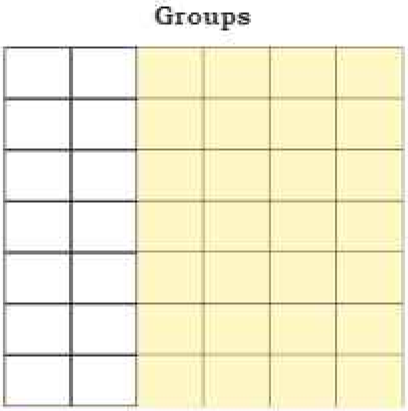


Chapter

6

p-BLOCK ELEMENTS

Objectives

After studying this chapter, 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.

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.

In Inter I yr., 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 Inter I yr., you will learn the chemistry of the elements of subsequent groups in this chapter.

GROUP 15 ELEMENTS

6.1 Introduction

Group 15 includes nitrogen, phosphorus, arsenic, antimony and bismuth. 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 and bismuth and moscovium are typical metals.

Occurrence

Molecular nitrogen comprises 78% by volume of the atmosphere. In the earth's $_3$ (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 $_4)_6 \cdot CaF_2$) 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 this group elements along with their electronic configurations are given in Table 6.1.

Table 6.1: Atomic and Physical Properties of Group 15 Elements

Property			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			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	
Covalent radius/pm^a		70		121	141	148
Melting point/K		—	317^b	1089^c	904	544
Boiling point/K		77.2*	554^b	888^d	1860	1837
Density/[g cm^{-3}(298 K)]		0.879^e	1.823	5.778^f	6.697	9.808

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

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

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.

Atomic and Ionic Radii

Covalent and ionic (in a particular state) radii increase 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.

$\Delta \qquad \Delta \qquad \Delta$

$\rightarrow$

$\pi \quad \pi$

elements of this group do not form $p\pi$-$p\pi$ 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 *sigma* and two *pi*) 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 $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

Table 6.2: 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 because the elements in the higher oxidation state exert more polarising power. 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_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Example 6.1

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 6.2

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

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

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

6.2 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 6.1).

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 high temperature, it directly combines with Li and Mg metals to form nitrides.

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

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

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

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

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

$$N_2 + O_2(g) \rightleftharpoons 2NO(g)$$

Uses: 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 6.3 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

6.3 Why is N_2 less reactive at room temperature?

6.3 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.

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

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.

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

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 773 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. 6.1. Earlier, iron was used as a catalyst with molybdenum as a promoter.

The moisture present in ammonia may be removed by using quick lime, CaO. Ammonia cannot be dried by conc.H_2SO_4, anhydrous $CaCl_2$ and P_4O_{10} as it reacts with these reagents.

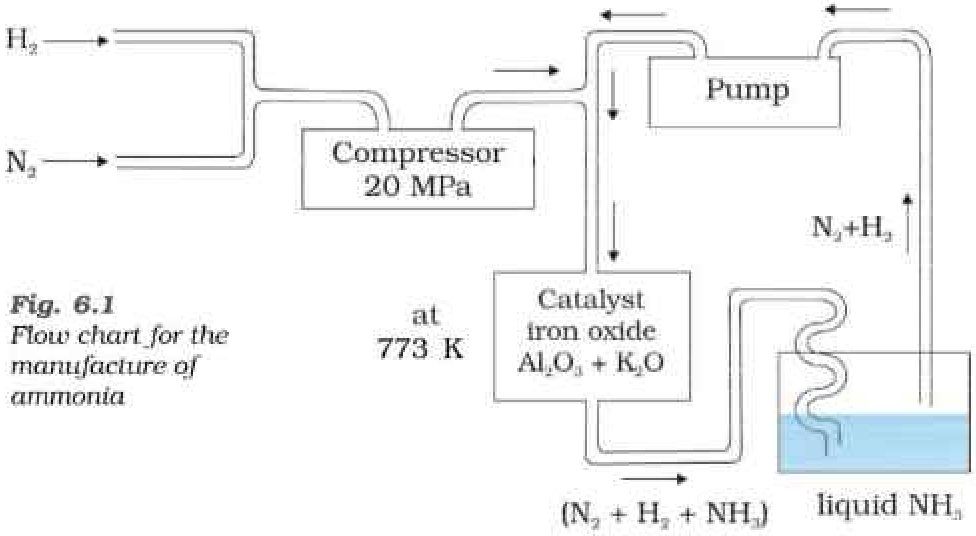
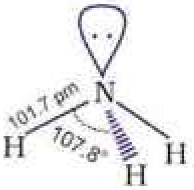


Fig. 6.1
Flow chart for the manufacture of ammonia

Properties



Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 195.2 K 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 (one volume of water can dissolve about 1000 volumes of ammonia gas at 273 K). 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,

$$ZnSO_4(aq) + 2NH_4OH(aq) \rightarrow \underset{\text{(white ppt)}}{Zn(OH)_2(s)} + (NH_4)_2SO_4(aq)$$

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

$$\rightleftharpoons$$

$$^{+}(\quad) + \quad ^{-}(\quad) \rightarrow \qquad (\,)$$

$$(\,) + \qquad (\quad) \rightarrow [\quad (\qquad)\,] \quad (\quad)$$

Uses:

Example 6.4

Solution

Intext Questions

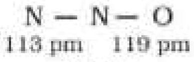
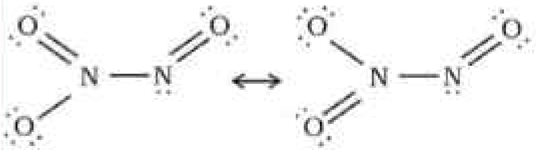
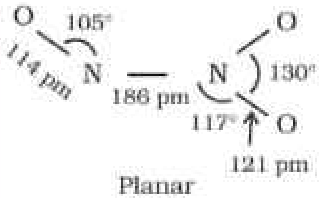
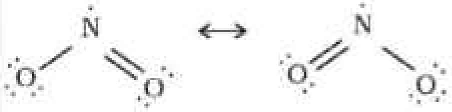
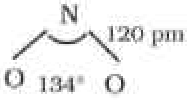
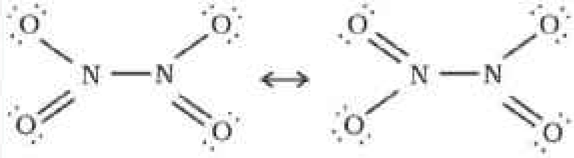
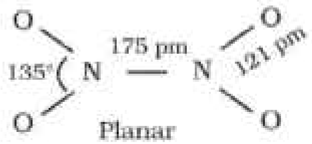
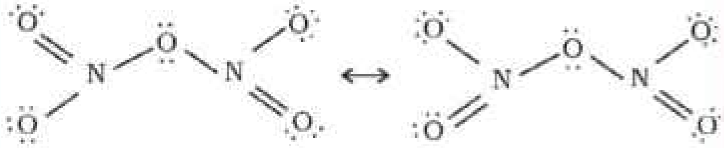
6.4 Oxides of Nitrogen

			$\longrightarrow$ $+$ $+$ $\rightarrow$ $+ \quad +$ $+ \quad \longrightarrow$ $+ \quad \longrightarrow$	

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 6.4.

Table 6.4: Structures of Oxides of Nitrogen

Formula	Resonance Structures	Bond Parameters
N_2O		 Linear
NO		
N_2O_3		 Planar
NO_2		 Angular
N_2O_4		 Planar
N_2O_5		 Planar

Example 6.5

Solution

Intext Question

6.6

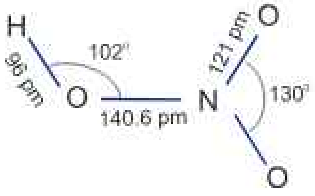
6.5 Nitric Acid

$+ \quad \rightarrow \quad +$

$(\;) + \quad (\;) \longrightarrow \quad (\;) + \quad (\;)$

$(\;) + \quad (\;) \rightleftharpoons \quad (\;)$

$(\;) + \quad (\;) \rightarrow \quad (\;) + \quad (\;)$



$\rightarrow \quad ^{-}$

depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

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

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

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

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

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

Some metals (e.g., Fe, Ni, 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.

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

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

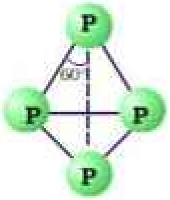
Uses: The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the *pickling of stainless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

6.6 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 of CO_2 giving PH_3.

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



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}.

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

Fig. 6.2
White phosphorus

It consists of discrete tetrahedral P_4 molecules as shown in Fig. 6.2. These discrete P_4 molecules are held by van der Waals forces.

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.

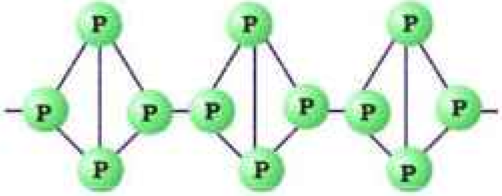


Fig.6.3: *Red phosphorus*

It is polymeric, consisting of chains of P_4 tetrahedra linked together through covalent bonds in the manner as shown in Fig. 6.3.

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 673K.

6.7 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.

$+ \quad \rightarrow \quad +$

$+ \quad \rightarrow \quad +$

$+ \quad \rightarrow$

Uses:

Example 6.6

Solution

$+ \quad \rightarrow$

Intext Questions

6.8 Phosphorus Halides

$+ \quad \rightarrow$

$+ \quad \rightarrow \quad + \quad +$

$+ \quad \rightarrow$

$-$

$+ \rightarrow +$

$+ \rightarrow +$

$+ \rightarrow$

$+ \rightarrow +$

$+ \rightarrow +$

$+ \rightarrow +$

$\longrightarrow +$

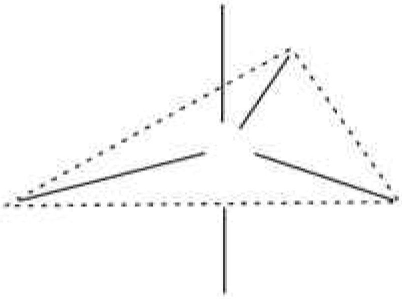
$-$

$+ \rightarrow + +$

$+ \rightarrow +$

$+ \rightarrow +$

$+ \rightarrow +$



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Example 6.7

Solution

+ →

Example 6.8

Solution

Intext Questions

6.9 Oxoacids of Phosphorus

			– –	
			– –	
			– –	
			– – –	
			– –	
			–	
			– – –	
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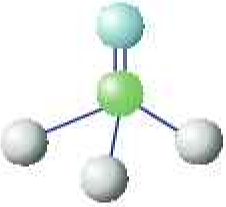

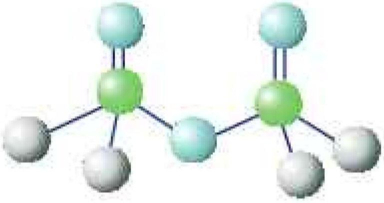

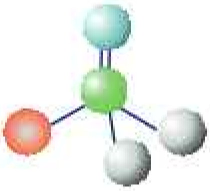

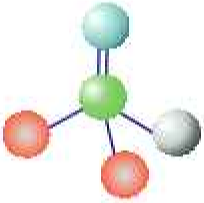

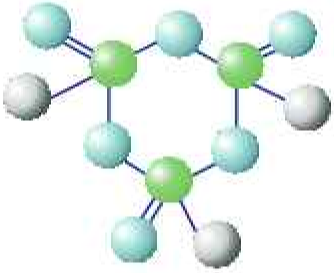

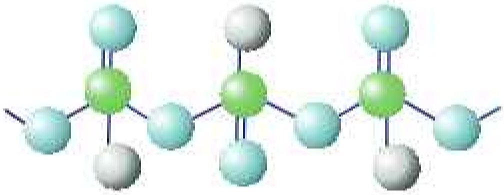

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Example 6.9

Solution

Intext Questions

6.11 What is the basicity of H_3PO_4?

6.12 What happens when H_3PO_3 is heated?

GROUP 16 ELEMENTS

6.10 Introduction

Oxygen, sulphur, selenium, tellurium and polonium constitute Group 16 of the periodic table. This is sometimes known as group of *chalcogens* (ore forming elements). 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.

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 properties of Lv.

Here, except for livermorium, important atomic and physical properties of Group16 along with electronic configuration are given in Table 6.6. Some of the atomic, physical and chemical properties and their trends are discussed below.

Electronic Configuration

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

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.

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.

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.

Example 6.10

Solution

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Example 6.11

Solution –

Intext Questions

6.11 Dioxygen

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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 Ch. 3 of Inter I yr.).

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:

$$2Ca + O_2 \rightarrow 2CaO \qquad 4Al + 3O_2 \rightarrow 2Al_2O_3$$

$$P_4 + 5O_2 \rightarrow P_4O_{10} \qquad C + O_2 \rightarrow CO_2$$

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \qquad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Some compounds are catalytically oxidised. For example,

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3 \quad 4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

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

6.16 Which of the following does not react with oxygen directly?

Zn, Ti, Pt, Fe

6.17 Complete the following reactions:

(i) $C_2H_4 + O_2 \rightarrow$ (ii) $4Al + 3\ O_2 \rightarrow$

6.12 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, metal oxides are basic.

Some metal oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides (SiO_2, ZnO, PbO, Al_2O_3, Sb_2O_3, BeO, SnO_2). They react with acids as well as alkalies. For example, Al_2O_3 reacts with acids as well as alkalies.

$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \rightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$
$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \rightarrow 2Na_3[Al(OH)_6](aq)$$

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.

6.13 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. 101.1 K) 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.

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

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

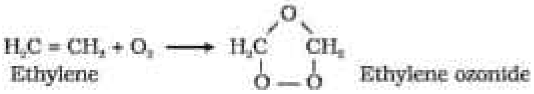
When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Metals like Ag and Hg are oxidised to their respective oxides.

$$2Ag + O_3 \rightarrow Ag_2O + O_2 \qquad 2Hg + O_3 \rightarrow Hg_2O + O_2$$

Due to the dissolution of Hg_2O in Hg, mercury loses its meniscus and starts sticking to the sides of the glass (container). This is called **'tailing of mercury'**. However, the meniscus can be regained by shaking it with water, which dissolves Hg_2O.

When Ozone is bubbled through the solution of an alkene or alkyne in an inert solvent like CH_2Cl_2, CCl_4 etc., at 195 K, ozonides are formed.

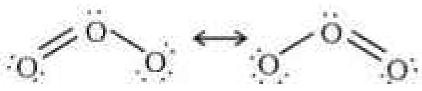


Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

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

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

6.18 Why does O_3 act as a powerful oxidising agent?

6.19 How is O_3 estimated quantitatively?

6.14 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.

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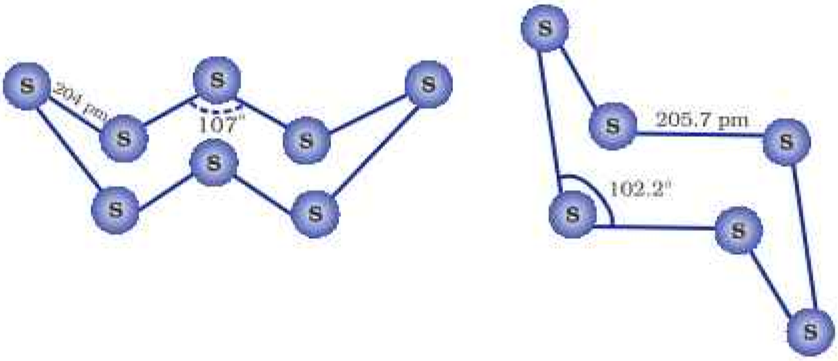

Example 6.12

Solution

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6.15 Sulphur Dioxide

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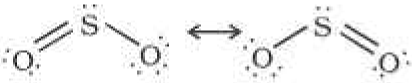

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Uses:

Intext Questions

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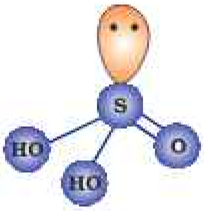
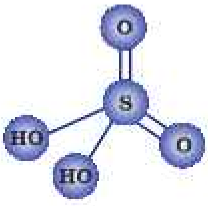
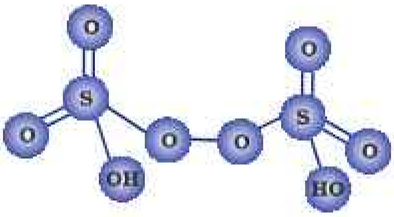
6.16 Oxoacids of Sulphur



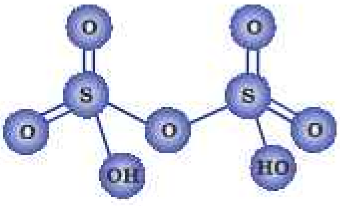
Sulphurous acid (H_2SO_3)



Sulphuric acid (H_2SO_4)



Peroxodisulphuric acid ($H_2S_2O_8$)



Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

6.17 Sulphuric Acid

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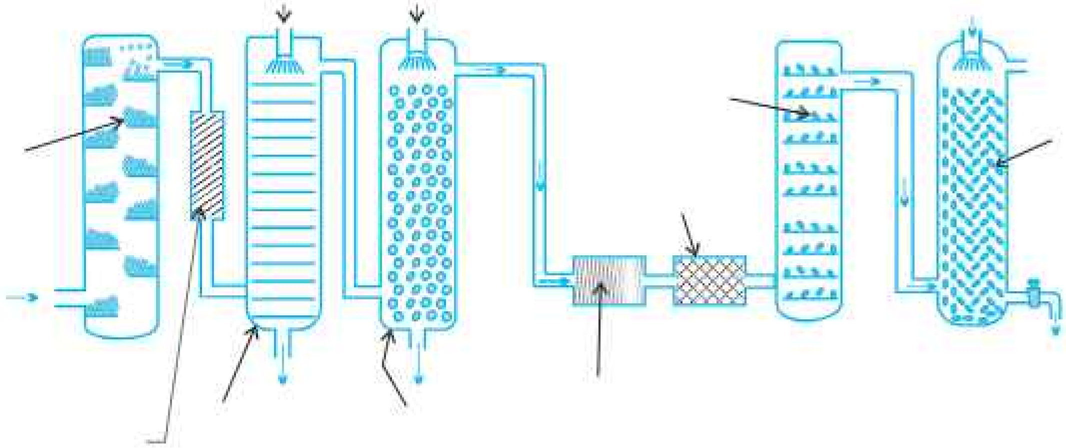

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Uses:

Example 6.13 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

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

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

6.25 Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water ?

GROUP 17 ELEMENTS

6.18 Introduction

Fluorine, chlorine, bromine, iodine and astatine 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.

Occurrence

Fluorine and chlorine are fairly abundant compared to bromine and iodine. 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 are given in Table 6.8.

Table 6.8: 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	–
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	–

	F_2	Cl_2	Br_2	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 $X_2(g) + 2e^- \rightarrow 2X^-(aq)$.

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 element could be prepared. Also its half life is in milliseconds only. That is why its chemistry could not be established.

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

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.

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.

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.

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 2*p* orbitals of fluorine and thus, the incoming electron does not experience much attraction.

Electronegativity

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

Example 6.14

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.

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Example 6.15

Solution

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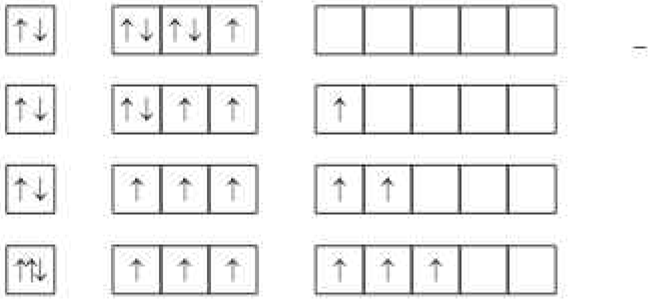

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Example 6.16 –

Solution

Intext Questions

6.19 Chlorine

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Uses:

Example 6.17

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Solution

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Intext Questions

6.20 Hydrogen Chloride

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Uses:

Example 6.18

Solution

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6.21 Oxoacids of Halogens

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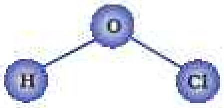
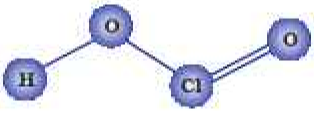
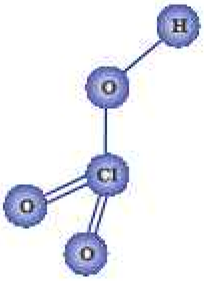


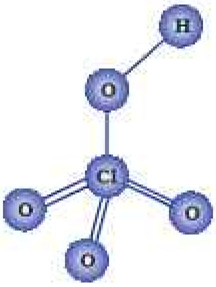
Hypochlorous acid



Chlorous acid



Chloric acid



Perchloric acid

6.22 Interhalogen Compounds

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$+ \xrightarrow{\quad\quad} \qquad + \rightarrow$

$+ \rightarrow$

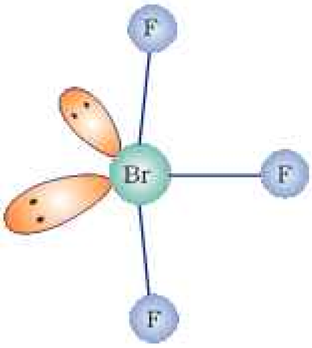
$+ \rightarrow \qquad + \rightarrow$

		α	–
		β	–

+ → +

Example 6.19

Solution



Uses:

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Intext Question

GROUP 18 ELEMENTS

6.23 Introduction

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

Occurrence

All the noble gases except radon 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.

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

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

$$^{249}_{98}\mathrm{Cf} + ^{48}_{20}\mathrm{Ca} \rightarrow ^{294}_{118}\mathrm{Og} + 3\mathrm{n}$$

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 has been made.

Example 6.20

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.

Here, except for oganesson, important atomic and physical properties of the Group 18 elements along with their electronic configurations are given in Table 6.12. The trends in some of the atomic, physical and chemical properties of the group are discussed here.

Table 6.12: Atomic and Physical Properties of Group 18 Elements

Property	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*

Electronic Configuration

All noble gases have general electronic configuration ns^2np^6 except helium which has $1s^2$ (Table 6.12). Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

Example 6.21

Solution

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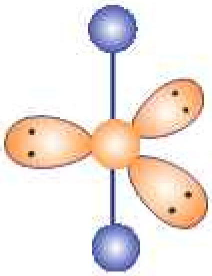

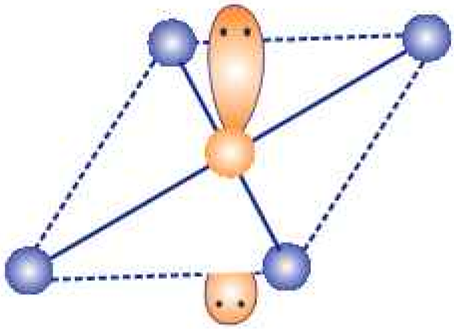

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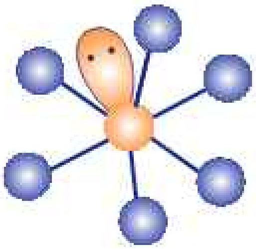

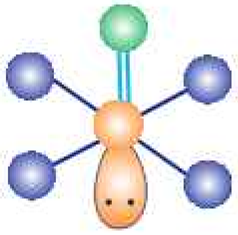

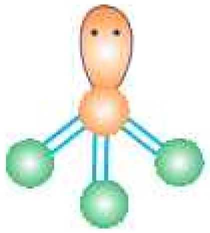

Example 6.22

Solution

Uses:

Intext Questions

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Chapter

The presence of incompletely filled *d* orbitals in their atoms makes the study of *d*-block elements and their compounds different from that of the main group elements. However, the usual theory of valence as applicable to the main group elements can also be applied successfully to the *d*-block elements.

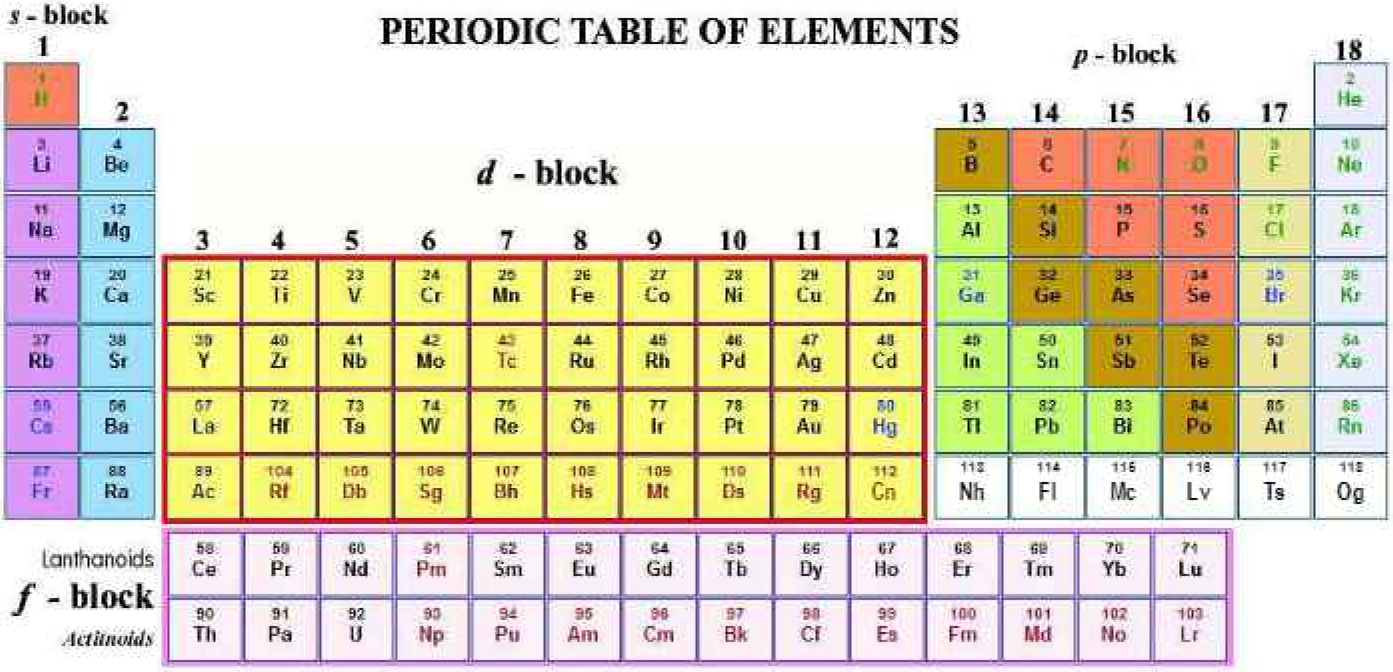
Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium form part of the *d*-block elements.

In this chapter, we shall deal with the electronic configuration, general properties of the *d* and *f* block elements with special emphasis on the trends in the properties of the first row (3*d*) *d*-block elements and the preparation and properties of some of their important compounds. Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their atomic state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the three transition series, their chemistry is also studied along with the chemistry of the transition metals. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the *f*-block elements.

THE TRANSITION ELEMENTS (*d*-BLOCK)

7.1 Position in the Periodic Table

The *d*–block occupies the large section between *s*– and *p*– blocks in the periodic table. The very name transition elements given to *d*-block is due to their properties which are transitioned between the electropositive *s*-block metals and the electronegative *p*-block elements. The *d*–orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals, i.e., 3*d*, 4*d* and 5*d*. The fourth row of 6*d* is still incomplete. These series of the transition elements are shown in Table 7.1.



PERIODIC TABLE OF ELEMENTS

s - block

d - block

p - block

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

f - block

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

Periodic Table of Elements

7.2 Electronic Configuration

In general the electronic configuration of these elements is $(n\text{-}1)d^{1-10}ns^{1-2}$. The (n–1) stands for the penultimate shell containing *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 ns orbitals. Furthermore, half filled and completely filled sets of orbitals give stability to atoms. A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the 3*d* series. Cr, for example, which has $3d^5 4s^1$ instead of $3d^4 4s^2$; the energy gap between the two sets (3*d* and 4*s*) of orbitals is small and hence the electron enters the 3*d* orbital. Similarly in case of Cu, the configuration is $3d^{10}4s^1$ and not $3d^9 4s^2$. The outer electronic configurations of the transition elements are given in Table 7.1.

Table 7.1: Outer Electronic Configurations of Transition Elements

3*d* - series		4*d* - series	
Element	Configuration	Element	Configuration
Sc	$3d^1 4s^2$	Y	$4d^1 5s^2$
Ti	$3d^2 4s^2$	Zr	$4d^2 5s^2$
V	$3d^3 4s^2$	Nb	$4d^4 5s^1$
Cr	$3d^5 4s^1$	Mo	$4d^5 5s^1$
Mn	$3d^5 4s^2$	Tc	$4d^6 5s^1$
Fe	$3d^6 4s^2$	Ru	$4d^7 5s^1$
Co	$3d^7 4s^2$	Rh	$4d^8 5s^1$
Ni	$3d^8 4s^2$	Pd	$4d^{10} 5s^0$
Cu	$3d^{10} 4s^1$	Ag	$4d^{10} 5s^1$
Zn	$3d^{10} 4s^2$	Cd	$4d^{10} 5s^2$

5*d* - series		6*d* - series	
Element	Configuration	Element	Configuration
La	$5d^1 6s^2$	Ac	$6d^1 7s^2$
Hf	$5d^2 6s^2$	Rf	$6d^2 7s^2$
Ta	$5d^3 6s^2$	Db	$6d^3 7s^2$
W	$5d^4 6s^2$	Sg	$6d^4 7s^2$
Re	$5d^5 6s^2$	Bh	$6d^5 7s^2$
Os	$5d^6 6s^2$	Hs	$6d^6 7s^2$
Ir	$5d^7 6s^2$	Mt	$6d^7 7s^2$
Pt	$5d^9 6s^1$	Ds	$6d^8 7s^2$
Au	$5d^{10} 6s^1$	Rg	$6d^{10} 7s^1$
Hg	$5d^{10} 6s^2$	Cn	$6d^{10} 7s^2$

The electronic configurations of Zn, Cd, Hg and Cn are represented by the general formula $(n\text{-}1)d^{10}ns^2$. The *d*- orbitals in these elements are completely filled in the atomic state as well as in their common oxidation states. Therefore, they are not regarded as transition elements. A transition element is defined as that which contains at least one unpaired *d*-electron in its atom or ions with common oxidation state.

The *d* orbitals of the transition elements are less penetrating than the other orbitals (i.e., *s* and *p*). Hence, they are more influenced by the atoms or ions or molecules bound to them. In some respects, ions with same number of unpaired electrons in a given period of the *d*- block have similar magnetic and electronic properties. With partly filled *d* orbitals these elements exhibit certain characteristic properties such as exhibition of different oxidation states, formation of aqueous coloured ions and ability to form complex compounds with a variety of ligands.

The transition metals and some of their compounds also exhibit catalytic property and different magnetic behaviours. All these characteristics have been discussed in detail later in this chapter.

There are greater horizontal similarities in the properties of the transition elements in contrast to the main group 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 7.1 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 atomic 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

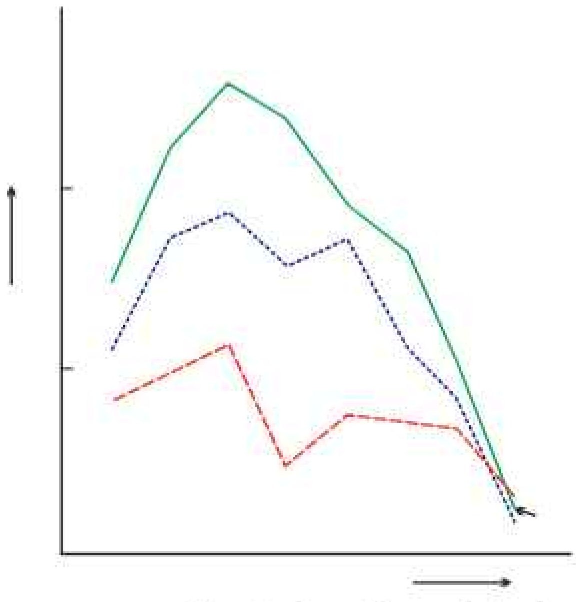
Silver atom has completely filled *d* orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

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

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 close packed structures at normal temperatures.

hcp	hcp	bcc	bcc	X	bcc	hcp	ccp	ccp	hcp
hcp	hcp	bcc	bcc	hcp	hcp	ccp	ccp	ccp	hcp
hcp	hcp	bcc	bcc	hcp	hcp	ccp	ccp	ccp	X

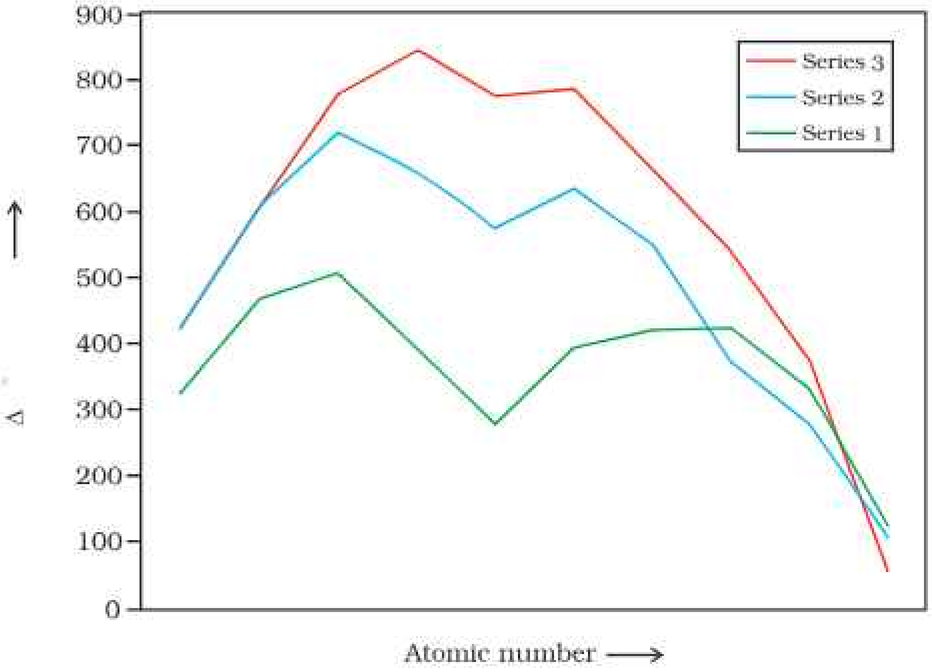
(bcc = body centred cubic; hcp = hexagonal close packed; ccp = cubic close packed; X = complex structure).



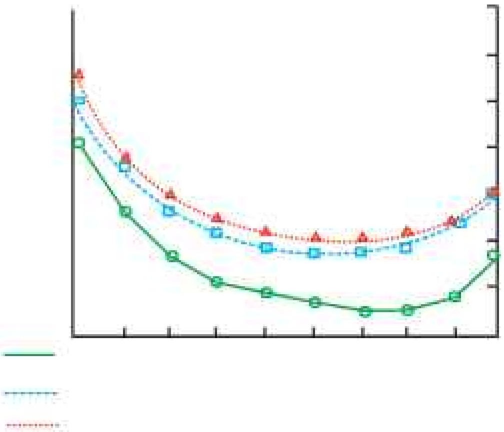
Trends in melting points of transition elements

The transition metals (with the exception of Zn, Cd and Hg) are very much hard and have low volatility. Their melting and boiling points are high. Fig. 7.1 depicts the melting points of the 3*d*, 4*d* and 5*d* transition metals. 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 n*s* 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. 7.2. The maxima at about the middle of each series indicate that one unpaired electron per *d* orbital is particularly 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. 7.2 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.



Trends in enthalpies of atomisation of transition elements



Trends in atomic radii of transition elements

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. 7.3 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 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 7.2).

	21	22	23	24	25	26	27	28	29	30
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]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	–	–
	$\Delta_a H^\ominus$	–								
	326	473	515	397	281	416	425	430	339	126

	Δ										
$\Delta_i H^{\ominus}$	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	3829
	M	164	147	135	129	137	126	125	125	128	137
	M^{2+}	–	–	79	82	82	77	74	70	73	75
	M^{3+}	73	67	64	62	65	65	61	60	–	–
	M^{2+}/M	–	–1.63	–1.18	–0.90	–1.18	–0.44	–0.28	–0.25	+0.34	-0.76
	M^{3+}/M^{2+}	–	–0.37	-0.26	-0.41	+1.57	+0.77	+1.97	–	–	–
		3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1

Example 7.2

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

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?

Due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals, there is an increase in ionisation enthalpy along each series of the transition elements from left to right. However, many small variations occur. Table 7.2 gives the values for the first three ionisation enthalpies of the first row elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. Although the first ionisation enthalpy, in general, increases, the magnitude of the increase in the second and third ionisation enthalpies for the successive elements, in general, is much higher.

The irregular trend in the first ionisation enthalpy of the 3*d* metals, 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. So the unipositive ions have d^n configurations with no 4*s* electrons. There is thus, a reorganisation energy accompanying ionisation with some gains in exchange energy as the number of electrons increases and from the transference of *s* electrons into *d* orbitals. There is the generally expected increasing trend in the values as the effective nuclear charge increases. However, the value of Cr is lower because of the absence of any change in the *d* configuration and the value for Zn higher because it represents an ionisation from the 4*s* level. 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 energies is required in addition to the enthalpy of atomisation for each element. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where the d^5 and d^{10} configurations of the M^+ ions are disrupted, with considerable loss of exchange energy. The value for Zn is correspondingly low as the ionisation consists of the removal of an electron which allows the production of the 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 superimposed upon the general increasing trend. In general, the third ionisation enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}. Also the high values for 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.

One of the notable features of a transition element is the great variety of oxidation states it may show in its compounds. Table 7.3 lists the common oxidation states of the first row transition elements.

	+2	+2	+2					+1	
+3	+3	+3		+3			+3		
		+4	+4	+4	+4	+4	+4		
			+5	+5					
				+6	+6				

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 ($Ti^{IV}O_2$, $V^{V}O_2^{+}$, $Cr^{VI}O_4^{2-}$, $Mn^{VII}O_4^{-}$) 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 7.3

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

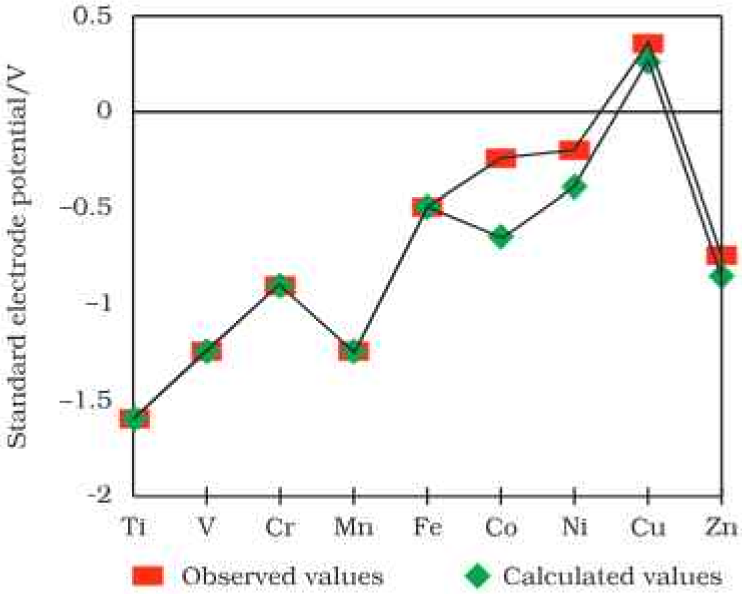
Solution

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

Intext Question

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

Table 7.4 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 7.4 are compared in Fig. 7.4.



Observed and calculated values for the standard electrode potentials

($M^{2+} \rightarrow M^\circ$) of the elements Ti to Zn

Example 7.4

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. On the other hand, the change from Mn^{2+} to Mn^{3+} results in the half-filled (d^5) configuration which has extra stability.

Intext Question

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

	$\Delta\ ^{\ominus}$	$\Delta\ ^{\ominus}$	$\Delta\ ^{\ominus}$	$\Delta\ ^{\ominus}$	$^{\ominus}$
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

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.

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 $\Delta_{hyd}H^{\ominus}$.

An examination of the $E^{\ominus}(M^{3+}/M^{2+})$ values (Table 7.2) 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).

Table 7.5 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^{V} 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 = Cl, Br or 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:

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

+ 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: $X = F \rightarrow I$; $X^I = F \rightarrow Br$; $X^{II} = F, Cl$; $X^{III} = Cl \rightarrow I$

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 7.6) 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}.

+ 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

Example 7.5

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

Solution

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

Intext Question

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

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 7.2) 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 $E^{\ominus}$ 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 7.2) 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 7.6

For the first row transition metals the $E^{\ominus}$ values are:

$\ominus$	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 non-regularity in the above values.

Solution

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

Example 7.7

Why is the $^{\ominus}$ 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 ^{5} to ^{4}) is mainly responsible for this. This also explains why the +3 state of Mn is of little importance.

Intext Questions

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

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

When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: and (chapter 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 . 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.

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 7.7. The experimental data are mainly for hydrated ions in solution or in the solid state.

Sc^{3+}	3 ^{0}	0	0	0
Ti^{3+}	3 ^{1}	1	1.73	1.7 - 1.8
Ti^{2+}	3 ^{2}	2	2.84	2.7 - 2.9
V^{2+}	3 ^{3}	3	3.87	3.7 - 3.9
Cr^{2+}	3 ^{4}	4	4.90	4.8 - 4.9
Mn^{2+}	3 ^{5}	5	5.92	5.7 - 6.0
Fe^{2+}	3 ^{6}	4	4.90	5.3 – 5.5
Co^{2+}	3 ^{7}	3	3.87	4.4 – 5.2
Ni^{2+}	3 ^{8}	2	2.84	2.9 – 3.4
Cu^{2+}	3 ^{9}	1	1.73	1.8 – 2.2
Zn^{2+}	3 ^{10}	0	0	

Example 7.8

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 ^{5} configuration (five unpaired electrons). The magnetic moment, μ is

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

Intext Question

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

When an electron from a lower energy orbital of a metal ion in a complex is excited to a higher energy orbital of the same value, the energy of excitation corresponds to the frequency of light absorbed. 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 7.8. A few coloured solutions of –block elements are illustrated in Fig. 7.5.

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 dealtwith in detail in co-ordination compounds). 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 orbitals for bond formation.

$3d^0$	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

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 and 4 electrons for bonding). This has the effect of increasing the concentration of reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowered). 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.

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

An explanation of this catalytic action can be given as:

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

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

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 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.

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 7.9

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

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

7.4 Some Important Compounds of Transition Elements

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_2^+ 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, $Na_2Cr_2O_7.\ 2H_2O$ 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.

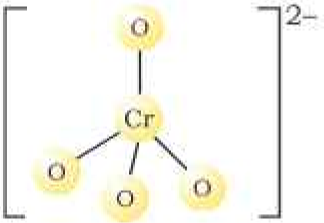
$$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$$

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.

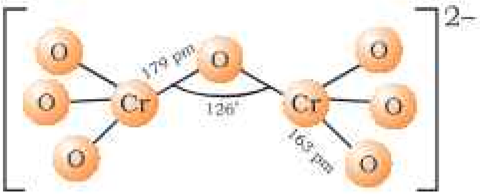
$$2\ CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

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

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:

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

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 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).

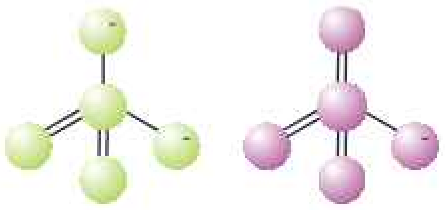
$$\underset{}{MnO_2} \xrightarrow{\text{Fused with KOH, oxidised with air or } KNO_3} \underset{\text{manganate ion}}{MnO_4^{2-}} \quad ; \quad \underset{\text{manganate}}{MnO_4^{2-}} \xrightarrow{\text{Electrolytic oxidation in alkaline solution}} \underset{\text{permanganate ion}}{MnO_4^-}$$

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 weak temperature dependent paramagnetism. These can be explained by the use of molecular orbital theory which is beyond the present scope.

The manganate and permanganate ions are tetrahedral; the green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

The π-bonding takes place by overlap of orbitals of oxygen with orbitals of manganese.

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,

$$MnO_4^- + e^- \rightarrow MnO_4^{2-} \qquad (^\circ = +\ 0.56\ V)$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \qquad (^\circ = +\ 1.69\ V)$$

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

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(II) ions are present or the temperature is raised.

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

In acid solutions:

(a) Iodine is liberated from potassium iodide :

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

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

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

(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:

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

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

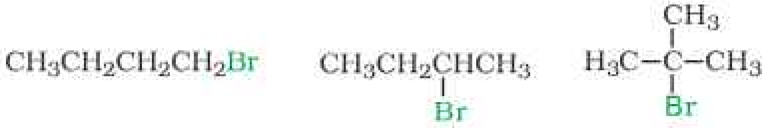
(e) Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

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

(f) Nitrite is oxidised to nitrate:

$5NO^- + 2MnO^- + 6H^+ \longrightarrow 2Mn^{2+}$

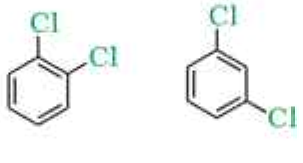
The boiling points of isomeric haloalkanes decrease with increase in branching (Ch. 13 of Inter I yr.). For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.



$CH_3CH_2CH_2CH_2Br$ $\quad$ $CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_3$ $\quad$ $H_3C-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

b.p./K 375 364 346

Boiling points of isomeric dihalobenzenes are very nearly the same. However, the isomers are high melting as compared to their and isomers. It is due to symmetry of isomers that fits in crystal lattice better as compared to - and -isomers.



b.p / K	453	446	448
m.p / K	256	249	323

Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms (Table 11.3).

n–C_3H_7Cl	0.89	CH_2Cl_2	1.336
n–C_3H_7Br	1.335	$CHCl_3$	1.489
n-C_3H_7I	1.747	CCl_4	1.595

In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and to break the hydrogen bonds between water molecules. Less energy would be released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents. This is because the intermolecular attractions between haloalkanes and solvent molecules have the same strength as that between haloalkane - haloalkane molecules and solvent - solvent molecules.

Intext Question

11.6 Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

11.5 Chemical Reactions

Reactions of Haloalkanes

The reactions of haloalkanes may be divided into the following categories:

(i) Nucleophilic substitution
(ii) Elimination reactions
(iii) Reaction with metals.

(i) *Nucleophilic substitution reactions*

In this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

It is one of the most useful classes of organic reactions of alkyl halides in which halogen is bonded to sp^3 hybridised carbon. The products formed by the reaction of haloalkanes with some common nucleophiles are given in Table 11.4.

Table 11.4: Nucleophilic Substitution of Alkyl Halides (R–X)

$$R - X + Nu^- \rightarrow R - Nu + X^-$$

Nucleophile product R–Nu	Reagent (Nu⁻)	Substitution product	Class of main
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	$R'O^-$	ROR′	Ether
NaI	I^-	R—I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″NH	RNR′R″	Tert. amine
KCN	$\overset{-}{C}\equiv N:$	RCN (cyanide)	Nitrile
AgCN	$\overline{N}C$	RNC (isocyanide)	Isonitrile
KNO_2	$O=N—O^-$	R—O—N=O	Alkyl nitrite
$AgNO_2$	$\underset{\overset{\downarrow}{O}}{\overline{N}}=O$	$R—NO_2$	Nitroalkane
R′COOAg	$R'COO^-$	R′COOR	Ester
$LiAlH_4$	H^-	RH	Hydrocarbon
$R'^- M^+$	R'^-	RR′	Alkane

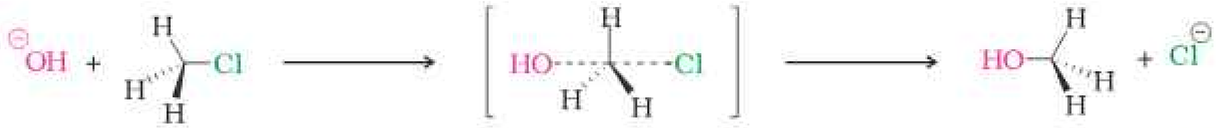
$\ominus$ $\equiv$ $\leftrightarrow$

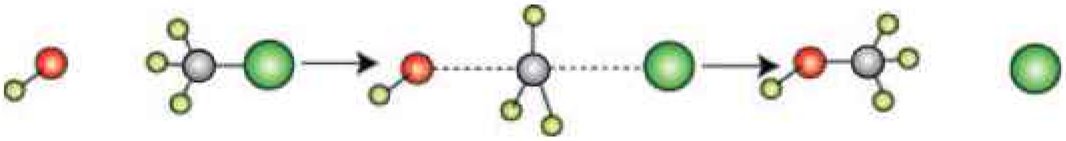
$\ominus$

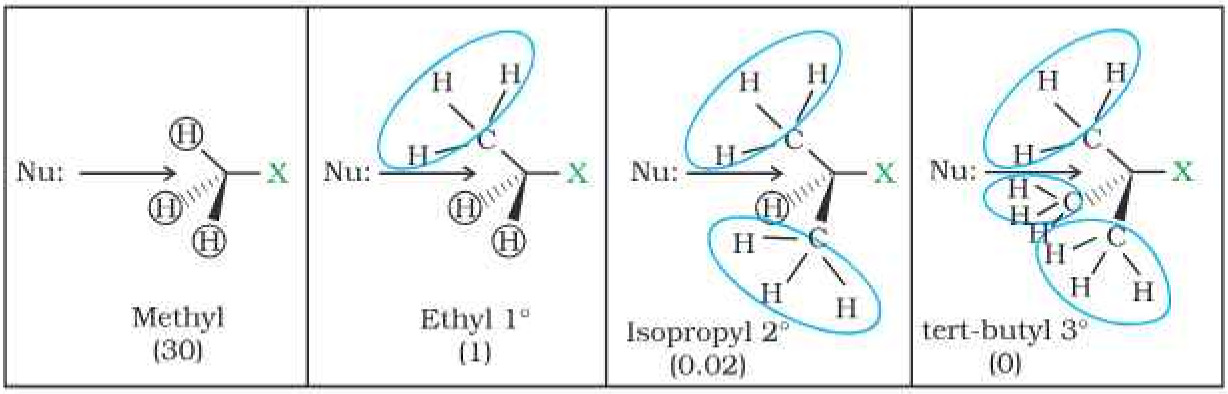
$\cdot\cdot$

Example 11.5

Solution



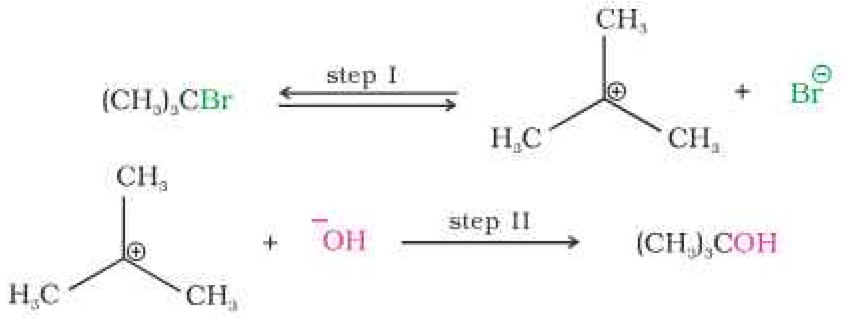


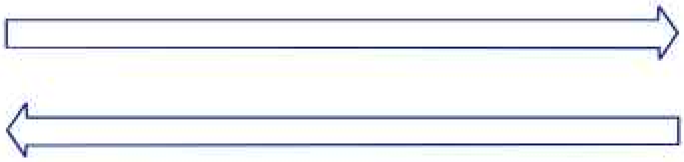


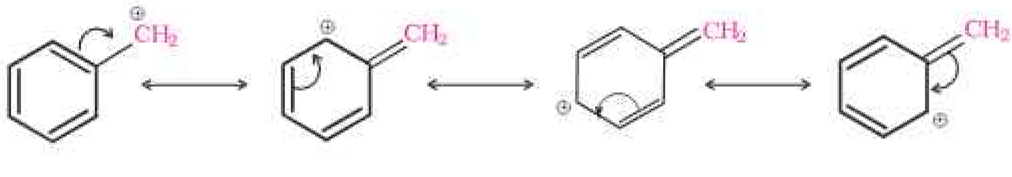
$$(CH_3)_3CBr + {}^{-}OH \longrightarrow (CH_3)_3COH + Br^{-}$$

2-Bromo-2-methylpropane

2-Methylpropan-2-ol


(CH3)3CBr
step I
CH3
H3C
CH3
Br
CH3
H3C
CH3
OH
step II
(CH3)3COH




CH2
CH2
CH2
CH2

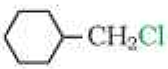
Example 11.6


and

;

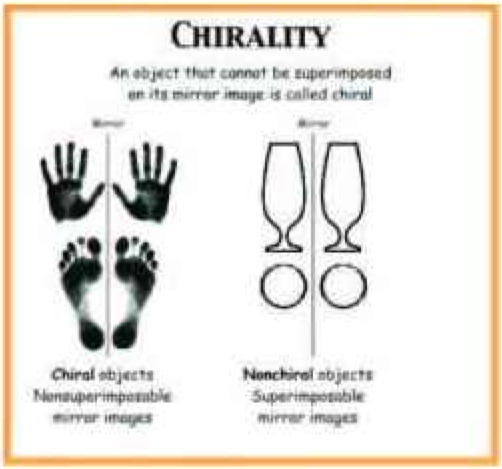
and

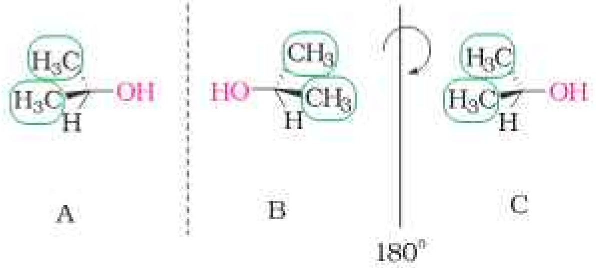

Solution



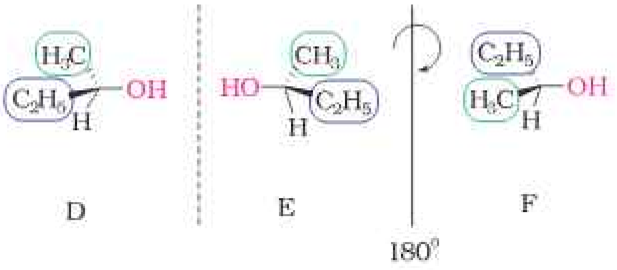
Example 11.7

Solution


CHIRALITY
An object that cannot be superimposed on its mirror image is called chiral
Mirror
Mirror
Chiral objects
Nonsuperimposable mirror images
Nonchiral objects
Superimposable mirror images



C obtained by rotating B by 180°
C is superimposable on its mirror image A

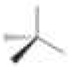


F obtained by rotating E by 180°
F is non superimposable on its mirror image D

±

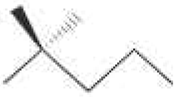
±

Example 11.8



|

Solution



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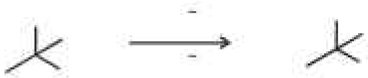
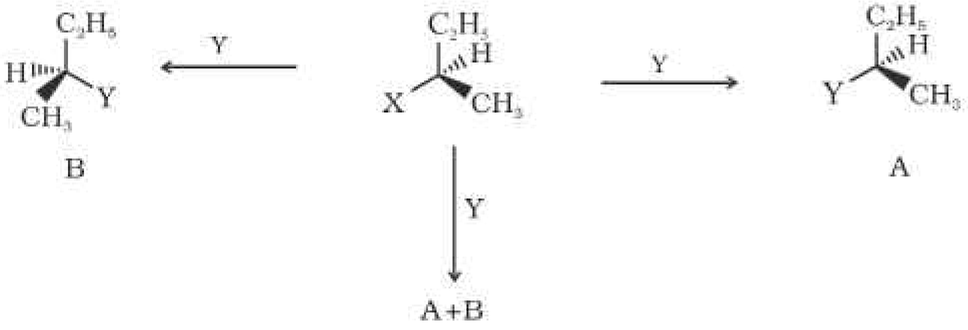
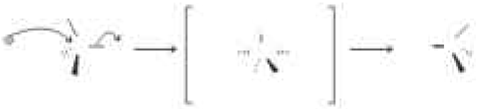
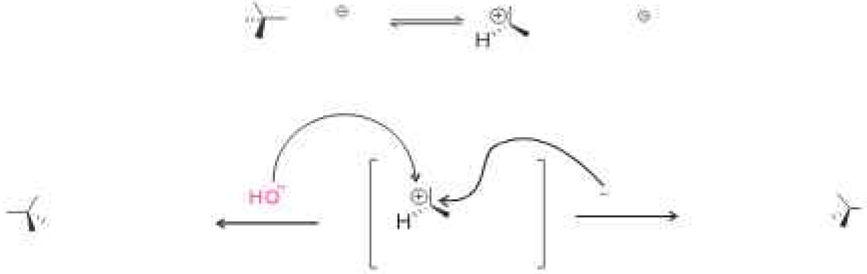



C2H5
H
Y
CH3
B
Y
C2H5
H
X
CH3
Y
C2H5
H
Y
CH3
A
Y
A+B



±



β

β

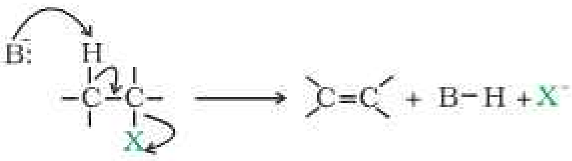
α

β

β

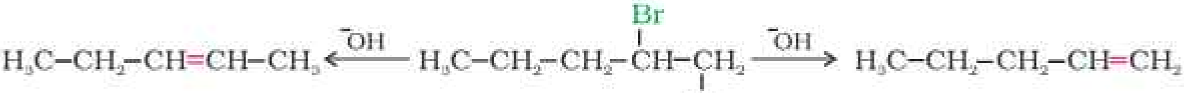
α

β



B=Base ; X=Leaving group

β

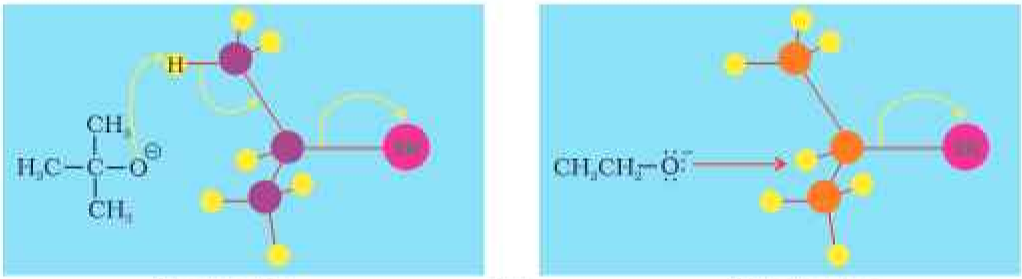


$$H_3C-CH_2-CH=CH-CH_3 \xleftarrow{^-OH} H_3C-CH_2-CH_2-\overset{Br}{\overset{|}{C}}H-\underset{H}{\underset{|}{C}}H_2 \xrightarrow{^-OH} H_3C-CH_2-CH_2-CH=CH_2$$

Pent-2-ene (81%) 2-Bromopentane Pent-1-ene (19%)

Elimination versus substitution

β



Elimination *vs* Substitution

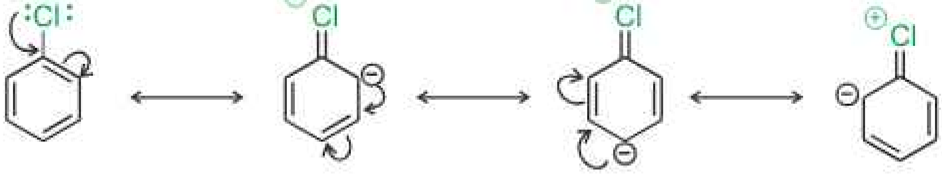
$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

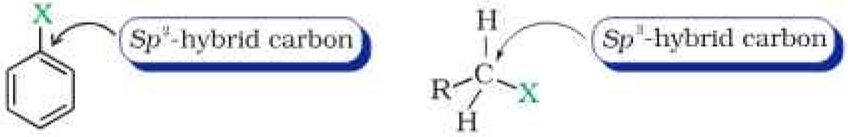
$$\overset{\delta-}{R}-\overset{\delta+}{Mg}\,\overset{\delta-}{X}$$

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

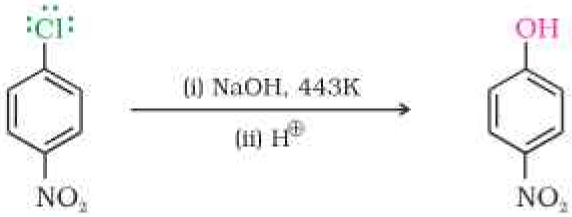
$$2RX + 2Na \longrightarrow RR + 2NaX$$

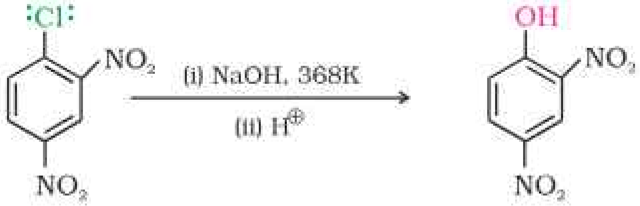
π

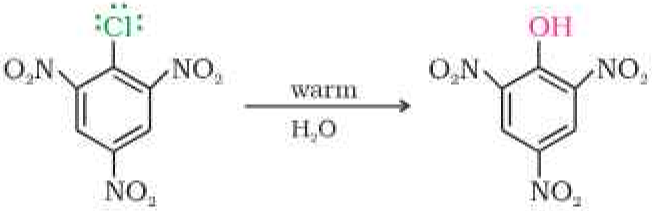


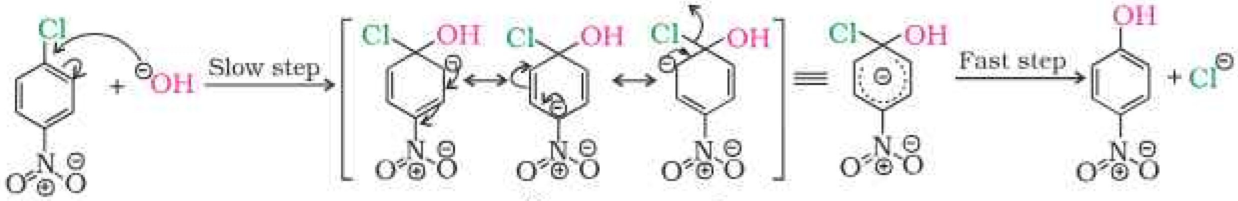

X
Sp²-hybrid carbon
H
R
C
X
H
Sp³-hybrid carbon

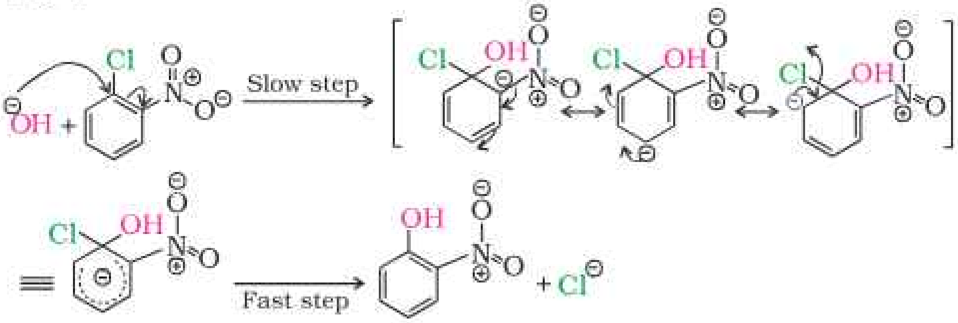

Cl
(i) NaOH, 623K, 300 atm
(ii) H⊕
OH

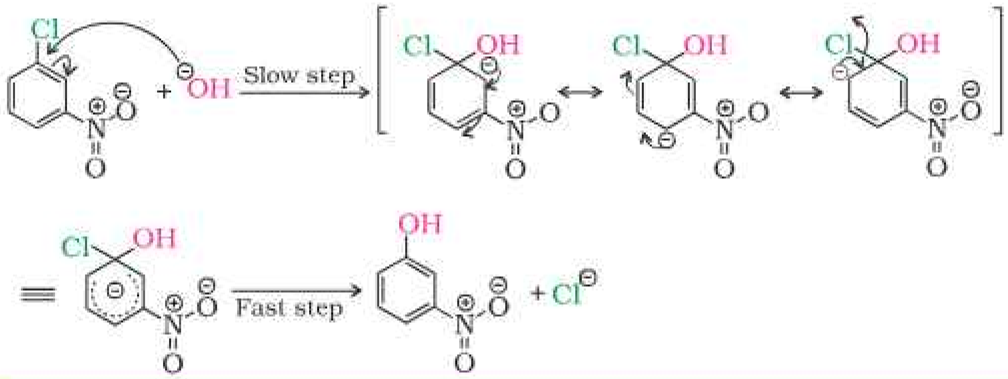

Cl
NO₂
(i) NaOH, 443K
(ii) H⊕
OH
NO₂

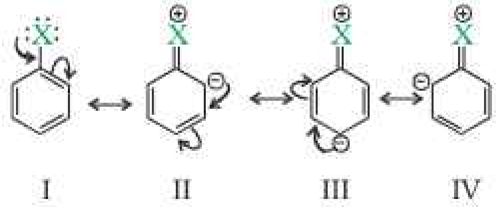

Cl
NO₂
NO₂
(i) NaOH, 368K
(ii) H⊕
OH
NO₂
NO₂

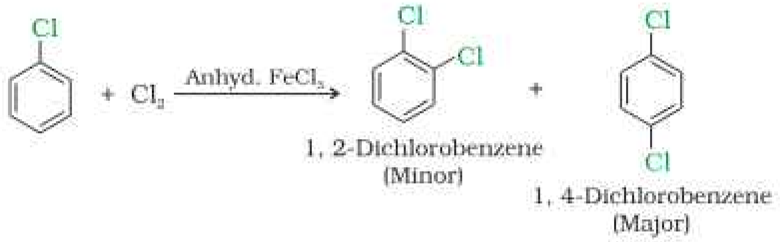

warm
H₂O


Slow step
Fast step


Slow step
Fast step


Slow step
Fast step



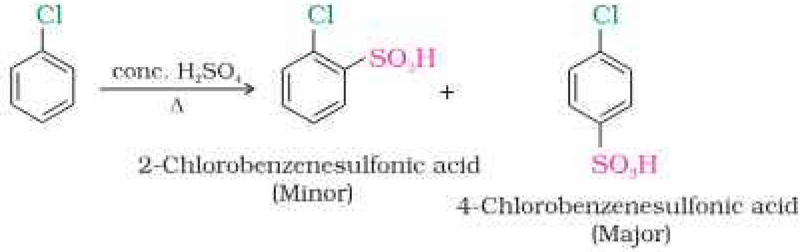


1, 2-Dichlorobenzene
(Minor)

1, 4-Dichlorobenzene
(Major)

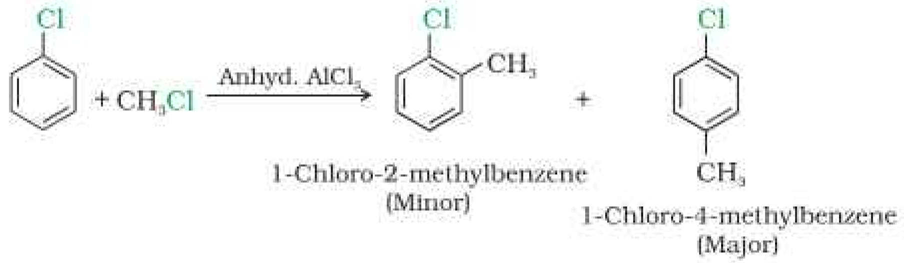
1-Chloro-2-nitrobenzene
(Minor)

1-Chloro-4-nitrobenzene
(Major)



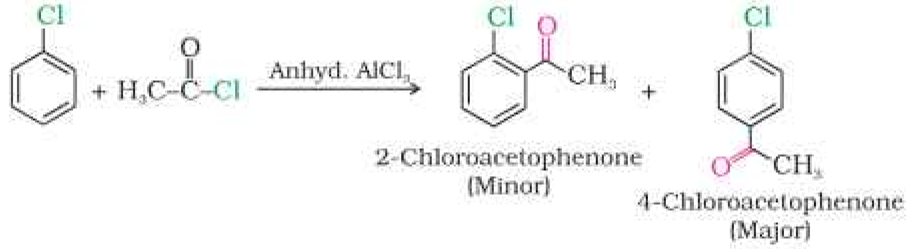
2-Chlorobenzenesulfonic acid
(Minor)

4-Chlorobenzenesulfonic acid
(Major)



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)

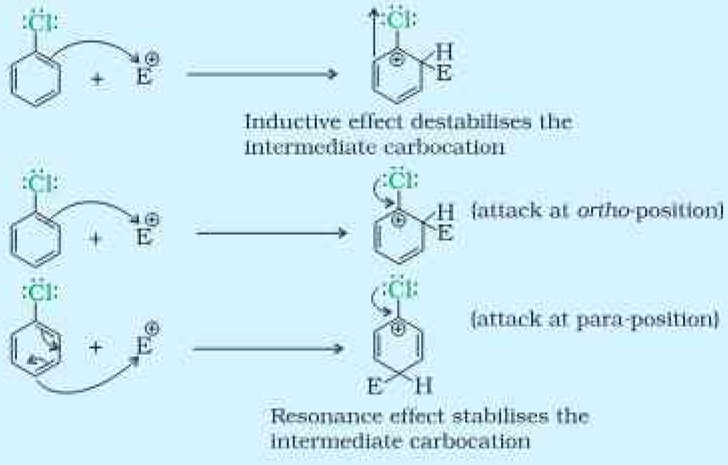


2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

Example 11.9

Solution



Inductive effect destabilises the intermediate carbocation

Resonance effect stabilises the intermediate carbocation

3. *Reaction with metals*

Wurtz-Fittig reaction

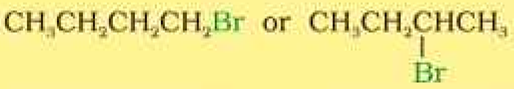
A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.

Fittig reaction

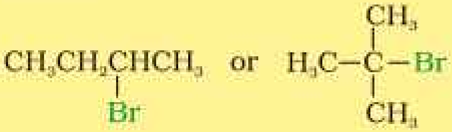
Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.

Intext Questions

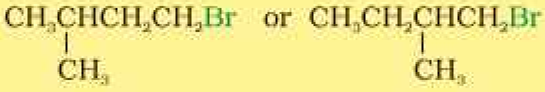
11.7 Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

(i) 

$CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

(ii) 

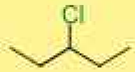
$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ or $H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-Br$

(iii) 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2Br$ or $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Br$

11.8 In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

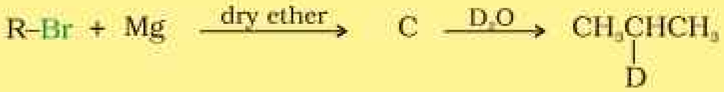
(i) 

and 

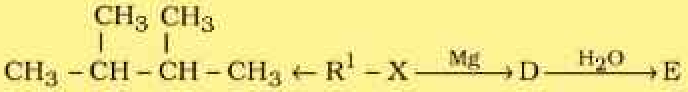
(ii) 

and 

11.9 Identify A, B, C, D, E, R and R^1 in the following:



$R{-}Br + Mg \xrightarrow{\text{dry ether}} C \xrightarrow{D_2O} CH_3\underset{\displaystyle D}{\underset{|}{C}}HCH_3$



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}H-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_3 \leftarrow R^1-X \xrightarrow{Mg} D \xrightarrow{H_2O} E$

11.6 Polyhalogen Compounds

Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

Dichloromethane (Methylene chloride)

Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

Trichloromethane (Chloroform)

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether. As might be expected from its use as an anaesthetic, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.

$$2CHCl_3 + O_2 \xrightarrow{light} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Triiodomethane (Iodoform)

It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Tetrachloromethane (Carbon tetrachloride)

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve