrCl_2(ox)_2]^{3-}$

Out of the two, (a) *cis* - $[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

9.4.3 Linkage Isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN. Jørgensen discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-NO_2$).

9.4.4 Coordination Isomerism

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}.

9.4.5 Ionisation Isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

9.4.6 Solvate Isomerism

This form of isomerism is known as '**hydrate isomerism**' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

Intext Questions

9.3 Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(i) $K[Cr(H_2O)_2(C_2O_4)_2]$
(ii) $[Co(en)_3]Cl_3$
(iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$
(iv) $[Pt(NH_3)(H_2O)Cl_2]$

9.4 Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionisation isomers.

9.5 Bonding in Coordination Compounds

Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions like:

(i) Why only certain elements possess the remarkable property of forming coordination compounds?
(ii) Why the bonds in coordination compounds have directional properties?
(iii) Why coordination compounds have characteristic magnetic and optical properties?

Many approaches have been put forth to explain the nature of bonding in coordination compounds *viz.* Valence Bond Theory (VBT), Crystal Field Theory (CFT), **Ligand Field Theory** (LFT) and Molecular Orbital Theory (MOT). We shall focus our attention on elementary treatment of the application of VBT and CFT to coordination compounds.

9.5.1 Valence Bond Theory

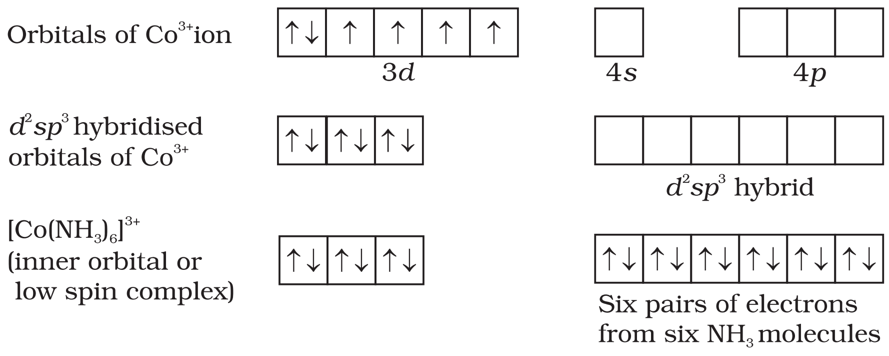
According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)*d*, n*s*, n*p* or n*s*, n*p*, n*d* orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on (Table 9.2). These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. This is illustrated by the following examples.

Table 9.2: Number of Orbitals and Types of Hybridisations

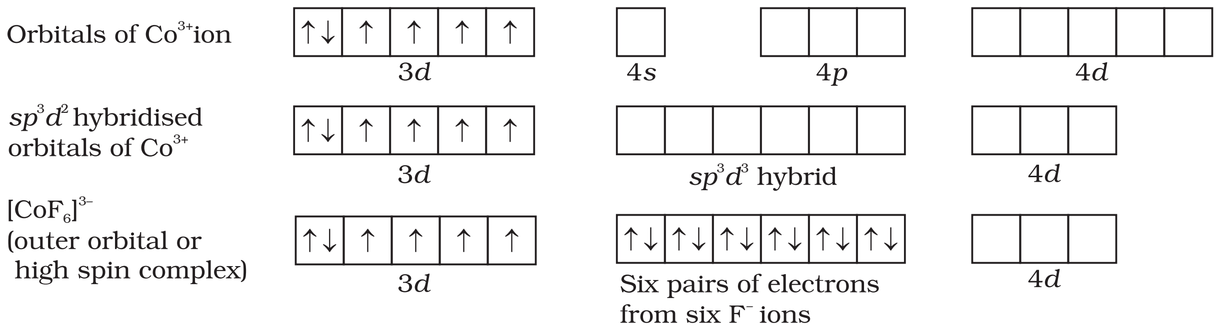
Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.

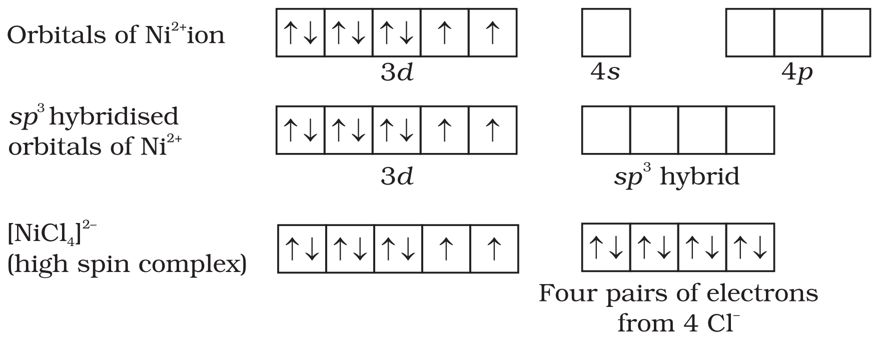
In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in diagram.



Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner *d* orbital (3*d*) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an **inner orbital** or **low spin** or **spin paired complex**. The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4*d*) in hybridisation (sp^3d^2). It is thus called **outer orbital** or **high spin** or **spin free complex**. Thus:

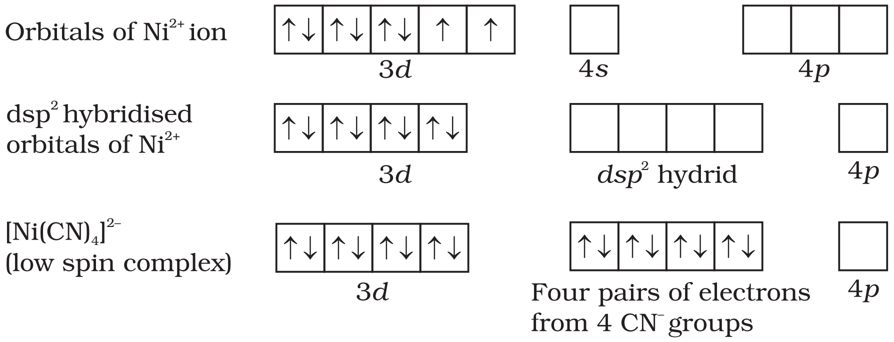


In tetrahedral complexes one *s* and three *p* orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for $[NiCl_4]^{2-}$. Here nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram.



Each Cl^- ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.

In the square planar complexes, the hybridisation involved is dsp^2. An example is $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram:



Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

9.5.2 Magnetic Properties of Coordination Compounds

The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the number of unpaired electrons (page 228) and hence structures adopted by metal complexes.

A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with upto three electrons in the *d* orbitals, like Ti^{3+} (d^1); V^{3+} (d^2); Cr^{3+} (d^3); two vacant *d* orbitals are available for octahedral hybridisation with 4*s* and 4*p* orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3*d* electrons are present, the required pair of 3*d* orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6 (Fe^{2+}, Co^{3+}) cases, a vacant pair of *d* orbitals results only by pairing of 3*d* electrons which leaves two, one and zero unpaired electrons, respectively.

The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ions. However, with species containing d^4 and d^5 ions there are complications. $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_{6-}]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

Example 9.7 The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion ?

Solution Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d* orbitals.

9.5.3 Limitations of Valence Bond Theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

(i) It involves a number of assumptions.
(ii) It does not give quantitative interpretation of magnetic data.
(iii) It does not explain the colour exhibited by coordination compounds.
(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
(vi) It does not distinguish between weak and strong ligands.

9.5.4 Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules. The five *d* orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.,* they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the *d* orbitals is lifted. It results in splitting of the *d* orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

(a) Crystal field splitting in octahedral coordination entities

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal *d* orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal *d* orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the *d* orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the

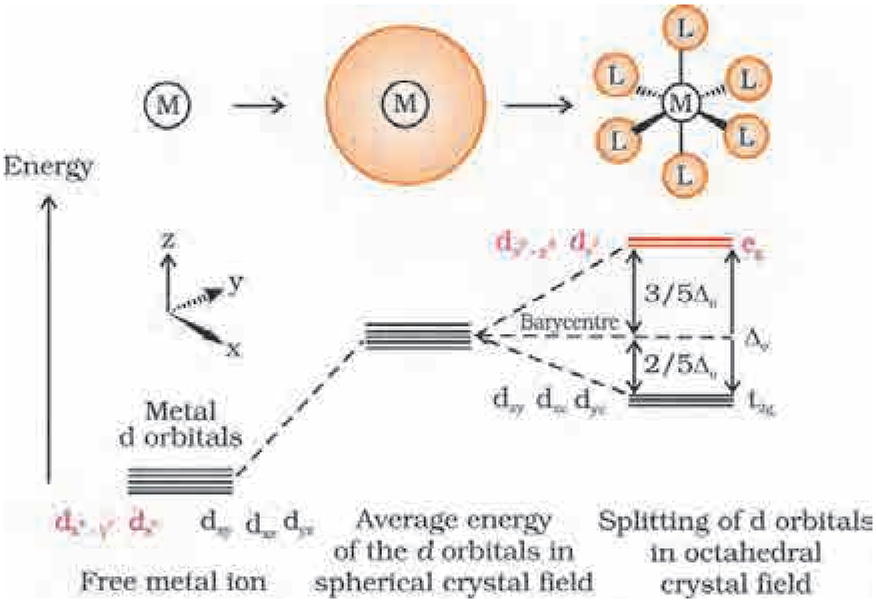


Fig.9.8: *d orbital splitting in an octahedral crystal field*

degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting** and the energy separation is denoted by Δ_o (the subscript o is for octahedral) (Fig.9.8). Thus, the energy of the two e_g orbitals will increase by (3/5) Δ_o and that of the three t_{2g} will decrease by $(2/5)\Delta_o$.

The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of *d* orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < \text{edta}^{4-} < NH_3 < \text{en} < CN^- < CO$$

Such a series is termed as **spectrochemical series**. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the *d* orbitals of metal ion in octahedral coordination entities. Obviously, the single *d* electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the *d* electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the e_g level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

(i) If Δ_o < P, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which Δ_o < P are known as *weak field ligands* and form high spin complexes.

(ii) If Δ_o > P, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as *strong field ligands* and form low spin complexes.

Calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.

(b) Crystal field splitting in tetrahedral coordination entities

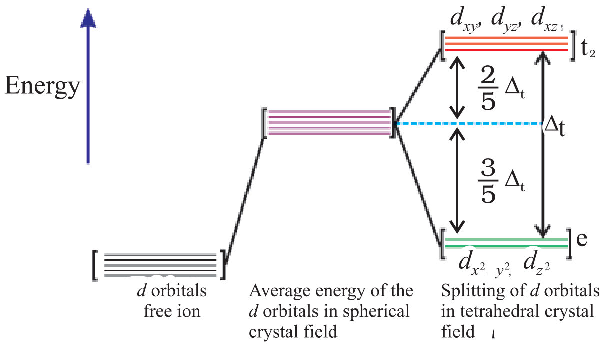


Fig.9.9: *d orbital splitting in a tetrahedral crystal field.*

In tetrahedral coordination entity formation, the *d* orbital splitting (Fig. 9.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\ \Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed. The 'g' subscript is used for the octahedral and square planar complexes which have centre of symmetry. Since tetrahedral complexes lack symmetry, 'g' subscript is not used with energy levels.

9.5.5 Colour in Coordination Compounds

In the previous Unit, we learnt that one of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red. Table 9.3 gives the relationship of the different wavelength absorbed and the colour observed.

Table 9.3: Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

Coordinaton entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow 🟨	Violet 🟪
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green 🟩	Red 🟥
$[Co(NH_3)_6]^{3+}$	475	Blue 🟦	Yellow Orange 🟧
$[Co(CN)_6]^{3-}$	310	Ultraviolet Not in visible region	Pale Yellow 🟨
$[Cu(H_2O)_4]^{2+}$	600	Red 🟥	Blue 🟦
$[Ti(H_2O)_6]^{3+}$	498	Blue Green 🟩	Violet 🟪

The colour in the coordination compounds can be readily explained in terms of the crystal field theory. Consider, for example, the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal *d* orbital is in the t_{2g} level in the ground state of the complex. The next higher state available for the electron is the empty e_g level. If light corresponding to the energy of blue-green region is absorbed by the complex, it would excite the electron from t_{2g} level to the e_g level ($t_{2g}{}^1 e_g{}^0 \rightarrow t_{2g}{}^0 e_g{}^1$). Consequently, the complex appears violet in colour (Fig. 9.10). The crystal field theory attributes the colour of the coordination compounds to *d-d* transition of the electron.

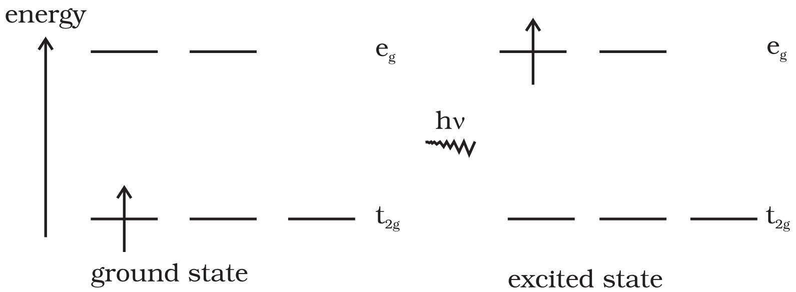


Fig.9.10: *Transition of an electron in* $[Ti(H_2O)_6]^{3+}$

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour. The influence of the ligand on the colour of a complex may be illustrated by considering the $[Ni(H_2O)_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water. If the didentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratios en:Ni, 1:1, 2:1, 3:1, the following series of reactions and their associated colour changes occur:

$$[Ni(H_2O)_6]^{2+}\,(aq) + en\,(aq) = [Ni(H_2O)_4(en)]^{2+}(aq) + 2H_2O$$

green pale blue

$$[Ni(H_2O)_4\,(en)]^{2+}(aq) + en\,(aq) = [Ni(H_2O)_2(en)_2]^{2+}(aq) + 2H_2O$$

blue/purple

$$[Ni(H_2O)_2(en)_2]^{2+}(aq) + en\,(aq) = [Ni(en)_3]^{2+}(aq) + 2H_2O$$

violet

This sequence is shown in Fig. 9.11.

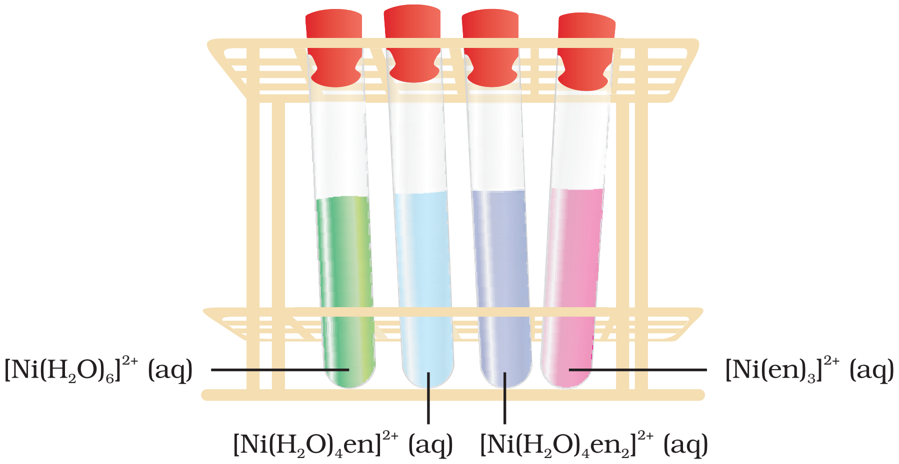


Fig.9.11
Aqueous solutions of complexes of nickel(II) with an increasing number of ethane-1, 2-diamine ligands.

Colour of Some Gem Stones

The colours produced by electronic transitions within the *d* orbitals of a transition metal ion occur frequently in everyday life. Ruby [Fig.9.12(a)] is aluminium oxide (Al_2O_3) containing about 0.5-1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+}. We may view these chromium(III) species as octahedral chromium(III) complexes incorporated into the alumina lattice; *d–d* transitions at these centres give rise to the colour.

In emerald [Fig.9.12(b)], Cr^{3+} ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$). The absorption bands seen in the ruby shift to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.

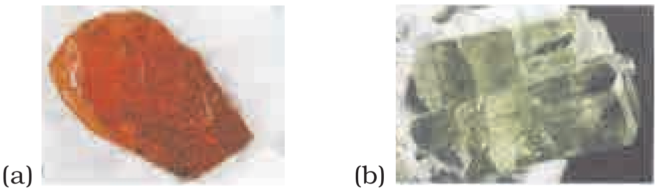


Fig.9.12: *(a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.*

9.5.6 Limitations of Crystal Field Theory

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent. However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series. Further, it does not take into account the covalent character of bonding between the ligand and the central atom. These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory which are beyond the scope of the present study.

Intext Questions

9.5 Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

9.6 $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

9.7 $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

9.8 Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

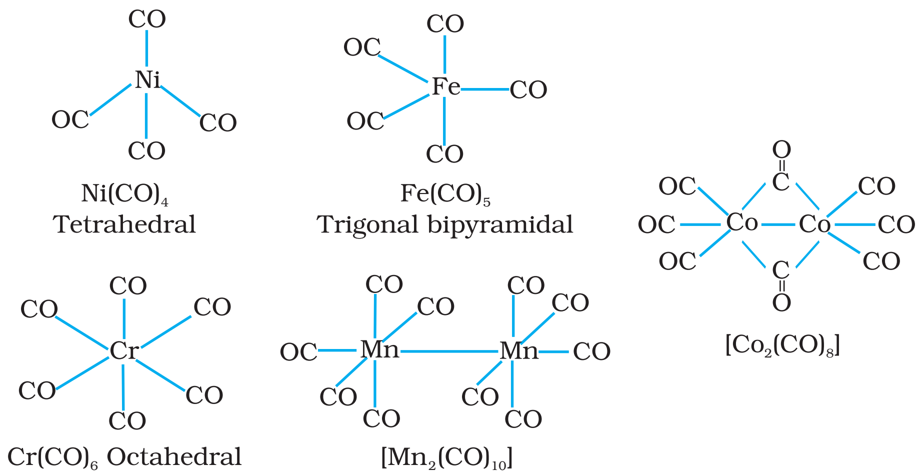
9.9 Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

9.10 The hexaquo manganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

9.6 Bonding in Metal Carbonyls

The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral, pentacarbonyliron(0) is trigonalbipyramidal while hexacarbonyl chromium(0) is octahedral.

Decacarbonyldimanganese(0) is made up of two square pyramidal $Mn(CO)_5$ units joined by a Mn – Mn bond. Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups (Fig.9.13).


$Ni(CO)_4$ Tetrahedral

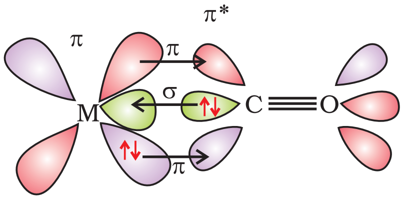
$Fe(CO)_5$ Trigonal bipyramidal

$[Co_2(CO)_8]$

$Cr(CO)_6$ Octahedral

$[Mn_2(CO)_{10}]$

Fig. 9.13 *Structures of some representative homoleptic metal carbonyls.*



Synergic bonding

Fig. 9.14: *Example of synergic bonding interactions in a carbonyl complex.*

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled *d* orbital of metal into the vacant antibonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fig.9.14).

9.7 Stability of Coordination Compounds

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the equilibrium constant (stability or formation) for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + 4L \rightleftharpoons ML_4$$

then the larger the stability constant, the higher the proportion of ML_4 that exists in solution. Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

$$\begin{array}{lllllll}
M & + & L & \rightleftharpoons & ML & K_1 = & [ML]/[M][L] \\
ML & + & L & \rightleftharpoons & ML_2 & K_2 = & [ML_2]/[ML][L] \\
ML_2 & + & L & \rightleftharpoons & ML_3 & K_3 = & [ML_3]/[ML_2][L] \\
\hline
ML_{(n-1)} & + & L & \rightleftharpoons & ML_n & K_4 = & [ML_n]/[ML_{(n-1)}][L]
\end{array}$$

where K_1, K_2, ... K_n, etc., are **stepwise stability constants.** The **overall stability constant** (β) of the formation of species ML_n from M and L can be given as:

$$M + nL \rightleftharpoons ML_n \qquad \beta = [ML_n]/[M][L]^n$$

The stepwise and overall stability constant are therefore related as follows:

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots K_n$$

If we take cuprammonium ion as an example, following species will be formed step wise by addition of ammonia molecules one by one: $[Cu(NH_3)]^{2+}$, $[Cu(NH_3)_2]^{2+}$, $[Cu(NH_3)_3]^{2+}$ and $[Cu(NH_3)_4]^{2+}$.

If K_1, K_2, K_3 and K_4 are stability constants of the successive reactions respectively then β_4 would be written as follows:

$$\beta_4 = [Cu(NH_3)_4{}^{2+}]/[Cu^{2+}][NH_3]^4$$

The addition of the four amine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are:

$$\log K_1 = 4.0,\ \log K_2 = 3.2,\ \log K_3 = 2.7,\ \log K_4 = 2.0 \text{ or } \log \beta_4 = 11.9$$

The **instability constant or the dissociation constant** of coordination compounds is defined as the reciprocal of the formation constant.

Intext Question

9.11 Calculate the overall complex dissociation equilibrium constant for the $Cu(NH_3)_4{}^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

9.8 Importance and Applications of Coordination Compounds

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.
- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc (Unit 6).
- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: *cis*–platin and related compounds.

Summary

The **chemistry of coordination compounds** is an important and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of bonding and molecular structure, novel breakthroughs in **chemical industry** and vital insights into the functioning of critical components of **biological systems**.

The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by **A. Werner**. His theory postulated the use of two types of **linkages** (**primary** and **secondary**) by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognised as the ionisable (ionic) and non-ionisable (covalent) bonds, respectively. Using the property of isomerism, Werner predicted the geometrical shapes of a large number of coordination entities.

The Valence Bond Theory (VBT) explains with reasonable success, the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and has nothing to say about the optical properties of these compounds.

The Crystal Field Theory (CFT) to coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of *d* orbital energies of the central metal atom/ion. The splitting of the *d* orbitals provides different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimations of orbital separation energies, magnetic moments and spectral and stability parameters. However, the assumption that ligands consititute point charges creates many theoretical difficulties.

The metal–carbon bond in **metal carbonyls** possesses both σ and π character. The ligand to metal is σ bond and metal to ligand is π bond. This unique synergic bonding provides stability to metal carbonyls.

The stability of coordination compounds is measured in terms of **stepwise stability (or formation) constant (K) or overall stability constant** (β). The stabilisation of coordination compound due to chelation is called the **chelate effect**. The stability of coordination compounds is related to Gibbs energy, enthalpy and entropy terms.

Coordination compounds are of great importance. These compounds provide critical insights into the functioning and structures of vital components of biological systems. Coordination compounds also find extensive applications in **metallurgical processes, analytical and medicinal chemistry**.

Exercises

9.1 Explain the bonding in coordination compounds in terms of Werner's postulates.

9.2 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

9.3 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

9.4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

9.5 Specify the oxidation numbers of the metals in the following coordination entities:

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$
(ii) $[CoBr_2(en)_2]^{+}$
(iii) $[PtCl_4]^{2-}$
(iv) $K_3[Fe(CN)_6]$
(v) $[Cr(NH_3)_3Cl_3]$

9.6 Using IUPAC norms write the formulas for the following:

(i) Tetrahydroxidozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanidonickelate(II)
(v) Pentaamminenitrito-O-cobalt(III)
(vi) Hexaamminecobalt(III) sulphate
(vii) Potassium tri(oxalato)chromate(III)
(viii) Hexaammineplatinum(IV)
(ix) Tetrabromidocuprate(II)
(x) Pentaamminenitrito-N-cobalt(III)

9.7 Using IUPAC norms write the systematic names of the following:

(i) $[Co(NH_3)_6]Cl_3$
(ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
(iii) $[Ti(H_2O)_6]^{3+}$
(iv) $[Co(NH_3)_4Cl(NO_2)]Cl$
(v) $[Mn(H_2O)_6]^{2+}$
(vi) $[NiCl_4]^{2-}$
(vii) $[Ni(NH_3)_6]Cl_2$
(viii) $[Co(en)_3]^{3+}$
(ix) $[Ni(CO)_4]$

9.8 List various types of isomerism possible for coordination compounds, giving an example of each.

9.9 How many geometrical isomers are possible in the following coordination entities?

(i) $[Cr(C_2O_4)_3]^{3-}$
(ii) $[Co(NH_3)_3Cl_3]$

9.10 Draw the structures of optical isomers of:

(i) $[Cr(C_2O_4)_3]^{3-}$
(ii) $[PtCl_2(en)_2]^{2+}$
(iii) $[Cr(NH_3)_2Cl_2(en)]^{+}$

9.11 Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2(en)_2]^+$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$ (iii) $[Co(NH_3)_2Cl_2(en)]^+$

9.12 Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

9.13 Aqueous copper sulphate solution (blue in colour) gives:

(i) a green precipitate with aqueous potassium fluoride and
(ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

9.14 What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

9.15 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[CoF_6]^{3-}$

9.16 Draw figure to show the splitting of *d* orbitals in an octahedral crystal field.

9.17 What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

9.18 What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of *d* orbitals in a coordination entity?

9.19 $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

9.20 A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

9.21 $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

9.22 Discuss the nature of bonding in metal carbonyls.

9.23 Give the oxidation state, *d* orbital occupation and coordination number of the central metal ion in the following complexes:

(i) $K_3[Co(C_2O_4)_3]$ (iii) $(NH_4)_2[CoF_4]$
(ii) cis-$[CrCl_2(en)_2]Cl$ (iv) $[Mn(H_2O)_6]SO_4$

9.24 Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (iii) $[CrCl_3(py)_3]$ (v) $K_4[Mn(CN)_6]$
(ii) $[Co(NH_3)_5Cl_{-}]Cl_2$ (iv) $Cs[FeCl_4]$

9.25 What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

9.26 What is meant by the *chelate effect*? Give an example.

9.27 Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems (iii) analytical chemistry
(ii) medicinal chemistry and (iv) extraction/metallurgy of metals.

9.28 How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

(i) 6 (ii) 4 (iii) 3 (iv) 2

9.29 Amongst the following ions which one has the highest magnetic moment value?

(i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Zn(H_2O)_6]^{2+}$

9.30 The oxidation number of cobalt in $K[Co(CO)_4]$ is

(i) +1 (ii) +3 (iii) –1 (iv) –3

9.31 Amongst the following, the most stable complex is

(i) $[Fe(H_2O)_6]^{3+}$ (ii) $[Fe(NH_3)_6]^{3+}$ (iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[FeCl_6]^{3-}$

9.32 What will be the correct order for the wavelengths of absorption in the visible region for the following:

$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

Answers to Some Intext Questions

9.1 (i) $[Co(NH_3)_4(H_2O)_2]Cl_3$
(ii) $K_2[Ni(CN)_4]$
(iii) $[Cr(en)_3]Cl_3$
(iv) $[Pt(NH_3)BrCl(NO_2)]^-$
(v) $[PtCl_2(en)_2](NO_3)_2$
(vi) $Fe_4[Fe(CN)_6]_3$

9.2 (i) Hexaamminecobalt(III) chloride
(ii) Pentaamminechloridocobalt(III) chloride
(iii) Potassium hexacyanidoferrate(III)
(iv) Potassium trioxalatoferrate(III)
(v) Potassium tetrachloridopalladate(II)
(vi) Diamminechlorido(methanamine)platinum(II) chloride

9.3 (i) Both geometrical (*cis*-, *trans*-) and optical isomers for *cis* can exist.
(ii) Two optical isomers can exist.
(iii) There are 10 possible isomers. (Hint: There are geometrical, ionisation and linkage isomers possible).
(iv) Geometrical (*cis*-, *trans*-) isomers can exist.

9.4 The ionisation isomers dissolve in water to yield different ions and thus react differently to various reagents:

$[Co(NH_3)_5Br]SO_4 + Ba^{2+} \rightarrow BaSO_4$ (s)
$[Co(NH_3)_5SO_4]Br + Ba^{2+} \rightarrow$ No reaction
$[Co(NH_3)_5Br]SO_4 + Ag^+ \rightarrow$ No reaction
$[Co(NH_3)_5SO_4]Br + Ag^+ \rightarrow AgBr$ (s)

9.6 In $Ni(CO)_4$, Ni is in zero oxidation state whereas in $NiCl_4^{2-}$, it is in +2 oxidation state. In the presence of CO ligand, the unpaired *d* electrons of Ni pair up but Cl^- being a weak ligand is unable to pair up the unpaired electrons.

9.7 In presence of CN^-, (a strong ligand) the 3*d* electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming inner orbital complex. In the presence of H_2O, (a weak ligand), 3*d* electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital complex containing five unpaired electrons, it is strongly paramagnetic.

9.8 In the presence of NH_3, the 3*d* electrons pair up leaving two *d* orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex in case of $[Co(NH_3)_6]^{3+}$.

In $Ni(NH_3)_6^{2+}$, Ni is in +2 oxidation state and has d^8 configuration, the hybridisation involved is sp^3d^2 forming outer orbital complex.

9.9 For square planar shape, the hybridisation is dsp^2. Hence the unpaired electrons in 5*d* orbital pair up to make one *d* orbital empty for dsp^2 hybridisation. Thus there is no unpaired electron.

9.11 The overall dissociation constant is the reciprocal of overall stability constant i.e. $1/\beta_4 = 4.7 \times 10^{-14}$