CHAPTER

11

Standard Electrode Potentials

Electrode Potential

When a metal piece is placed in water or in water solution containing one of its salts (*i.e.* the solution contains the metal ions. *e.g.* Zn in $ZnSO_4$ solution), the metal atoms tend to lose electrons and hence become positively charged ions. Thus the solution, due to the presence of positively charged metal ions, becomes positively charged.

The conversion of metal atoms into positively-charged ions is due to the attractive force of polar water molecules which remove the metal ions from the metal surface and send them into the solution. The electrons removed from the metal atoms are left on the metal itself and hence the metal becomes negatively charged. Thus :

$$\textit{Metal} - \textit{Electrons} \rightleftarrows \textit{Positively charged metal ions}$$

↓	↓
Are left on the metal to make the metal negatively-charged.	*Go into the solution to make the solution positively-charged.*

The positively-charged metal ions which have passed from the metal into the solution cluster around the surface of the negatively- charged metal and form a *double electric layer* (Fig. 11.1). This double electric layer can be compared with an electric capacitor in which one plate is the charged metal surface and the other is layer of ions near it. The double electric layer thus formed develops a definite potential difference between the metal and the solution. This potential difference is called electrode potential of the metal or electrode. Thus :

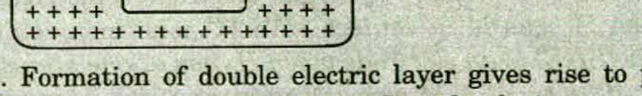


Fig. 11.1. Formation of double electric layer gives rise to potential difference between the metal (Zn metal) and solution containing its own ions (Zn^{2+} ions) which is called electrode potential.

The potential difference between a metal and a solution containing its own ions (in equilibrium) is called **electrode potential** *of that metal or electrode.*

The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons, *i.e.* it is a measure of the relative tendency of the metal to undergo oxidation (loss of electrons) or reduction (gain of electrons).

Oxidation Electrode Potential and Reduction Electrode Potential

Depending on the tendency of a metal to lose or gain electrons, the electrode potential may be of two types namely *oxidation potential and reduction potential. Oxidation potential of a metal indicates its electron losing tendency while reduction potential represents the electron gaining capacity of the metal.*

The unit of electrode potential is *volt which is the potential required to flow one coulomb of electric current per second through a uniform thread of mercury, 106.3 cm. long containing 14.4521 gm. mercury at 0°C.*

The potential of a single electrode cannot be measured directly. Actually what we do is that, first of all, we assign an arbitrary electrode potential to a reference or standard electrode and then the potential of the given electrode is measured with respect to this standard electrode. A universally adopted standard electrode is the hydrogen electrode which will be described a little later.

Factors Affecting the Magnitude of Electrode Potential

The magnitude of electrode potential depends on the following factors :

1. Nature of metal or electrode. The metals have different tendency to lose or accept the electrons and hence have different electrode potential. Na, being extremely active, has a strong tendency to lose electrons and hence has high electrode potential. On the other hand, Cu, being less active, has lower tendency to lose electrons and hence has lower electrode potential.

2. Concentration of metal ions in solution. Consider Zn rod dipped in $ZnSO_4$ solution (*i.e.* in Zn^{2+} ions)

$$Zn \rightleftarrows Zn^{2+} + 2e^-$$

As the concentration of Zn^{2+} ions increases, the equilibrium will shift to the left side and the hence the electrode potential will decrease. Similarly as the concentration of Zn^{2+} ions decreases, electrode potential increases.

3. Temperature. The change in the temperature of the solution also changes the electrode potential.

Standard Hydrogen Electrode (SHE)

We have already said that it is not possible to measure the potential of a singal electrode (half-cell). However, it is measured with respect to some standard electrode (half-cell) which is usually hydrogen electrode. This electrode is a half-cell developed when H_2 gas is in contact with H^+ ions in a solution. *Standard Hydrogen Electrode (SHE) is an electrode when H_2 gas at one atmosphere pressure is in contact with H^+ ions of 1 M concentration at 25°C.* This electrode is also called *Normal Hydrogen Electrode (NHE). It is assigned a potential of zero.* This electrode is obtained and works as follows (Also see Fig. 11.2).

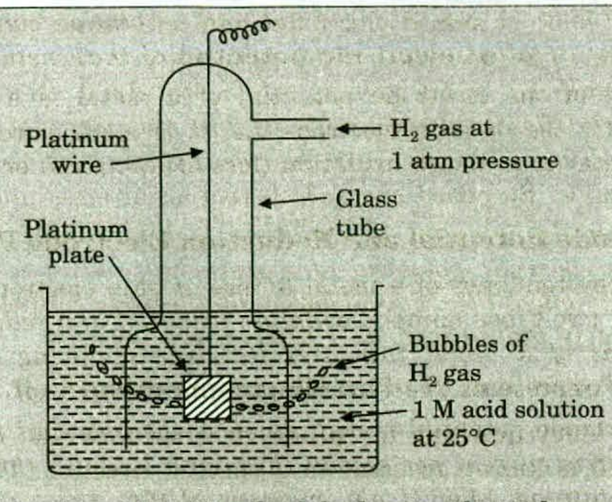


Fig. 11.2. Standard hydrogen electrode.

(*i*) 1M HCl or H_2SO_4 solution is taken in a glass vessel and maintained at 25°C.

(*ii*) A platinum wire fused in a glass tube and having a small platinum plate coated with finely divided platinum black is used as the electrode. The platinum plate provides a large surface for hydrogen to get adsorbed on it.

(*iii*) The electrode (*i.e.* platinum wire and platinum plate) is surrounded by a glass tube which has an inlet at its top for bubbling pure H_2 gas (at 1 atmosphere pressure) into the acid solution contained in the glass vessel and has a number of holes at its base for the escape of excess of H_2 gas. A part of H_2 gas is absorbed on the surface of the platinised Pt electrode while the excess of H_2 gas escapes through the holes.

Hydrogen electrode thus obtained forms one of the two half-cells of a given voltaic cell. When this half-cell is connected with any other half-cell, it begins to work. For example when it is connected with a Zn–Zn^{2+} half-cell, the electrons given up by Zn – Zn^{2+} half-cell are used up at the hydrogen electrode bringing about the reduction of H^+ (*aq*) ions to H_2 gas.

$$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$$

$$2H^+\ (aq) + 2e^- \rightarrow H_2\ (g)$$

Thus we see that here hydrogen electrode acts as a cathode and hence is represented as $H_2\ (g)/2H^+(aq)$ and is placed at the right hand of the complete cell.

$$\xrightarrow{\qquad \textit{Flow of electrons} \qquad}$$

Zn (s) | Zn²⁺(aq) |	*| 2H⁺ (aq) | H₂(g)*
Anode (–)	*Cathode* (+)
(Oxidation half-cell)	*(Reduction half-cell)*

Standard Electrode Potential (E°)

We have already pointed out that since it is not possible to determine the electrode potential of a given single electrode (half-cell), it is measured with respect to that of some standard electrode (half-cell) which is usually standard hydrogen electrode. *The potential difference between the standard hydrogen half-cell and the half-cell in question is called* **standard electrode potential,** *provided that all the dissolved species are at unit molarity (1M); all gases are at one atmosphere pressure; all solids are in their most stable form and the temperature is maintained at 25°C.* Standard electrode potential is represented as E°.

Since the electrode potential of standard hydrogen half-cell is arbitrarily taken as zero, the electrode potential of a given half-cell is called its standard electrode potential when the concentration of the ions is 1M, temperature is 25°C and pressure is maintained at 1 atmosphere pressure.

Electromotive Force (e.m.f.) of an Electrochemical Cell

The flow of electrons taking place in the two half-reactions of an electrochemical cell is known to occur in a specific direction. The voltage of the cell is read by the voltmeter and is called **electromotive force (e.m.f.)** of the cell. *The standard e.m.f. of a given cell ($E°_{cell}$) is equal to the difference of the standard reduction potential of the cathode (i.e. right hand electrode), $E°_{cathode}$ and the standard reduction potential of the anode (i.e. left hand electrode), Thus :*

$$\boxed{\begin{aligned}\mathbf{E°}_{cell} &= \mathbf{E°}_{cathode} - \mathbf{E°}_{anode}\\ &= \mathbf{E°}_{right} - \mathbf{E°}_{left}\end{aligned}}$$

Measurement of Standard Electrode Potential

For measuring the standard electrode potential of a given electrode, a voltaic cell is set up with two half-cells one of which has the electrode whose standard electrode potential is to be determined and the other has a standard hydrogen electrode. 1M solutions are used in both the half-cells and the temperature is maintained at 25°C. The electrodes are connected with a voltmeter and the e.m.f. of the cell is noted from the deflection of the needle of the voltmeter. The reading noted in the voltmeter gives the standard electrode potential of the electrode in question with respect to hydrogen electrode. This procedure can be understood by considering the following examples :

1. Determination of standard electrode potential of Zn/Zn^{2+} electrode. In order to determine the electrode potential of Zn electrode dipped in 1M $ZnSO_4$ solution, it is combined with the standard hydrogen electrode to form the complete cell.

The deflection of the needle of the voltmeter towards Zn electrode indicates that the conventional current is flowing from H electrode to Zn electrode and hence *the electrons are flowing from Zn electrode through the connecting wire towards H electrode* as shown in Fig. 11.3. Thus here Zn electrode acts as an *anode* and H electrode acts as a *cathode* and the cell can, therefore, be represented as :

—— *Flow of electrons* ⟶	
⟵ *Flow of current* ——	
$Zn(s)/Zn^{2+}(aq)$ |	**| $2H^+(aq)/H_2(g)$**
***Anode* (–)**	***Cathode* (+)**
(*Oxidation half-cell*)	**(*Reduction half-cell*)**

The two half-cell reactions are :

Oxidation half-reaction (Anode reaction) :

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

Reduction half-reaction (Cathode reaction) :

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

The complete cell-reaction is obtained by adding the above two half-cell reactions.

$$Zn(s) + 2H^+(aq) \rightarrow H_2(g) + Zn^{2+}(aq)$$

The voltmeter reads 0.76 volts which is the observed e.m.f. of the cell, *i.e.*

$$E^\circ_{cell} = 0.76 \text{ volts}$$

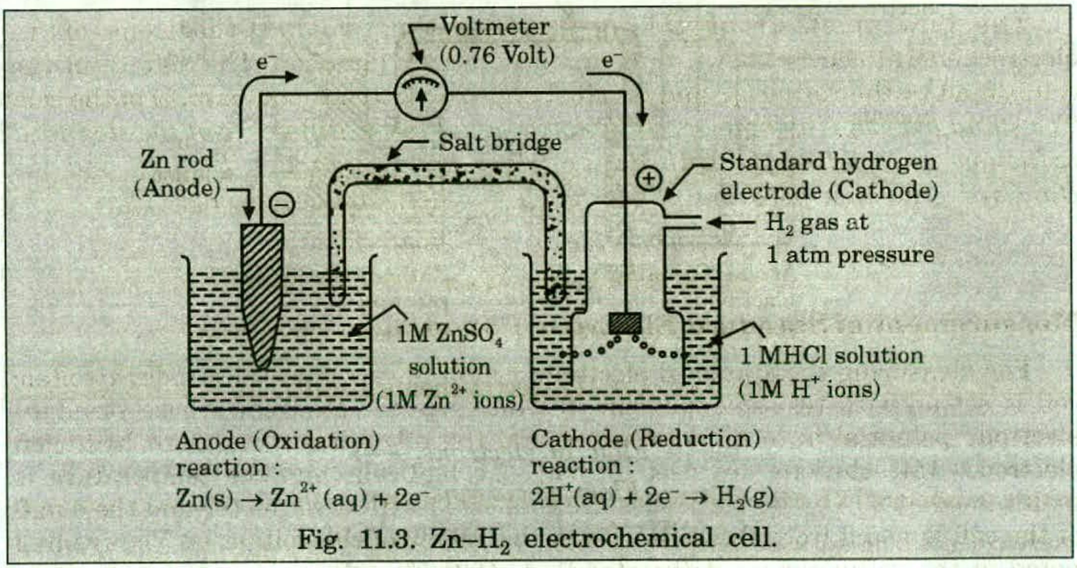


Fig. 11.3. Zn–H_2 electrochemical cell.

Now, as we have already seen that :

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

or $$0.76 = E^\circ_{2H^+/H_2} - E^\circ_{Zn^{2+}/Zn}$$

or $$0.76 = 0 - E^\circ_{Zn^{2+}/Zn} \qquad (\text{Since } E^\circ_{2H^+/H_2} = 0)$$

$$\therefore \quad E^\circ_{Zn^{2+}/Zn} = -\,0.76 \text{ volt.}$$

Here negative sign indicates that 0.76 volt is the standard reduction potential of Zn^{2+}/Zn electrode, *i.e.*, 0.76 volt is the standard potential corresponding to the reduction reaction :

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s);\ E^\circ_{Zn^{2+}/Zn} = -\,0.76 \text{ volt}$$

In order to get the standard oxidation potential of Zn/Zn^{2+} electrode, (*i.e.* standard electrode potential corresponding to the oxidation reaction, $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$) we have to reverse the sign of standard reduction potential obtained as above. Thus :

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-\ ;\ E^\circ_{Zn/Zn^{2+}} = +\,0.76 \text{ volt.}$$

2. Determination of standard electrode potential of Cu^{2+}/Cu electrode. In order to determine the electrode potential of Cu electrode dipped in 1M $CuSO_4$

solution, it is combined with the standard H-electrode to form the complete cell. Here the deflection of the needle of the voltmeter is towards H-electrode, indicating that the conventional current is flowing from Cu electrode to H-electrode and hence the *electrons are flowing from H-electrode through the connecting wire towards Cu electrode* as shown in Fig. 11.4. Thus here H-electrode acts as anode and Cu-electrode acts as cathode and the cell can be represented as :

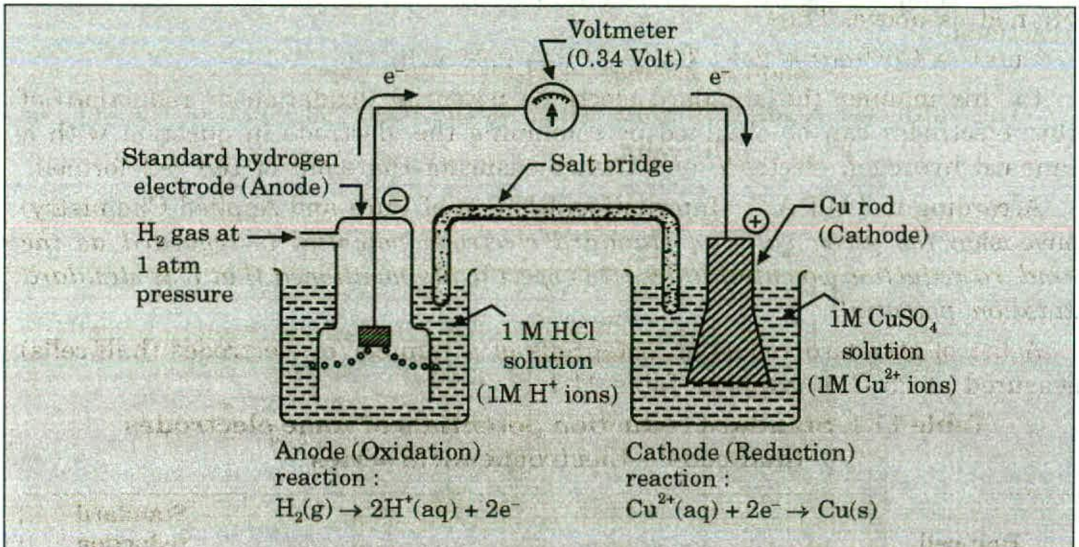


Fig. 11.4. Cu–H_2 electro-chemical cell.

—— *Flow of electrons* ⟶

⟵ *Flow of current* ——

$$H_2(g)/2H^+\ (aq)\,|\quad |\,Cu^{2+}(aq)/Cu(s)$$

Anode (–) *Cathode* (+)

The two half-reactions are :

Oxidation half-reaction (Anode reaction)

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

Reduction half-reaction (Cathode reaction)

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The *complete cell reaction* is obtained by adding the above two half-cell reactions. Thus :

$$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s)$$

Voltmeter reads 3.34 which is the observed e.m.f. of the cell, *i.e.*

$$E^\circ_{cell} = 0.34 \text{ volts}$$

Now, $$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

or $$0.34 = E^\circ_{Cu^{2+}/Cu} - E^\circ_{2H^+/H_2}$$

or $$0.34 = E^\circ_{Cu^{2+}/Cu} - 0$$

or $$E^\circ_{Cu^{2+}/Cu} = 0.34 \text{ volt.}$$

0.34 volt is the standard reduction potential of Cu^{2+}/Cu electrode, *i.e.* 0.34 volt is the standard potential corresponding to the reduction reaction :

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)\ ;\ E^\circ_{Cu^{2+}/Cu} = +\ 0.34 \text{ volt.}$$

In order to get the standard oxidation potential of Cu/Cu^{2+} electrode (*i.e.*, standard electrode potential corresponding to the oxidation reaction $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$) we have to reverse the sign of standard reduction potential obtained as above. Thus :

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-\ ;\ E^\circ_{Cu/Cu^{2+}} = -\ 0.34 \text{ volt.}$$

In this manner the standard electrode potential (oxidation or reduction) of other electrodes can be obtained by combining the electrode in question with a standard hydrogen electrode and then measuring the e.m.f of the cell formed.

According to I.U.P.A.C. (International Union of Pure and Applied Chemistry) convension *the given value of standard electrode potential is regarded as the standard reduction potential unless it is specifically mentioned that it is standard oxidation potential.*

A list of standard reduction potentials of a number of electrodes (half-cells) measured at 25°C is given in Table 11.1.

Table 11.1. Standard reduction potentials of some electrodes (half-cells)—Electrochemical series

Half-cell (Electrode or couple)	**Half-cell reaction (Reduction reaction)**		**Standard reduction potential (volts) (E° values)**
	↓ Oxidising power decreasing	↓ Reducing power increasing	↓ E° values decreasing
	Oxidising agent	Reducing agent	
$F_2/2F^-$	$F_2 + 2e^-$	$\rightarrow 2F^-$	+ 2.85
	Strongest oxidising agent	Weakest reducing agent	
O_3/O_2	$O_3 + 2H^+ + 2e^-$	$\rightarrow O_2 + H_2O$	+ 2.07
$S_2O_3^{2-}/SO_4^{2-}$	$S_2O_3^{2-} + 2e^-$	$\rightarrow 2SO_4^{2-}$	+ 2.01
H_2O_2/H_2O	$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	+ 1.77
MNO_4^-/MnO_2	$MnO_4^- + 4H^+ + 3e^-$	$\rightarrow MnO_2 + 2H_2O$	+ 1.69
Au^+/Au	$Au^+ + e^- +$	$\rightarrow Au$	+ 1.68
$HClO_3/HClO$	$HClO_3 + 2H^+ + 2e^-$	$\rightarrow HClO + H_2O$	+ 1.64
$HClO/Cl_2$	$2HClO + 2H^+ + 2e^-$	$\rightarrow Cl_2 + 2H_2O$	+ 1.64
Ce^{4+}/Ce^{3+}	$Ce^{4+} + e^-$	$\rightarrow Ce^{3+}$	+ 1.61
$2BrO_3^-/Br_2$	$2BrO_3^- + 12H^+ + 10e^-$	$\rightarrow Br_2 + 6H_2O$	+ 1.52
MnO_4^-/Mn^{2+}	$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	+ 1.51
Au^{3+}/Au	$Au^{3+} + 3e^-$	$\rightarrow Au$	+ 1.42
$Cl_2/2Cl^-$	$Cl_2 + 2e^-$	$\rightarrow 2Cl^-$	+ 1.36
$Cr_2O_7^{2-}/2Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
$2IO_3^-/I_2$	$2IO_3^- + 12H^+ + 10e^-$	$\rightarrow I_2 + 6H_2O$	+ 1.20
Pt^{2+}/Pt	$Pt^{2+} + 2e^-$	$\rightarrow Pt$	+ 1.20

Table 11.1. (Contd.)

IO_3^-/I^-	↓ Oxidising power decreasing ↓	$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$	↓ Reducing power increasing ↓	+ 1.09	↓ E° values decreasing ↓
$Br_2/2Br^-$		$Br_2 + 2e^- \rightarrow 2Br^-$		+ 1.06	
Hg^{2+}/Hg		$Hg^{2+} + 2e^- \rightarrow Hg$		+ 0.85	
Ag^+/Ag		$Ag^+ + e^- \rightarrow Ag$		+ 0.80	
Fe^{3+}/Fe^{2+}		$Fe^{3+} + e^- \rightarrow Fe^{2+}$		+ 0.77	
O_2/H_2O_2		$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$		+ 0.68	
H_3AsO_4/H_3AsO_3		$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$		+ 0.56	
$I_2/2I^-$		$I_2 + 2e^- \rightarrow 2I^-$		+ 0.53	
Cu^+/Cu		$Cu^+ + e^- \rightarrow Cu$		+ 0.52	
O_2/H_2O		$O_2 + 4H^+ + e^- \rightarrow 2H_2O$		+ 0.40	
Cu^{2+}/Cu		$Cu^{2+} + 2e^- \rightarrow Cu$		+ 0.34	
Bi^{3+}/Bi		$Bi^{3+} + 3e^- \rightarrow Bi$		+ 0.32	
Cu^{2+}/Cu^+		$Cu^{2+} + e^- \rightarrow Cu^+$		+ 0.15	
Sn^{4+}/Sn^{2+}		$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$		+ 0.15	
$S_4O_6^{2-}/S_2O_3^{2-}$		$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$		+ 0.09 = 0.00	
$2H^+/H_2$		$2H^+ + 2e^- \rightarrow H_2$		(By definition)	
Pb^{2+}/Pb		$Pb^{2+} + 2e^- \rightarrow Pb$		− 0.13	
Sn^{2+}/Sn		$Sn^{2+} + 2e^- \rightarrow Sn$		− 0.14	
Ni^{2+}/Ni		$Ni^{2+} + 2e^- \rightarrow Ni$		− 0.24	
Co^{2+}/Co		$Co^{2+} + 2e^- \rightarrow Co$		− 0.28	
Cd^{2+}/Cd		$Cd^{2+} + 2e^- \rightarrow Cd$		− 0.40	
Cr^{3+}/Cr^{2+}		$Cr^{3+} + e^- \rightarrow Cr^{2+}$		− 0.41	
Fe^{2+}/Fe		$Fe^{2+} + 2e^- \rightarrow Fe$		− 0.44	
S/S^{2-}		$S + 2e^- \rightarrow S^{2-}$		− 0.51	
Cr^{3+}/Cr		$Cr^{3+} + 3e^- \rightarrow Cr$		− 0.71	
Zn^{2+}/Zn		$Zn^{2+} + 2e^- \rightarrow Zn$		− 0.76	
Mn^{2+}/Mn		$Mn^{2+} + 2e^- \rightarrow Mn$		− 1.05	
Al^{3+}/Al		$Al^{3+} + 3e^- \rightarrow Al$		− 1.67	
Be^{2+}/Be		$Be^{2+} + 2e^- \rightarrow Be$		− 1.70	
$H_2/2H^-$		$H_2 + 2e^- \rightarrow 2H^-$		− 2.24	
Mg^{2+}/Mg		$Mg^{2+} + 2e^- \rightarrow Mg$		− 2.38	
Na^+/Na		$Na^+ + e^- \rightarrow Na$		− 2.71	
Ca^{2+}/Ca		$Ca^{2+} + 2e^- \rightarrow Ca$		− 2.76	
Sr^{2+}/Sr		$Sr^{2+} + 2e^- \rightarrow Sr$		− 2.89	
Ba^{2+}/Ba		$Ba^{2+} + 2e^- \rightarrow Ba$		− 2.90	
M^+/M (M = K, Rb or Cs)		$M^+ + e^- \rightarrow M$		− 2.92	
Li^+/Li		$Li^+ + e^- \rightarrow Li$		− 3.04	
		Weakest oxidising agent Strongest reducing agent			

Here it should be noted that the standard reduction potentials given in the table are so called because these are for the reduction reactions :

$$M + e \rightarrow M^-$$

If these values are to be converted into standard oxidation potentials, their magnitude will remain the same but their sign will have to be reversed and the values so obtained are called standard oxidation potentials because they are for the oxidation reactions :

$$M \rightarrow M^+ \times e^-$$

For example for the reduction reaction :

$$Zn^{2+} + 2e^- \rightarrow Zn,$$

standard reduction potential (from Table 11.1), $E^\circ_{Zn^{2+}/Zn} = -\ 0.76$ V.

Now if the E° value is to be written for the oxidation reaction :

$$Zn \rightarrow Zn^{2+} + 2e^-,$$

then the magnitude of E° will remain the same but the sign will be reversed, *i.e.*, *standard oxidation potential*, $E^\circ_{Zn/Zn^{2+}} = +\ 0.76$ V.

Moreover, any reaction equation may be suitably multiplied on both sides in order to balance the electrons gained and lost, in a redox reaction but *values of reduction potential are not multiplied by any coefficient.* For example, Table 11.1. shows that for the reduction reaction :

$$Ag^+(aq) + e^- \rightarrow Ag(s);\ E^\circ_{Ag^+/Ag} = +\ 0.80\ \text{V}$$

For two electrons the equation becomes :

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s);\ E^\circ_{2Ag^+/2Ag} = +\ 0.80\ \text{V}$$

Thus :

$$E^\circ_{Ag^+/Ag} = E^\circ_{2Ag^+/2Ag} = E^\circ_{3Ag^+/3Ag} = \ldots\ldots = +\ 0.80\ \text{volts.}$$

Electrochemical Series or e.m.f. Series

The list of elements or ions arranged in the decreasing order of their standard reduction potential values, as in Table 11.1, is called electro-chemical or e.m.f. series or activity series.

From this series the following points should be noted and should be borne in mind while studying the uses of this series.

1. The forward reaction shown in the central column of the series is a *reduction reaction* and hence the standard electrode potential values are *standard reduction potential values.*

2. The species given at the left hand side of the reduction reaction accept electrons and are reduced into the species shown at the right hand side. Thus the species shown at the left hand side act as oxidising agents while those given at the right hand side of the reduction reaction act as reducing agents.

3. The values of standard reduction potential (E° values) are decreasing as we proceed from $F_2/2F^-$ (E° = + 2.85 V) to Li^+/Li (E° = – 3.04 V) through $2H^+/H_2$ (E° = ± 0.00 V). Thus E° values are decreasing from top to bottom in the series, *i.e.* positive E° values (*e.g.* $F_2/2F^-$, E° = + 2.85 V) → zero E° value (*e.g.*

$2H^+/H_2$, E° = ± 0.00 V) → negative E° values (*e.g.* Li^+/Li, E° = – 3.04 V). Thus the species lying above hydrogen have positive E° values while those lying below hydrogen have negative E° values.

4. With the decrease of E° values from + 2.85 V ($F_2/2F^-$) to – 3.04 V (Li^+/Li), the oxidising power of the oxidising agents is decreasing from top to bottom (*i.e.* from F_2 to Li^+ ion) while the reducing power of the reducing agents is increasing in the same direction (*i.e.* from F^- ion to Li metal). Thus F_2 is the strongest oxidising agent while Li^+ ion is the weakest oxidising agent. Similarly F^- ion is the weakest reducing agent while Li metal is the strongest reducing agent.

Uses of Electrochemical Series

1. To compare the oxidising and reducing power of metals or non-metals.

The magnitude of E° value of a metal or a non-metal gives a measure of its tendency to gain electrons to get reduced and hence to act as an oxidising agent or to lose electrons to get oxidised and hence to act as a reducing agent.

Gain of electrons (Reduction)

$$\underset{\text{Oxidising agent}}{M} + e^- \rightarrow \underset{\text{Reducing agent.}}{M^-}$$

Loss of electrons (Oxidation)

$$\underset{\text{Reducing agent}}{M} \rightarrow \underset{\text{Oxidising agent}}{M^+ + e^-}$$

Thus the oxidising or reducing property of a given element in solution is measured by the magnitude of its E° value.

Oxidising agents. The species having positive E° values *i.e.*, the species lying above hydrogen in the electrochemical series show a strong tendency to gain electrons to undergo reduction and hence they are strong oxidising agents. As already said, with the decrease of E° value of a given species, the tendency of that species to gain electrons to undergo reduction decreases and hence the oxidising power of that species also decreases.

Examples. (*i*) The metals like Au, Pt, Hg, Ag, Cu etc. which have positive E° values are strong oxidising agents. The oxidising power of these metals is in the order: Au > Pt > Hg > Ag > Cu, since Au has the maximum E° value while Cu has the minimum E° value as shown below :

$$\begin{aligned} Au^{3+} + 3e^- &\rightarrow Au,\ E^\circ = +1.42\ V \\ Pt^{2+} + 2e^- &\rightarrow Pt,\ E^\circ = +1.20\ V \\ Hg^{2+} + 2e^- &\rightarrow Hg,\ E^\circ = +0.85\ V \\ Ag^+ + e^- &\rightarrow Ag,\ E^\circ = +0.80\ V \\ Cu^{2+} + 2e^- &\rightarrow Cu,\ E^\circ = +0.34\ V \end{aligned}$$

E° values decreasing ↓

Oxidising power decreasing ↓

(*ii*) The non-metals like F_2, Cl_2, Br_2, I_2 and O_2 which have positive E° values are all strong oxidising agents. F_2 which has the maximum E° value is the strongest oxidising agent while O_2 which has the lowest E° value is the weakest oxidising agent. Thus the oxidising power of these non-metals is in the order :

$$F_2 > Cl_2 > Br_2 > I_2 > O_2,$$

since E° values are also decreasing in the same fashion as shown below :

$$\begin{array}{rl} F_2 + 2e^- \rightarrow 2F^-, & E^\circ = +2.85\text{ V} \\ Cl_2 + 2e^- \rightarrow 2Cl^-, & E^\circ = +1.36\text{ V} \\ Br_2 + 2e^- \rightarrow 2Br^-, & E^\circ = +1.06\text{ V} \\ I_2 + 2e^- \rightarrow 2I^-, & E^\circ = +0.53\text{ V} \\ O_2 + 2H^+ + 2e^- \rightarrow 2OH^-, & E^\circ = +0.40\text{ V} \end{array} \left| \begin{array}{c} \text{E° values} \\ \text{decreasing} \\ \downarrow \end{array} \right| \begin{array}{c} \text{Oxidising power} \\ \text{decreasing} \\ \downarrow \end{array}$$

(*iii*)Among the oxidising agents shown in Table 11.1, with the decrease of E° values from F_2 to Li^+ ion, the tendency of these species to gain electrons to undergo reduction decreases and hence their oxidising power decreases from F_2 to Li^+ ion. Thus among the oxidising agents shown in Table 11.1 F_2 is the strongest oxidising agent while Li^+ ion is the weakest oxidising agent.

Reducing agents. The species having negative values of standard reduction potentials (E° values), *i.e.* the species lying below hydrogen in the electrochemical series show a strong tendency to lose electrons to undergo oxidation and hence they are strong reducing agents. As already said, with the decreases of E° value of a given species (*i.e.*, as E° value becomes more negative), the tendency of that species to lose electrons to undergo oxidation increases and hence the reducing power of that species also increases.

Examples. (*i*) To illustrate the above rule we can consider the reducing property of alkali metals (group I A) and alkaline earth metals (group II A). E° values of these metals are given below :

Alkali metals (Group I A)	**Alkaline earth metals (Group II A)**
$Li^+ + e^- \rightarrow Li$, $E^\circ = -3.04$ V	$Be^{2+} + 2e^- \rightarrow Be$, $E^\circ = -1.70$ V
$Na^+ + e^- \rightarrow Na$, $E^\circ = -2.71$ V	$Mg^{2+} + 2e^- \rightarrow Mg$, $E^\circ = -2.38$ V
$K^+ + e^- \rightarrow K$, $E^\circ = -2.92$ V	$Ca^{2+} + 2e^- \rightarrow Ca$, $E^\circ = -2.76$ V
$Rb^+ + e^- \rightarrow Rb$, $E^\circ = -2.92$ V	$Sr^{2+} + 2e^- \rightarrow Sr$, $E^\circ = -2.89$ V
$Cs^+ + e^- \rightarrow Cs$, $E^\circ = -2.92$ V	$Ba^{2+} + 2e^- \rightarrow Ba$, $E^\circ = -2.90$ V

E° values of alkali metals show that these metals have high negative values and hence are strong reducing agents. Since Li has the minimum E° value (*i.e.* Li has maximum negative E° value), it is the strongest reducing agent of all the alkali metals. Similarly all the alkaline earth metals have high negative E° values and hence, like alkali metals, behave as strong reducing agents. Since E° values are decreasing (*i.e.* E° values are becoming more and more negative) from Be to Ba, the reducing power of these metals is also increasing in the same direction, *i.e.* Be with maximum E° value (*i.e.* with minimum negative E° value) is the weakest reducing agent while Ba which has minimum E° value (*i.e.* maximum negative E° value) is the strongest reducing agent.

When we compare the E° values of alkali metals with those of alkaline earth metals, we find that E° values increase on moving from group I A to group II A (*i.e.* E° values become less negative). Due to this increase in E° values, alkaline earth metals are weaker reducing agents than alkali metals.

(*ii*) Among the reducing agents shown in Table 11.1, with the decrease of E° values from F^- ion to Li metal, the tendency of these species to lose the electrons to undergo oxidation increases and hence their reducing power increases from F^- ion to Li metal. Thus among the reducing agents shown in Table 11.1 F^- ion is the weakest reducing agent while Li metal is the strongest reducing agent.

2. Electropositive Character of Metals.

Metals like K, Ca, Na etc. which lie at the bottom of the series readily lose their outer-most shell electrons to form metal cations and hence are *strongly electropositive* (*i.e. weakly electronegative*) while those lying at the top are not able to lose the outer-most shell electrons to form the cations and hence are *weakly electropositive* (*strongly electronegative*).

3. To Predict the Relative Chemical Reactivity of Metals.

Generally speaking the reactivity of a metal depends on its tendency to lose electrons to change into metal cation (M^+) which in turn, as we have already said, depends on the magnitude of its standard reduction potential. *Greater the value of standard reduction potential of a given metal (M), smaller its tendency to loss electrons to change into metal cation (M^+) and hence smaller its chemical reactivity. Thus with the decrease of standard reduction potential values on descending the electro-chemical series, the chemical reactivity of the metals increases in the same direction.* For example :

(*a*) Although alkali metals (Li, Na, K, Rb) and coinage metals (Cu, Ag and Au) both have one electron in their respective valence-shell, yet alkali metals are *highly reactive* while coinage metals are *least reactive*. For example alkali metals react with cold H_2O to give metallic hydroxides and H_2 gas. Coinage metals, on the other hand, do not react at all with water and steam and hence are called noble metals. These metals are attacked by strong oxidising agents like HNO_3, H_2SO_4 etc. The difference in reactivity is because of the fact that alkali metals have the lowest values (*i.e.* high negative values) of standard reduction potentials while the coinage metals have high positive values of standard reduction potentials.

(*b*) Metals like Pb, Sn, Ni, Co and Cd which lie a little down the series *react very slowly with very hot steam* to liberate H_2 gas.

(c) Metals like, Fe, Cr, Zn, Mn, Al and Mg which lie still down the series *react* with steam to produce the metallic oxides and H_2 gas. For example :

$$3Fe + 4H_2O\ (steam) \rightarrow Fe_3O_4 + 4H_2 \uparrow$$

Example. *Four metals A, B, C and D have their standard reduction potential values (in volt) equal to + 0.40, – 0.54, + 0.14 and – 1.36 respectively. Arrange these metals in the decreasing order of their reactivity.*

Solution : Since the standard reduction potential values of these metals are in the order : A(= + 0.40 V) > C(= + 0.14 V) > B(= – 0.54 V) > D(= – 1.36 V), the reactivity of these metals will be in the reverse order as shown below :

$$A < C < B < D$$

or

$$D > B > C > A$$

4. To predict whether a given metal will displace another metal from aqueous solution of its salt.

A metal with lower standard reduction potential will displace another metal with higher standard reduction potential from the aqueous solution of its salt and the metal with higher standard reduction potential gets precipitated. This means that a *metal will displace another metal from the aqueous solution of its salt that lies above it in the electrochemical series.*

Examples. (*i*) If a piece of Fe is placed in a solution of $CuSO_4$ some of Fe goes into solution as Fe^{2+} (*aq*) ions and Cu metal gets precipitated, *i.e.* Fe displaces Cu from $CuSO_4$ solution as shown below :

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu$$

or $$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + \underset{\text{ppt.}}{Cu(s)}$$

The displacement of Cu from $CuSO_4$ solution by Fe is because of the fact that $E^\circ_{Fe^{2+}/Fe}$ (= – 0.44 V) is less than $E^\circ_{Cu^{2+}/Cu}$ (= + 0.34 V).

Why the displacement of Cu from $CuSO_4$ solution by Fe is possible or why the reaction :

$$\underset{\substack{\text{Reducing}\\\text{agent}}}{Fe(s)} + \underset{\substack{\text{Oxidising}\\\text{agent}}}{Cu^{2+}(aq)} \rightarrow \underset{\substack{\text{Oxidising}\\\text{agent}}}{Fe^{2+}(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Cu(s)}$$

occurs spontaneously can also be explained by saying that since the reducing agent *viz.* Fe lies below the oxidising agent namely Cu^{2+} ions in the electrochemical series, the reaction shown above is possible to occur.

(*ii*) Zn does not displace Mg from a solution of $MgSO_4$, *i.e.* the reaction shown below is not possible to occur.

$$Zn + MgSO_4 \rightarrow ZnSO_4 + Mg$$

or $$Zn(s) + Mg^{2+}(aq) \rightarrow Zn^{2+}(aq) + \underset{\text{ppt}}{Mg(s)}$$

For this reaction to occur it is essential that $E^\circ_{Zn^{2+}/Zn}$ should be less than $E^\circ_{Mg^{2+}/Mg}$, but actually the former is greater than the latter ($E^\circ_{Zn^{2+}/Zn}$ = – 0.76 V, $E^\circ_{Mg^{2+}/Mg}$ = –2.34 V). This means that the reverse of the above reaction will proceed spontaneously, *i.e.* Mg will displace Zn from $ZnSO_4$ solution as shown below :

$$Mg + ZnSO_4 \rightarrow MgSO_4 + Zn$$

or $$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + \underset{\text{ppt}}{Zn(s)}$$

In the reaction :

$$\underset{\substack{\text{Reducing}\\\text{agent}}}{Zn(s)} + \underset{\substack{\text{Oxidising}\\\text{agent}}}{Mg^{2+}(aq)} \rightarrow \underset{\substack{\text{Oxidising}\\\text{agent}}}{Zn^{2+}(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Mg(s)}$$

since the reducing agent *viz.* Zn lies above the oxidising agent namely Mg^{2+} in the electrochemical series, the reaction is not possible to occur in the direction shown. However, the reverse reaction :

$$\underset{\substack{\text{Oxidising}\\\text{agent}}}{Zn^{2+}(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Mg(s)} \rightarrow \underset{\substack{\text{Reducing}\\\text{agent}}}{Zn(s)} + \underset{\substack{\text{Oxidising}\\\text{agent}}}{Mg^{2+}(aq)}$$

takes place spontaneously because the reducing agent *viz.* Mg lies below the oxidising agent namely Zn^{2+} ions in the electrochemical series.

(*iii*) The reaction :

$$\mathrm{Zn}(s) + \mathrm{Fe}^{2+}(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Fe}(s)$$

is predictable, since $E^\circ_{Zn^{2+}/Zn}$ (= – 0.76 V) is less than $E^\circ_{Fe^{2+}/Fe}$ (= – 0.44 V).

This reaction is used for galvanising Fe with Zn to prevent rusting of Fe. Zn coating on Fe prevents the oxidation of Fe to Fe^{2+} by air. If the galvanised Fe is scratched and some iron is oxidised to Fe^{2+} by air, Fe^{2+} thus produced is immediately reduced by Zn to Fe and thus the rusting of Fe is prevented.

(*iv*) Since $E^\circ_{Cu^{2+}/Cu}$ (= + 0.34 V) > $E^\circ_{Sn^{2+}/Sn}$ (= – 0.14 V) > $E^\circ_{Zn^{2+}/Zn}$ (= – 0.76 V), Zn can displace both Sn and Cu from aqueous solutions of their respective salts; Sn, on the other hand, can displace Cu from aqueous solution of its salt, but it cannot displace Zn from an aqueous solution containing Zn^{2+} ions, *i.e.*, the reactions (*a*), (*b*) and (*c*) are possible but reaction (*d*) is not feasible.

Reducing agent **Oxidising agent** **Oxidising agent** **Reducing agent**

(*a*) $$\mathrm{Zn}\ (s) + \mathrm{Sn}^{2+}\ (aq) \rightarrow \mathrm{Zn}^{2+}\ (aq) + \underset{\mathrm{ppt}}{\mathrm{Sn}\ (s)}$$

(*b*) $$\mathrm{Zn}\ (s) + \mathrm{Cu}^{2+}\ (aq) \rightarrow \mathrm{Zn}^{2+}\ (aq) + \underset{\mathrm{ppt}}{\mathrm{Cu}\ (s)}$$

(*c*) $$\mathrm{Sn}\ (s) + \mathrm{Cu}^{2+}\ (aq) \rightarrow \mathrm{Sn}^{2+}\ (aq) + \underset{\mathrm{ppt}}{\mathrm{Cu}\ (s)}$$

In reactions (*a*) and (*b*) since the reducing agent *viz.* Zn lies below the oxidising agents namely Sn^{2+} and Cu^{2+} ions and in reaction (*c*) the reducing agent *viz.* Sn lies below the oxidising agent namely Cu^{2+} ion, these reactions are possible to occur. In reaction (*d*) since the reducing agent Sn lies above the oxidising agent *viz.* Zn^{2+}, this reaction is not predictable.

(*v*) Since $E^\circ_{Ag^+/Ag}$ (= + 0.80 V) > $E^\circ_{Cu^{2+}/Cu}$ (= + 0.34 V), Cu can displace Ag from an aqueous solution containing Ag^+ ions but Ag cannot displace Cu from an aqueous solution containing Cu^{2+} ions. This means that the reaction :

$$\mathrm{Cu}\ (s) + 2\mathrm{Ag}^+\ (aq) \rightarrow \mathrm{Cu}^{2+}\ (aq) + \underset{\mathrm{ppt.}}{2\mathrm{Ag}\ (s)}$$

is possible while the reaction :

$$2\mathrm{Ag}\ (s) + \mathrm{Cu}^{2+}\ (aq) \rightarrow 2\mathrm{Ag}^+\ (aq) + \underset{\mathrm{ppt}}{\mathrm{Cu}\ (s)}$$

is not possible.

5. To Predict Whether a Give Non-metal will Displace Another Non-metal from Aqueous Solution of its Salt.

A non-metal with higher standard reduction potential will displace another non-metal with lower standard reduction potential. This means that *a non-metal will displace another non-metal that lies below it in the electrochemical series.* For example Cl_2 can displace both Br_2 and I_2 from their salt solutions, since Br_2 and I_2 both lie below Cl_2 in the electrochemical series. Thus in the preparation of Br_2 gas when Cl_2 gas is passed through sea-water (containing $MgBr_2$), Br_2 of $MgBr_2$ is displaced by Cl_2 and Br_2 gas is thus obtained.

$$Cl_2 + MgBr_2 \rightarrow MgCl_2 + Br_2$$

or $$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(g)$$

Note that $E^\circ_{Cl_2/2Cl^-}$ (= + 1.36 V) is greater than $E^\circ_{Br_2/2Br^-}$ (= + 1.06V)

The reaction :

$$\underset{\text{Oxidising agent}}{Cl_2(g)} + \underset{\text{Reducing agent}}{2Br^-(aq)} \rightarrow \underset{\text{Reducing agent}}{2Cl^-(aq)} + \underset{\text{Oxidising agent}}{Br_2(g)}$$

takes place spontaneously in the direction shown, since the reducing agent *viz.* Br^- lies below the oxidising agent namely Cl_2 in the electrochemical series.

Similarly Cl_2 can displace I_2 from KI solution.

$$Cl_2 + KI \rightarrow 2KCl + I_2$$

or $$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

6. To Predict Whether a Metal will Liberate Hydrogen Gas from dil. Acids or not.

The metal (M) which has a strong tendency to lose electrons to form metal ions (M^+) will displace H^+ ions from acid solution and thus will liberate H_2 gas as shown below :

$M(s) + 2H^+ (aq)$ (*From acid*) $\rightarrow M^{2+} (aq) + H_2 (g) \uparrow$

We have already pointed out that greater the value of standard reduction potential of a metal, smaller its tendency to lose electrons to form metal ions and hence smaller its tendency to displace H^+ ions from acid solution to liberate H_2 gas. *Thus with the decrease of standard reduction potential values on descending the electrochemical series, the tendency of the metals to liberate H_2 gas from dil. acids increases in the same direction.*

In general it has been observed that the metals like Au, Pt, Ag, Cu etc. which are lying *above* hydrogen in the electrochemical series are not able to liberate H_2 gas from dil. HCl at all while the metals like Zn, Mg, Ca etc. which are lying *below* hydrogen in the electrochemical series can liberate H_2 gas from dil. HCl.

7. To Predict Whether a Given Metal can Liberate H_2 Gas from Water.

Fe and all other metals which lie below it in the electrochemical series can displace H_2 gas from H_2O. Alkali metals and alkaline earth metals liberate H_2 from H_2O at ordinary temperature while the metals from Fe to Mg in the electrochemical series can do so with boiling water or steam.

$$2Na + H_2O \rightarrow NaOH + H_2$$
$$3Fe \text{ (red hot)} + 4H_2O \text{ (steam)} \rightarrow Fe_3O_4 + 4H_2O$$
$$Mg + H_2 \text{ (boiling)} \rightarrow MgO + H_2$$

8. Decomposition of Oxides of Metals.

The oxides of Hg and of the metals lying *above* Hg in the electrochemical series get decomposed on heating to give the free metal and O_2 while the oxides of the metals lying *below* Hg in the electrochemical series do not undergo decomposition. For example HgO gets decomposed on heating to give Hg and O_2

while the oxides of the metals Ag, Mg, Ca, Ba, etc. which are lying below Hg in the electrochemical series do not undergo the decomposition. Thus :

$$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

$$Ag_2O,\ MgO,\ CaO \text{ or } BaO \xrightarrow{\Delta} \text{Do not decompose.}$$

9. To Calculate the e.m.f. of a Given Galvanic Cell.

The values of standard reduction potentials given in electrochemical series can also be used to calculate the *e.m.f.* of a given galvanic cell. *The standard e.m.f. of a cell (E°_{cell}) is equal to the difference of the standard reduction potential of the cathode (i.e. right hand electrode), $E^\circ_{cathode}$ and the standard reduction potential of the anode (i.e. left hand electrode), E°_{anode}.* Thus :

$$\boxed{\begin{aligned} \mathbf{E^\circ_{cell}} &= \mathbf{E^\circ_{cathode} - E^\circ_{anode}} \\ &= \mathbf{E^\circ_{right} - E^\circ_{left}} \end{aligned}}$$

This application can be illustrated by the following solved examples.

Example 1. *Write the half-cell reactions for the following cell and calculate its standard e.m.f.*

$$\underset{Anode}{Mg \mid Mg^{2+}} \mid\mid \underset{Cathode}{Cu^{2+} \mid Cu}$$

Solution. Obviously the two half-cell reactions occuring in the cell are :

Oxidation half-reaction (Anode reaction) :

$Mg \rightarrow Mg^{2+} + 2e^-$; $E^\circ_{Mg/Mg^{2+}} = +\ 2.38$ V (From Table 11.1)

or $E^\circ_{Mg^{2+}/Mg} = -2.38$ V

Reduction half-reaction (Cathode reaction) :

$Cu^{2+} + 2e^- \rightarrow Cu$; $E^\circ_{Cu^{2+}/Cu} = +\ 0.34$ V (From Table 11.1)

$$\begin{aligned} \therefore \quad E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Mg^{2+}/Mg} = [0.34 - (-\ 2.38)] \text{ volt} \\ &= +\ 2.72 \text{ volt.} \end{aligned}$$

Example 2. *Two half-cell reactions and their standard electrode potentials are given below :*

$$Zn \rightarrow Zn^{2+} + 2e^- \ ;\ E^\circ = +\ 0.76 \text{ volt}$$

$$Cu \rightarrow Cu^{2+} + 2e^- \ ;\ E^\circ = -\ 0.34 \text{ volt.}$$

What overall chemical reaction will take place in the electrochemical cell formed by the combination of these two half-cells? Calculate the e.m.f. of this cell under standard conditions. *(Punjab B.Sc. 1975; Punjabi 1975)*

Solution. It is obvious from the half-cell reactions given in the question that the E° values are oxidation potential values. Reduction potential values, therefore, are as :

$E^\circ_{Zn^{2+}/Zn} = -\ 0.76$ volt and $E^\circ_{Cu^{2+}/Cu} = +\ 0.34$ volt

Again we know that the electrode having negative value of reduction potential acts as an anode while that having positive value acts as a cathode. Thus Zn/Zn^{2+}

electrode which has negative reduction potential value acts as anode while Cu^{2+}/Cu electrode with positive value acts as a cathode and consequently :

Oxidation or anode reaction :

$Zn \rightarrow Zn^{2+} + 2e^-$; $E^\circ_{Zn/Zn^{2+}} = +\ 0.76$ volt (given)

or $E^\circ_{Zn^{2+}/Zn} = -\ 0.76$ volts.

Reduction or cathode reaction :

$Cu^{2+} + 2e^- \rightarrow Cu$; $E^\circ_{Cu^{2+}/Cu} = +\ 0.34$ volt

∴ Overall cell reaction is represented as :

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

and its e.m.f., E°_{cell} is given by :

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} = [0.34 - (-\ 0.76)] \text{ volt} \\ &= 1.10 \text{ volt} \end{aligned}$$

Example 3. *Calculate the e.m.f. of Cu–Ag cell.*

Solution. First of all we have to decide which of the electrodes namely $Cu(s)/Cu^{2+}$ (*aq*) and Ag (*s*)/Ag^+(*aq*) will act as an anode and which will act as a cathode.

The electrode having lower value of reduction potential acts as an anode while that having higher value of reduction potential acts as a cathode. Thus, since $E^\circ_{Cu^{2+}/Cu}$ (= + 0.34 V) is lower than $E^\circ_{Ag^+/Ag}$ (= + 0.80 V), $Cu(s)/Cu^{2+}$ (*aq*) electrode acts as anode and Ag^+ (*aq*)/Ag (*s*) acts as cathode. Thus the cell can be represented as :

⟶ Flow of electrons ⟶

$$Cu(s) | Cu^{2+}(aq) \quad || \quad Ag^+(aq) | Ag(s)$$

Anode (–) Cathode (–)

(Oxidation half-cell) (Reduction half-cell)

Obviously two half-cell reactions taking place in the above cell are :

(*i*) Oxidation or anode reaction :

$Cu(s) \rightarrow Cu^{2+}$ (*aq*) + $2e^-$; $E^\circ_{Cu/Cu^{2+}} = -\ 0.34$ volt (From Table 11.1)

or $E^\circ_{cu^{2+}/cu} = +\ 0.34$ volt

(*ii*) Reduction or cathode reaction :

$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$; $E^\circ_{2Ag^+/2Ag} = +\ 0.80$ volt (From Table 11.1)

∴ Cell reaction can be represented as :

$$Cu\ (s) + 2Ag^+\ (aq) \rightarrow Cu^{2+}(aq) + 2Ag(s),$$

and

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{2Ag^+/2Ag} - E^\circ_{cu^{2+}/cu} = 0.80 - 0.34 \\ &= 0.46 \text{ volt} \end{aligned}$$

Example 4. *Write the cell reaction and calculate the cell e.m.f. from the following half-reactions :*

$$Ag^+ + e^- \rightarrow Ag;\ E^\circ = +\ 0.799\ V$$

$$Ni^{2+} + 2e^- \rightarrow Ni;\ E^\circ = -\ 0.250\ V$$

Solution. We know that the electrode having negative value of reduction potential acts as anode while that having positive value acts as cathode. Thus the cell can be represented as :

$$\longrightarrow \text{Flow of electrons} \longrightarrow$$

$$\underset{\text{Anode}}{\mathrm{Ni}\,|\,\mathrm{Ni}^{2+}}\;\Big|\quad\Big|\;\underset{\text{Cathode}}{\mathrm{Ag}^{+}\,|\,\mathrm{Ag}}$$

and hence the two half-reactions are :

Oxidation half-reaction (Anode reaction) :

$$\mathrm{Ni} \rightarrow \mathrm{Ni}^{2+} + 2e^- \;;\; E^\circ_{\mathrm{Ni/Ni}^{2+}} = +\,0.250 \text{ V}$$

or $$E^\circ_{\mathrm{Ni}^{2+}/\mathrm{Ni}} = -\,0.250 \text{ V}$$

Reduction half-reaction (Cathode reaction) :

$$2 \times [\mathrm{Ag}^+ + e^- \rightarrow \mathrm{Ag}] \;;\; E^\circ_{2\mathrm{Ag}^+/2\mathrm{Ag}} = +\,0.799 \text{ V}$$

The complete cell reaction is obtained by adding the above two reactions :

$$\mathrm{Ni} + 2\mathrm{Ag}^+ \rightarrow \mathrm{Ni}^{2+} + 2\mathrm{Ag}$$

and its e.m.f. is given by :

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{2\mathrm{Ag}^+/2\mathrm{Ag}} - E^\circ_{\mathrm{Ni}^{2+}/\mathrm{Ni}} = 0.799 - (-\,0.250) \\ &= 1.049 \text{ volt.} \end{aligned}$$

Example 5. *Represent the cell with the reaction :*

$$Cd + 2Ag^+ \rightarrow Cd^{2+} + 2Ag$$

and calculate the standard e.m.f. of the cell.

Solution. The above reaction is composed of the following two half-reactions;

(*i*) Oxidation or anode reaction :

$$\mathrm{Cd} \rightarrow \mathrm{Cd}^{2+} + 2e^- \;;\; E^\circ_{\mathrm{Cd/Cd}^{2+}} = +\,0.40 \text{ V} \qquad \text{(From Table 11.1)}$$

or $$E^\circ_{\mathrm{Cd}^{2+}/\mathrm{Cd}} = -\,0.40 \text{ V}$$

(*ii*) Reduction or cathode reaction :

$$2\mathrm{Ag}^+ + 2e^- \rightarrow 2\mathrm{Ag};\; E^\circ_{2\mathrm{Ag}^+/2\mathrm{Ag}} = +\,0.80 \text{ V} \qquad \text{(From Table 11.1)}$$

By convention Cd/Cd^{2+} electrode will act as anode and $2Ag^+/2Ag$ electrode will act as cathode, since oxidation occurs at anode and reduction takes place at cathode. Thus the cell can be represented as :

$$\longrightarrow \text{Flow of electrons} \longrightarrow$$

$$\underset{\substack{\text{Anode }(-)\\ \text{(Oxidation}\\ \text{half-cell)}}}{\mathrm{Cd}\,|\,\mathrm{Cd}^{2+}}\;\Big|\quad\Big|\;\underset{\substack{\text{Cathode }(-)\\ \text{(Reduction}\\ \text{half-cell)}}}{\mathrm{Ag}^{+}\,|\,\mathrm{Ag}}$$

Obviously,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{2\mathrm{Ag}^+/\mathrm{Ag}} - E^\circ_{\mathrm{Cd}^{2+}/\mathrm{Cd}} \\ &= +\,0.80 - (-\,0.40) \\ &= 1.20 \text{ volt.} \end{aligned}$$

10. To Predict Whether a Given Galvanic Cell will Work or Not.

The cell will work only when its standard electrode potential, E°_{cell} *is a positive quantity.* For example we can show whether the cell represented as :

$$\underset{Anode\ (-)}{Pb \mid Pb^{2+}} \;\|\; \underset{Cathode\ (+)}{Mg^{2+} \mid Mg}$$

will work or not, *i.e.* whether the cell representation is correct or not.

Now

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{Mg^{2+}/Mg} - E^\circ_{Pb^{2+}/Pb} \\ &= +2.38 - (-0.13) \qquad \text{(From Table 11.1)} \\ &= -2.25 \text{ volt.} \end{aligned}$$

Since E°_{cell} *is negative, the representation is not correct. The correct cell representation can be obtained by interchanging the position of cathode and anode. Thus the correct representation will be :*

$$\underset{Anode}{Mg \mid Mg^{2+}} \;\|\; \underset{Cathode}{Pb^{2+} \mid Pb}$$

The correctness of this representation is evident from the fact that the value of E°_{cell} *of this cell comes out to be a positive quantity as shown below :*

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= E^\circ_{Pb^{2+}/Pb} - E^\circ_{Mg^{2+}/Mg} \\ &= -0.13 - (-2.38) \qquad \text{(From Table 11.1)} \\ &= +2.25 \text{ volt.} \end{aligned}$$

Example. *Referring* E° *values for the electrodes* Sn^{2+}/Sn *and* Pb^{2+}/Pb *in Table 11.1, calculate the e.m.f. of the cell :*

$$Sn \mid Sn^{2+}\,(1.0M) \;\|\; Pb^{2+}(0.001M) \mid Pb$$

Predict whether the cell will function or not.

Solution. E° values for the electrodes are as : $E^\circ_{Sn/Sn^{2+}} = +0.14$ V and $E^\circ_{Pb^{2+}/Pb} = -0.13$ V and E°_{cell} is given by :

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{right} - E^\circ_{left} \\ &= E^\circ_{Pb^{2+}/Pb} - E^\circ_{Sn^{2+}/Sn} \\ &= -0.13 - (-0.14) = +0.01 \text{ volt} \end{aligned}$$

Since E°_{cell} is a positive quantity, the cell will function in the manner shown here.

11. To Predict Whether a Given Redox Reaction is Likely to Occur or Not.

A given redox reaction will take place spontaneously in the direction as represented by a given net cell equation, if E°_{cell} *is positive,* because in that case the standard free energy change of the reaction (ΔG°) would be negative ($\Delta G^\circ = nFE^\circ_{cell}$). *If* E_{cell} *is a negative quantity, the given redox reaction will not take place in the direction from left to right but it will take place in the direction from right to left (i.e. in the reverse direction).* In order to illustrate this application let us see whether the reaction :

$$Cu(s) + Zn^{2+}\,(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$$

will take place spontaneously or not. In order to answer this problem we proceed as follows :

The half-cell reactions of which the above reaction is composed are :

Oxidation half-reaction (Anode reaction) :

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$; $E^\circ_{Cu/Cu^{2+}} = -0.34$ volt (From Table 11.1)

Reduction half-reaction (Cathode reaction) :

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$; $E^\circ_{Zn^{2+}/Zn} = -0.76$ V (From Table 11.1)

Thus the cell can be represented as :

$$\underset{\text{Anode}}{Cu(s) \mid Cu^{2+}(aq)} \;\Big|\Big|\; \underset{\text{Cathode}}{Zn^{2+}(aq) \mid Zn(s)}$$

and

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= -0.76 - (+0.34) \\ &= -1.10 \text{ volt.} \end{aligned}$$

Since E°_{cell} is a negative quantity, the cell reaction shown above does not take place spontaneously in the direction as written. However the reaction takes place spontaneously in the reverse direction as shown below :

$$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s).$$

An Important Rule.

We know that each reaction consists of one oxidising agent and one reducing agent on the left hand and similarly one oxidising agent and one reducing agent on the right hand side as shown below for the reaction between Cu(s) and $Zn^{2+}(aq)$ discussed above.

$$\underset{\substack{\text{Oxidising}\\\text{agent}}}{Cu^{2+}(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Zn(s)} \rightarrow \underset{\substack{\text{Oxidising}\\\text{agent}}}{Zn^{2+}(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Cu(s)} \quad ...(i)$$

We have already seen that the reaction (*i*) can take place spontaneously in the direction as shown. Why this reaction takes place spontaneously in the direction from left to right can also be explained with the help of a rule which says that :

A given oxidising agent (given at the left hand side of the reduction reactions shown in the electrochemical series) will react with any reducing agent (given at the right hand side of the reduction reactions shown in the electrochemical series) whose standard reduction potential is less than that of the oxidising agent. In other words *a given oxidising agent will react (i.e. will oxidise or will be reduced by) with that reducing agent which lies below the oxidising agent in the electrochemical series. Similarly a given reducing agent will react with (i.e. will reduce or will be oxidised by) that oxidising agent which lies above the reducing agent in the electrochemical series.*

Thus, according to the above rule, the reaction (*i*) in which Cu^{2+} ions act as oxidising agent and Zn metal acts as reducing agent, takes place spontaneously in a direction from left to right, since $E^\circ_{Zn^{2+}/Zn}$ (= − 0.76 volt) < $E^\circ_{Cu^{2+}/Cu}$ (= + 0.34 volt)

Now let us use the above rule to explain why the reaction :

$$\underset{\substack{\text{Reducing}\\\text{agent}}}{Cu(s)} + \underset{\substack{\text{Oxidising}\\\text{agent}}}{Zn^{2+}(aq)} \rightarrow \underset{\substack{\text{Oxidising}\\\text{agent}}}{Cu^{2+}(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Zn(s)}$$

cannot take place spontaneously in the direction from left to right. The values of $E^\circ_{Cu^{2+}/Cu}$ (= + 0.34 volt) and $E^\circ_{Zn^{2+}/Zn}$ (= – 0.76 volt) show that $E^\circ_{Cu^{2+}/Cu}$ is not less than $E^\circ_{Zn^{2+}/Zn}$ and hence the reaction shown above does not take place in the direction from left to right

Examples to Illustrate the Rule.

The above rule can also be explained with the help of the following examples.

1. *Oxidation of Cu metal to Cu^{2+} ions by Ag^+ ions.* In the oxidation of Cu metal to Cu^{2+} ions by Ag^+ ions, Ag^+ ions are reduced to Ag metal.

$$\underset{\substack{\text{Oxidising}\\\text{agent}}}{2Ag^+(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Cu(s)} \rightarrow \underset{\substack{\text{Oxidising}\\\text{agent}}}{Cu^{2+}(aq)} + \underset{\substack{\text{Reducing}\\\text{agent}}}{2Ag(s)}$$

The oxidation of Cu metal by Ag^+ ions is feasible because

$$E^\circ_{Cu^{2+}/Cu} (= +0.34\ V) < E^\circ_{2Ag^+/2Ag} = (+0.80\ V).$$

2. *Oxidation of I^- ions to I_2 molecule by Fe^{3+} ions.* In this redox reaction Fe^{3+} ions are reduced to Fe^{2+} ions.

$$\underset{\substack{\text{Oxidising}\\\text{agent}}}{2Fe^{3+}} + \underset{\substack{\text{Reducing}\\\text{agent}}}{2I^-} \rightarrow \underset{\substack{\text{Reducing}\\\text{agent}}}{2Fe^{2+}} + \underset{\substack{\text{Oxidising}\\\text{agent}}}{I_2}$$

The above reaction takes place in the direction shown because

$$E^\circ_{I_2/2I^-} (= +0.53\ V) < E^\circ_{Fe^{3+}/Fe^{2+}} = (+0.77\ V).$$

3. *Oxidation of Cu metal to Cu^{2+} ions by I_2.* In this redox reaction I_2 molecule is itself reduced to I^- ions.

$$\underset{\substack{\text{Oxidising}\\\text{agent}}}{I_2} + \underset{\substack{\text{Reducing}\\\text{agent}}}{Cu} \rightarrow \underset{\substack{\text{Oxidising}\\\text{agent}}}{Cu^{2+}} + \underset{\substack{\text{Reducing}\\\text{agent}}}{2I^-}$$

The oxidation of Cu metal to Cu^{2+} ions is feasible because $E^\circ_{Cu^{2+}/Cu}$ (= + 0.34 V) < $E^\circ_{I_2/2I^-}$ (= + 0.53 V)

On the same lines of argument it can be explained why the oxidation of Bi metal to Bi^{3+} ions and of H_2 molecule to H^+ ions by I_2 molecule is feasible.

Oxidising agent *Reducing agent* *Oxidising agent* *Reducing agent*

$$3I_2 + 2Bi \rightarrow 2Bi^{3+} + 6I^-;\ E^\circ_{I_2/2I^-} = +0.53\ V,\ E^\circ_{Bi^{3+}/Bi} = +0.32\ V$$

$$I_2 + H_2 \rightarrow 2H^+ + 2I^-;\ E^\circ_{I_2/2I^-} = +0.53\ V,\ E^\circ_{2H^+/H_2} = +0.00\ V$$

On similar grounds with the help of E° values of $I_2/2I^-$, $2Ag^+/2Ag$, $Br_2/2Br^-$, $Cl_2/2Cl^-$ and $F_2/2F^-$ electrodes given as : $E^\circ_{I_2/2I^-} = +0.53$ V, $E^\circ_{2Ag^+/2Ag} = +0.80$ V, $E^\circ_{Br_2/2Br^-} = +1.06$ V, $E^\circ_{Cl_2/2Cl^-} = +1.36$ V, $E^\circ_{F_2/2F^-} = +2.85$ V, it can be explained why oxidation of Ag to Ag^+ ions, Br^- to Br_2, Cl^- to Cl_2 and F^- to F_2 by I_2 is not possible, *i.e.* the following redox reactions can not occur in the direction as shown below :

Oxidising agent		*Reducing agent*		*Oxidising agent*		*Reducing agent*	
I_2	+	2Ag	→	$2Ag^+$	+	$2I^-$ ...	*Not possible*
I_2	+	$2Br^-$	→	Br_2	+	$2I^-$ ...	*Not possible*
I_2	+	$2Cl^-$	→	Cl_2	+	$2I^-$ ...	*Not possible*
I_2	+	$2F^-$	→	F_2	+	$2I^-$ ...	*Not possible*

4. *Reduction of Fe^{2+} ions to Fe metal by Zn metal.* In this redox reaction Zn metal itself is oxidised to Zn^{2+} ions.

$$\underset{\text{Reducing agent}}{Zn} + \underset{\text{Oxidising agent}}{Fe^{2+}} \rightarrow \underset{\text{Oxidising agent}}{Zn^{2+}} + \underset{\text{Reducing agent}}{Fe}$$

The reduction of Fe^{2+} ions to Fe metal by Zn metal is possible because $E°_{Z^{2+}/Zn}$ (= – 0.76 V) < $E°_{Fe^{2+}/Fe}$ (= – 0.44 V).

On the same lines of argument it can be explained why the reduction of H^+ ions to H_2 and Cu^{2+} ions to metallic Cu by Zn metal is feasible.

Reducing agent		*Oxidising agent*		*Reducing agent*	*Oxidising agent*	
Zn	+	2H+	→	H_2	+ Zn^{2+} ;	$E°_{Zn^{2+}/Zn} = -0.76$ V, $E°_{2H^+/H_2} = +0.00$ V
Zn	+	Cu^{2-}	→	Cu	+ Zn^{2+} ;	$E°_{Zn^{2+}/Zn} = +0.76$ V, $E°_{Cu^{2+}/Cu} = +0.34$ V

On similar grounds with the help of E° values of Al^{3+}/Al, Mg^{2+}/Mg and K^+/K electrodes given as $E°_{Al^{3+}/Al} = 1.67$ V, $E°_{Mg^{2+}/Mg} = -2.38$ V and $E°_{K^+/K} = -2.92$ V, it can be explained why the reduction of Al^{3+} to Al, of Mg^{2+} to Mg and of K^+ to K by Zn metal is not possible, *i.e.* the redox reactions given below can not occur in the direction shown.

Oxidising agent		*Reducing agent*		*Oxidising agent*		*Reducing agent*	
Al^{3+}	+	Zn	→	Zn^{2+}	+	Al ...	*Not possible*
Mg^{2+}	+	Zn	→	Zn^{2+}	+	Mg ...	*Not possible*
K^+	+	Zn	→	Zn^{2+}	+	K ...	*Not possible*

Effect of Metal Ion Concentration on the Magnitude of Electrode Potential—Nerst Equation

We know that the standard oxidation potential of Zn/Zn^{2+} electrode in which the Zn rod is dipped in IM solution of $ZnSO_4$ is + 0.76 volt. If the concentration of the solution is not 1M, then the oxidation potential corresponding to the reaction :

$$Zn \rightarrow Zn^{2+} + 2e^-$$

is not equal to + 0.76 volt but is given by :

$$E = E°_{Zn/Zn^{2+}} - \frac{0.0592}{n} \log \frac{[Zn^{2+}]}{[Zn]}$$

where n = No. of electrons in the electrode reaction = 2.

Now since the concentration of the elements and solids = 1, [Zn] = 1 and hence :

$$E = E^\circ_{Zn/Zn^{2+}} - \frac{0.0591}{2} \log [Zn^{2+}]$$

In general :

$$E = E^\circ - \frac{0.0591}{n} \log [\text{Ion}]$$

This is called **Nerst equation.**

This is the equation for a half-cell oxidation reaction and hence :

$$E_{ox} = E^\circ - \frac{0.0591}{n} \log [\text{Ion}]$$

The value of E_{red} for the half-cell reduction reaction is given by reversing the sign of E_{ox}, *i.e.*

$$E_{red} = -E_{ox} = -\left[E^\circ - \frac{0.0591}{n} \log [\text{Ion}]\right]$$

or

$$E_{red} = -E^\circ + \frac{0.0591}{n} \log [\text{Ion}]$$

Effect of Metal Ion Concentration on the Magnitude of e.m.f of a Given Cell

We have seen that the standard e.m.f. of Daniell cell represented as :

$$Zn \mid Zn^{2+}(1M) \mid \quad \mid Cu^{2+}(1M) \mid Cu$$

in which the concentration of each of the metal ions is unity is given by :

$$\begin{aligned}\text{Standard e.m.f.} = E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode}\\ &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}\\ &= 0.34 - (-0.76)\\ &= +1.10 \text{ volt}\end{aligned}$$

If the concentration of each of the metal ions is different as in the cell :

$$Zn \mid Zn^{2+}(0.1M) \mid \quad \mid Cu^{2+}(0.01M) \mid Cu,$$

the e.m.f. is given by :

$$\boxed{\begin{gathered}E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]},\\ \text{where } n = \text{No. of electrons involved in the redox reaction} = 2 \text{ (see below)}\end{gathered}}$$

The value of [Products]/[Reactants] is obtained from the cell reaction, remembering that oxidation occurs at the anode and the reduction occurs at the cathode. This is illustrated for the above cell as follows :

Oxidation half-reaction (Anode reaction)

$$Zn \rightarrow Zn^{2+}(0.1M) + 2e^-$$

Reduction half-reaction (Cathode reaction)

$$Cu^{2+}(0.01M) + 2e^- \rightarrow Cu$$

∴ *Cell reaction is represented as :*

$$Zn + Cu^{2+}(0.01M) \rightarrow Zn^{2+}(0.1M) + Cu \ (n = 2)$$

$$\therefore \quad \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[Zn^{2+}]\,[Cu]}{[Zn^{2+}]\,[Cu^{2+}]}$$

Now since concentration of the elements and solids = 1, [Cu] or [Zn) = 1 and hence :

$$\frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.1}{0.01}$$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

$$= 1.10 - 0.0295 \times 1$$

$$= 1.0705 \text{ volt.}$$

This example clearly shows how the metal ion concentration changes the magnitude of the e.m.f. of the cell.

Questions with Answers

Q.1 Explain the following :

(*i*)Co^{3+} is not stable in aqueous solution. Given that $E^\circ_{Co^{3+}/Co^{2+}} = +1.82$ V and $E^\circ_{H_2O/O_2} = -1.23$ V.

Ans : In aqueous solution, Co^{3+} is reduced to Co^{2+} according to the following equation.

$$\underset{\substack{(Co\,=\,+3)\\ OA}}{4Co^{3+}} + \underset{\substack{(O\,=\,-2)\\ RA}}{2H_2O} \rightarrow \underset{(O\,=\,+2)}{4Co^{2+}} + 4H^+ + \underset{(O\,=\,0)}{O_2}$$

This reaction takes place (*i.e.*, Co^{3+} gets reduced to Co^{2+} ion and hence is unstable), since E° reaction is positive as shown below :

$$E^\circ_{reaction} = (E^\circ_{red})_{OA} - (E^\circ_{red})_{RA}$$

$$= E^\circ_{Co^{3+}/Co^{2+}} - E^\circ_{O_2/H_2O}$$

$$= +1.82 - (+1.23)$$

$$= +1.82 - 1.23 = \mathbf{+0.59\ V}$$

(*ii*) When I_2 and F_2 are added to a soultion containing 1M each of I^- and F^- ions, only I^- ions are oxidised to I_2 but F^- ions are not oxidised to F_2. (Given that : $E^o_{I_2/2I^-} = +0.54$ V and $E^\circ_{F_2/2F^-} = +2.87$ V).

Ans : The oxidation of F^- and I^- ions to F_2 and I_2 respectively can be represented as :

(*a*) $\underset{RA}{2F^-} + \underset{OA}{I_2} \rightarrow F_2 + 2I^-$

(*b*) $$\underset{\text{RA}}{2I^-} + \underset{\text{OA}}{F_2} \rightarrow I_2 + 2F^-$$

In reaction (*a*), since E°_{OA} (= $E^\circ_{I_2/2I^-}$ = 0.54 V) < E°_{RA} (= $E^\circ_{F_2/2F^-}$ = +2.87 V), this reaction is not feasible, *i.e.* F^- ions cannot be oxidised to F_2 by I_2. In reaction (*b*), since E°_{OA} (= $E^\circ_{F_2/2F^-}$ = +2.87 V) > E°_{RA} (= $E^\circ_{I_2/2I^-}$ = +0.54 V), this reaction is feasible, *i.e.* I^- ions can be oxidised to I_2 by F_2.

(*iii*) When aqueous solution of NaCl is electrolysed, only H_2 gas and not Na metal is liberated at cathode. (Given that $E^\circ_{Na^+/Na} = -2.71$ V and $E^\circ_{H_2O/H_2} = -0.83$ V).

Ans : On electrolysis aqueons solution of NaCl gives $Na^+(aq)$ and $Cl^-(aq)$ ions.

$$NaCl\,(aq) \xrightarrow{\text{Ionisation}} Na^+\,(aq) + Cl^-\,(aq)$$

On cathode $Na^+\,(aq)$ and $H_2O\,(l)$ both can undergo reduction to give Na metal and $H_2\,(g)$ respectively.

$$\underset{(Na\,=\,+1)}{Na^+\,(aq) + e^-} \xrightarrow{\text{Reduction}} \underset{(Na\,=\,0)}{Na\,(s)}, \; E^\circ_{Na^+/Na} = -2.71\text{ V}$$

$$\underset{(H\,=\,+1)}{H_2O\,(l) + 2e^-} \xrightarrow{\text{Reduction}} \underset{(H\,=\,0)}{H_2\,(g) + 2OH^-\,(aq)}, \; E^\circ_{H_2O/H_2} = -0.83\text{ V}$$

Now since $E^\circ_{H_2O/H_2}$ (= – 0.83 V) > $E^\circ_{Na^+/Na}$ (= –2.71 V), H_2O is more easily reduced to H_2 gas than Na^+ ion is reduced to Na metal.

(*iv*) The reducing power of halide ions (X^-) is in the order : $I^- > Br^- > Cl^- > F^-$.

Ans : When the halide ions (X^-) act as reducing agents, they are oxidised to their respective halogen molecules (X_2) as shown below :

$$2F^- \xrightarrow{\text{Oxidation}} F_2 + 2e^-, \; E^\circ_{2F^-/F_2} = -2.87\text{ V}$$

$$2Cl^- \xrightarrow{\text{Oxidation}} Cl_2 + 2e^-, \; E^\circ_{2Cl^-/Cl_2} = -1.36\text{ V}$$

$$2Br^- \xrightarrow{\text{Oxidation}} Br_2 + 2e^-, \; E^\circ_{2Br^-/Br_2} = -1.08\text{ V}$$

$$2I^- \xrightarrow{\text{Oxidation}} I_2 + 2e^-, \; E^\circ_{2I^-/I_2} = -0.54\text{ V}$$

E°_{ox} values given above show that these values are in the order :

$$\begin{array}{ccccccc} E^\circ_{2I^-/I_2} & > & E^\circ_{2Br^-/Br_2} & > & E^\circ_{2Cl^-/Cl_2} & > & E^\circ_{2F^-/F_2} \\ -0.54\text{ V} & & -1.08\text{ V} & & -1.36\text{ V} & & -2.87\text{ V} \end{array}$$

Since $E^\circ_{2I^-/I_2}$ is the largest value, I^- ions are most easily oxidised to I_2 molecules, *i.e.* I^- ions are the strongest reducing agents. On the other hand, since $E^\circ_{2F^-/F_2}$ is the smallest value, F^- ions are least readily oxidised to F_2, *i.e.* F^- ions are the weakest reducing agents.

(*v*) The oxidising power of halogen molecules (X_2) is the order : $F_2 > Cl_2 > Br_2 > I_2$.

Ans : When halogen molecules (X_2) act as oxidising agents, they are reduced to their respective halide ions (X^-) as shown below :

$$F_2 + 2e^- \xrightarrow{\text{Reduction}} 2F^-,\ E^\circ_{F_2/2F^-} = +2.87\text{ V}$$

$$Cl_2 + 2e^- \xrightarrow{\text{Reduction}} 2Cl^-,\ E^\circ_{Cl_2/Cl^-} = +1.36\text{ V}$$

$$Br_2 + 2e^- \xrightarrow{\text{Reduction}} 2Br^-,\ E^\circ_{Br_2/2Br^-} = +1.08\text{ V}$$

$$I_2 + 2e^- \xrightarrow{\text{Reduction}} 2I^-,\ E^\circ_{I_2/2I^-} = +0.54\text{ V}$$

E°_{red} values given above show that these values are in the order :

$$\begin{array}{ccccccc} E^\circ_{F_2/2F^-} & > & E^\circ_{Cl_2/2Cl^-} & > & E^\circ_{Br_2/2Br^-} & > & E^\circ_{I_2/2I^-} \\ +2.87\text{ V} & & +1.36\text{ V} & & +1.08 & & +0.54\text{V} \end{array}$$

Since $E^\circ_{F_2/2F^-}$ is the largest value, F_2 is most readily reduced to F^- ions, *i.e.* F_2 is the strongest OA. On the other hand, since $E^\circ_{I_2/2I^-}$ is the smallest value, I_2 is least readily reduced to I^- ions, *i.e.* I_2 is the weakest OA.

Q.2 Arrange the following metals in the order in which they can displace each other. Fe, Cu, Zn, Ag, Mg and Al. Given that $Fe^{2+}/Fe = -0.44$ V, $Cu^{2+}/Cu = +0.34$ V, $Zn^{2+}/Zn = -0.76$ V, $Ag^+/Ag = +0.80$ V, $Mg^{2+}/Mg = -2.37$ V and $Al^{3+}/Al = -1.66$ V.

Ans : The given metals displace each other in the following order :

$$\xrightarrow{\text{Mg, Al, Zn, Fe, Cu, Ag}}$$

This order shows that a given metal can displace all those metals given on its RHS.

Explanation : Arrange E° values in the decreasing order :

$E^\circ_{Ag^+/Ag}$	$E^\circ_{Cu^{2+}/Cu}$	$E^\circ_{Fe^{2+}/Fe}$	$E^\circ_{Zn^{2+}/Zn}$	$E^\circ_{Al^{3+}/AL}$	$E^\circ_{Mg^{2+}/Mg}$
+0.80 V	+0.34 V	–0.44 V	–0.76 V	–1.66 V	–2.37 V

$$\xrightarrow{\qquad\qquad E^\circ \text{ values decreasing} \qquad\qquad}$$

We know that a metal having lower value of E° can displace the metal/metals from its/their salt solution with higher E° value. Now :

(*a*) Since $E^\circ_{Mg^{2+}/Mg}$ (= –2.37 V) value is the lowest (most negative), Mg can displace all other metals from their salt solutions.

(*b*) Since $E^\circ_{Al^{3+}/Al}$ (= –1.66 V) value is lower than E° values for all other metals lying to its left, Al can displace Zn, Fe, Cu and Ag from their salt solutions. Note that Al can not displace Mg from Mg salt solution.

(*c*) Since $E^\circ_{Zn^{2+}/Zn}$ (= –0.76 V) value is lower than E° values for all other metlas lying to its left, Zn can displace Fe, Cu and Ag from their salt solutions. Note that Zn cannot displace Al and Mg from their salt solutions.

(*d*) Since $E^\circ_{Fe^{2+}/Fe}$ (= –0.44 V) is lower than E° values for both the metals lying to its left, Fe can displace Cu and Ag from their salt solutions. Note that Fe cannot displace Zn, Al and Mg from their salt solutions.

(*e*) Since $E^\circ_{Cu^{2+}/Cu}$ (= +0.34 V) is lower than $E^\circ_{Ag^+/Ag}$ (= +0.80 V), Cu can displace Ag from its salt solution. Note that Cu cannot displace Fe, Zn, Al and Mg from the salt solutions of these metals.

(*f*) Since $E^\circ_{Ag+/Ag}$ (= +0.80 V) is the highest, Ag cannot displace any of the other metals from the solutions of their salts.

Q.3 On the basis of the following redox reactions arrange Mg, Zn, Cu and Ag in the decreasing order of their E° values.

$$\mathbf{Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag}$$
$$\mathbf{Mg + Zn^{2+} \rightarrow Mg^{2+} + Zn}$$
$$\mathbf{Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}}$$

Ans : Indicate oxidising agents (OA) and reducing agents (RO) in the given reactions.

(*i*) $\underset{RA}{Cu} + \underset{OA}{2Ag^{+}} \rightarrow Cu^{2+} + 2Ag$

(*ii*) $\underset{RA}{Mg} + \underset{OA}{Zn^{2+}} \rightarrow Mg^{2+} + Zn$

(*iii*) $\underset{RA}{Zn} + \underset{OA}{Cu^{2+}} \rightarrow Cu + Zn^{2+}$

We know that in a redox reaction $E°_{OA} > E°_{RA}$. Thus :

In reaction (*i*) $E°_{Ag^{+}/Ag} > E°_{Cu^{2+}/Cu}$,

In reaction (*ii*) $E°_{Zn^{2+}/Zn} > E°_{Mg^{2+}/Mg}$ and

In reaction (*iii*) $E°_{Cu^{2+}/Cu} > E°_{Zn^{2+}/Zn}$

On combining the above relations we get :

$$E°_{Ag^{+}/Ag} > E°_{Cu^{2+}/Cu} > E°_{Zn^{2+}/Zn} > E°_{Mg^{2+}/Mg}$$

Q. 4 For M^{2+}/M and M^{3+}/M^{2+} systems, E° values for some metals are as : $Cr^{2+}/Cr = -0.9$ V, $Cr^{3+}/Cr^{2+} = -0.4$ V, $Mn^{2+}/Mn = -1.2$ V, $Mn^{3+}/Mn^{2+} = +1.5$ V, $Fe^{2+}/Fe = -0.4$ V and $Fe^{3+}/Fe^{2+} = +0.8$ V.

(*a*) Compare the stabilty of Fe^{3+} in acid solution with that of Cr^{3+} and Mn^{3+}.

(*b*) Arrange Cr, Mn and Fe in the decreasing order of the ease with which these metals are oxidised.

Ans : (*a*) Write E° values for Fe^{3+}/Fe^{2+}, Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} systems as shown below :

$$Mn^{3+} + e^{-} \xrightarrow{\text{Reduction}} n\ Mn^{2+},\ E° = +1.5\ V$$

$$Fe^{3+} + e^{-} \xrightarrow{\text{Reduction}} Fe^{2+},\ E° = +0.80\ V$$

$$Cr^{3+} + e^{-} \xrightarrow{\text{Reduction}} Cr^{2+},\ E° = -0.40\ V$$

Since E° value for Mn^{3+}/Mn^{2+} is higher (= +1.5 V) than that for Fe^{3+}/Fe^{2+} (= +0.80 V), Mn^{3+} ion can more easily be reduced to Mn^{2+} than Fe^{3+} ion can be reduced to Fe^{2+}. Thus Mn^{3+} ion is less stable than Fe^{3+} ion ($Mn^{3+} < Fe^{3+}$). In other words Fe^{3+} ion is more stable than Mn^{3+} ion ($Fe^{3+} > Mn^{3+}$).

Since E° value for Fe^{3+}/Fe^{2+} is positive and that for Cr^{3+}/Cr^{2+} is negative, Fe^{3+} ion can easily be reduced to Fe^{2+} while Cr^{3+} ion cannot be reduced to Cr^{2+} ion. Thus Fe^{3+} ion is less stable than Cr^{3+} ion. ($Fe^{3+} < Cr^{3+}$) In short we say that Fe^{3+} is more stable then Mn^{3+} but less stable then Cr^{3+}.

(*b*) Write $E°_{ox}$ values for Cr/Cr^{2+}, Mn/Mn^{2+} and Fe/Fe^{2+} systems in the decreasing order as shown below :

$$Mn \xrightarrow{\text{Oxidation}} Mn^{2+},\ E^\circ_{ox} = +1.2\ V$$

$$Cr \xrightarrow{\text{Oxidation}} Cr^{2+},\ E^\circ_{ox} = +0.9\ V$$

$$Fe \xrightarrow{\text{Oxidation}} Fe^{2+},\ E^\circ_{ox} = +0.4\ V$$

We know that with the decrease in the values of E°_{ox}, the ease with which the metals are oxidised also decreases. Thus the ease with which the given metals get oxidised is in the order : Mn > Cr > Fe.

Q. 5 Calculate the value of standerd emf of reaction :

$$\mathbf{Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}}$$

Given : $E^\circ_{Fe^{2+}/Fe} = -0.441$ V and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ V.

Ans : The given reaction can be broken into the following half-reactions.

$$Fe \xrightarrow{\text{Oxidation}} Fe^{2+} + 2e^-,\ E^\circ_{ox} = E^\circ_{Fe/Fe^{2+}} = +0.441\ V$$

$$Fe^{3+} + e^- \xrightarrow{\text{Reduction}} Fe^{2+}\ ] \times 2,\ E^\circ_{red} = E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771\ V$$

$$Fe + 2Fe^{3+} \rightarrow Fe^{2+} + 2Fe^{2+},\ E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

$$= 0.441 + 0.771$$

$$= \mathbf{1.212\ V}$$ **Ans.**

Q. 6 Two half-reactions with their E° values are given below :

$$\mathbf{2I^- \rightarrow I_2 + 2e^-,\ E^\circ = -0.54\ V}$$

$$\mathbf{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O,\ E^\circ = +1.33\ V.}$$

(*a*) Write the cell reaction which is composed of these half-reactions.

(*b*) Calculate the value of the cell reaction.

Ans : (*a*) In order to find out the cell reaction proced as follows :

(*i*) Write both the given half-reactions as reduction half-reactions with their E_0 values. Both the reduction half-reactions should have the same number of electrons.

$$I_2 + 2e^- \xrightarrow{\text{Reduction}} 2I^-$$

or $$3I_2 + 6e^- \xrightarrow{\text{Reduction}} 6I^-,\ E^\circ = +0.54\ V$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \xrightarrow{\text{Reduction}} 2Cr^{3+} + 7H_2O,\ E^\circ = +1.33\ V.$$

(*ii*) Now subtract the reduction half-reaction with lower value of E° from that having higher value of E°

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

$$+ 3I_2 + 6e^- \rightarrow +6I^-,\ E^\circ = +0.54\ V\ (\textit{Lower value})$$

On subtracting : $Cr_2O_7^{2-} + 14H^+ - 3I_2 \rightarrow 2Cr^{3+} + 7H_2O - 6I^-$

or $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$.

This is the required cell reaction.

(*b*) $E^\circ_{\text{cell reaction}} = E^\circ_{\text{higher}} - E^\circ_{\text{lower}}$

$$= +1.33 - 0.54$$

$$= \mathbf{0.79\ V}$$ **Ans.**

Q.7 The emf (E°_{cell}) of the cell reaction

$$3Sn^{4+} + 2Cr \rightarrow 3Sn^{2+} + 2Cr^{3+}$$

is 0.89 V. Calculate ΔG° for the reaction

(F = (96, 500 C mol^{-1} and VC = J.)

Ans : The value of ΔG° for a reaction is given by :

$$\Delta G^\circ = -\, n\, F\, E^\circ_{cell}$$

Calculation of the value of *n*

$$Cr \xrightarrow{\text{Oxidation}} Cr^{3+} + 3e^-] \times 2$$

$$Sn^{4+} + 2e^- \xrightarrow{\text{Reduction}} Sn^{2+}] \times 3$$

$$2Cr + 3Sn^{4+} \rightarrow 2Cr^{3+} + 3Sn^{2+} \text{ (Cell reaction)}$$

For this reaction $n = 6$

$\therefore \Delta G^\circ = -\, nFE^\circ_{cell} = -\, 6 \times (96500 \text{ C mol}^{-1}) \times (0.89 \text{ V})$

$= -515310 \text{ CV mol}^{-1}$

= –515310J mol^{-1} Ans. (∵ CV = J)

Q.8 The half-cell reactions for rusting of iron are :

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O,\ E^\circ = +1.23 \text{ V}$$

$$Fe^{2+} + 2e^- \rightarrow Fe(s),\ E^\circ = -\ 0.44 \text{ V}$$

Calculate the value of ΔG° (in KJmol^{-1}) for the overall reaction.

Ans : We know that the value of ΔG° for a reaction is given by :

$$\Delta G^\circ = -n\ FE^\circ_{cell}$$

E°_{cell} is given by :

$E^\circ_{cell} = E^\circ_{Higher} - E^\circ_{Lower} = 1.23 - (-\ 0.44)$

$= 1.23 + 0.44 = 1.67 \text{ V}$

The given half-reactions show that n = 2. F = 96500 C mol^{-1}.

$\therefore \Delta G^\circ = -n\ FE^\circ_{cell}$

$= -2 \times (96500 \text{ Cmol}^{-1}) \times (1.67 \text{ V})$

$= -2 \times 96500 \times 1.67 \text{ CV mol}^{-1}$

$= -2 \times 96500 \times 1.67 \text{ Jmol}^{-1}$ (CV = J)

$= -322310 \text{ J mol}^{-1}$

$= \frac{-322310}{1000} \text{ KJ mol}^{-1}$

= –322.31 KJ mol^{-1} Ans.

Q.10 (*i*) Calculate the cell e.m.f. at 25°C for the following cell :

Mg (*s*) | Mg^{2+} (0.01 M) || Sn^{2+} (0.1 M) Sn (*s*)

Given E° Mg^{2+}/Mg = –2.34 V, $E^\circ_{Sn^{2+}/Sn}$ = –0.136 V, 1F = 96,500 C mol^{-1}

(*ii*) Calculate the maximum work that can be accompalished by the operation of this cell.

Ans : (*i*) Since concentrations of Mg^{2+} and Sn^{2+} ions are different from 1M,e.m.f of the cell will be calculated by Nernst equation.

Calculation of the value of $E°_{cell}$. The value of $E°_{cell}$ is given by :

$$E_{cell} = E_{cathode} - E_{anode} = E_{Sn2+/Sn} - E_{Mg2+/Mg}$$
$$= -0.136 - (-2.340) = -0.136 + 2.340$$
$$= 2.204 \text{ V}$$

Calculation of the value of *n*. Cell reaction is :

$Mg\ (s) + Sn^{2+}\ (0.1\ M) \rightarrow Mg^{2+}\ (0.01\ M) + Sn\ (s)$.

For this reaction $n = 2$

Applying Nernst equation, we get :

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log \frac{[Mg^{2+}]}{[Sn^{2+}]}$$
$$= 2.204 - \frac{0.0591}{2} \log \frac{0.01}{0.1}$$
$$= 2.204 - 0.02955 \log \frac{1\times10^{-2}}{1\times10^{-1}}$$
$$= 2.204 - 0.02955 \times \log 10^{-1}$$
$$= 2.204 - 0.02955 \times (-1)$$
$$= 2.204 + 0.02955 = \mathbf{2.23355\ V\ Ans.}$$

(*ii*)
$$W_{max} = nF\ E°_{cell}$$
$$= 2 \times (96500 \text{ C mol}^{-1}) \times (2.204 \text{ V})$$
$$= 2 \times 96500 \times 2.204 \text{ CV mol}^{-1}$$
$$= 2 \times 96500 \times 2.204 \text{ J mol}^{-1} \qquad (CV = J)$$
$$= \frac{2\times96500\times2.204}{1000} \text{ KJ mol}^{-1}$$
$$= \mathbf{425.372\ KJ\ mol^{-1}\ Ans.}$$

Q.10 The standard electrode potentials (E°) for OCl^-/Cl^- and $Cl^-/\frac{1}{2}Cl_2$ respectively are 0.94 V and –13.6 V. Calculate E° value for $OCl^-/\frac{1}{2}Cl_2$ electrode.

Ans : The reduction half-reactions for the given electrodes can be written as :

(*i*) $OCl^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O\ (n_1 = 2),\ E°_{OCl^-/Cl^-} = +0.94$ V
$(Cl = +1) \qquad (Cl = -1)$

(*ii*) $\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-\ (n_2 = 1),\ E°_{\frac{1}{2}Cl_2/Cl^-} = +\ 1.36$ V
$(Cl = 0) \qquad (Cl = -1)$

(*iii*) $OCl^- + 2H^+ + e^- \rightarrow \frac{1}{2}Cl_2 + H_2O\ (n_3 = 1),\ E°_{OCl^-/\frac{1}{2}Cl_2} = ?$
$(Cl = +1) \qquad (Cl = 0)$

EFM diagram showing the reduction process $OCl^- \rightarrow \frac{1}{2}Cl_2 \rightarrow Cl^-$ can be shown in Fig.11.5.

$$\begin{tikzcd}[column sep=huge]
\underset{(Cl\,=\,+1)}{OCl^-} \arrow[r, "E^\circ_{OCl^-/\frac{1}{2}Cl_2} = ?", "(n_3 = 1)"'] \arrow[rr, bend right=40, "E^\circ_{OCl^-/\,Cl^-} = +0.94\text{ V}", "(n_1 = 2)"'] & \frac{1}{2}\underset{(Cl\,=\,0)}{Cl_2} \arrow[r, "E^\circ_{\frac{1}{2}Cl_2/Cl^-} = +1.36\text{ V}", "(n_2 = 1)"'] & \underset{(Cl\,=\,-1)}{Cl^-}
\end{tikzcd}$$

Fig. 11.5. EMF diagram showing the reduction process $OCl^- \rightarrow \frac{1}{2}Cl_2 \rightarrow Cl^-$.

The EMF diagram shows that :

$$E^\circ_{OCl^?/\frac{1}{2}Cl_2} \times n_3 + E^\circ_{\frac{1}{2}Cl_2/Cl^-} \times n_1 = E^\circ_{OCl^-/Cl^-} \times n_2$$

or $$E^\circ_{OCl^-/\frac{1}{2}Cl_2} \times 1 + 1.36 \times 1 = 0.94 \times 2$$

or $$E^\circ_{OCl^-/\frac{1}{2}Cl_2} = 0.94 \times 2 - 1 \times 1.36$$

$$= \mathbf{0.52\ V\ (Ans.)}$$

Q.11 Calculate the electrode potential of Cu^+/Cu half cell. Given that the standard reduction protentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are o.337 V and 0.153 V respectively.

Ans : Half reduction reactions for the given electrodes can be written as :

(*i*) $Cu^+ + e^- \rightarrow Cu$ ($n_1 = 1$), $E^\circ_{Cu^+/Cu} = ?$

(*ii*) $Cu^{2+} + 2e^- \rightarrow Cu$ ($n_2 = 2$), $E^\circ_{Cu^{2+}/Cu} = +0.337$ V

(*iii*) $Cu^{2+} + e^- \rightarrow Cu^+$ ($n_3 = 1$), $E^\circ_{Cu^{2+}/Cu} = +0.153$ V

Note that the number of Cu-atoms in all three equations is the same. EMF diagram showing the reduction processes $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu$ can be shown in Fig.11.6.

$$\begin{tikzcd}[column sep=huge]
Cu^{2+} \arrow[r, "E^\circ_{Cu^{2+}/Cu^+} = +0.153\text{ V}", "(n_3 = 1)"'] \arrow[rr, bend right=40, "E^\circ_{Cu^{2+}/Cu} = +0.337\text{ V}", "(n_2 = 2)"'] & Cu^+ \arrow[r, "E^\circ_{Cu^+/Cu} = ?", "(n_1 = 1)"'] & Cu^0
\end{tikzcd}$$

Fig.11.6. EMF diagram showing the reduction process $Cu^{2+} \rightarrow Cu^+ \rightarrow Cu$.

EMF diagram shows that :

$$E^\circ_{Cu^{2+}/Cu^+} \times n_3 + E^\circ_{Cu^+/Cu} \times n_1 = E^\circ_{Cu^{2+}/Cu} \times n_2$$

or $$0.153 \times 1 + E^\circ_{Cu^+/Cu} \times 1 = +0.337 \times 2$$

$$E^\circ_{Cu^+/Cu} = 2 \times 0.337 - 1 \times 0.153$$

$$= 0.674 - 0.153$$

$$= \mathbf{0.521\ V\ Ans.}$$

Q.12 Calculate E° value for the half-cell reaction : $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$.

Given that :

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$, E° = +1.51 V

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$, E° = +1.23 V.

Ans : The given reduction half-reactions can be shown in the form of EMF diagram given in Fig.11.7.

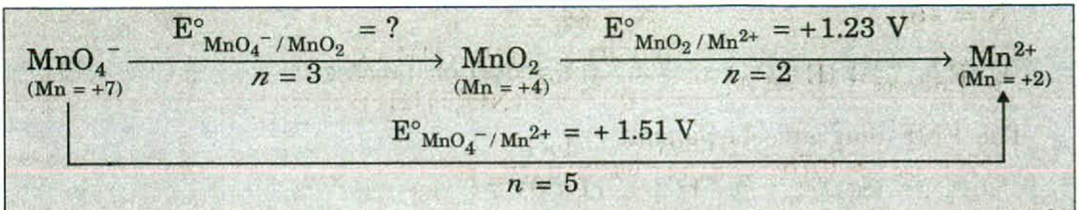


Fig.11.7. EMF diagram for reduction reactions involving MnO_4^-, MnO_2 and Mn^{2+}.

The diagram clearly shows that :

$$3 \times E^\circ_{MnO_4^-/MnO_2} + 2 \times E^\circ_{MnO_2/Mn^{2+}} = 5 \times E^\circ_{MnO_4^-/Mn^{2+}}$$

or $$3 \times E^\circ_{MnO_4^-/MnO_2} + 2 \times 1.23 = 5 \times 1.51$$

or $$E^\circ_{MnO_4^-/MnO_2} = \frac{5 \times 1.51 - 2 \times 1.23}{3}$$

$$= \frac{7.55 - 2.46}{3} = \frac{5.09}{3}$$

$$= \mathbf{1.69\ V\ Ans.}$$

Q.13 Calculate EMF of the following cell.

$Pt \mid H_2(P_1) \mid H^+\ (aq) \mid H_2\ (P_2) \mid Pt$.

Ans : Cell reaction can be obtained by adding the oxidation and reduction half-reactions taking place on anode and cathode respectively. Cell reaction also gives the value of n.

$$H_2(P_1) \xrightarrow{\text{Oxidation}} 2H^+\ (aq) + 2e^-\ (\textit{At anode})$$

$$2H^+\ (aq) + 2e^- \xrightarrow{\text{Reduction}} H_2(P_2)\ (\textit{At cathode})$$

Cell reaction : $H_2\ (P_1) + 2H^+ (aq) \rightarrow 2H^+(aq) + H_2(P_2)$ ($n = 2$)

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ_{2H^+/H_2} - E^\circ_{2H^+/H_2} = 0 - 0 = 0$$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \log \frac{[H^+]^2\,[H_2]}{[H_2]\,[H^+]^2}$$

$$= 0 - \frac{RT}{2F} \log \frac{(1)^2 \times P_2}{P_1 \times (1)^2} = -\frac{RT}{2F} \log \frac{P_2}{P_1}$$

or $$E_{cell} = \frac{RT}{2F} \log \frac{P_1}{P_2}$$

Q. 14 The standard reduction potential for the half-cell NO_3^- (*aq*) + $2H^+$ (*aq*) + $e^- \rightarrow NO_2 + H_2O$ is 0.78 V.

(*i*) Calculate the reduction potential in 8 M H^+.

(*ii*) What will be the reduction potential of the half-cell in a neutral soluiton ? Assume all the other species to be at unit concentration.

Ans : (*i*) Reduction electrode reaction can be written as :

$NO_3^- + 2H^+ (8M) + e^- \rightarrow NO_2 + H_2O$ (n = 1), $E°_{red}$ = 0.78 V

(N = +5) (N = +4)

$$\therefore (E_{red})_{elec} = (E°_{red})_{elec} - \frac{0.0591}{n} \log \frac{[NO_2][H_2O]}{[NO_3^-][H^+]^2}$$

$$= 0.78 - \frac{0.0591}{1} \log \frac{1 \times 1}{1 \times (8)^2}$$

$$= 0.78 - 0.0591 \times [\log 1 - \log 8^2]$$

$$= 0.78 - 0.0591\ [0 - 2 \log 8]$$

$$= 0.78 + 0.0591 \times 2 \times \log 8$$

$$= 0.78 + 0.0591 \times 2 \times 0.903$$

$$= 0.78 + 0.106$$

$$= \mathbf{0.886\ V\ Ans.}$$

(*ii*) Neutral solution means pH = 7

or $[H^+] = 10^{-7}$ M.

Electrode reduction reaction can be written as :

$NO_3^- + 2H^+ (10^{-7}\ M) + e^- \rightarrow NO_2 + H_2O$ (n = 1)

$$\therefore (E_{red})_{elec} = (E°_{red})_{elec} - \frac{0.0591}{1} \log \frac{[NO_2][H_2O]}{[NO_3^-][H^+]^2}$$

$$= 0.78 - 0.0591 \times \log \frac{1 \times 1}{1 \times (10^{-7})^2}$$

$$= 0.78 - 0.0591 \times [\log 1 - \log 10^{-14}]$$

$$= 0.78 - 0.0591 \times [-(-14) \log 10]$$

$$= 0.78 - 0.0591 \times 14 \times 1$$

$$= -0.78 - 0.8274 = \mathbf{-\ 0.0474\ V\ Ans.}$$

Q. 15 The standard reduction potential of Cu^{++}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 volt respectively. Construct the galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of Ag^+ will the e.m.f. of the cell at 25°C be zero if the concentration of Cu^{++} is 0.01 M ?

Ans : (*i*) $E°_{Cu^{2+}/Cu}$ = 0.337 V, $E°_{Ag^+/Ag}$ = 0.799 U and E_{cell} = 0. Now since $E°_{Ag^+Ag}$ (= 0.799 V) > $E°_{Cu^{2+}/Cu}$ (= 0.337 V), Ag/Ag^+ electrode will act as cathode and Cu/Cu^{2+} electrode will work as anode. Hence the cell can be represented as :

Cu | Cu^{2+} | | Ag^+ | Ag

Anode Cathode

(*ii*) Cell reaction is :

$Cu + 2Ag^+ (c) \rightarrow Cu^{2+}$ (0.01 M *or* 10^{-2} M) + 2Ag ($n = 2$)

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Cu^{2+}][Ag]^2}{[Cu][Ag^+]^2}$$

$$\text{or} \quad 0 = (E^\circ_{cathode} - E^\circ_{anode}) - \frac{0.0591}{n} \log \frac{[Cu^{2+}][Ag]^2}{[Cu][Ag^+]^2}$$

$$= (E^\circ_{Ag+/Ag} - E^\circ_{Cu^{2+}/Cu}) - \frac{0.0591}{n} \log \frac{[Cu^{2+}][Ag]^2}{[Cu][Ag^+]^2}$$

$$= (0.799 - 0.337) - \frac{0.0591}{2} \log \frac{10^{-2} \times (1)^2}{1 \times c^2}$$

$$= 0.462 - 0.02955\ [\log 10^{-2} - \log c^2]$$

$$= 0.462 + 0.02955 \times [-2 -2 \log c]$$

$$= 0.462 + 2 \times 00.2955 + 2 \times 0.02955 \log c$$

$$0 = 0.462 + 0.0591 + 0.0591 \log c$$

$$\therefore \quad \log c = \frac{-0.462 - 0.0591}{0.0591} = \frac{-0.5211}{0.0591} = -8.8712$$

$\therefore$ c = Antilog − 8.8172 = **1.523×10^{-9} M Ans.**

Q. 16 The EMF of the following cell is found to be 0.20 V at 298 K

$Cd \mid Cd^{2+} (?) \parallel Ni^{2+} (2.0\ M)\ Ni$

What is the molar concentraction of Cd^{2+} ions in the solution ?

($E^\circ_{Cd^{2+}/Cd} = -\ 0.40$ V, $E^\circ_{Ni^{2+}/Ni} = -\ 0.25$ V).

Ans : To calculate E°_{cell}.

$E^\circ_{cell} = E^\circ_{higher} - E^\circ_{lower} = -0.25 - (-0.40)$

$= -0.25 + 0.40 = \mathbf{+\ 0.15\ V}$

To write the cell reaction. The representation of the cell given in the question shows that the cell reaction is the sum of the oxidation and reduction half-reactions given below.

$$Cd \xrightarrow{\text{Oxidation}} Cd^{2+} + 2e^-$$

$$Ni^{2+} + 2e^- \xrightarrow{\text{Reduction}} Ni$$

Cell reaction : $Cd + Ni^{2+} \rightarrow Cd^{2+} + Ni$ ($n = 2$)

or $Cd + Ni^{2+}$ (2.0 M) $\rightarrow Cd^{2+}$ (?) + Ni

Suppose concentration of Cd^{2+} ions is c M. Then from Nernst equation, we have :

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Cd^{2+}][Ni]}{[Cd][Ni^{2+}]}$$

$$\text{or} \quad 0.20 = 0.15 - 0.02955 \log \frac{c \times 1}{1 \times 2}$$

or $$\log\frac{c}{2} = \frac{0.15-0.20}{0.02955} = -\frac{0.05}{0.02955}$$

or $$\log\frac{c}{2} = -1.69$$

or $$\log c - \log 2 = -1.69$$

or $$\log c = -1.69 + \log 2 = -1.69 + 0.3021$$

$$= -1.3879$$

$\therefore$ $$c = \text{Antilog } -1.3879$$

$$= \mathbf{0.0409\ M\ Ans.}$$

Q. 17 Calculate the potential of a hydrogen electrode in contact with a solution whose pH is 10.

Ans : $\text{pH} = 10$

or $-\log[H^+] = 10$

or $\log[H^+] = -10$

or $[H^+] = \text{Antilog}(-10) = 10^{-10}$ M

Reduction reaction taking place on hydrogen electrode can be written as :

$$2H^+ + 2e^- \rightarrow H_2\ (n = 2)$$

$$\therefore\quad E_{2H^+/H_2} = E^0_{2H^+/H_2} - \frac{0.0591}{n}\log\frac{[H_2]}{[H^+]^2}$$

$$= 0 - \frac{0.0591}{2}\log\frac{1}{(10^{-10})^2}$$

$$= \frac{0.0591}{2}[\log 1 - \log 10^{-20}]$$

$$= +\frac{0.0591}{2}\times(-20)\log 10$$

$$= -0.0591 \times 10 = \mathbf{-0.591\ V\ Ans.}$$

Q. 18 At what pH of HCl solution will hydrogen gas electrode show electrode potential of – 0.118 V ? H_2 gas is bubbled at 298 K and 1 atm pressure.

Ans : Hydrogen gas electrode is represented as :

$$H^+/\tfrac{1}{2}H_2\ (1\text{ atom}),\quad E_{H^+/\frac{1}{2}H_2} = -0.118\text{ V}$$

Reduction reaction taking place at hydrogen gas electrode is :

$$H^+ + e^- \rightarrow \frac{1}{2}H_2\ (1\text{ atm})\ (n = 1)$$

Applying Nernst equation to the above reduction half-reaction, we get :

$$E_{H^+/\frac{1}{2}H_2} = E^\circ_{H^+/\frac{1}{2}H_2} - \frac{0.0591}{n}\log\frac{[H_2]^{1/2}}{[H^+]} \quad ...(i)$$

Now since H_2 gas is at 1 atm. pressure, $[H_2] = 1$. Hence equation (*i*) becomes

$$E_{H^+/\frac{1}{2}H_2} = E^\circ_{H^+/\frac{1}{2}H_2} - \frac{0.0591}{1}\log\frac{1}{[H^+]}$$

or $$-0.118 = 0 - 0.0591\ \{-\log[H^+]\}$$

or $$\frac{-0.118}{-0.059} = -\log[H^+]$$

or $$1.99 = -\log[H^+]$$

or $$2 = pH \qquad (\because pH = -\log[H^+])$$

Thus pH of the solution = **2 Ans.**

University Questions

1. Differentiate between ionisation potential and electrode potential of a metal. *(VBS Purvanchal 2002)*

2. Give reason fro the fact that E° of Cu is + 0.34 V while that of Zn is – 0.76 V. *(Delhi 2002)*

Answer. We know that a less reactive metal has higher value of E° than a more reactive metal. Thus Cu has higher value of E° (= +0.34 V) than Zn (= – 0.76 V), since Cu is less reactive than Zn.

3. (*a*) What is electrode potential ? How does it differ from ionisation energy ?

(*b*) Predict whether the following reaction will occur spontaneously or not ?

$Ni\ (s) + Cu^{2+}\ (aq) \rightarrow Ni^{2+}\ (ag) + Cu\ (s)$

Given that : $E^\circ_{Ni/Ni^{2+}} = +0.25$ V and $E^\circ_{Cu/Cu^{2+}} = -0.337$ V.

(*c*) What is electrochemical series ? Describe its uses in explaning chemical reactions. *(VBS Purvanchal 2003)*

4. Consider the following EMF diagram for broming and answer the following :

$$\begin{tikzcd}
E^\circ_A & BrO_3^- \arrow[r, "1.49"] \arrow[rrr, bend left, "1.44"] & HOBr \arrow[r, "1.59"] \arrow[rr, bend right, "E"'] & \frac{1}{2}Br_2(l) \arrow[r, "1.07"] & Br^-
\end{tikzcd}$$

$$\begin{tikzcd}
E^\circ_A & BrO_3^- \arrow[r, "0.54"] \arrow[rrr, bend left, "0.61"] & BrO^- \arrow[r, "0.45"] & \frac{1}{2}Br_2(l) \arrow[r, "1.07"] & Br^-
\end{tikzcd}$$

(*a*) Calcualte the value of E.

(*b*) State whether the following statements are true or false. Give reasons to your answer.

(*i*) Bromine disproportionates into bromide and hypobromate ions in basic medium but not in acidic medium.

(*ii*) BrO_3^- is better oxidizing agent in acid solution than in basic solution. *(Rohilkhand 2003)*

5. (*a*) Calculate the equilibrium constant for the reaction

$Zn + Cu^{+2} \rightarrow Cu + Zn^{+2}$ at 25°C

$E^\circ_{Zn/Zn^{+2}} = 0.763$ Volts, $E^\circ_{Cu/Cu^{+2}} = -0.337$ Volts (*b*) The e.m.f. of following cell

Pt, H_2 | H^+ a_{H+} = 1 | Solution | 0.1 M KCl | Hg_2Cl_2 | Hg is 0.93 volts. [$E_{calomel}$ = 0.34 volts]. Calculate the pH of the solution. (*Gujrat 2003*)

6. Calculate e.m.f. of the concentration cell given below at 25°C

Zn | Zn^{2+} (M) || Cu^{2+}(M) | Cu

$E^\circ_{Cu^{2+}/Cu} = 0.34$ V, $E^\circ_{Zn^{2+}/Zn} = 0.76$ V (*Meerut 2004*)

7. Calculate free energy change of the following cell at 25°C.

Sn | $Sn^{2+}(a = 0.6)$ || $Pb^{2+}(a = 0.3)$ | Pb

Given that $E^\circ_{cell} = 0.014$ V (*Meerut 2004*)

8. Calculate the e.m.f. of the following cell at 25°C.

Ag | $AgNO_3$(0.01 M) || $AgNO_3$(0.1 M) | Ag (*C.S.J.M. Kanpur 2005*)

9. Write a note on "Nernst Equation." (*Meerut 2006*)

10. Define electrode potential. Derive Nernst equation for a single electrode potential. How do you decide the sign of electrodes according to IUPAC system of and galvanic cell. (*Meerut 2007*)

11. Write a note on "Glass Electrode". (*C.S.J.M. Kanpur 2008*)

12. Write a note on "Single Electrode Potential". (*Meerut 2008*)

13. Predict whether Zn and Ag react with 1N H_2SO_4 to give out H_2 gas or not. Given that $E^\circ_{Zn^{2+}/Zn} = -0.76$ V and $E^\circ_{Ag^+/Ag} = 0.80$ V.

(*C.S.J.M. Kanpur 2009*)

CHAPTER

12

Modern Concepts of Acids and Bases

Following are the important modern concepts of acids and bases :

Arrhenius Concept : Water Ion System

According to this concept, an acid is any hydrogen containing compound which gives H^+ ions in aqueous solution and a base which gives OH^- ions in aqueous solution. Thus HCl is an acid and NaOH is a base and the neutralisation process can be represented by a reaction involving the combination of H^+ and OH^- ions to form H_2O.

$$HCl \overset{H_2O}{\rightleftharpoons} H^+ + Cl^-$$

$$NaOH \overset{H_2O}{\rightleftharpoons} Na^+ + OH^-$$

$$H^+ + OH^- \longrightarrow H_2O$$

Utility. (*i*) Since the reaction representing neutralisation process involves the combination H^+ and OH^- ions, the approximately constant molar heat of neutralisation would be expected. Thus the constant heat of neutralisation of a strong acid by a strong base is readily understandable in terms of this concept.

(*ii*) This concept has offered a means of correlating catalytic behaviour with the concentration of the H^+ ion.

Limitations. (*i*) According to this concept, HCl is regarded as an acid only when dissolved in H_2O and not in some other solvent such as C_6H_6. or when it exists in the gaseous form.

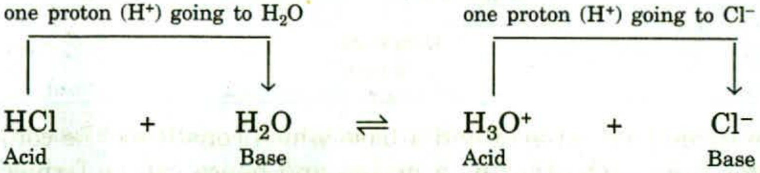
(*ii*) It cannot account for the acidic and basic character of the materials in non-aqueous solvents, *e.g.*, NH_4NO_3 in liq. NH_3 acts as an acid, though it does not give H^+ ions. Similarly many organic materials and NH_3, which do not have OH^- ions at all, are actually known to show basic character.

(*iii*) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in many other solvents and even in the absence of solvents.

(*iv*) It cannot explain the acidic character of certain salts such as $AlCl_3$ in aqueous solution.

Bronsted-Lowry Concept : Proton-Donor Acceptor System

Bronsted and Lowry in 1923 independently proposed a more general definition of acids and bases. According to them, *an acid is defined as any hydrogen* *containing material* (a molecule or a cation or an anion) *that can release a proton (H^+) to any other substance, whereas a base is any substance* (a molecule or a cation or an anion) *that can accept a proton from any other substance.* In short, *an acid is a proton-donor and a base is a proton-acceptor.* As an example consider the reaction between HCl and H_2O as given below :



$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{Cl^-}$$

In this reaction HCl donates a proton to H_2O and is, therefore, an acid. Water, on the other hand, accepts a proton from HCl, and is, therefore, a base. In the reverse reaction which at equilibrium proceeds at the same rate as the forward reaction, H_3O^+ ion donates a proton to Cl^- ion and hence H_3O^+ ion is an acid. Cl^- ion, because it accepts a proton from H_3O^+ ion, is a base.

Examples of Bronsted-Lowry Acids and Bases

As already stated, Bronsted-Lowry acids and bases may be molecular, cationic and anionic species. Examples of such species are given below :

Type of species	Acids	Bases
Molecular	HCl, HBr, $HClO_4$, HNO_3, H_2SO_4, H_3PO_4, H_2O	NH_3, N_2H_4, amines, H_2O, NH_2OH
Cationic	NH_4^+, $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)^{3+}$, H_3O^+,	$[Fe(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_5(OH)]^{2+}$
Anionic	HCO_3^-, HSO_4^-	Cl^-, Pr^-, I^-, OH^-, CO_3^{2-}, SO_4^{2-}, H^-, NH_2^- OH^-, HS^-

Conjugate Acid-Base Pairs

Let us again consider the reaction between HCl and H_2O as given below :

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{Cl^-}$$

In this reaction Cl^- ion (base) formed by the loss of one proton from HCl (acid) is called the conjugate base of the acid, HCl. Thus HCl and Cl^- is a conjugate acid-base pair. Similarly if we consider the reverse reaction, H_2O (base) formed by the loss of one proton from H_3O^+ (acid) is called the conjugate base of the acid, H_3O^+. Thus H_3O^+ and H_2O is another conjugate acid-base pair. Now if the acid HCl is labelled as $Acid_1$ and its conjugate base *viz.* Cl^- as $Base_1$ and further, if H_2O is designated as $Base_2$ and its conjugate acid *viz.* H_3O^+ as $Acid_2$, then the two conjugate acid-base pairs can be shown as :

Conjugate acid-base pair

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Cl^-}$$

Conjugate
acid-base
pair

It may be noted that an acid and a base which constitute the conjugate acid-base pair differ from each other by a proton and hence can be formed from each other by the loss or gain of a proton as shown below :

$$\text{Acid} \underset{\substack{\text{Gain of proton} \\ (+H^+)}}{\overset{\substack{\text{Loss of proton} \\ (-H^+)}}{\rightleftarrows}} \text{Base}$$

e.g. $\underset{\text{Acid}}{HCl} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} \underset{\text{Base}}{Cl^-}$ and $\underset{\text{Acid}}{H_3O^+} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} \underset{\text{Base}}{H_2O}$

Some common conjugate acid-base pairs are given below :

Conjugate acid-base pair

Conjugate
acid base pair

Acid		*Base*		*Acid*		*Base*
$HClO_4$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	ClO_4
H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
$[Al(H_2O)_6]^{3+}$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$[Al(H_2O)_5(OH)]^{2+}$
$[Fe(H_2O)_6]^{3+}$	+	H_2O	$\rightleftharpoons$	H_3O^+	+	$[Fe(H_2O)_5(OH)]^{2+}$
NH_4^+	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NH_3
H_2O	+	CN^-	$\rightleftharpoons$	HCN	+	OH^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3	+	OH^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
HCl	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
CH_3COOH	+	NH_3	$\rightleftharpoons$	NH_4^+	+	CH_3COO^-
HSO_4^-	+	NH_3	$\rightleftharpoons$	NH_4^+	+	SO_4^{2-}

An Important Rule

It has been observed that acid-base reactions proceed in a direction to form the weak acid and weak base and hence in these reactions a strong acid reacts with a strong base to form a weak acid and a weak base. Consequently in these reactions the strong acid and weak base form one conjugate acid-base pair and similarly a strong base and a weak acid form another conjugate acid-base pair. Thus in the reaction :

$$\overset{\textit{Strong acid}}{HCl} + \overset{\textit{Strong base}}{H_2O} \rightleftarrows \overset{\textit{Weak acid}}{H_3O^+} + \overset{\textit{Weak base}}{Cl^-},$$

since HCl is a strong acid, its conjugate base *viz.* Cl^- ion is a weak base, *i.e.* HCl (strong acid) Cl^- (weak base) is one conjugate acid-base pair and similarly H_3O^+ (weak acid) —H_2O (strong base) is another conjugate acid-base pair. In general :

Conjugate acid-base pair

$$\overset{\text{Strong acid}}{HA} + \overset{\text{Strong base}}{B} \rightleftarrows \overset{\text{Weak acid}}{HB^+} + \overset{\text{Weak base}}{A^-}$$

Conjugate acid-base pair

Thus conjugate base of a strong acid is always a weak base and the conjugate acid of a strong base is always a weak acid.

Dual Behaviour of Water

Water can act both as an acid (*i.e.* proton donor) and as a base (*i.e.* proton acceptor). For example H_2O acts as an acid towards NH_3 and acts as a base towards HCl as shown below :

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_3} \rightleftarrows \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{OH^-}$$

$$\underset{\text{Base}}{H_2O} + \underset{\text{Acid}}{HCl} \rightleftarrows \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{Cl^-}$$

The dual behaviour of H_2O has been used to explain the alkaline, acidic and neutral behaviour of the aqueous solution of salts. For example aqueous solution of Na_2CO_3 is alkaline, that of $FeCl_3$, $Al_2(SO_4)_3$, $NiSO_4$, $CuNO_3$ etc. is acidic while that of NaCl, K_2SO_4 etc. is neutral.

When Na_2CO_3 is dissolved in water, CO_3^{2-}ion, being a strong proton-acceptor, acts as a base and H_2O molecule which loses the proton behaves as an acid. Thus OH^- ions are produced and these ions make the solution alkaline.

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{CO_3^{2-}} \rightleftarrows \underset{\text{Acid}}{HCO_3^-} + \underset{\text{Base}}{OH^-}$$

In case of the aqueous solution of the salts of Fe^{3+}, Al^{3+} etc. cations, these strongly hydrated and highly charged small cations are strong proton-donors and hence readily give up a proton to H_2O which becomes H_3O^+. Due to the presence of H_3O^+ cations the solution is acidic.

$$\underset{\text{Acid}}{[Fe(H_2O)_6]^{3+}} + \underset{\text{Base}}{H_2O} \rightleftarrows \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{[Fe(H_2O)_5(OH)]^{2+}}$$

$$\underset{\text{Acid}}{[Al(H_2O)_6]^{3+}} + \underset{\text{Base}}{H_2O} \rightleftarrows \underset{\text{Acid}}{H_3O^+} + \underset{\text{Base}}{[Al(H_2O)_5(OH)]^{2+}}$$

In case of the aqueous solutions of NaCl, K_2SO_4 etc. the hydrated cations are poor proton donors and hence the aqueous solutions are neutral.

Basicity or Protocity of an Acid

The number of H^+ (or H_3O^+) ions liberated by one molecule of an acid in aqueous solution is known as its basicity. On the basis of the basicity of a given acid, it may be a *monobasic or monoprotic* (*e.g.* HCl, HNO_3), *dibasic or diprotic* (*e.g.* H_2SO_4, H_2CO_3), and *tribasic* or *triprotic* (*e.g.* H_3PO_4). These acids liberate one, two and three or H^+ or H_3O^+ ions in aqueous solution respectively.

Acidity or Hydroxity of a Base

The number of OH^- ions liberated by one molecule of a base in aqueous solution is known as its acidity or hydroxity. On the basis of the acidity of a given base, it may be *monoacidic* or *monohydroxic* (*e.g.* NaOH, NH_4OH), *diacidic* or *dihydroxic* [*e.g.* $Ca(OH)_2$, Mg $(OH)_2$] and *triacidic* or *trihydroxic* [*e.g.* Al $(OH)_3$, Fe $(OH)_3$]. These bases liberate one, two and three OH^- ions in aqueous solution respectively.

Relative Strength of Acids and Bases

We know that acids and bases are also electrolytes and hence ionise in water. Acids and bases dissociate to give H^+ or H_3O^+ ions and bases ionise to give OH^- ions in aqueous solutions.

The strength of an acid or a base is defined as its capacity to give H^+ and OH^- ions in equimolar solutions in water respectively. Thus relative strength of two acids or bases can be compared by comparing their H^+ ion or OH^- ion concentrations in their equimolar solutions in water respectively.

Those acids and bases which ionise almost completely in solution are called strong acids and strong bases while those which are ionised only to a limited extent in solution are termed as weak acids and weak bases. Examples of strong acids are HNO_3, H_2SO_4, $HClO_4$, HCl, HBr, HI and those of strong bases are NaOH, KOH, $(CH_3)_4NOH$.

For an aqueous solution of an acid, HA, the equilibrium is shown as :

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

For the above equilibrium the value of equilibrium constant, K is given by :

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Now since water which is used as a solvent is present in large quantity, $[H_2O]$ = constant. Thus :

$$\frac{[H_3O^+][A^-]}{[HA]} = K \times [H_2O] = K_a \qquad ...(i)$$

Here K_a is called *acid dissociation constant.*

Similarly for a weak base, B the corresponding equilibrium is :

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

and the value of *base dissociation constant*, K_b is given by :

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad ...(ii)$$

Equation (*i*) shows that *larger the value of K_a, higher the concentration of H_3O^+ ions and consequently stronger the acid. Thus higher the value of acid dissociation constant, K_a of an acid, stronger is the acid.* For example in case of CH_3COOH and HCN acids the values of acid dissociation constants are as follows.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_{CH_3COOH} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8\times10^{-5}$$

$$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$$

$$K_{HCN} = \frac{[CN^-][H_3O^+]}{[HCN]} = 7.1\times10^{-10}$$

Since K_{CH_3COOH} is higher than K_{HCN}, CH_3COOH is much stronger than HCN.

Similarly equation (*ii*) shows that *larger the value of K_b higher the concentration of OH^- ions and consequently stronger the base. Thus higher the value of base dissociation constant, K_b of a base, stronger is the base.* For example since K_b for NH_4OH (= 1.81×10^{-5}) is smaller than that for $C_2H_5NH_2 = 5.60 \times 10^{-4}$), $C_2H_5NH_2$ is a stronger base.

Values of dissociation constants (at 25°C) and relative strengths of some acids and bases are given in Table 12.1.

Table 12.1. Dissociation of some constants of some acids and bases at 25°C and their relative strength

Acid or base	Dissociation	K_a or K_b	Relative strength
Acids			
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	Very large	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	Very large	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large	Very strong
HSO_4^-	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-2}	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-4}	Weak
CH_3COOH	$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	1.8×10^{-5}	Weak
H_2CO_3 $(H_2O + CO_2)$	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.4×10^{-7}	Weak
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	Weak
NH_4^+	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	Weak
HCO_3^-	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}	Weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16}	Very weak

Bases			
NaOH	$NaOH \rightleftharpoons Na^+ + OH^-$	Very high	Very strong
KOH	$KOH \rightleftharpoons K^+ + OH^-$	Very high	Very strong
$Ca(OH)_2$	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	High	Strong
NH_4OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.81×10^{-5}	Weak
CH_3NH_2	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.38×10^{-4}	Weak
$C_6H_5NH_2$	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.7×10^{-10}	Very weak

Acidity and Basicity of Molecules

We have seen that according to Bronsted-Lowry concept, if a molecule is to act as an acid, it should contain H-atom which it should donate as a proton (H^+). The degree of acidity of a given molecule is determined by the case with which the molecule can lose (*i.e.* donate) a proton.

There are many factors which influence the acidity (*i.e.* acidic strength) and basicity of a given molecule. Here we shall consider only one factor namely *electron delocalisation*. It has been observed that with the increase of volume available to the electron, the electron delocalisation also increases. The increase in electron delocalisation decreases the electron density and hence the attraction for a proton also decreases. The decrease in the attraction for a proton means that the basicity also decreases. The effect of the increase of electron delocalisation in decreasing the basicity is evident from the following examples.

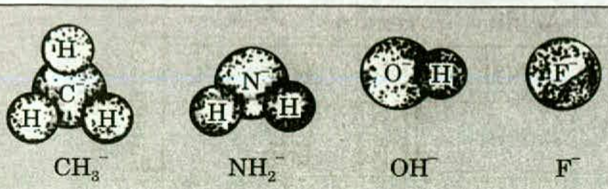
1. Relative order of the acidity of CH_4, NH_3, H_2O and HF molecules.

In order to find the order of acidity of these molecules, let us find out the relative order of the basicity of their conjugate bases *viz.* CH_3^- (methide ion), NH_2^- (amide ion), OH^- (hydroxide ion) and F^- (fluoride ion) respectively. The structures of these ions as shown in Fig. 12.1 make it clear that (*i*) in CH_4^- ion 3/4 of the volume of carbon atom carrying the negative charge is occupied by three H-atoms. Thus the negative charge on C-atom exists only on 1/4 volume of the carbon atom (*ii*) in NH_4^+ ion 2/3 of the volume of N-atom carrying negative charge is occupied by two H-atoms. Thus the negative charge on N-atom exists only on 1/3 volume of N-atom (*iii*) in OH^- ion the negative charge on O-atom exists on more volume of O-atom, and (*iv*) in F^- ion the negative charge on F-atom exists on the whole volume of F-atom. Thus the volume available to electron increases as we pass from CH_3^- to F ion. The increase in this volume increases the electron delocalisation from CH_3^- to F^- ion. As the electron delocalisation increases, the electron density and hence the attraction for a proton decreases. The decrease in the attraction for a proton means that the basicity of these conjugate bases decreases from CH_3^- to F^- as shown below :

$$CH_3^- \text{ (Strongest base)} > NH_2^- > OH^- > F^- \text{ (Weakest base)}$$

We have already learnt that a stronger base has a weaker acid as its conjugate acid. Thus the conjugate acid of CH_3^- base (namely CH_4) should be the weakest acid and the conjugate acid of F^- base (namely HF) should be the strongest acid, *i.e.* the acidity of CH_4, NH_3, H_2O and HF molecules should be in the order :

$$CH_4 \text{ (Weakest acid)} < NH_3 < H_2O < HF \text{ (Strongest acid)}$$



—Volume available to electron increasing→
—Electron delocalisation increasing→
—Electron density decreasing→
—Attraction for proton decreasing→
—Basicity decreasing→

Fig. 12.1. The basicity of CH_3^-, NH_2^-, OH^- and F^- ions decreases as we pass from CH_3^- to F^- ion through NH_2^- and OH^- ions.

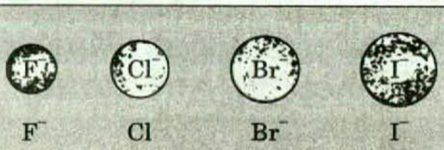
2. Relative order of the acidity of HF, HCl, HBr and HI acids.

To find the order of the acidity of the halogen acids, let us find out the relative order of the basicity of their conjugate bases, *viz*. F^-, Cl^-, Br^- and I^-.

When we move from F^- to I^-, the volume available to electron increases from F^- to I^-. This results in an increase in electron delocalisation and decrease in electron density from F^- to I^-. Consequently, the attraction for proton and basicity decrease in the order :

F^- (Strongest base) > Cl^- > Br^- > I^- (Weakest base)

The above conclusions are depicted in Fig. 12.2.



—Volume available to electron increasing→
—Electron delocalisation increasing→
—Electron density decreasing→
—Attraction for proton decreasing→
—Basicity decreasing→

Fig. 12.2. The basicity of F^-, Cl^-, Br^- and I^- ions decreases as we pass from F^- to I^- ion through Cl^- and Br^- ions.

It may now be inferred that F^- is the strongest base and its conjugate acid HF is the weakest acid. Similarly, I^- is the weakest base and its conjugate acid HI is the strongest acid among the halogen acids. The order of acidity of halogen acid is, therefore, as shown below :

HF (Weakest acid) < HCl < HBr < HI (Strongest acid)

In general, the acidity of binary acids increases on moving down a periodic group and also across a period from left to right.

Acidity increasing →

CH_4	NH_3	H_2O	HF
		H_2S	HCl
		H_2Se	HBr
			HI

Acidity increasing ↓

3. Relative order of acidity of oxyacids.

The acidic character of the oxy-acids having the same central atom in different oxidation number increases with the increase in the oxidation number of the central atom. For example :

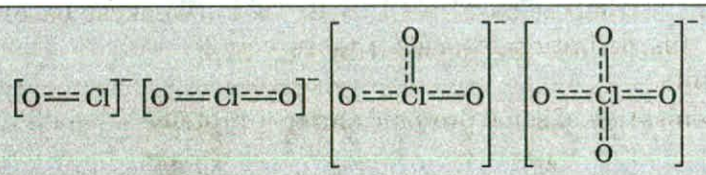
(*a*) $HCl^{+}O < HCl^{3+}O_2 < HCl^{5+}O_3 < HCl^{7+}O_4$

(*b*) $H_2S^{4+}O_3 < H_2S^{6+}O_4$

(*c*) $HN^{+}O < HN^{3+}O_2 < HN^{5+}O_3$.

Let us explain the relative order of acidity of the oxy-acids of chlorine. In order to do so let us find out the relative order of the basicity of the conjugate bases *viz* ClO^-, ClO_2^-, ClO_3^- and ClO_4^- of these acids. With the increase in the number of oxygen atoms in the conjugate bases, the delocalisation of the π bond becomes more and more extended. This results in decrease in electron density. Consequently, proton attraction and basicity also decrease (Fig. 12.3) in the order :

ClO^- (Strongest base) > ClO_2^- > ClO_3^- > ClO_4^- (Weakest base)



ClO^- (Cl = + 1) ClO_2^- (Cl = + 3) ClO_3^- (Cl = + 5) ClO_4^- (Cl = + 7)

—Oxidation number of chlorine increasing→

—Number of oxygen atoms increasing→

—Delocalized π bond becomes more extended→

—Electron delocalization increasing→

—Electron density decreasing→

—Attraction for proton decreasing→

—Basicity decreasing→

Fig. 12.3. The basicity of ClO^-, ClO_2^-, ClO_3^- and ClO_4^- ions decreases as we pass from ClO^- ion to ClO_4^- ion through ClO_2^- and ClO_3^-, ions.

It may now be inferred that ClO^- is the strongest base and its conjugate acid HClO is the weakest acid. Similarly ClO_4^- is the weakest base and its conjugate acid $HClO_4$ is the strongest acid among the oxyacids of chlorine. The order of acidity of oxyacids of chlorine is, therefore, as shown below :

HClO (Weakest acid) < $HClO_2$ < $HClO_3$ < $HClO_4$ (Strongest acid)

Cady-Esley Concept : General Theory of Solvent System

The protonic definition of acid and bases given by Bronsted can be extended to the reactions occurring in non-aqueous solvents containing hydrogen such as NH_3, N_2H_4, HF, H_2SO_4, CH_3COOH, HCN, and alcohols.

In an attempt to have a more general definition of acids and bases applicable to protonic and non-protonic solvents, several definitions have been proposed. One of these is due to Cady and Elsey (1928) according to whom *an acid is a solute that, either by direct association or by reaction with the solvent, gives the anion characteristic of the solvent and a base is a solute that either by direct association or by reaction with the solvent, gives the anion characteristic of the solvent.* If, for example, we consider the solvent H_2O, its characteristic cation and anion are H_3O^+ and OH^- respectively as shown below :

$$\overset{\text{Acid}}{H_2O} + \overset{\text{Base}}{H_2O} \rightleftarrows \overset{\text{Acid}}{H_3O^+} + \overset{\text{Base}}{OH^-}$$

Thus all those compounds which can give H_3O^+ ions in H_2O will act as acids and all the compounds which can give OH^- ions in H_2O will behave as bases.

Similarly in N_2O_4 as solvent, substances such as NOCl which yield NO^+ ions are acids and the substances such as $NaNO_3$ which yield NO_3^- ions are bases.

$$\overset{\text{Acid}}{N_2O_4} + \overset{\text{Base}}{N_2O_4} \rightarrow \overset{\text{Acid}}{2NO^+} + \overset{\text{Base}}{2NO_3^-}$$

Evidently this definition of acids applies equally well to protonic and non-protonic solvents.

The auto-ionisation of some protonic and non-protonic solvents is shown below.

Protonic solvents :

$$\overset{\text{Acid}}{H_2O} + \overset{\text{Base}}{H_2O} \rightleftharpoons \overset{\text{Acid}}{H_2O^+} + \overset{\text{Base}}{OH^-}$$

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$CH_3COOH + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$$

Non-protonic solvents :

$$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO_3^-$$

$$COCl_2 + COCl_2 \rightleftharpoons (COClCOCl_2)^+ + Cl^-$$

$$BrF_3 + BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$N_2O_4 + N_2O_4 \rightleftharpoons 2NO^+ + 2NO_3^-$$

Just as with the Arrhenius definition, neutralisation is a reaction between an acid and a base to produce a salt and the solvent. Neutralisation reactions in some non-aqueous solvents are given below :

	Acid	*Base*	*Salt*	*Solvent*
In liq. NH_3 :	NH_4Cl +	$NaNH_2$	$\rightleftharpoons$ NaCl	+ $2NH_3$
In N_2O_3 :	NOCl +	$NaNO_3$	$\rightleftharpoons$ NaCl	+ N_2O_4
In CH_3COOH :	HCl +	CH_3COONa	$\rightleftharpoons$ NaCl	+ CH_3OOH
In liq. SO_2 :	$SOCl_2$ +	$[N(CH_3)_4]_2SO_3$	$\rightleftharpoons$ $2[N(CH_3)_4]Cl$	+ $2SO_2$

It may be seen from the following reactions that there is a complete analogy between solvolytic and amphoteric behaviours in aqueous solvents.

Solvolytic behaviour :

In liq. NH_3 : $AlCl_3 + NH_3 \rightarrow [Al(NH_3)]^{2+} + H^+ + 3Cl^-$

In H_2O : $AlCl_3 + H_2O \rightarrow [Al(OH)]^{2+} + H^+ + 3Cl^-$

Amphoteric behaviour :

In liq NH_3 : $Zn(NH_2)_2 + 2NH_2^- \rightarrow [Zn(NH_2)_4]^{2-}$

In H_2O : $Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$

Utility of the concept. Evidently, this concept of solvent system can be used to explain the acid-base reactions occurring in aqueous and non-aqueous solvents (protonic and non-protonic both).

Limitations. (*i*) This theory does not consider a number of acid-base reactions included in the protonic definition.

(*ii*) It limits acid-base phenomena to solvent systems only. Thus it does not explain the acid-base reactions which may occur in the absence of solvent.

(*iii*) It cannot explain the neutralisation reactions occurring without the presence of ions.

Thus this theory can simply be said to be an extension of the Arrhenius water-ion system.

Lux-Flood Concept

This concept was proposed by Lux (1939) and extended by Flood (1947). This concept considers the acid-base reactions in terms of oxide ion. Accordingly, *an acid (like* SiO_2*,* CO_2*,* P_4O_{10}*, etc.) is an oxide ion-acceptor while a base (like CaO, BaO, PbO, etc.) is an oxide ion-donor*. Some examples of acid-base reactions, in terms of the Lux-Flood concept, are given below :

Base		*Acid*		*Salt*
CaO	+	SiO_2	→	$CaSiO_3$
BaO	+	CO_2	→	$BaCO_3$
$6\ Na_2O$	+	P_4O_{10}	→	$4Na_3PO_4$
PbO	+	SO_3	→	$PbSO_4$
TiO_2	+	$Na_2S_2O_7$	→	$TiOSO_4 + Na_2SO_4$

Amphoteric substances, in terms of this concept, show a tendency to lose and gain an oxide ion. Thus :

$$\underset{\text{(Amphoteric)}}{ZnO} \overset{+O^{2-}}{\rightleftarrows} ZnO_2^{2-}$$

$$ZnO \overset{-O^{2-}}{\rightleftarrows} Zn^{2+} + O^{2-}$$

$$\underset{\text{(Amphoteric)}}{Al_2O_3} \overset{+O^{2-}}{\rightleftarrows} 2AlO_2^-$$

$$Al_2O_3 \overset{-3O^{2-}}{\rightleftarrows} 2Al^{3+} + 3O^{2-}$$

This concept is particularly useful in explaining reactions which take place at high temperatures such as in metallurgical operations and during the manufacture of glass and ceramics. It can be extended to include transfer of any anion like halide, sulphide, carbanion, etc.

Lewis Concept: Electron-Donor Acceptor System

Each of the concepts discussed above had its own weaknesses and hence a need was felt for a new concept which could explain all the hitherto known properties of acids and bases. Lewis who is one of the early exponents of covalent bonding suggested that :

An acid is any species (molecule, radical or ion) which can accept an electron pair and a base is any species that can donate an electron pair. Thus an acid is an electron pair acceptor and a base is an electron-pair donor.

Consequently, a base should have a lone pair of electrons, which is used in making a coordinate covalent bond from the base to the acid, when an acid combines with a base.

Electron pair being donated by base to acid

$$\underset{\text{Lewis acid}}{\text{Acid}} \quad + \quad \underset{\text{Lewis base}}{(:)\text{Base}} \rightarrow \underset{\text{Adduct}}{[\text{Acid} \leftarrow \text{Base}]}$$

A Lewis acid is often described as an *electrophilic reagent* (or simply an *electrophile*), since an electrophilic reagent, as its name implies, is an *electron-lover* or *electron-seeker* species (*electro* = electron, *philic* = lover), *i.e.*, it loves to accept the electrons (lone pairs). Thus Lewis acids are deficient of electrons. These may be positively-charged ions (*e.g.* H^+, RCO^+, etc.), metal cations (*e.g.*, Co^{3+}, Fe^{3+} etc.), molecules (*e.g.* CO_2, BF_3, SO_2 etc.) or metals in zero oxidation state.

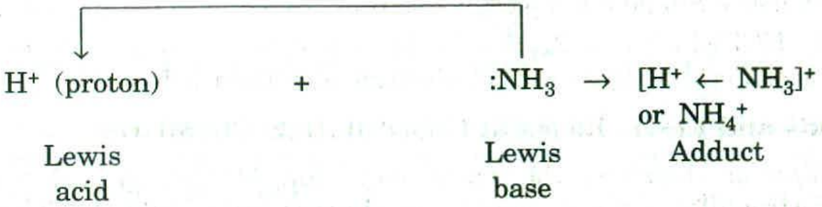
In keeping with the definition of Lewis acid given above, a Lewis base is often described as a *nucleophic reagent* (or *nucleophile*), since a nucleophilic reagent, as its name suggests, is a *nucleus-lover* or *nucleus-seeker species* (*nucleo* = nucleus, *philic* = lover), *i.e.* it loves to donate electrons to a nucleus—in fact—to a positively-charged ion. Lewis bases have unshared pair of electrons (lone pairs). Since the nucleus is electrically positive, Lewis bases (or nucleophiles) may be negative ions (*e.g.* OH^-, F^-, NH_2^-, etc.) or electron rich molecules (*e.g.* NH_3, H_2O etc.).

Neutralisation Reactions in Terms of Lewis Concept

According to Lewis concept the process of neutralisation is simply the formation of a coordinate covalent bond between an acid and the donor atom of the base. The product formed is called a neutralisation product or an adduct. This adduct may be either non-ionisable or may undergo dissociation or condensation reaction depending on its stability.

The neutralisation reaction between a proton (H^+) and : NH_3 molecule takes place as shown below :

An electron pair from :NH_3 being transferred to H^+



$$H^+ \text{ (proton)} + :NH_3 \rightarrow [H^+ \leftarrow NH_3]^+ \text{ or } NH_4^+$$

Evidently in the above reaction proton (H^+) accepts one electron pair from :NH_3 molecule and is, therefore, an acid, whereas :NH_3 molecule which donates an electron pair, is a base. The adduct is NH_4^+ ion.

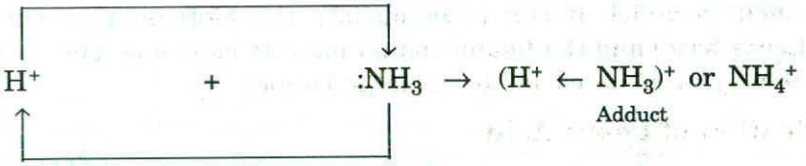
Arrhenius Acids *Vs* Lewis Acids

Arrhenius considered those substances as acids which could donate proton (H^+). Since proton can accept an electron pair from a base, *all Arrhenius acids are also Lewis acids.*

Bronsted Bases *Vs* Lewis Bases

According to Bronsted a base is a substance which accepts proton while according to Lewis, a base is any species which can donate an electron pair. Bronsted base can accept proton only when it has an unshared pair of electrons in it. *Thus all Bronsted bases are also Lewis bases.* This fact can be made evident from the following neutralisation reaction in which NH_3 behaves both as Bronsted base as well as Lewis base.

NH_3 accepts proton (H^+) and, therefore, is a Bronsted base.



$$H^+ + :NH_3 \rightarrow (H^+ \leftarrow NH_3)^+ \text{ or } NH_4^+$$

NH_3 donates its lone pair of electrons to H^+ and, therefore is a Lewis base.

Solvent System *Vs* Lewis System

Solvent system considers NH_4^+ ion as an acid and NH_2^- ion as a base in liquid NH_3 as shown below :

$$\underset{Acid}{NH_4^+} + \underset{Base}{NH_2^-} \rightleftarrows \underset{Acid}{NH_3} + \underset{Base}{NH_3}$$

In the above reaction, NH_2^- ion donates a lone pair of electrons to NH_4^+ ion to produce two molecules of NH_3. Since NH_4^+ ion is nothing but an ammoniated proton and the proton (H^+) can accept a lone pair of electrons from a base (*i.e.* NH_2^- ion), NH_4^+ and NH_2^- ions which are acid and base respectively in liquid NH_3 are also Lewis acid and Lewis base.

Bronsted Acids *Vs* Lewis Acids

There are many Lewis acids (*e.g.* SO_3, halides of B, Al, Fe (III) and Zn) which cannot be treated as Bronsted acids. The central atom of these acids is electron-deficient and hence can accept a pair of electrons from a base to complete its octet.

Similarly HCl which is a Bronsted acid cannot be called a Lewis acid, since it has no vacant orbital to accept an electron pair from a base.

Lewis Acids and Lewis Bases in Coordination Chemistry

In coordination chemistry, the central metal ion, M^{n+} is regarded as a Lewis acid (*i.e.* electrophile), since it accepts an electron pair while the ligand, L is regarded as Lewis base (*i.e.* nucleophile), since it donates an electron pair. The compound formed by the combination of metal cation (M^{n+}) and ligand (L) is called a *complex* or an *adduct*.

Electron pair being donated by L to M^{n+}

M^{n+}	+	$:L$	$\rightarrow$	$[M^{n+} \leftarrow L]^{n+}$
Lewis acid (Electrophile or Electron pair acceptor)		Lewis base (Nucleophile or Electron pair donor)		Complex or adduct

M^{n+} and L are linked together by a coordinate covalent bond from L to M^{n+} ($M^{n+} \leftarrow L$ bond). Thus the reaction between a metallic cation, M^{n+} and a ligand, L shown above can be considered as an acid-base reaction according to Lewis concept.

The metallic cation (Lewis acid) must have at least one vacant orbital in its valence-shell in which it can accommodate the electron pair donated by the ligand (Lewis base) and the ligand should have at least one lone pair of electrons so that it may be donated to the metallic cation.

Classification of Lewis Acids

Any Lewis acid must contain at least one empty orbital in the valence shell of one of its atoms to accept an electron pair from a Lewis base. Lewis acids may be classified as :

1. Molecules containing a central atom with incomplete octet. Typical examples of this class of acids are electron-deficient molecules such as alkyls and halides of Be, B and Al. Some reactions of this type of Lewis acids with Lewis bases are shown below :

Lewis acid		Lewis base		Adducts
F_3B	+	$O(C_2H_5)_2$	$\rightarrow$	$F_3B \leftarrow O(C_2H_5)_2$
Cl_3Al	+	NC_5H_5	$\rightarrow$	$Cl_3Al \leftarrow NC_5H_5$
Me_3B	+	N_2H_4	$\rightarrow$	$Me_3B \leftarrow N_2H_4$

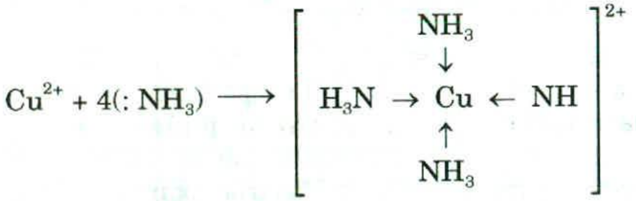
2. Molecules containing a central atom with vacant d-orbitals. The central atom of the halides such as SiX_4, GeX_4, $TiCl_4$, SnX_4, PX_3, PF_5, SF_4, $TeCl_4$, etc.

have vacant *d*-orbitals. These substances can, therefore, accept an electron pair from the Lewis base to accommodate in their vacant *d*-orbital and can thus form adducts with a number of halide ions and organic bases. These substances are, therefore, Lewis acids. These halides are vigorously hydrolysed by H_2O to form an oxy acid or oxide of the central atom and the appropriate HX. The hydrolytic reactions take place presumably through the intermediate formation of unstable adducts with H_2O.

3. Simple cations. Theoretically all simple cations are potential Lewis acids. Reactions of some cations as Lewis acids with Lewis bases are shown below. It will be seen that these reactions are identical with those which produce Werner complexes.

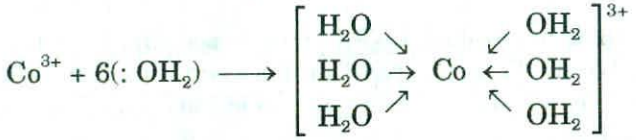
Lewis acid **Lewis base** **Adduct or addition compounds**

Ammonation : $Ag^+ + 2(:NH_3) \longrightarrow [NH_3) \rightarrow Ag \leftarrow NH_3]^+$

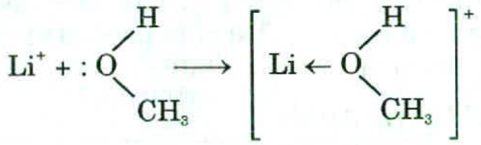


$$Cu^{2+} + 4(:NH_3) \longrightarrow \left[\begin{array}{c} NH_3 \\ \downarrow \\ H_3N \rightarrow Cu \leftarrow NH \\ \uparrow \\ NH_3 \end{array}\right]^{2+}$$

Hydration :



Alcoholation :

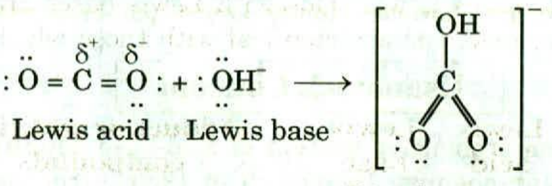


The Lewis acid strength or coordinating ability of the simple cations which, according to Lewis, are Lewis acids, increases with (*a*) an increase in the positive charge carried by the cation (*b*) an increase in the nuclear charge for atoms in any period of the periodic table (*c*) a decrease in ionic radius (*d*) a decrease in the number of shielding electron shells.

Evidently the acid strength of simple cations increases for the elements on moving from left to right in a period and from bottom to top in a group of periodic table. Thus:

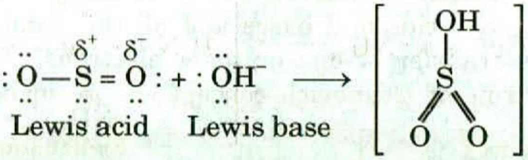
$Fe^{2+} < Fe^{3+}$ (positive charge increases from +2 to +3)
$K^+ < Na^+$ (on moving from bottom to top in a group)
$Li^+ < Be^{2+}$ (on moving from left to right in a period)
——Strength of Lewis acids increasing——→

4. Molecules having a multiple bond between atoms of dissimilar electronegativity. Typical examples of molecules falling in this class of Lewis acids are CO_2, SO_2 and SO_3. In these compounds the oxygen atoms are more electronegative than S or C-atom. As a result, the electron density of π-electrons is displaced away from carbon or sulphur atoms which are less electronegative than oxygen, towards the O-atom. The C or S-atom thus becomes electron deficient and is, therefore, able to accept an electron pair from a Lewis base such as OH^- ions to form dative bond.



Bicarbonate ion

SO_2 also reacts in the same manner with OH^- ion



Bisulphate ion

5. Elements with an electron sextent. Oxygen and sulphur atoms contain six electrons in their valence shell and can, therefore, be regarded as Lewis acids. The oxidation of SO_3^{2-} to SO_4^{2-} ion by oxygen and to $S_2O_3^{2-}$ ion by sulphur are the acid-base reactions.

Lewis base		**Lewis acid**		**Adduct**
SO_3^{2-}	+	$:\overset{..}{\underset{..}{O}}$	→	$[O \leftarrow SO_3]^{2-}$
SO_3^{2-}	+	$:\overset{..}{\underset{..}{S}}$	→	$[S \leftarrow SO_3]^{2-}$

Utility of Lewis Concept

(*i*) This concept also includes those reactions in which no protons are involved.

(*ii*) Lewis concept is more general than the Bronsted-Lowry concept (*i.e.* protonic concept) in that acid-base behaviour is not dependent on the presence of one particular element or on the presence or absence of a solvent.

(*iii*) It explains the long accepted basic properties of metallic oxides and acidic properties of non-metallic oxides.

(*iv*) This theory also includes many reactions such as gas-phase, high temperature and non-solvent reaction as neutralisation processes.

(*v*) The Lewis approach is, however, of great value in cases where the protonic concept is inapplicable, for example, in reaction between acidic and basic oxides in the fused state.

Limitations of Lewis Concept.

(*i*) Since the strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength. Thus, for example, experiments show that fluoride complex of Be^{2+} ion is more stable than that of Cu^{2+} ion, indicating that Be^{2+} ion is more acidic than Cu^{2+} ion. On the other hand amine complex of Cu^{2+} is more stable than that of Be^{2+} ion indicating that Cu^{2+} is more acidic than Be^{2+} ion.

(*ii*) According to the phenomenological criteria, an acid-base reaction should be a rapid reaction. There are, however, many Lewis acid-base reactions which are slow.

Usanovich Concept

This is the most comprehensive concept of acid-base definition. This concept was proposed by Russian chemist, Usanovich in 1939. According to this concept *an acid is any chemical species which is capable of combining with anions or electrons or giving up cations. Conversely a base is any chemical species which is capable of giving up anions or electrons or combining with cations.* This definition includes all Lewis acids and bases and all the redox reactions which may consist of complete transfer of one or more electrons. Some examples of acid-base reactions in terms of Usanovich concept are given below :

Acid-base reactions	**Explanation**
Acid **Base** **Salt**	
$SO_3 + Na_2O \rightarrow Na_2SO_4$	Base, Na_2O gives up O^{2-} ion; acid, SO_3 combines with O^{2-} ion. $Na_2O \rightarrow 2Na^+ + O^{2-}$ $SO_3 + O^{2-} \rightarrow SO_4^{2-}$ $2Na^+ + SO_4^{2-} \rightarrow Na_2SO_4$ (salt)
$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$	Base, KCN gives up CN^- ion, acid $Fe(CN)_2$ combines with CN^- ion. $4KCN \rightarrow 4K^+ + 4CN^-$ $Fe(CN)_2 + 4CN^- \rightarrow [Fe(CN)_6]^{4-}$ $4K^+ + [Fe(CN)_6]^{4-} \rightarrow K_4[Fe(CN)_6]$
$Cl_2 + 2Na \rightarrow 2NaCl$	Base, Na atom loses an electron; acid, Cl combines with this electron. $2Na \rightarrow 2Na^+ + 2e^-$ $2Cl + 2e^- \rightarrow 2Cl^-$ $2Na^+ + 2Cl^- \rightarrow 2NaCl$

Utility of the concept.

This concept is particularly advantageous in classifying together all examples of acids and bases. It is thus the most general of all acid-base concepts.

Limitations of the concept.

(*i*) This concept is like a synthesis of all the previous acid-base concepts and hence in this respect this concept becomes extremely general.

(*ii*) It includes many reactions such as oxidation-reduction reactions which can perhaps be better considered from some other point of view.

(*iii*) This concept virtually considers all the chemical reactions as acid-base reactions.

Conclusion

The study of all the acid-base concepts as made above makes it evident that it is difficult to make an appropriate choice for the best concept. As a matter of fact, each concept has its own advantages and disadvantages and the knowledge of all the concepts is essential.

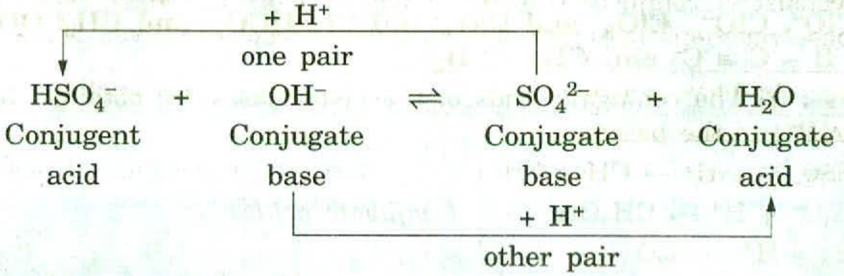
Questions with Answers

Q.1 Indicate the two conjugate acid-base pairs in the following reactions :

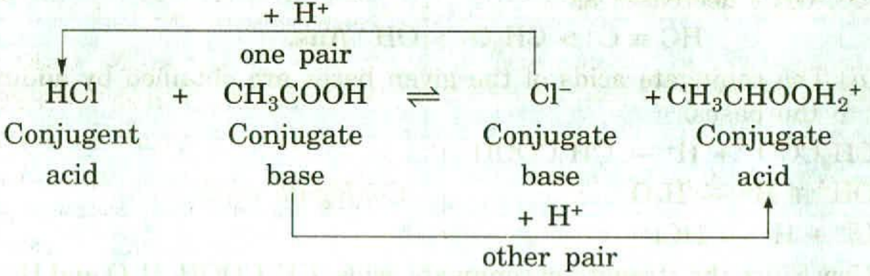
(*i*) $HSO_4^- + OH^- \rightleftharpoons SO_4^{2-} + H_2O$

(*ii*) $HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$

Ans : (*i*) HSO_4^- – SO_4^{2-} and H_2O – OH^- are two conjugate acid-base pairs as shown below :



(*ii*) HCl – Cl^- and $CH_3OOH_2^+$ – CH_3COOH are two conjugate acid-base pairs as shown below



Q.2 Which of the species given in the following sets act as Bronsted acids and Bronsted bases (amphoteric character) (*i*) H_2O, HCO_3^-, NH_3, H_2S (*ii*) HSO_4^-, NH_3, OH^- (*iii*) HNO_3, HCO_3^-, H_2O, NH_3 (*iv*) HCl, H_3PO_4, HCO_3^-

Ans. (*i*) H_2S can donate a proton (H^+) to form HS^- but cannot accept a proton. Hence H_2S acts only as as Bronsted acid. H_2O, HCO_3^- and NH_3 can donate a proton to form OH^-, CO_3^{2-} and NH_2^- respectively. Thus these species can act as acids. These species can also accept H^+ to give H_3O^+, H_2CO_3 and NH_4^+

respectively. Thus these can also act as bases. In other words HCO_3^-, NH_3 and H_2S show amphoteric character.

(ii) All the three species can donate a proton (H^+) to form SO_4^{2-}, NH_2^- and O_2^- respectively. Thus they can act as acids. These species can also accept a proton to give H_2SO_4, NH_4^+ and H_2O respectively. Hence these species can also act as bases. Thus all the given three species show amphoteric character.

(iii) HNO_3 can only donate a proton (H^+) to form NO_3^- but cannot accept a proton to give $H_2NO_3^+$. Thus HNO_3 is an acid. HCO_3^-, H_2O and NH_3 can donate as well as accept H^+ to form (CO_3^{2-}, OH^-, NH_2^-) and (H_2CO_3, H_3O^+, NH_4^+) respectively. Thus HCO_3^-, H_2O and NH_3 show amphoteric character.

(iv) HCl and H_3PO_4 cannot accept a proton. Hence these species donot act as bases. These species can donate a proton to form Cl^- and $H_2PO_4^-$. Hence these species act acids. HCO_3^- can donate a proton to form CO_3^{2-}. Thus it can act as an acid. This ion can also accept a proton to form H_2CO_3. Hence HCO_3^- can also act as a base. Consequently HCO_3^- can act both as an acid and as a base *i.e.* HCO_3^- shows amphoteric character.

Q.3 Arrange the following bases in the decreasing order of their basic strength : *(i)* $CH \equiv C^-$, CH_3O^- and OH^- *(ii)* CH_3COO^-, OH^- and Cl^- *(iii)* ClO^-, ClO_2^-, ClO_3^- and ClO_4^- *(iv)* Cl^-, HCO_3^- and CH_3COO^- *(v)* OH^-, NH_2^-, $H - C \equiv C^-$ and $CH_3 - CH_2^-$.

Ans : *(i)* The conjugate acids of the given bases are obtained by odding a proton (H^+) to the bases.

$$\left.\begin{aligned} &CH \equiv C^- + H^+ \rightarrow CH \equiv CH \\ &CH_3O^- + H^+ \rightarrow CH_3OH \\ &OH^- + H^+ \rightarrow H_2O \end{aligned}\right\} \textit{Conjugate acids}$$

Now since the strength of conjugate acids ($CH \equiv CH$, CH_3OH, H_2O) increases as : $HC \equiv CH < CH_3OH < H_2O$, the strength of their conjugate bases ($CH \equiv C^-$, CH_3O^-, OH^-) decreases as :

$$HC \equiv C^- > CH_3O^- > OH^- \textbf{ Ans.}$$

(ii) The conjugate acids of the given bases are obtained by adding a proton (H^+) to the bases.

$$\left.\begin{aligned} &CH_3COO^- + H^+ \rightarrow CH_3COOH \\ &OH^- + H^+ \rightarrow H_2O \\ &Cl^- + H^+ \rightarrow HCl \end{aligned}\right\} \textit{Conjugate acids}$$

Now Since the strength of conjugate acids (CH_3COOH, H_2O and HCl) increases as : $H_2O < CH_3COOH < HCl$, the strength of their conjugate bases (CH_3COO^-, OH^-, Cl^-) decreases as :

$$OH^- > CH_3COO^- > Cl^- \textbf{ Ans.}$$

(iii) The conjugate acids of the given bases are obtained by adding a proton (H^+) to the bases.

$ClO^- + H^+ \rightarrow HClO$, $\quad ClO_2^- + H^+ \rightarrow HClO_2$

$ClO_3^- + H^+ \rightarrow HClO_3$, $\quad ClO_4^- + H^+ \rightarrow HClO_4$

Now since the strength of the conjugate acids ($HClO$, $HClO_2$, $HClO_3$ and $HClO_4$) increases as : $HClO < HClO_2 < HClO_3 < HClO_4$, the strength of their conjugate bases (ClO^-, ClO_2^-, ClO_3^- and ClO_4^-) decreases as : $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$ **Ans.**

(*iv*) The conjugate acids of the given bases are HCl, H_2CO_3 and CH_3COOH respectively ($Cl^- + H^+ \rightarrow HCl$, $HCO_3^- + H^+ \rightarrow H_2CO_3$, $CH_3COO^- + H^+ \rightarrow CH_3COOH$). Since the strength of the conjugate acids increases as : $CH_3COOH < H_2CO_3 < HCl$, the strength of their conjugate bases decreases as :

$$CH_3COO^- > HCO_3^- > Cl^-$$

(*v*) The conjugate acids of the given bases are H_2O, NH_3, $H-C\equiv C-H$ and CH_3-CH_3 respectively ($OH^- + H^+ \rightarrow H_2O$, $NH_2^- + H^+ \rightarrow NH_3$, $H-C\equiv C^- + H^+ \rightarrow H-C\equiv C-H$, $CH_3-CH_2^- + H^+ \rightarrow CH_3-CH_3$). Since the strength of conjugate acids increases as : $CH_3-CH_3 < NH_3 < H-C\equiv C-H < H_2O$, the strength of their conjugate bases decreases as :

$$CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$$ **Ans.**

Q.4 Which of the following species is the weakest base (*i*) H^-, CH_3^-, CH_3O^-, Cl^- (*ii*) $C_2H_5O^-$, CN^-, CH_3COO^-, NO_3^- (*iii*) $C_2H_5O^-$, NO_3^-, F^-, CH_3COO^-.

Ans : (*i*) The conjugate acids of the given species (bases) are obtained as shown below : $H^- + H^+ \rightarrow \times$, $CH_3^- + H^+ \rightarrow CH_4$, $CH_3O^- + H^+ \rightarrow CH_3OH$, $Cl^- + H^+ \rightarrow HCl$. Out of CH_4, CH_3OH and HCl, since HCl is the strongest conjugate acid, its conjugate base *viz* Cl^- is the weakest base.

(*ii*) The given acids of the given bases are obtained as shown below :

$C_2H_5O^- + H^+ \rightarrow C_2H_5OH$, $CN^- + H^+ \rightarrow HCN$

$CH_3COO^- + H^+ \rightarrow CH_3COOH$, $NO_3^- + H^+ \rightarrow HNO_3$

Out of C_2H_5OH, HCN, CH_3COOH and HNO_3, HNO_3 is the strongest acid. Hence its conjugate base (NO_3^-) is the weakest base.

(*iii*) The conjugate acids of the given species are C_2H_5OH, HNO_3, HF and CH_3COOH. Out of these acids, since HNO_3 is the strongest acid, its conjugate base (*i.e.* NO_3^-) is the weakest base.

Q.5 Which species in the following sets has the highest proton affinity.

(*i*) I^-, HS^-, NH_2^-, F^-

(*ii*) SbH_3, AsH_3, PH_3, NH_3

Ans : (*i*) The species which is the strongest base has the higest proton affinity. Thus we should select the strongest base. The conjugate acids of the given species are HI, H_2S, NH_3 and HF respectively. Among these acids, since NH_3 is the weakest acid, its conjugate base (*i.e.* NH_2^-) is the strongest base. Consequently NH_2^- has the highest proton affinity.

(*ii*) If a substence has proton affinity it can accept the proton and will act as a base. Larger is the size of the central atom (M) in MH_3 molecules, lesser is the tendency of MH_3 molecule to accept a proton and hence lesser is the basic character of MH_3 molecule. Thus since the size of M-atom (central atom) increases from N to Sb, the proton affinity (*i.e.* basic character) of the given molecules decreases from NH_3 to SbH_3 ($NH_3 > PH_3 > AsH_3 > SbH_3$). Thus NH_3 has the highest proton affinity.

Another explanation : The central atom in all the given MH_3 molecules has one *lp* of electrons. Since N atom is the smallest in size, the lone pair electron density on N-atom in NH_3 molecule is the highest and hence the proton affinity of NH_3 is the highest.

Q.6 Which of the following molecules acts as a Lewis acid : $(CH_3)_2O$, $(CH_3)_3P$, $(CH_3)_3N$, $(CH_3)_3B$.

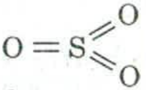
Ans : The structures of $O(CH_3)_2$, $P(CH_3)_3$ and $N(CH_3)_3$ show that O, P and N-atoms (central atom) of these molecules have an octet of electrons (complete octet) round them. Thus these molecules cannot accept electrons. Hence these molecules cannot act as Lewis acids. B-atom (central atom) in $B(CH_3)_3$ has incomplete of octet of electrons (it has six electrons round it), it can accept electrons and hence $B(CH_3)_3$ molecule is Lewis acid.

Q.7 Which of the species given in the follwoing sets is not a Lewis acid ?

(*i*) $SnCl_2$, $AlCl_3$, CCl_4, $SiCl_4$

(*ii*) CO, $SiCl_4$, SO_3, Zn^{2+}

Ans : (*i*) Central atom of $SnCl_2$ and $SiCl_4$ molecules have empty *d*-orbitals. Hence these molecules are Lewis acids. Al atom (central atom) in $AlCl_3$ has incomplete octet of electrons. Hence $AlCl_3$ is also Lewis acis. Since C-atom in CCl_4 has complete octet of electrons, it is not a Lewis acid.

(*ii*) We know that the molecules having empty *d*-orbitals (*e.g.* $SiCl_4$), molecules having multiple bonds between different atoms [e.g. SO_3 or ] and simple cations (*e.g.* Zn^{2+}) are Lewis acids. Since CO does not have any of the above characteristics, it is not a Lewis acid.

Q.8 Which of the species given in the following sets is not a Lewis base.

(*i*) CN^-, ROH, NH_3, $AlCl_3$

(*ii*) Ag^+, H_2O, CN^-, C_2H_5OH

Ans : (*i*) CN^-, ROH and NH_3 all have unshared electron pairs which can be donated. Thus these species are Lewis bases. Since Al atom in $AlCl_3$ has empty *d*-orbitals, $AlCl_3$ is a Lewis acid, *i.e.* $AlCl_3$ is not a Lewis base.

(*ii*) H_2O, CN^- and C_2H_5OH all have unshared electron pairs which can be donated. Thus these species act as Lewis bases. Ag^+ is a simple cation. Hence it as a Lewis acid *i.e.* Ag^+ is not Lewis base.

Q.9 Identify Lewis acids and Lewis bases in the following reactions.

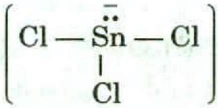
(*i*) $BrF_3 + F^- \rightarrow [BrF_4]^-$

(*ii*) $I^- + I_2 \rightarrow I_3^-$

(*iii*) $[SnCl_3]^- + (CO)_5\,MnCl \rightarrow (CO)_5\,Mn\,(SnCl_3) + Cl^-$

Ans : (*i*) Reaction (*i*) is a Lewis acid – Lewis base reaction. In this reaction F^- ion has four *lps* of electrons which are donated to BrF_3 molecule to form $F_3Br \leftarrow F^-$ or BrF_4^-. Thus F^- ion acts a Lewis base (donor). In BrF_3 molecule Br atom is sp^3d hybridised. Br atom has four emply 4*d* orbitals (unhybridised orbitals) which accept electron pair donated by F^- ion (Lewis base). Thus BrF_3 molecule acts a Lewis acid (acceptor).

(*ii*) Reaction (*ii*) is also a Lewis acid-Lewis base reaction. In this reaction I^- ion has four *lps* of electrons and hence acts as Lewis base. In I_2 molecule $\left(:\underset{\cdot\cdot}{\ddot{I}} - \underset{\cdot\cdot}{\ddot{I}}:\right)$ each I-atom is sp^3 hybridised. 5*d* orbitals in I-atom are lying empty. These orbitals accept electrons donated by one I^- ion to form $:\underset{\cdot\cdot}{\ddot{I}}-\underset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{I}} \leftarrow \underset{\cdot\cdot}{\overset{-}{\ddot{I}}}:$ or I_3^- ion. Thus I_2 molecule acts as Lewis acid.

(*iii*) This reaction is not a Lewis acid-Lewise base reaction. Sn atom in $SnCl_3^-$ ion has one *lp* of electrons  $\left[\mathrm{Cl}-\underset{\underset{\mathrm{Cl}}{|}}{\overset{-}{\ddot{\mathrm{Sn}}}}-\mathrm{Cl}\right]$. Hence this ion acts as a Lewis base. In $(CO)_5MnCl$, Cl^- ion is also a Lewis base. In the given reaction Lewis base, $SnCl_3^-$ replaces Cl^- ion (Lewis base) present in $(CO)_5MnCl$ to from $(CO)_5\ Mn(SnCl_3)$.

Q.10 Four acids A, B, C and D have their *pKa* values as A = 1.0, B = 3.0, C = 2.0 and D = 4.5. Which of these acids is the strongest ?

Ans : We Know that lower is the value of *pKa* of an acid, stronger is the acid. Thus since A has the lowest value of *pKa* (= 1.0), it is the strongest acid.

Q.11 Which of the following acids is the strongest acid : $ClO_3(OH)$, $ClO_2(OH)$, $SO(OH)_2$, $SO_2(OH)_2$?

Ans : Given oxy acids can be written as $HClO_4$, $HClO_3$, H_2SO_3, H_2SO_4. Since central atom (Cl-atom) in $HClO_4$ has the highest O.S. (= +7), this acid is the strongest acid.

Q.12 Explain the following :

(*i*) Tricovalent phosphorus compounds like PCl_3 can act both as Lewis acid and Lewis base.

Ans : In PCl_3 molecule, P-atom has a *lp* of electrons. This *lp* of electrons can be donated to a metal ion. Thus PCl_3 can act as a Lewis base. Since P-atom (central atom) in PCl_3 molecule has empty 3*d* orbitals, these orbitals can receive electrons donated by an electron-rich metal in low oxidation state. Thus PCl_3 can also act as Lewis acid. In $[Ni(PCl_3)_4]^0$, PCl_3 acts as a Lewis acid.

(*ii*) NH_2^- is better base than PH_2^- towards proton.

Ans : NH_2^- and PH_2^- both act as bases since they can accept a proton (H^+) to form NH_3 and PH_3 respectively. Both the given ions have two *lps* of electrons on their central atom. Since N-atom is smaller in size than P-atom, lone pair electron density on N-atom in NH_2^- is higher than that on P-atom in PH_2^-. Due to higher electron density, NH_2^- is better base towards proton.

(iii) The acid strength of $[Fe(H_2O)_6]^{2+}$, $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ ions in aqueons solution decreases as $[Al(H_2O)_6]^{3+} > [Fe(H_2O)_6]^{3+} > [Fe(H_2O)_6]^{2+}$

Ans : The given aqua ions have Fe, Al and Fe in +2, +3 and +3 oxidation state respectively. Since Fe in $[Fe(H_2O)_6]^{3+}$ has higher charge (= +3) than in $[Fe(H_2O)_6]^{2+}$ (Fe = +2), $[Fe(H_2O)_6]^{3+}$ has higher acid strength than $[Fe(H_2O)_6]^{2+}$.

Thus :

$$[Fe^{3+}(H_2O)_6]^{3+} > [Fe^{2+}(H_2O)_6]^{2+} \quad ...\ (i)$$

Since Fe and Al in $[Fe(H_2O)_6]^{3+}$ and $[Al(H_2O)_6]^{3+}$ have the same charge (= +3), the acid strength of these ions dependes on the size of Fe^{3+} and Al^{3+} ions. Since Al^{3+} ion is smaller in size than Fe^{3+}, $[Al(H_2O)_6]^{3+}$ has higher acid strength than $[Fe(H_2O)_6]^{3+}$

$$[Al^{+3}(H_2O)_6]^{3+} > [Fe^{3+}(H_2O)_6]^{3+} \quad ...\ (ii)$$

On combining the two relations (*i*) and (*ii*) given above we get :

$$[Al^{3+}(H_2O)_6]^{3+} > [Fe^{3+}(H_2O)_6]^{3+} > [Fe^{2+}(H_2O)_6]$$

(iv) When aqueous solution of $CuSO_4$ is added to the aqueous solution of $(NH_4)_2SO_4$, the acidity of $(NH_4)_2SO_4$ solution increases.

Ans : When $CuSO_4$ solution is added to $(NH_4)_2SO_4$, H_2SO_4 or protons (H^+) are released.

$$CuSO_4 + 2(NH_4)_2SO_4 \rightarrow [Cu(NH_3)_4]SO_4 + 2H_2SO_4$$

or $$Cu^{2+} + 4NH_4^+ \rightarrow [Cu(NH_3)_4]^{2+} + 4H^+$$

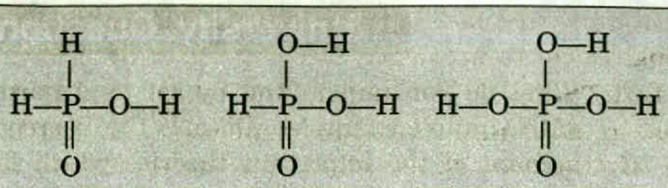
Due to the production of H^+ ions, the acidity of aqueous soultion of $(NH_4)_2SO_4$ increases.

(v) PCl_5 is a better Lewis acid than PCl_3.

Ans : P-atom (central atom) in both the given molecules has vacant *d*-orbitals. Hence both the molecules can act as Lewis acids (electron pair acceptors). Since O.N. of P-atom in PCl_5 (P = +5) is higher than that in PCl_3 (P = +3), EN of P-atom in PCl_5 would be higher than that of the same element (*i.e.* P-atom) in PCl_3. Due to higher EN of P-atom in PCl_5, PCl_5 is a better electron pair acceptor (Lewis acid).

(vi) The acidity (acidic character) of H_3PO_2, H_3PO_3 and H_3PO_4 acids decreases as : $H_3PO_2 > H_3PO_3 > H_3PO_4$.

Ans : The decreasing order of acidity of the given acids can not be explained on the basis of oxidation state of P-atom. Their acidity is explained on the basis of inductive effect of the pronated O-atoms in these acids. The structres of these acids are given below in Fig.12.4.



H_3PO_2 (Mono-basic) H_3PO_3 (Dibasic) H_3PO_4 (Tri-basic)

		H_3PO_2	H_3PO_3	H_3PO_4
No. of protonated O-atoms	=	1	2	3
No. of unprotonated O-atoms	=	1	1	1

Fig. Structures of H_3PO_2, H_3PO_3 and H_3PO_4 molecules

It may be seen from the structers that the number of unprotonated O-atoms in all three acids is the same (=1) but the number of protonated O-atoms increases as 1 → 2 → 3 in H_3PO_2, H_3PO_3 and H_3PO_4 respectively. With the increases in the number of protonated O-atoms, the inductive effect of these O-atoms decreases from H_3PO_2 to H_3PO_4. Due to the decrease in inductive effect of protonated O-atoms, the acidity of acids decreases from H_3PO_2 to H_3PO_4.

Q.13 Classify the following as hard/soft acids or bases. H^-, Ni^{4+}, I^+, H^+.

Ans : Characteristics of the given species are given below. On the basis of these characteristics the nature of the species can be predicated.

Characteristics

Species	Charge	Size	EN	Polaribility	Conclusion
(*i*) H^-	Negative charge	Larger in size than H-atom	Low	Due to large size it has high polarisability.	Soft base
(*ii*) Ni^{4+}	High positive charge	It has smaller size than Ni^{2+}	High	Due to smaller size it has low polarisability.	Hard acid
(*iii*) I^+	Low positive charge	It has larger size	Low	Due to larger size it has high polarisability.	Soft acid
(*iv*) H^+	High positive charge	Smallest size	High	Due to the smallest size it has very low polarisability.	Hard acid

University Questions

1. (*i*) What do you understand by soft and hard acids and bases ? Explain with suitable examples. Discuss the Pearson's principle and give a brief account of the important theories which favour this principle.

(*ii*) Explain why do Ca and Mg occur as oxides and carbonates but not as sulphides in nature. (*Lucknow 2002*)

2. Lewis strength of BBr_3 is greater than that of BCl_3 and BF_3. Explain. (*Lucknow 2002*)

3. Explain why all Bronsted bases are Lewis bases but all Bronsted acids are not Lewis acids. (*Lucknow 2002*)

4. (*a*) What are hard and soft acids and bases ? Explain with examples.

(*b*) On the basis of SHAB principle, explain why HgS is insoluble and $Hg(OH)_2$ is soluble in dil. HCl. (*Nagpur 2002*)

5. Discuss the Pearson's hard and soft acid and base principle for the classification of acids and bases. Explain theoretical behaviour of hardness and softness. Predict the relative strength of HF, HBr and HI in aqueous solution in the light of the above concept. (*VBS Purvanchal 2003*)

6. Explain Bronsted-Lowry concept of acids and bases with suitable examples. (*VBS Purvanchal 2003*)

7. Explain Lewis concept of acids and bases. (*VBS Puravanchal 2003*)

8. Discuss the concept of hard and soft acids and bases.

9. (*a*) What are Lewis acids and bases ? How are they classified ?

(*b*) Discuss the concept of the following, giving suitable examples : (*i*) Lux flood concept of acids and bases (*ii*) Hard and soft acids and bases.

10. (*a*) BCl_3 is stronger acid than BF_3. Explain.

(*b*) Which is a Lewis acid in the following ? (*i*) NaCl (*ii*) $BaCl_2$ (*iii*) $AlCl_3$. (*VBS Purvanchal 2003*)

11. (*a*) Enumerate the factors which govern the hardness and softness in acids and bases.

(*b*) Illustrate HSAB principle. Give reasons for the following on the basis of HSAB principle : (*i*) AgI_2^- is stable but AgF_2^- is not ; (*ii*) CsF reacts with LiI but the reverse is not true.

(*c*) Identity Lewis acid or base in the following : Ag^+, BF_3, CO, PCl_3. (*Rohikhand 2003*)

12. (*a*) Explain the terms conjugate acids and conjugate bases with the help of siutable examples.

(*b*) Discuss the effect of substituents on the strength of carboxylic acid.

(*c*) Which is the stronger acid of each pair. H_3O^+ or H_2O, NH_4^+ or H_2S or HS^- and H_2O or OH ? (*Delhi 2003*)

13. (*a*) Apply SHAB principle in : (*i*) Occurrence of metal minerals and (*ii*) predicting the stability of halogen acids.

(*b*) Classify the following as hard and soft acids : Ca^{2+} and Hg^{2+}.

(*Nagpur 2003*)

14. (*a*) Discuss the Bronsted-Lowery concept of acid and bases. What are its applications and limitations ?

(*b*) Explain the following :

(*i*) Arrhenius hypothesis (*ii*) Lux-Flood acid-base hypothesis.

(*c*) Explain the following :

(*i*) Hard acid and soft base (*ii*) Hard base and soft base

(*iii*) Lewis acid and Lewis base. (*Bhopal 2004*)

15. (*a*) Out of BCl_3 and BF_3 which is more acidic ?

(*b*) BF_3 is a Lewis acid where as CCl_4 is not a Lewis acid. Explain.

(*GND Amritsar, 2004*)

16. What are hard and soft acids and bases ? (*Bhopal 2004*)

17. Boron trihalides are called Lewis acids. Explain why. (*Meerut 2004*)

18. Give Lewis definition of acid and base giving suitable examples.

(*Banglore 2005, Nagpur 2005*)

19. What are different kinds of Lewis acids ? (*Calcutta 2005*)

20. What is HSAB principle ? (*Calcutta 2005*)

21. Explain Bronsted-Lowery theory of acids and bases. Give its limitations.

(*Meerut 2006*)

22. What the limitations of HSAB concept ? (*H.N. Bahunguna 2006*)

23. (*a*) What do you understand by conjugate acid-base pair ? Show that a strong acid has a weak conjugate base and a weak acid has a strong conjugate base ?

(*b*) All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases. Discuss. (*C.S.J.M Kanpur 2007*)

24. Discuss Bronsted-Lowery and Lewis concept of acids and bases with suitable examples. (*Agra 2007*)

25. (*a*) Discuss in brief about conjugate acids and conjugate bases.

(*b*) How does pKa value charge with strength of acids.

(*C.S.J.M. Kanpur 2008*)

26. Describe Lewis acid-base concept with suitable examples. (*Meerut 2008*)

(*a*) Which one is hard base : F^- or I^-.

(*b*) What are characteristics of hard acids ? (*H.N. Bahuguna 2008*)

27. (*a*) Explain Lux-Flood acids and bases.

(*b*) Explain amphoteric substences. (*C.S.J.M Kanpur 2009*)

CHAPTER

13

Non-aqueous Solvents

Classification of Solvents

Solvents have been classified in a number of ways depending on their physical and chemical properties.

1st classification :

This is a common classification which is based on *proton-donor* and *proton-acceptor property* of the solvents. On the basis of this classification the solvents may be classified into three types :

1. Protic or protonic solvents. These solvents have hydrogen atom in their formulae and are of two types. (*a*) *Acidic or protogenic solvents.* These have *strong tendency to donate protons* (*e.g.* H_2SO_4. HF. CH_3COOH, HCN etc.) (*b*) *Basic or protonic solvents.* These have *strong tendency to accept protons* (*e.g.*, NH_3, C_5H_5, amines, N_2H_4).

2. Aprotic or non-protonic solvents. These may or may not have hydrogen in their formula and *neither donate nor accept protons* (*e.g.*, C_6H_6, $CHCl_3$, SO_2, CCl_4, BrF_3).

3. Amphi-protic or amphoteric solvents. These have hydrogen in their formula and donate or accept protons depending on the nature of reacting species, *i.e.*; *these can act both as acids and bases and consequently are amphoteric in nature.* These solvents dissociate feebly into protons and anions. Examples are CH_3COOH, H_2O.

2nd classificaton :

This classification is based on the fact that *"like dissolve like"*. Thus this classification gives (1) *Ionising (polar or ionic) solvents* and *(2) Non-ionising (non-polar or non-ionic) solvents.*

1. Ionising solvents. Ionising solvents are polar or ionic in nature and hence dissolve ionic compounds and initiate ionic reactions. These exist as ions in their pure state and thus are weak conductors of electricity. These have high values of dielectric constants. Because of their polar nature they have strong tendency to form associated structures. Examples are H_2O, NH_3, HF, SO_2 etc. These solvents undergo self-ionisation as shown below.

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^- : NH_3 + NH_3 \rightleftarrows NH_4^+ + NH_2^- ;$$
$$SO_2 + SO_2 \rightleftarrows SO^{2+} + SO_3^{2-}$$

2. Non-ionising solvents. These are non-polar or non-ionic in nature and hence dissolve only non-polar or neutral compounds and do not initiate ionic reactions. These have low dielectric constants. They have little associating and solvating tendency between the solute and solvents. Examples are C_6H_6, CCl_4 etc. These solvents do not undergo self-ionisation.

3rd Classification : Aqueous and Non-aqueous Solvents.

The solvents other than water are called non-aqueous solvents. The groups obtained as a result of self-ionisatjon of H_2O and non-aqueous solvents are analogous to each other, *e.g.*, H_3O^+ and OH^- groups obtained from the self ionisation of H_2O are analogous to NH_4^+ and NH_2^- groups respectively resulted from the self ionisation of liq. NH_3. This is called *parent solvent concept* and a large number of chemical reactions have been correlated in terms of this concept.

Some of the parent solvents and analogous groups are given below :

$$\begin{aligned} H_2O + H_2O &\rightleftarrows H_3O^+ + OH^- \\ NH_3 + NH_3 &\rightleftarrows NH_4^+ + NH_2^- \\ NH_2OH + NH_2OH &\rightleftarrows NH_3OH^+ + NHOH^- \\ \underbrace{H_2S + H_2S}_{\text{Solvents}} &\rightleftarrows \underbrace{H_3S^+ + SH^-}_{\text{Analogous groups}} \end{aligned}$$

In this chapter we shall confine our attention to the study of ionising solvents only in which inorganic substances ionise and give ionic reactions similar to water. Non-ionising solvents are of interest particularly in organic chemistry.

Liquid Ammonia as Solvent

Liquid NH_3 is one of the most comprehensively studied water-like solvent. It is a protonic solvent and is able to dissolve a wide variety of substances. The physical data for liquid NH_3 are as : melting point = 175.3K; boiling point = 239.62K; dielectric constant = 23 at 239.62K; specific conductance = 5×10^{-11} per ohm per cm.

Solubility of Substances in liq. NH_3

1. Inorganic compounds. Since dielectric constant of NH_3 is much less than that of H_2O, liq. NH_3 is a poorer solvent for ionic substances. Molecules having many electrons such as iodine compounds and non-polar substances such as hydrocarbons are, however, soluble in liq. NH_3. Nitrates, thiocyanates, perchlorates and most cyanides are soluble. Oxides, hydroxides, sulphates, carbonates, phosphates, sulphites, and most sulphides, are insoluble. The general order of the solubility of halides in liq. NH_3 is $I^- > Br^- > F^-$. Most iodides are soluble, bromides are less soluble, only NH_4^+, Be^{2+} and Na^+ chlorides are soluble and most fluorides are insoluble.

Most of the ammonium salts (except those of multivalent anions) such as NH_4NO_3, NH_4SCN, $NH_4(CH_3COO)$ are soluble in liq. ammonia. All the metal amides, except those of alkali metals, are insoluble. LiNH is also insoluble.

2. Organic compounds. Alcohols, halogen compounds (*e.g.* chloroform etc.), ketones, esters,, simple ethers and phenol and its derivatives are soluble. The aromatic hydrocarbons are in general sparingly soluble.

3. Non-metals. The non-metals (*e.g.* P, S and I) dissolve in liq. NH_3 reacting with it.

$$\tfrac{5}{4}S_8 + 16NH_3 \rightarrow N_4S_4 + 6(NH_4)_2S$$

Reactions Taking Place in Liquid Ammonia

The various reactions carried out in liquid ammonia are as follows :

1. Auto-ionization of Liquid Ammonia. The extent of auto-ionization of liquid ammonia is less than that of water.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

It is indicated from its low -specific conductance and also from its ion product constant, *i.e.*,

$$H_2O = [H^+][OH^-] = 1 \times 10^{-14} \text{ at } 293 \text{ K}$$
$$2NH_3 = [NH_4^+][NH_2^-] = 1.9 \times 10^{-33} \text{ at } 218 \text{ K.}$$

2. Acid-base Reactions. On the basis of Bronsted-Lowry concept ammonium ions would behave as acids while amide ions as bases in liquid ammonia.

$$\begin{array}{ccccccc} NH_3 & + & NH_3 & \rightleftharpoons & NH_4^+ & + & NH_2^- \\ H_2O & + & H_2O & \rightleftharpoons & H_3O^+ & + & OH^- \\ \text{Acid (I)} & & \text{Base (I)} & & \text{Acid (II)} & & \text{Base (II)} \end{array}$$

The strongest acid available in liquid ammonia is the ammonium ion which is analogue of hydronium ions in aqueous system. A typical neutralization is the reaction of ammonium bromide with potassium amide.

$$\underset{\text{Acid}}{NH_4Br} + \underset{\text{Base}}{KNH_2} \rightarrow \underset{\text{Salt}}{KBr} + \underset{\text{Solvent}}{2NH_3}$$

Reactions of solutions of metal ions in liquid ammonia result in the precipitation of metal amides, imides or nitrides which are analogues to the precipitation of metal hydroxides and oxides in aqueous system.

$$AgNO_3 + KNH_2 \xrightarrow{\text{Liq. } NH_3} AgNH_2 + KNO_3$$
$$PbI_2 + KNH_2 \longrightarrow PbNH + KI + HI$$
$$3HgI_2 + 2KNH_2 \longrightarrow Hg_3N_2 + 2KI + 4HI$$

Many metal amides, imides and nitrides dissolve in solution of potassium amide in liquid ammonia to from complexes.

$$AgNH_2 + KNH_2 \xrightarrow{\text{Liq. } NH_3} K[Ag(NH_2)_2]$$
$$NaNH_2 + 2KNH_2 \longrightarrow K_2[Na(NH_2)_3]$$

3. Precipitation Reactions. Because of the differences in the solubilities of various substances in liquid ammonia and water, a large number of reactions which do not occur in water have been reported to be carried out in liquid ammonia. Following examples are illustrative.

(*i*) When solutions of silver chloride and barium nitrate in liquid ammonia are brought together, a white ppt. of $BaCl_2$ is obtained.

$$2AgCl + Ba(NO_3)_2 \overset{\text{Liq. } NH_3}{\rightleftarrows} \underset{\text{white ppt,}}{BaCl_2} + 2AgNO_3$$

(*ii*) Similarly, a white ppt. of KCl is obtained by mixing solution of KI with NH_4Cl solution in liquid ammonia.

$$KI + NH_4Cl \overset{\text{Liq. } NH_3}{\rightleftarrows} \underset{\text{white ppt.}}{KCl} + NH_4I$$

4. Complex Formation Reactions. Many complex formation reactions have been reported which are similar to reactions occurring in water system. When KCN is added to silver nitrate solution in liquid ammonia or in water, a ppt. of silver cyanide is first formed which dissolves in excess of KCN yielding the complex compound, $[KAg(CN)_2]$.

$$AgNO_3 + KCN \longrightarrow \underset{\text{ppt.}}{AgCN} + KNO_3$$

$$AgCN + KCN \longrightarrow KAg(CN)_2$$

5. Ammonolysis Reactions. These reactions are also termed as solvolysis reactions. Liquid ammonia is regarded as an ideal solvent medium for many ammonolysis reactions. Some of these are as follows :

(*i*) Alkali metal and alkaline earth metal hydrides are ammonolysed to the corresponding metal amides and hydrogen.

$$M^+H^- + NH_3 \longrightarrow MNH_2 + H_2$$

(*ii*) Many covalent halides undergo ammonolysis in liquid ammonia.

$$HgCl_2 \xrightarrow{\text{Liq. } NH_3} HgNH_2Cl$$

$$SiCl_4 \longrightarrow Si(NH_2)_4$$

$$GeI_4 \longrightarrow Ge(NH_2)_4$$

6. Solvation Reactions. In solvation reactions, solvent gets bonded to a solute species (molecule or ion). Such reactions taking place in water are called ammonation reactions. Some examples of solvation reactions are :

$$BF_3 + NH_3 \longrightarrow BF_3.NH_3$$

$$SiF_4 + 2NH_3 \longrightarrow SiH_4.2NH_3$$

$$SO_3 + 2NH_3 \longrightarrow SO_3.2NH_3$$

7. Metal-ammonia Solutions and Their Reactions. (*i*) *Solutions of metals in liquid ammonia.* Metals that have low ionisation energies, low energies of sublimation and high energies of solvation, alkali metals, alkaline earth metals, Al, europium and ytterbium readily dissolve in liq. NH_3 and give metal-ammonia solutions. These are blue in colour in dilute and bronze-coloured in concentrated solutions. The absorption spectra of the blue solutions are alike, regardless of the metal dissolved in the solution. The blue solutions are excellent electrolytes. The bronze-coloured solutions (*i.e.* concentrated solutions) have high thermal coefficient of electrical conductance approaching that of the free metal whereas the electrolytic conductance of the blue-coloured solutions (*i.e.* dilute solutions) is of the magnitude of an electrolytic solution.

By simply evaporating the alkali metal-ammonia solutions, alkali metal can be recovered. Alkaline earth metal-ammonia solutions on evaporation give hexammonate, $M(NH_3)_6$, where M = alkaline earth metal, indicating that the solvent action is chemical.

All metal ammonia solutions, upon long standing or in presence of a suitable catalyst, undergo decomposition and give H_2 gas and the metal amide.

$$M + nNH_3 \longrightarrow M(NH_2)_n + \frac{n}{2}H_2\uparrow$$

This decomposition reaction proceeds rapidly in presence of small amounts of certain catalysts such as Fe_2O_3 or Pt-black.

The blue metal ammonia dilute solutions are paramagnetic in character (*i.e.* if these solutions are placed in magnetic field, they will be attracted into the field), indicating the presence of unpaired electrons. As the concentration of the solutions increases, the magnetic susceptibility per mole of the solute decreases.

It is now believed that in concentrated solutions the electrons are largely free, *i.e.*

$$M \rightleftarrows M^+ + e^- \qquad ...(1)$$

On the other hand in dilute solutions the electrons and the metal ions, M^+ are solvated (*i.e.* ammoniated) reversibly as :

$$M^+ + xNH_3 \rightleftarrows \underset{\substack{\text{Ammoniated}\\ \text{cation}}}{[M(NH_3)_x]^+} \qquad ...(2)$$

$$e^- + yNH_3 \rightleftarrows \underset{\substack{\text{Ammoniated}\\ \text{electron}}}{[e(NH_3)_y]^-} \qquad ...(3)$$

Thus the properties of metal-ammonia solutions are best accounted for in terms of an equilibrium represented by (4) obtained by adding (1), (2) and (3),

$$e^- + M + (x + y)\ NH_3 \rightleftarrows [M(NH_3)]^+ + [e(NH_3)_y]^-$$

or

$$M \overset{NH_3(l)}{\rightleftarrows} M^+_{(am)} + e^-_{(am)} \qquad ...(4)$$

where the ammoniated cation and ammoniated electron have been represented as $M^+_{(am)}$ and $e^-_{(am)}$ respectively.

The electrons are believed to occupy the cavities in the solvent surrounded by NH_3 molecules whose protons are oriented towards the free electrons. As the concentration increase, the $M^+_{(am)}$ cations tend to bond together by $e^-_{(am)}$ into aggregates such as M_2, M_3, etc. In the concentrated bronze-coloured solutions, the $M^+_{(am)}$ cations and $e^-_{(am)}$ are bonded together in a manner which is similar to that of ordinary metal ions of the same size in a molten metal.

(ii) Reactions of metal-ammonia solutions. Since the blue metal-ammonia solutions contain highly mobile, ammoniated electrons, such solutions can act as strong reducing agents, particularly for reducing those substances which are soluble in liq. NH_3.

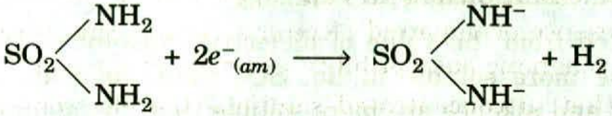
Now since the reducing agents which are stronger than hydrogen, react with water to liberate hydrogen, these cannot generally be used in aqueous solutions. It is for this reason that many metal ammonia solutions which are strong reducing agents are widely used to bring about a number of reductions reaction. Some typical reactions are mentioned below :

(*a*) If metal-ammonia solution is treated with non-metallic element, reduction products are obtained by direct combination.

(*b*) Metal-ammonia solutions are quickly decolorised by ammonium salts or by other acids which are reduced.

$$NH_4^+ + e^-_{(am)} \longrightarrow NH_3 + \tfrac{1}{2} H_2$$

This further supports the view that the blue colour is due to ammoniated electrons.



$$SO_2(NH_2)_2 + 2e^-_{(am)} \longrightarrow SO_2(NH^-)_2 + H_2$$

(*c*) Many organic compounds undergo reduction in metal ammonia solutions.

$$\underset{\text{Acetylenic hydrocarbon}}{RC \equiv CH} + e^-_{(am)} \xrightarrow[NH_3(l)\text{ not in excess}]{\text{Metal dissolved in}} \underset{\text{Acetylide ion}}{RC \equiv C^-} + H$$

$$RC \equiv CH + \tfrac{1}{2}H_2 \xrightarrow[\text{in } NH_3(l)\text{ in excess}]{\text{Metal dissolved}} \underset{\text{Ethylenic derivatives}}{RC = CH_2}$$

(*d*) A large number of organometallic compounds of various types can react with metal-ammonia solutions and form a series of compounds containing metal bonds.

Liquid Sulphur Dioxide as Solvent

Liquid sulphur dioxide is a water-like solvent and as such is used extensively for carrying out a number of chemical reactions. Its boiling point is –10°C and freezing point –75.5°C. Since the liquid range is sufficiently high, it can be used as a solvent.

The auto-ionisation occurring in liq. SO_2 takes place as follows :

$$SO_2 + SO_2 \rightleftarrows SO^{2+} + SO_3^{2-}$$

The thionyl ion (SO^{2+}) is analogous to the hydronium ion (H_3O^+) and NH_4^+ ion and SO_3^{2-} ion corresponds to OH^- and NH_3^- ion of the aqueous and liq. NH_3 system.

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$
$$NH_3 + NH_3 \rightleftarrows NH_4^+ + NH_2^-$$

Dipole moment of SO_2 is 1.61 D. Its dielectric constant is 17.27 (at –16.5°C) and it can dissolve many salts.

Solubility of Inorganic Materials in liq. SO_2

In general, iodides are most soluble followed by thiocyanates. The solubilities of alkali metal halides decrease in the order MI > MBr > MCl > MF. Alkali metal sulphites and acetates are soluble. Metal sulphates, alkali metal thiocyanates and cyanides are soluble. Metal sulphates, sulphides, oxides and hydroxides are virtually insoluble. Many of the ammonium, thallium and mercuric salts are soluble. The substances such as IBr, PBr_3, CCl_4, $SiCl_4$, $GeCl_4$ and $SnCl_4$ are quite soluble in liq. SO_2.

Many substances such as Br_2, ICl, BCl_3, PCl_3, $AsCl_3$, CS_2, $POCl_3$, $SOCl_2$, $SO(CH_3COO)_2$ and many sulphuryl compounds, SO_2X_2, are completely miscible with liq. SO_2. The miscible nature of $SOCl_2$ has been utilised in the preparation of a large number of thionyl derivatives by the metathetical reactions of liq. SO_2.

Solubility of Organic Compounds in liq. SO_2

As might be expected from the value of dielectric constant of SO_2, covalent organic compounds are more soluble in liq. SO_2 than the ionic compounds. Aromatic hydrocarbons and alkenes are more soluble than the alkanes. Liq. SO_2 has also been used as a medium for conducting a number of organic reactions such as Friedel-Crafts' sulphonation and bromination reactions.

Conductivity of Salt Solutions in liq. SO_2

The solutions of alkali metals, ammonium and teraalkyl ammonium chlorides, bromides, iodides and thiocyanates in liq. SO_2 are moderately good conductors. On the other hand the mono-, di- and tri-alkyl ammonium salts are very poor conductors.

The conductivity of electrolyte solutions in liq. SO_2 roughly increases with the size of the cation. Thus the order of conductivity may be shown as: $Na^+ < NH_4^+ < K^+ < Rb^+ < (CH_3)_3S^+ < (CH_3)_4N^+$ etc. The conductivity of the anions increases in the order : $SCN^- < ClO_4^- < Cl^- < I^-$ etc.

Many covalent compounds such as Br_2, I_2, PBr_5, $AsBr_3$, $SbCl_5$, S_2Br_2, IBr, ICl, ICl_3, $SOBr_2$, $(C_6H_5)_3CCl$ etc. behave as electrolytes in liq. SO_2.

The solutions of many tri-substituted hydronium salts such as $[(C_2H_5)_3O]BF_4$, $[(CH_3)_3O]BF_4$ and $[(C_2H_5)_3O]_5SbCl_6$ in liq. SO_2 are moderately good conductors.

Chemical Reactions That Can Occur in Liquid Sulphur Dioxide

Chemical reactions that can occur in liq. SO_2 can be classified under the following headings :

1. Acid-base Reactions. Auto-ionisation of liquid SO_2 is in accordance with following equation.

$$2\ SO_3 \rightleftarrows SO^{2+} + SO_3^{2-}$$

The compounds which contain or make available sulphite ions (SO_3^{2-}) on dissolving in liquid SO_2 would act as typical bases. Therefore, the alkali metal sulphites should behave as typical bases in liquid sulphur dioxide.

Similarly, such compounds which contain or make available thionyl ion (SO^{2+}) would act as typical acids in liquid SO_2. Therefore, thionyl compounds ($SOCl_2$, $SOBr_2$) would act as acids.

Some examples of acid-base reactions are as follows :

$$\begin{aligned} SOCl_2 + Cs_2SO_3 &\xrightarrow{\text{Liq. } SO_2} 2CsCl + 2SO_2 \\ SOBr_2 + [(CH_3)_4N]_2SO_3 &\longrightarrow 2[(CH_3)_4N]Br + 2SO_2 \\ \underset{\text{Acid}}{SO(SCN)_2} + \underset{\text{Base}}{K_2SO_3} &\longrightarrow \underset{\text{Salt}}{2KSCN} + \underset{\text{Solvent}}{2SO_2} \end{aligned}$$

2. Solvolytic Reactions. Solvolytic reactions of salts in liquid SO_2 are more complex than the true solvolytic processes in many protonic solvents. For example :

$$\begin{aligned} Zn(C_2H_5)_2 + 2SO_2 &\longrightarrow ZnSO_3 + SO(C_2H_5)_2 \\ PCl_5 + SO_2 &\longrightarrow POCl_3 + SOCl_2 \\ PBr_5 + SO_2 &\longrightarrow POBr_3 + SOBr_2 \\ NbCl_5 + SO_2 &\longrightarrow NbOCl_3 + SOCl_2 \\ UCl_6 + 2SO_2 &\longrightarrow UO_2Cl_2 + 2SOCl_2 \end{aligned}$$

3. Metathetical Reactions. There are a large number of neutralizations or acid-base reactions which may better be described as metathetical reactions. A few examples are :

$$5CH_3COOAg + SOCl_2 \xrightarrow{\text{Liq. } SO_2} 2AgCl(s) + (CH_3COO)_2SO$$

$$2CH_3COONH_4 + SOCl_2 \xrightarrow{\text{Liq. } SO_2} 2NH_4Cl(s) + (CH_3COO)_2SO$$

$$3KI + SOCl_2 \xrightarrow{\text{Liq. } SO_2} 2KCl + SOI_2$$

4. Reactions with Organic Compounds. Because many organic compounds are soluble in liquid SO_2 and because it is itself inert to many of them, a large number of organic reactions have been carried out in this solvent. In such reactions there is a sulphonation of aomatic hydrocarbons by sulphur trioxide or chlorosulphonic acid.

$$C_6H_6 + SO_3 \xrightarrow{\text{Liq. } SO_2} C_6H_5SO_2OH$$

$$C_6H_6 + ClSO_3H \xrightarrow{\text{Liq. } SO_2} C_6H_5SO_2OH + HCl$$

5. Complex Formation Reactions. A large number of complex ion formation in liquid SO_2 have been reported. For example, the solubility of iodine in liquid SO_2 is greatly increased by the addition of potassium or rubidium iodide. This is due to the formation of complexes like RbI_3 or KI_3.

$$\begin{aligned} KI + I_2 &\longrightarrow KI_3 \\ RbI + I_2 &\longrightarrow RbI_3 \end{aligned}$$

Similarly, the solubilities of potassium iodide and mercuric iodide in liquid SO_2 are greatly increased owing to the formation of complexes.

$$HgI_2 + 2KI \longrightarrow K_2HgI_4$$

6. Amphoterism in Liquid Sulphur Dioxide. Several reactions have been reported in liquid SO_2 which may be compared to the behaviour of amphoteric hydroxides in aqueous system. When a solution of tetramethylammonium sulphate is added to a solution of aluminium chloride in liquid SO_2, a gelatinous ppt. of aluminium sulphite is formed.

$$2AlCl_3 + 3(Me_4N)_2SO_4 \longrightarrow \underset{\text{ppt.}}{Al_2(SO_3)_3} + 6Me_4NCl$$

Similar reaction has been reported with gallium trichloride. It gives a ppt. with tetramethyl ammonium sulphite.

$$2GaCl_3 + 3\ (Me_4N)_2SO_3 \longrightarrow \underset{\text{ppt.}}{Ga_2(SO_3)_3} + 6Me_4NCl$$

7. Oxidation Reduction Reactions. In many oxidation- reduction reactions studied in SO_2, the solvent acts merely as an inert carrier. A solution of $FeCl_2$ quantitatively oxidizes KI to I_2.

$$2FeCl_3 + 2KI \longrightarrow 2FeCl_2 + 2KCl + I_2$$

Similarly a solution of $SbCl_5$ oxidises KI to I_2

$$6KI + 3SbCl_5 \longrightarrow 2K_3SbCl_6 + SbCl_3 + 3I_2.$$

Questions with Answers

Q.1 (*a*) Classify the following solvents as ionising and non-ionising solvents: HF, liq. SO_2, liq. N_2O_4, H_2SO_4, $POCl_3$, pyridine and acetic acid.

(*b*) Classify the following solvents as protonic (protic) or non-protonic (aprotic) solvents: HF, liq. SO_2, C_6H_6, H_2SO_4 and liq. NH_3.

Ans : (*a*) *Ionising solvents* : HF, H_2SO_4, acetic acid

Non-ionising solvents : liq. SO_2, liq. N_2O_4, $POCl_3$, pyridine.

(*b*) *Protic solvents* : HF, H_2SO_4, liq. NH_3

Aprotic solvents : liq. SO_2, C_6H_6

Q.2 What will be the effect of adding (*a*) KNH_2 (*b*) Li_3N (*c*) CH_3COOK to liq. NH_3 on the acidity/bascity of the solvent.

Ans : (*a*) Since KNH_2 gives NH_2^- ions (amide ions) in liq. NH_3, it behaves as a base in this solvent. Thus the addition of KNH_2 to liq. NH_3 increases the basisc character of the solvent

$$KNH_2 \xrightarrow{\text{Liq.}NH_3} K^+ + NH_2^-$$

(*b*) Since Li_3N produces nitride ions (N^{3-} ions) in liq. NH_3, it behaves as a base in this solvent. Thus the addition of Li_3N to liq. NH_3 increases the basic nature of the solvent.

$$Li_3N \xrightarrow{\text{Liq.}NH_3} 3Li^+ + N^{3-}$$

(*c*) Since CH_3COOK does not have any of the ions *viz* NH_4^+, NH_2^-, NH^{2-}, N^{3-}, the addition of this compound to liq. NH_3 has no effect on the acidity/bascity of liq. NH_3.

Q.3 Guess the reaction between $Zn(NH_2)_2$ and CH_3COONH_4.

Ans : Auto-ionisation of liq. NH_3 gives NH_4^+ (ammono acid ion) and NH_2^- (ammono base ion) ions. Thus Zn $(NH_2)_2$ will act as a base and CH_3COONH_4 will act as an acid in liq. NH_3 and the reaction between these substances is a neutralisation reaction.

Ammono base *Ammono acid* *Salt* *Solvent*

$$Zn(NH_2)_2 + 2CH_3COONH_4 \longrightarrow Zn(CH_3COO)_2 + 4NH_3$$

Zn^{2+} ions obtained by the dissociation of $Zn(CH_3COO)_2$ will react with $4NH_3$ to give tetramminezinc (II) ion, $[Zn(NH_3)_4]^{2+}$

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$

Q.4 How do the following solutes behave in the solvents given in parentheses ? (*a*) KNH_2 (NH_3) (*b*) $(NH_4)_2SO_4$ (NH_3) (*c*) $SiCl_4$ (NH_3) (*d*) SO_2Cl_2 (NH_3) (*e*) PCl_5 (SO_2) (*f*) AgCl (NH_3) (*g*) $Zn(C_2H_5)_2$ (SO_2) (*h*) Cs_2SO_3 (SO_2) (*i*) $NbCl_5$(SO_2).

Ans : (*a*) KNH_2 behaves as a base in liq. NH_3, since it gives NH_2^- (base anion) in this solvent.

$$KNH_2 \xrightarrow{\text{Liq.}NH_3} K^+ + NH_2^-$$

(*b*) $(NH_4)_2SO_4$ behaves as an acid in liq. NH_3, since NH_4^+ ions are produced.

$$(NH_4)_2SO_4 \xrightarrow{\text{Liq.}NH_3} 2NH_4^+ + SO_4^{2-}$$

(*c*) $SiCl_4$ is covalent and hence undergoes ammonolysis reaction in liq. NH_3. In this reaction the concentration of NH_2^- ions is increased due to the prodution of $Si(NH_2)_4$.

$$\begin{tikzcd} SiCl_4 + 8NH_3 \arrow[r] & Si(NH_2)_4 + 4NH_4\,Cl \arrow[d, "0^\circ"'] & \\ & Si\,(NH)\,(NH_2)_2 \arrow[r, "1200^\circ"] & Si_3N_4 \end{tikzcd}$$

(*d*) SO_2Cl_2 undergoes ammonolysis reaction in liq. NH_3, since $SO_2(NH_2)_2$ is produced. This compound increases the concentration of NH_2^- ions.

$$SO_2Cl_2 + 4NH_3 \longrightarrow SO_2(NH_2)_2 + 2NH_4\,Cl$$

(*e*) In liq. SO_2, PCl_5 undergoes solvolysis reaction and $POCl_3$ is formed.

$$PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$$

(*f*) AgCl dissolves in liq. NH_3 due to the formation of a complex compound, $[Ag(NH_3)_2]Cl$.

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]\,Cl$$

(*g*) The reaction between $Zn(C_2H_5)_2$ and liq. SO_2 is an example of solvolysis reaction

$$Zn(C_2H_5)_2 + 2SO_2\,(l) \longrightarrow ZnSO_3 + (C_2H_5)_2SO$$

(*h*) Since Cs_2SO_3 gives SO_3^{2-} ions in liq. SO_2, this compound acts as a base in this solvent

$$Cs_2SO_3 \xrightarrow{\text{Liq. }SO_2} 2Cs^+ + SO_3^{2-} \textit{ (Base ion)}$$

(*i*) $NbCl_5$ shows solvolysis reaction in liq. SO_2.

$$NbCl_5 + SO_2\,(l) \longrightarrow NbOCl_3 + SOCl_2$$

Q.5 How will the following solutes react with the solvents given in the parenthesis. State whether the solution formed in each case will be more acidic or more basic than the solvent.

$H_2SO_4(H_2O)$, $H_2SO_4(NH_3)$, $CH_3COOH(H_2SO_4)$, $SOCl_2(SO_2)$ and $CH_3CONH_2(NH_3)$.

Ans : The reactions between the solutes and the solvents are given below. The nature of the solution is given in parenthesis.

Solute		*Solvent*					
H_2SO_4	+	H_2O	$\longrightarrow$	HSO_4^-	+	$\boxed{H_3O^+}$	(*Acidic*)
H_2SO_4	+	NH_3	$\longrightarrow$	HSO_4^-	+	$\boxed{NH_4^+}$	(*Acidic*)
CH_3COOH	+	H_2SO_4	$\longrightarrow$	$CH_3COOH_2^+$	+	$\boxed{HSO_4^-}$	(*Basic*)
$SOCl_2$	+	SO_2	$\longrightarrow$	$2Cl^-$	+	$\boxed{SO^{2+}}$	(*Acidic*)
CH_3CONH_2	+	NH_3	$\longrightarrow$	CH_3COONH^-	+	$\boxed{NH_4^+}$	(*Acidic*)

Q.6 Complete the following equations :

(*i*) $C_2H_5OH + HF \longrightarrow$ .... (Guru Nanak Dev. 96)

(*ii*) $PbI_2 + KNH_2 \xrightarrow{\text{Liq. NH}_3}$ .... (P.U. 1977)

(*iii*) $Zn\ (NO_3)_2 + KNH_2 \xrightarrow{\text{Liq. NH}_3}$ .... (P.U. 1997)

(*iv*) $Na + NH_4Cl \xrightarrow{\text{Liq. NH}_3}$ .... (Kurukshetra 1977)

Ans : (*i*) In HF (solvent), C_2H_5OH (solute) behaves as a base, since HF_2^- ions (solvent anions) are produced.

C_2H_5OH (*solute*) + 2HF (*solvent*) $\longrightarrow C_2H_5OH_2^+ + HF_2^-$ (*Solvent anion - base anion*)

(*ii*) PbI_2 is a metal salt. It reacts with the base *viz* KNH_2 and gives the ppt. of lead imide (PbNH).

$PbI_2 + KNH_2$ (*Ammono base*) $\xrightarrow{\text{Liq. NH}_3} PbNH\downarrow + KI + HI$

(*iii*) $Zn\ (NO_3)_2$ is a metal salt. It reacts with the base, KNH_2 and gives the ppt. of $ZnNH_2$.

$Zn(NO_3)_2 + 2KNH_2$ (*Ammono base*) $\xrightarrow{\text{Liq. NH}_3} Zn(NH_2)_2 + 2KNO_3$

(*iv*) In liq. NH_3, Na metal reduces NH_4Cl to H_2.

$$\underset{(Na\,=\,0)}{2Na} + \underset{(H\,=\,+1)}{2NH_4Cl} \xrightarrow{\text{Liq. NH}_3} \underset{(Na\,=\,+1)}{2NaCl} + 2NH_3 + \underset{(H\,=\,0)}{H_2}$$

Q.7 Complete the following reactions in liq. SO_2.

(*i*) $HgI_2 + KI \longrightarrow$ ....

(*ii*) $SbCl_5 + NOCl_2 \longrightarrow$ ....

(*iii*) $Cr_2\ (SO_3)_3 + SOCl \longrightarrow$ ....

(*iv*) $C_6H_6 + SO_3 \longrightarrow$ .... (P.U. April 1996, Kurukshetra 1994)

Ans : (*i*) When HgI_2 is dissolved in liq. SO_2 in presence of KI, the solubility of HgI_2 in liq. SO_2 is increased due to the formation of $K_2[HgI_4]$ (a complex compound).

$$HgI_2 + 2KI \xrightarrow{\text{Liq. NH}_3} K_2[HgI_4]$$

(*ii*) The reaction between $SbCl_5$ (covalent halide) and NOCl in liq. SO_2 leads to the formation of hexachloro complex, $NO^+[SbCl_6]^-$

$$SbCl_5 + NOCl \xrightarrow{\text{Liq. } NH_3} NO^+[SbCl_6]^-$$

(*iii*) Since $Cr_2(SO_3)_3$ contains SO_3^{2-} ions, this compound acts as a base in liq. SO_2. Similarly, since $SOCl_2$ gives SO^{2+} ions in liq. SO_2, this salt behaves as an acid in liq. SO_2. Thus the reaction between $Cr_2(SO_3)_3$ and $SOCl_2$ in liq. SO_2 is an acid-base (neutralisation) reaction and gives salt and solvent (*i.e.* SO_2)

$$SOCl_2(acid) + CsSO_3\ (base) \xrightarrow{\text{Liq. } SO_2} 2CsCl\ (\text{salt}) + 2SO_2\ (\text{solvent})$$

(*iv*) In presence of liq. SO_2, C_6H_6 undergoes sulphonation.

$$C_6H_6 + SO_3 \xrightarrow{\text{Liq. } SO_2} C_6H_5SO_3H.$$

Q.8 Show whether each of the following compounds acts as an acid or a base in liq. HF.

BF_3, SbF_5, H_2O, CH_3COOH, C_6H_6.

Ans : We know that HF undergoes self-ionisation as follows:

$$3HF \rightleftharpoons \underset{\substack{\text{Solvent cations}\\ \text{(Acid ions)}}}{H_2F^+} + \underset{\substack{\text{Solvent anions}\\ \text{(Base ions)}}}{HF_2^-}$$

This equation shows that the compounds producing H_2F^+ ions in liq. HF act as acids in this solvent while the compounds giving HF_2^- ions behave as bases in this solvent. Thus:

$$\underset{\text{(Acid)}}{BF_3} + 3HF \rightleftharpoons H_2F^+ + BF_4^-$$

$$\underset{\text{(Acid)}}{SbF_5} + 2HF \rightleftharpoons H_2F^+ + SbF_6^-$$

$$\underset{\text{(Base)}}{H_2O} + 2HF \rightleftharpoons H_3O^+ + HF_2^-$$

$$\underset{\text{(Base)}}{CH_3COOH} + 2HF \rightleftharpoons CH_3COOH_2^+ + HF_2^-$$

$$\underset{\text{(Base)}}{C_6H_6} + 2HF \rightleftharpoons C_6H_7^+ + HF_2^-$$

Q.9 Account for the following, giving appropriate reasons.

(*i*) K_2SO_3 is soluble in liq. SO_2. ***[M.D. Rohtak 1997]***

(*ii*) SO_2 acts both as a Lewis acid and as a Lewis base. ***[M.D.Rohtak 1998]***

(*iii*) The electrical conductivity of liq. NH_3 is increased when NH_4Cl is dissolved in it. ***[M.D. Rohtak 1997, Agra 1993]***

(*iv*) A liq. NH_3 solution of phenolphthalein is colourless but becomes red coloured on addition of KNH_2. ***[M.D. Rohtak 1994]***

(*v*) Liq. NH_3 exhibits association whereas liq. SO_2 does not. ***[M.D. Rohtak 1992, Punjab* 1996]**

(*vi*) Acetamide behaves as a base in aqueous solution but shows acidic properties in liq. NH_3.

(*vii*) HNO_3 acts as an acid in aqueous solution but in HF it behaves as a base. ***[H.P.W. 1997]***

(*viii*) CH_3COOH behaves as a base in HF but SbF_6 behaves as an acid in this solvent **[*Guru Nanak pev 1997*]**

(*ix*) Liq. NH_3 behaves as a differentiating solvent for NaH, $NaNH_2$ and $NaOC_2H_5$.

(*x*) Solution of sodium metal in liq. NH_3 is blue and has strong reducing property and high electrical conductance. **[*Punjab 1996*]**

Ans : (*i*) K_2SO_3 is soluble in liq. SO_2, since this compound forms a solvate, $K_2SO_3.\ SO_2$ (an addition compound) with liq. SO_2. This solvate contains one molecule of SO_2 as sulphur dioxide of crystallisation. In this solvate, K_2SO_3 acts as a solute.

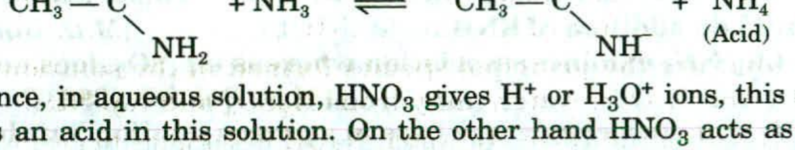
(*ii*) In the formation of solvates like $CaI_2.4SO_2$, $LiI_2.2SO_2$ etc, SO_2 donates electrons to the solutes and hence acts as Lewis base. In the formation of solvates like $C_5H_5N.SO_2$, $C_6H_7N.SO_2$. SO_2 accepts electrons from the solutes and hence acts as Lewis acid. Thus SO_2 acts both as a Lewis acid and as a Lewis base.

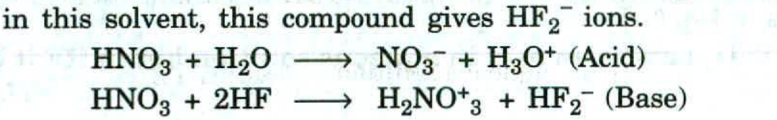
(*iii*) Since NH_4Cl gives NH_4^+ ions in liq. NH_3, this compound acts as an acid in this solvent. Due to the production of NH_4^+ ions, the concentration of these ions in liq. NH_3 increases. The increase of NH_4^+ ions increases the electrical conductivity of liq. NH_3.

(*iv*) Addition of KNH_2 to liq. NH_3 increases the concentration of NH_2^- ions and hence this solution behaves as an ammono base. As soon as the concentration of NH_2^- ions increases in solution, the solution behaves as a base and hence imparts red colour to phenolphathlein just as an aqueous basic solution imparts red (pink) colour.

(*v*) Due to small size and high electronegativity of N-atom, many molecules of liq. NH_3 get associated together through H-bonding. This type of association is not possible in case of liq. SO_2, since sulphur atom has bigger size. (N = 0.75 Å, S = 1.02Å) and lower electronegativity (N = 3.0, S = 2.5) than N-atom.

(*vi*) Since acetamide, CH_3CONH_2 gives OH^- ions in aqueous solution, this compound behaves as a base in water. On the other hand, since CH_3CONH_2 gives NH_4^+ ions in liq. NH_3, it behaves as an acid in this solvent.





(*vii*) Since, in aqueous solution, HNO_3 gives H^+ or H_3O^+ ions, this compound behaves as an acid in this solution. On the other hand HNO_3 acts as a base in HF, since, in this solvent, this compound gives HF_2^- ions.

$$HNO_3 + H_2O \longrightarrow NO_3^- + H_3O^+ \text{ (Acid)}$$
$$HNO_3 + 2HF \longrightarrow H_2NO^+{}_3 + HF_2^- \text{ (Base)}$$

(*viii*) CH_3COOH gives HF_2^- ions in HF by accepting H^+ ion.

$$CH_3COOH + 2HF \longrightarrow CH_3COOH_2^+ + HF_2^- \text{ (Base)}$$

SbF_5 ionises as an acid in HF by accepting F^- ion. Thus SbF_5 gives H_2F^+ ions

$$SbF_5 + 2HF \longrightarrow SbF_6^- + H_2F^+ \text{ (Acid)}$$

Here the self ionisation of HF can be noted as given below:

$$3HF \longrightarrow \underset{\substack{\text{Solvent cations}\\ \text{(Acid ions)}}}{H_2F^+} + \underset{\substack{\text{Solvent anions}\\ \text{(Base ions)}}}{HF_2^-}$$

(*ix*) When strong bases like NaH, $NaNH_2$ and $NaOC_2H_5$ react with H_2O (solvent), a proton is donated by H_2O molecule to these bases and NaOH is produced.

(a) $$H_2O + NaH \longrightarrow H_2 + NaOH$$

or $$\overbrace{H_2O + H^-}^{H^+} \longrightarrow H_2 + OH^-$$

(b) $$H_2O + NaNH_2 \longrightarrow NH_3 + NaOH$$

or $$\overbrace{H_2O + NH_2^-}^{H^+} \longrightarrow NH_3 + OH^-$$

(c) $$H_2O + NaOC_2H_5 \longrightarrow C_2H_5OH + NaOH$$

or $$\overbrace{H_2O + OC_2H_5^-}^{H^+} \longrightarrow C_2H_5OH + OH^-$$

Thus we see that these bases are levelled to the base strength of OH^- ions, and hence these bases cannot be differentiated as bases in aqueous solution. On the other hand, since liq. NH_3 is a poor proton donor, these bases can be differentiated as bases in liq. NH_3. Thus liq. NH_3 behaves as a differentiating solvent for NaH, $NaNH_2$ and $NaOC_2H_5$.

(*x*) Blue colour is due to an absorption band having its maximum at 5000Å. Strong reducing property and high electrical conductance shown by the solution of sodium in liq. NH_3 is due to the production of ammoniated cations, $[Na(NH_3)_x]^+$ and ammoniated electron, $[e\ (NH_3)_y]^-$.

$$Na \xrightarrow{\text{Liq. } NH_3} Na^+ + e^-$$

$$Na^+ + x\ NH_3 \longrightarrow [Na\ (NH_3)_x]^+$$

$$e^- + y\ NH_3 \longrightarrow [e\ (NH_3)_y]^-$$

Q.10 What are the principal species formed in the solutions of NaOH, $(NH_4)_2SO_4$ and H_2O in water, anhydrous H_2SO_4 and liq. NH_3?

Ans : NaOH (*a*) *In water* : In water, NaOH dissociates to give Na^+ and OH^- ions.

$$NaOH \xrightarrow{\text{Aqueous solution}} Na^+ + OH^-$$

(*b*) *In anhydrous H_2SO_4.* OH^- ions formed as above further react with H_2SO_4 to produce HSO_4^- and H_3O^+ ions.

$$OH^- + 2H_2SO_4 \longrightarrow 2HSO_4^- + H_3O^+$$

(*c*) *In liq.NH_3* : In liq. NH_3, no species are formed.

$(NH_4)_2SO_4$ (*a*) *In water* : NH_4^+ and SO_4^{2-} ions are formed.

$$(NH_4)_2SO_4 \xrightarrow{\text{Aqueous solution}} 2NH_4^+ + SO_4^{2-}$$

NH_4^+ ions formed as above react with H_2O to give H_3O^+ ions.

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H_3O^+$$

(*b*) *In anhydrous H_2SO_4*: NH_4^+ and SO_4^{2-} ions are obtained.

$$(NH_4)_2SO_4 \longrightarrow 2NH_4^+ + SO_4^{2-}$$

(*c*) *In liq.NH_3*: NH_4^+ and SO_4^{2-} ions are formed. Due to the production of NH_4^+ ions, the solution becomes acidic.

$$(NH_4)_2SO_4 \xrightarrow{\text{Liq. } NH_3} 2NH_4^+ + SO_4^{2-}$$

H_2O. (*a*) *In water* there will be no reaction

(*b*) *In anhydrous H_2SO_4.* Following reaction will occur.

$$H_2O + H_2SO_4 \longrightarrow HSO_4^- + H_3O^+$$

(*c*) *In liq. NH_3.* NH_4^+ ions will be obtained.

$$H_2O + NH_3 \longrightarrow NH_4^+ + OH^-$$

Q.11 Predict the behaviour of urea in water, liq. NH_3 and anhydrous H_2SO_4.

Ans : Urea is NH_2CONH_2.

In water : NH_2CONH_2 is expected to behave as a non-electrolyte.

In liq. NH_3 : NH_2CONH_2 behaves as a weak acid in liq. NH_3, since this compound produces NH_4^+ ion in this solvent.

$$NH_2CONH_2 + NH_3\,(l) \rightleftharpoons NH_4^+ + NH_2CONH^-$$

In anhydrous H_2SO_4 : When NH_2CONH_2 reacts with H_2SO_4, HSO_4^- ion is produced. Thus NH_2CONH_2 behaves as a base in H_2SO_4.

$$NH_2CONH_2 + H_2SO_4 \longrightarrow NH_2CONH_3^+ + HSO_4^-$$

University Questions

1. (*a*) Giving two examples in each, discuss the following reactions in liq. SO_2 (*i*) Acid - base reaction (*ii*) Precipitation reaction (*iii*) Complex formation reaction

   (*b*) Liq. SO_2 is a better solvent for organic liquids. Explain.

   (*c*) Write self - ionisation of liq. NH_3 by giving two examples.

   (*d*) In what respect is liq. NH_3 a better solvent than H_2O ?

   (*e*) Metal - liquid NH_3 solutions are good reducing agents. Explain.

   (*f*) Self ionisation reactions in H_2SO_4. (*Himachal Pradesh 2000*)

2. What are the advantages of non - aqueous solvents ? Discuss the following reactions occurring in liq. SO_2 medium. (*i*) Acid - base reactions (*ii*) Precipitation reactions (*iii*) Complex formation reactions. (*Kumaon 2000*)

3. How are solvents classified ? Taking liq. NH_3 as solvent, explain the following reactions and point out the differences from water as solvent (*i*) Precipitation reactions (*ii*) Solvolysis reactions (*iii*) Neutralisation reactions (*iv*) Solubility of alkali metals. (*Lucknow 2000*)

4. (*a*) Discuss in detail the classification of solvents.
  (*b*) Discuss the following in liquid NH_3 and liquid SO_2.
    (*i*) Oxidation-reduction reaction.
    (*ii*) Precipitation reaction. (*Nagpur 2002*)

5. Compare the self-ionisation of water, liq. NH_3 and anhydrons acetic acid.

(*Delhi 2002*)

6. (*a*) Predict the behaviour of the following solutes in liquid SO_2 :
    (*i*) $SOCl_2$ (*ii*) CS_2SO_3 (*iii*) $(CH_3)_4\ N^+\ Br^-$.
  (*b*) Predict the solubility of the following soultes in liquid SO_2.
    (*i*) NH_4SCN (*ii*) Na_2S.
  (*c*) Cmplete the following equations :
    (*i*) $PbI_2 + KNH_2 \xrightarrow{NH_3}$ ....
    (*ii*) $SO_2\ Cl_2 + NH_3 \xrightarrow{NH_3}$ .... (*Delhi 2002*)

7. (*a*) Explain chemical reactions in non-aqueous solvents with reference to those orruring in liq. NH_3.
  (*b*) Discuss the role of non-protonic solvents in chemical reactions with special refrence to the reactions occuring in liquid SO_2. (*VBS, Purvanchal 2003*)

8. (*a*) What is meant by protic and aprotic solvents ? Give examples.
  (*b*) Give only one example for each of the following in liquid sulpher dioxide:
    (*i*) Acid-base reaction (*ii*) Redox reaction (*iii*) Precipitation reaction (*iv*) Complex formation reaction (*v*) Reaction with organic compounds. (*Rohidkhand 2003*)

9. Explain the following reaction which take place in liq. SO_2 as medium :
  (*i*) Acid base reactions (*ii*) Precipitation reactions. (*Delhi 2003*)

10. (*a*) Classify the solvents on the basis of their proton-donor and proton-acceptor property. Give the following reaction in liquid NH_3.
    (*i*) Redox reaction (*ii*) Precipitation reaction.
  (*b*) Give the following reactions in liquid SO_2.
    (*i*) Solvolysis (*ii*) Complex formation. (*Nagpur 2003*)

11. (*a*) Write notes on (in non-aqueous solvent)

(*i*) Ammonolysis (*ii*) Acid-base reactions (*iii*) Redox reactions

(*b*) What are non-aqueous solvents ? Explain the following reactions in liquid HF.

(*i*) Auto ionisation reaction (*ii*) Precipitation reaction (*iii*) Solvation reactions (*iv*) Reaction with C_2H_5OH. (*Bhopal 2004*)

12. What do you understand by ionising and non-ionising solvents ? Give examples. (*GND Amritsar 2004*)

13. Discuss acid-base reaction in liq. SO_2 and metathetical reactions in liq. HF. (*GND Amritsar 2004*)

14. How do the following reactions proceed ?

(*i*) $HgI_2 + KNH_2 \xrightarrow{NH_2}$ ...... (*ii*) $Cs_2SO_3 + SOCl_2 \xrightarrow{SO_2}$ ....

(*GND Amritsar, 2004*)

15. (*a*) Write down the nature of products when AgCl is treated with $Ba(NO_3)_2$ in liq. NH_3.

(*b*) Complete the reaction :

$Zn(C_2H_5)_2 + 2SO_2\,(l) \rightarrow$ ...... (*C.S.J.M Kanpur, 2005*)

16. (*a*) Which of the following are protonic solvents : Liq. SO_2, C_6H_6, H_2SO_4, Liq. NH_3, HF ?

(*b*) What the advantages and disadvantages of liq. NH_3 as a solvent ? Using chemical equations illustrate the following types of reactions in liq. NH_3 : Complex formation and precipitation.

(*H.N. Bahuguna 2005*)

17. Explain amphoteric substances in a non-aqueous solvent.

(*C.S.J.M. Kanpur 2006*)

18. What are the advantages of non-aqueous solvents ? Discuss the following reactions occuring in liq. SO_2 medium. Acid-base reactions, precipitation reactions and complex formation reactions. (*H.N. Bahuguna 2006*)

19. Discuss the chemistry of liq. NH_3 as a solvent. What are the advantages and disadvantages of liq. NH_3 as a solvent. (*C.S.J.M. 2007*)

20. Explain the classification of non-aqueous solvents and describe their important characteristics. (*Agra 2007*)

21. (*a*) Which of the following is an amphoteric solvent : H_2SO_4, HCl, H_2O, $CHCl_3$?

(*b*) What are non-aqueous solvents ? Explain different types of chemical reactions in liq. NH_3 or in liq. SO_2. (*Agra 2008*)

22. (*a*) Which of the following is a non-aqueous solvent ? Liq. NH_3, Liq. SO_2, Liq HF.

(*b*) Write the following reactions with examples in liq. SO_2. Pricipitation, acid base neutralisation and solvolysis. (*H.N Bahuguna 2008*)

23. What do you mean by solvation and solvolysis in non-aqueous solvents. Explain in liq. NH_3. (*Gurukul Kangri 2008*)

CHAPTER

14

Principles and Processes of Metallurgy

What are Minerals and Ores ?

Metals occur in nature sometimes *free* (*i.e., in uncombined state*) but mostly in the *combined state* (*i.e., as compounds with other elements*). When a metal is found free or in uncombined state it is said to occur as **native.** Metals found in the native state are copper, silver, gold, mercury and platinum. Others are found in the combined state.

The natural materials found in the earth in which the metals occur in the combined state are called **minerals.** *Those minerals from which the metals may be extracted conveniently and economically are called* **ores.** *Thus all the ores are minerals but all the minerals are not ores.* For example, all clays contain aluminium but these are not ores of aluminium, since the extraction of aluminium metal from these clays is too much coumbersome and not economically worthwhile.

What is Mining ?

The process of taking out the ores from mines is called **mining.**

Occurrence of Metals in Nature

Most metals occur in the combined state. Only those metals which have little or no affinity for oxygen, moisture and other chemical reagents occur in the *free* (or *metallic* or *native*) *state*. Thus : (1) *In native state*. Examples are Ag, Au, Pt (2) *As oxide*. Examples are : bauxite, Al_2O_3; tin stone, SnO_2 ; rutile TiO_2 (3) *As carbonate*. Examples are : magnesite, $MgCO_3$; lime stone, $CaCO_3$ calamine, $ZnCO_3$ (4) *As sulphate*. Examples are : gypsum, $CaSO_4 . 2H_2O$; calestine, $SrSO_4$; barytes, $BaSO_4$ (5) *As silicate*. Examples are : beryl, $3\ BeO . Al_2O_3 . 6\ SiO_2$; spodumene, $LiAl\ (SiO_3)_2$ (6) *As phosphate*. Examples are : amblygonite, $LiF. AlPO_4$; triphylite, $(Li, Na)\ PO_4 . (Fe, Mn)_3\ (PO_4)_2$ (7) *As sulphide*. Examples are : galena, PbS; zinc blende, ZnS; cinnabar, HgS (8) *As halide*. Examples are : rock salt, NaCl; carnallite, $KCl.MgCl_2 . 6H_2O$; horn silver, AgCl.

Occurrence of Metals in India

India is fortunate to have rich mineral resources. This statement is true, since our country is gifted by nature with rich mineral resources. Some common minerals and the places of their occurrence are given in Table 14.1.

What is Metallurgy?

The process of extracting the metals from their ores and refining them is called **metallurgy.**

Table 14.1. Some common minerals and the places of their occurrence in India

Metal	Minerals found in India	Places of occurrence in India
Lithium	Lepidolite or lithium mica, (Li, Na, K)$_2$, Al$_2$ (SiO$_3$)$_3$.(F.OH)$_2$	Bihar, Rajasthan, Mysore and Kashmir
Sodium	Tincal or native borax, $Na_2B_4O_7.10H_2O$	Laddakh and Kashmir
Potassium	Nitre or Indian salt petre, KNO_3	Arid regions of Haryana and Bengal
Beryllium	Beryl, $3BeO.Al_2O_3.6SiO_2$	Bihar, Orissa, Nellore (Tamil Nadu) and Ajmer-Marwara (Rajasthan)
Magnesium	(*i*) Dolomite, $MgCO_3.CaCO_3$ (*ii*) Magnesite, $MgCO_3$	Both the ores occur in Salem (Madras)
Calcium	(*i*) Gypsum, $CaSO_4.2H_2O$	Jodhpur, Bikaner, Nagpur and Jaisalmer districts of Rajasthan, Trichirapalli and Coimbatore districts of Tamil Nadu and Dode and Baramulla districts of Jammu and Kashmir
	(*ii*) Lime stone (chalk or marble), $CaCO_3$	Jaipur and in some places of Madhya Pradesh
	(*iii*) Fluorspar, CaF_2	Near Jabbalpur
Barium	Barytes or heavy spar, $BaSO_4$	Alwar and Kurnool
Boron	Borax, $Na_2B_4O_7.10H_2O$	In Ladakh and Puga Valley of Kashmir
Aluminium	Bauxite, $Al_2O_3.2H_2O$	In Katni, Kolahpur, Rawa, Orissa, Jabbulpure and Balurghat district, Madras and Jammu
Tin	Tinstone, SnO_2	Hazaribagh (Bihar) and Orissa
Lead		India has no important deposits of lead ores. Recently lead ores have been located at Zawar mines near Udaipur (Rajasthan) and at Hazaribagh (Bihar)
Antimony	(*i*) Stibnite, Sb_2S_3	In small quantities in Punjab and Mysore
	(*ii*) Cu-Sb sulphide	In Madhya Pradesh
Copper	(*i*) Chalcopyrites or copper pyrites, $CuFeS_2$	Bihar, Orissa, Madhya Pradesh
	(*ii*) Malachite, $Cu(OH)_2.CuCO_3$	Singbhum, Hazaribagh, Jabalpur, Salimabad.
Silver		Gold from Kolar fields and Huthi mines (Karnataka) and lead and zinc ores of Zawar mines (Rajasthan) contain some silver
Gold	Native	Found in the free state in Karnataka, Andhra Pradesh in the alluvial sands of the Ganga, the Brahamputra and the Irrawaddy
Zinc	Zinc blende, ZnS	Zewar zinc mines near Udaipur (Rajasthan) containing 8—10% of Zn and 5% of Pb

Cadmium		Found in the zinc ore of Anji Valley of Kashmir to the extent of 0.175%
Chromium	Chromite or chrome iron ore, $FeO.Cr_2O_3$	Occurs in Karnataka, Bihar and Orissa, near Salem in Tamil Nadu and in the Andaman Islands
Manganese	Pyrolusite, MnO_2	Found in Panch Mahal (Bombay), Karnataka and Singbhum (Bihar)
Iron	Haematite, Fe_2O_3	In Mayurbhanj, Singbhum and Mysore
Cobalt	Cobaltite or cobalt glance, (Co, Fe) AsS	Found at Khetri
Nickel	Smaltite, (Fe, Co, Ni) As_2	Mixed with copper ores at Khetri and with gold bearing rocks of Kolar and Travancore

The process used for the metallurgy (*i.e.* extraction) of a metal depends on the nature of the ore from which the metal is being extracted and also on the properties of the metal. *Thus it is not possible to chalk out a universal method for the extraction of all the metals.*

Various Steps of Metallurgy

Various steps used in the metallurgy of metals from their respective ores are discussed below :

1. Grinding or Crushing the Ore

The rock ores after mining are generally obtained as big lumps. These lumps of the ore are crushed to smaller pieces by *hammering* or by means of *jaw-crusher* and *grinders.*

The jaw-crusher consists of two plates forming a sort of jaw. One of the plates is fixed and the other is movable. The lumps of the ore are put in between the plates and movable plate moves with the help of a mechanical device. The crushed ore is collected below. (See Fig. 14.1).

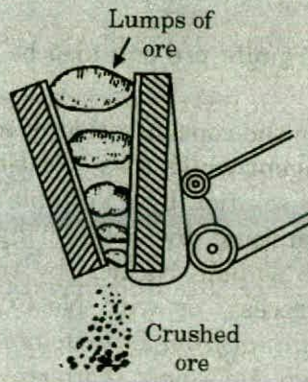


Fig. 14.1. A jaw-crusher used to crush the ore.

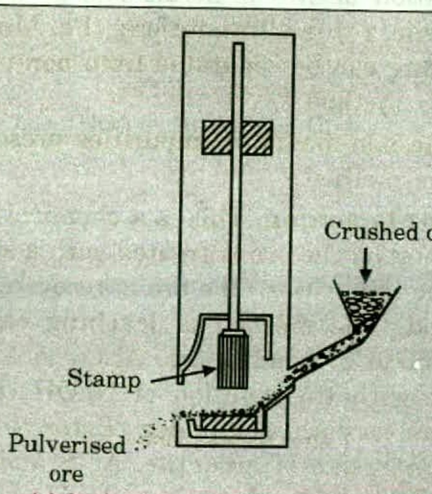


Fig. 14.2. A stamp mill used to pulverise the crushed pieces of the ore.

2. Pulverising the Ore

The crushed pieces of the ore are then taken to *stamp mills* or *pulverisers* in which the crushed pieces of the ore are finely powdered. The coarse ore is fed into the stamp mill from one side (See Fig. 14.2) and the fine powder is taken out by means of a stream of water. Sometimes ball mills are also employed for pulverisation.

3. Concentration of the Ore : Ore-dressing

Generally the ores are contaminated with impurities of earthy matter like sand, clay, lime stone etc. These impurities present in the ore are called **gangue** *or* **martix.** The *removal of these foreign impurities from the ore is called* **concentration** or **ore-dressing** and *the purified are is called* **concentrate.** The concentration is generally carried out by any of the following processes :

(*i*) **Hand picking.** When the impurities present are quite distinct from the ore so as to be easily differentiated with eye, picking by hands is done. This is done usually in the initial stage of concentration.

(*ii*) **Wilfley table and hydraulic classifier methods.** Both these methods are collectly called *gravity separation method*. Both are used for the concentration of *dense ores* like tin stone, SnO_2 (an ore of tin), haematite, Fe_2O_3 (an ore of iron) and are based on the difference in the densities of the gangue particles (*i.e.* impurity particles) and the ore particles.

(*iii*) **Froth flotation process.** This method is commonly used for the concentration of the low grade sulphide ores like *gelana*, PbS (ore of Pb), *copper pyrites*, CuS.FeS (ore of Cu) and *zinc blende*, ZnS (ore of Zn) and is based on the fact that *gangue and ore particles have different degree of wettability with water and oil (e.g. pine oil)—the gangue particles are preferentially wetted by water while the ore particles are wetted by oil.*

(*iv*) **Electromagnetic separation method.** This method is used for the separation of two minerals one of which is magnetic while the other is non-magnetic, *e.g.* wulframite ore, (Fe, Mn)WO_4 (ore of tungsten) which is magnetic in nature can be separated from non-magnetic tin stone ore, SnO_2 (an ore of tin) by this method.

The non-magnetic impurities present in wolframite ore can also be removed by this method.

(*v*) **Leaching.** This is a chemical method for the concentration of an ore. In this method the ore is treated with a suitable reagent which dissolves the ore but not the impurities. The ore is recovered from the solution by a suitable chemical method. The method of leaching can be understand by considering (*a*) the conversion of bauxite ore, Al_2O_3 (ore of Al) into soluble $NaAlO_2$ by treating it either with the solution of NaOH (Baeyer's process) or with Na_2CO_3 (Hall's process) as discussed under. *"Extraction of Aluminium from Bauxite ore"*, and (*b*) the conversion of argentite, Ag_2S and born silver, AgCl ores (both are the ores of Ag) into soluble $Na[Ag(CN)_2]$ by treating them with an aqueous solution of NaCN as discussed under "*Extraction of silver*".

4. Conversion of the Concentrated Ore into Metallic Oxide : Calcination and Roasting.

The conversion of the concentrated ore into the metallic oxide is done by the following methods :

(*i*) **Calcination.** *Calcination is a process in which the ore is heated strongly in the absence of air.* The process does the following things :

(*a*) It removes the volatile impurities like CO_2, SO_2, organic matter, moisture from the ore.

(*b*) It removes water from the hydrated oxide ore, *e.g.*

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} \xrightarrow{\text{Calcination}} \underset{\substack{\text{Anhydrous}\\\text{aluminium oxide}}}{Al_2O_3} + 2H_2O$$

$$\underset{\text{Limonite}}{2Fe_2O_3.3H_2O} \xrightarrow{\text{Calcination}} \underset{\substack{\text{Anhydrous}\\\text{iron oxide}}}{2Fe_2O_3} + 3H_2O$$

(*c*) It removes CO_2 from a carbonate ore, *e.g.*

$$\underset{\text{Lime stone}}{CaCO_3} \xrightarrow{\text{Calcination}} \underset{\text{Calcined oxide}}{CaO + CO_2}$$

$$\underset{\text{Malachite}}{Cu(CO_3).Cu(OH)_2} \xrightarrow{\text{Calcination}} \underset{\text{Copper oxide}}{2CuO} + CO_2 + H_2O$$

$$\underset{\text{Dolomite}}{CaCO_3.MgCO_3} \xrightarrow{\text{Calcination}} CaO + MgO + 2CO_2$$

Calcination is generally done in a *reverberatory furnace.*

(*ii*) **Roasting.** *Roasting is a process in which the ore (usually the sulphide ore) is heated strongly in the presence of excess of air. The heating should be done at a temperature below the melting point of the ore.* This process does the following things :

(*a*) It dries the ore.

(*b*) The volatile impurities like CO_2, SO_2 organic matter, moisture are all driven off.

(*c*) The ore is converted into metallic oxide which can easily be reduced to the metal. For example :

$$\underset{\text{Gelana}}{2PbS} + 3O_2 \xrightarrow{\text{Heat}} 2PbO + 2SO_2$$

$$\underset{\text{Cinnabar}}{2HgS} + 3O_2 \xrightarrow{\text{Heat}} 2HgO + 2SO_2$$

$$\underset{\text{Zinc blende}}{2ZnS} + 3O_2 \xrightarrow{\text{Heat}} 2ZnO + 2SO_2$$

$$\underset{\text{Copper glance}}{2Cu_2S} + 3O_2 \xrightarrow{\text{Heat}} 2Cu_2O + 2SO_2$$

Sometimes sulphide ores which are *insoluble* are converted into the corresponding sulphates which are *water soluble*. For example :

$$\underset{\text{(Insoluble)}}{CuS} + 2O_2 \xrightarrow{\text{Heat}} \underset{\text{(Soluble)}}{CuSO_4}$$

$$\underset{\text{(Insoluble)}}{ZnS} + 2O_2 \xrightarrow{\text{Heat}} \underset{\text{(Soluble)}}{ZnSO_4}$$

$$\underset{\text{(Insoluble)}}{PbS} + 2O_2 \xrightarrow{\text{Heat}} \underset{\text{(Soluble)}}{PbSO_4}$$

Roasting is generally done in a *reverberatory furnace* or in a *sinterer* (*or suction reaster*) or in a *blast furnace*.

5. Extraction of the Metal from Roasted or Calcined Ore.

The metal can be obtained from the roasted or calcined ore by any of the following methods :

(*i*) **Carbon reduction method : Smelting.** This method is used for the extraction of Pb, Zn, Fe, Cu and Sn. *Smelting is a process in which the oxide ore in the fused state is reduced by carbon to the free metal. In other words the extraction of a metal from its oxide ore by a process involving melting is called smelting.*

In this method the roasted oxide ore is mixed with carbon (charcoal, coal or coke) and a *flux* (*see below*) and then heated to a high temperature in a suitable furnace. Carbon reduces the oxide ore to the free metal. For reducing cassiterite ore, SnO_2 (an oxide ore of tin) powdered anthracite is used as a reducing agent. The metal obtained may be in the form of vapours (*e.g.* Zn) which are then condensed or in the form of molten metal (*e.g.* Fe, Sn). Examples illustrating the process of smelting are given below :

$$ZnO + C \xrightarrow{\Delta} Zn + \underset{\text{Vapours}}{CO}$$

$$\underset{\text{Cassiterite}}{SnO_2} + \underset{\substack{\text{Powered}\\\text{anthracite}}}{2C} \longrightarrow \underset{\substack{\text{Molten}\\\text{metal}}}{Sn} + 2CO$$

$$PbO + C \xrightarrow{\Delta} Pb + CO$$

$$\underset{\text{Heamatite}}{Fe_2O_3} + 3C \xrightarrow{\Delta} 2Fe + 3CO$$

$$CuO + C \xrightarrow{\Delta} Cu + CO$$

Usually the process of smelting is carried out in reverberatory furnace or blast furnace in a controlled supply of air.

In case of metals like Zn which are volatile, smelting cannot be carried out in an open furnace. It is rather done in a fire-clay vertical retorts in which heating is done by producer gas.

A flux *is a substance which is added to the furnace charge (roasted or calcined oxide ore and coke) during the process of smelting to remove the non-fusible impurities of earthy matter (e.g. metallic oxides, silica, silicates etc.) present in the roasted or calcined oxide ore.*

During smelting flux combines with the non-fusible impurity to convert it into a fusible material known as **slag.** Being light, the slag floats over the molten metal from where it can be removed. The slag is a material with low melting point. At high temperature the slag is a liquid which is insoluble in the molten metal.

Thus we see that *the function of flux is to remove the non-fusible impurity as fusible slag.* Fluxes are of two types :

(*a*) *Acidic fluxes* like *silica, borax etc.* which are added to remove *basic impurities* (*e.g.* metallic oxides like CaO, FeO) as fusible slag.

$$\begin{array}{ccccc} \textit{Basic impurity} & & \textit{Acidic flux} & & \textit{Fusible slag} \\ CaO & + & SiO_2 & \longrightarrow & CaSiO_3 \\ FeO & + & SiO_2 & \longrightarrow & FeSiO_3 \end{array}$$

(*b*) Basic *fluxes* like *lime stone* ($CaCO_3$), *magnesite* ($MgCO_3$), *haematite* (Fe_2O_3) etc. which are added to the furnace charge to remove the acidic impurities (*e.g.* silica, silicates etc.) as fusible slag.

$$\underset{\text{Acidic impurity}}{SiO_2} + \underset{\text{Basic flux}}{MgCO_3} \longrightarrow \underset{\text{Fusible slag}}{MgSiO_3} + CO_2$$

(*ii*) **Carbon monoxide reduction method.** In some cases CO gas produced in the furnace itself is used as a reducing agent, *e.g.*

$$Fe_3O_4 + 4CO \xrightarrow{\Delta} 3Fe + 4CO_2$$

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} \underset{\text{Molten metal}}{2Fe} + 3CO_2$$

$$PbO + CO \xrightarrow{\Delta} Pb + CO_2$$

$$CuO + CO \xrightarrow{\Delta} Cu + CO_2$$

(*iii*) **Hydrogen reduction method.** H_2 gas has also been used as a reducing agent. For example :

$$WO_3 + 3H_2 \xrightarrow{\Delta} W + 3H_2O$$

$$MoO_3 + 3H_2 \xrightarrow{\Delta} Mo + 3H_2O$$

$$GeO_2 + 2H_2 \xrightarrow{\Delta} Ge + 2H_2O$$

(*iv*) **Magnesium reduction method.** Oxides of some metals are reduced by Mg, *e.g.*

$$Rb_2O_3 + 3Mg \longrightarrow 3MgO + 2Rb$$

Ti is obtained by the reduction of $TiCl_4$ by Mg in an inert atmosphere of argon.

$$TiCl_4 + 2Mg \xrightarrow{\Delta} Ti + 2MgCl_2$$

(*v*) **Aluminium reduction method : Alumino-thermic method.** Certain metallic oxides cannot be reduced by carbon because the affinity of oxygen for the metal is greater than its affinity for carbon. Such metallic oxides can be reduced with the help of aluminum powder. The reduction of a metallic oxide into metal by Al powder is called *alumino-thermic process* and this process has been used to reduce TiO_2, Cr_2O_3 and Mn_3O_4 oxides into Ti, Cr and Mn metals respectively. The details of this process can be studied from "*Extraction of Cr metal from chromite ore, $FeO.Cr_2O_3$*" discussed in chapter 46.

Sr and Ba are obtained by the reduction of their oxides by Al in vacuo.

(*vi*) **Self-reduction method.** This method is also called *auto-reduction method* or *air-reduction method*. If the sulphide ores of some of the less electropositive metals like Hg, Cu, Pb, Sb etc. are heated in air, a part of these sulphide ores is changed into the oxide or sulphate which then reacts with the remaining part of the sulphide ore to give the metal and SO_2. The reactions illustrating the extraction of Hg, Cu and Pb from their sulphide ores are given below :

(*a*) $\underset{\text{Cinnabar}}{2HgS} + 3O_2 \longrightarrow 2HgO + 2SO_2$

$2HgO + HgS \longrightarrow 3Hg + SO_2$

(*b*) $Cu_2S + 3O_2 \longrightarrow 3Cu_2O + 2SO_2$

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

(*c*) $\underset{\text{Galena}}{2PbS} + 3O_2 \longrightarrow PbO + 2SO_2$

$2PbO + PbS \longrightarrow 3Pb + SO_2$

The extraction of Pb by heating its sulphide ore (PbS) in air can also be represented as :

$$PbS + 2O_2 \longrightarrow PbSO_4$$
$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$$

(*vii*) **Electrolytic reduction method.** The oxides of the active metals like alkali metals, alkaline earth metals, Al, Zn etc. are very stable and hence in order to reduce their oxides to the free metal, the oxides have to be heated at high temperature with carbon. But at high temperature these metals combine with carbon to form the metallic carbides. Thus such metals cannot be extracted by reducing their oxides with carbon. These are however, extracted by the electrolysis of their oxides, hydroxides or chlorides in the fused state. The metal is liberated at the cathode.

Some other salt may have to be added to lower the melting point of the compound taken.

As an example we may consider the manufacture of sodium metal by the electrolysis of a fused mixture of NaCl and $CaCl_2$ (*Down's process*). Various reactions taking place in the electrolytic cell are :

Fusion : $NaCl \rightleftarrows Na^+ + Cl^-$

These ions are mobile and hence go to the electrodes.

Electrolysis : (*a*) *At cathode (Negative electrode)*

$$Na^+ + e^- \longrightarrow Na \text{ (Reduction)}$$

(*b*) *At anode (Positive electrode)*

$$Cl^- \longrightarrow Cl + e^- \text{ (Oxidation)}$$

$$Cl + Cl \longrightarrow Cl_2 \uparrow$$

(*viii*) **Amalgamation process.** This process is used for the extraction of noble metals like silver and gold from their native ores. This process is based on the fact that noble metals dissolve in Hg and form amalgams. Hence the name *amalgamation process*. In this process the mixture of finely powdered ore and water, known as **slurry,** is allowed to flow over copper or brass plates coated with mercury and arranged in a slanting position. The metal particles form an amalgam with Hg and are retained on these plates. The amalgam is scrapped off from the plates and distilled in iron retorts, when mercury distills over leaving the free metal behind.

(*ix*) **Hydro-metallurgy process : Wet process.** In this method concentrated ore is leached with aqueous solution of some suitable chemical reagent whereby the metal is obtained in the form of its soluble salt. The metal is then recovered from this salt solution either by its electrolysis or by adding some electropositive metal to it when the metal to be extracted is obtained as a precipitate. This process is illustrated by the following examples :

(*a*) **Extraction of Cu.** A large heap of *copper glance ore*, Cu_2S is exposed to air and water. In about a year the ore is oxidised to $CuSO_4$. The solution of $CuSO_4$ is either electrolysed or scrap iron is added to it to get Cu as a precipitate.

$$\underset{\text{Copper glance}}{2Cu_2S} + 5O_2 \longrightarrow \underset{\text{Solution}}{2CuSO_4} + 2CuO$$

$$CuSO_4 + \underset{\text{Scrap iron}}{Fe} \longrightarrow FeSO_4 + \underset{\text{ppt.}}{Cu}$$

(*b*) **Extraction of Ag and Au.** For this see the conversion of argentite, Ag_2S or horn silver, AgCl (both are the ores of Ag) and gold into soluble Na $[Ag(CN)_2]$ and $Na[Au(CN)_2]$ complex compounds respectively by the use of an aqueous solution of NaCN as discussed in chapter 46.

6. Purification or Refining of Metals

The metals obtained by any of the methods described above need further purification as they may contain other metals, dissolved oxides, carbon, phosphorus, etc. as impurities.

The refining of metals is done in many ways depending upon the nature of the metal concerned. The common refining methods are :

(*i*) **Liquation.** This method is used to concentrate as well as to purify the metals like Bi, Sn, Pb, Hg, etc. whose melting points are lower than those of the impurities. Impure metal like tin or lead is placed on the sloping hearth of a reverberatory furnace. On being heated to a temperature slightly above its melting point, the metal flows down the hearth while the impurities are left behind on the hearth.

(*ii*) **Distillation.** Metals with low boiling points such as zinc, cadmium, mercury and bismuth can be separated from most impurities by distilling the impure metal in a retort. The vapours of the metal so produced are condensed in a suitable receiver while the impurities are left behind in the retort.

(*iii*) **Oxidation.** The method is used when the impurities present in the metal have a greater affinity for O_2 and are more readily oxidised than the metal. This method is usually employed for refining the metals like Pb, Ag, Cu, etc. In this method the molten impure metal is subjected to oxidation by various ways as given below :

(*a*) **Cupellation process.** In this process the molten impure metal is heated in a cupel (boat shaped dish made of bone ash or cement) and a blast of air is passed over the molted metal. The impurities are oxidised and the volatile oxides thus produced escape with the blast of air. The pure metal remains behind in the cupel. For example, the impurity of lead present in silver is removed by cupellation process.

(*b*) **Bessemerisation.** In this oxidation method the impure molten metal is heated in specially designed furnaces and a blast of compressed air is blown through the molten metal. Molten pig iron is purified by this method. The molten pig iron from the blast furnace is taken in a Bessemer converter and the impurities present in it are oxidised by a blast of compressed air (See "*Manufacture of steel by Bessemer's process*" discussed in chapter 46)

(*iv*) **Poling.** The impure metal containing oxide impurities can be purified by this method. It is melted and stirred with green poles of wood. Hydrocarbon gases escaping from the poles act as reducing agents and reduce the oxide impurities.

This method has been used for the purification of copper metal as discussed under "*Extraction of copper from copper pyrites.*"

(*v*) **Electrolytic method.** Large number of metals like copper, silver, gold, nickel and zinc are purified by this method. The impure metal is made the anode while the thin sheet of pure metal acts as the cathode. The electrolyte is generally an aqueous solution of a salt or a complex of the metal. On passing the electric current, the pure metal starts depositing on the cathode through the solution. The soluble impurities pass in the solution while the insoluble low electropositive impurities collect below the anode as **anode mud** or **anode sludge.** The valuable metals can be recovered from the anode mud.

The method can be understood by studying the purification of copper as discussed under "*Extraction of copper from copper pyrites.*"

(*vi*) **Vapour phase method.** Impure metal is converted to a stable volatile compound taking care that the impurities remain unaffected. The compound produced is then decomposed to obtain the pure metal. Titanium, zirconium and nickel have been purified by this method. The method based on the vapour phase technique used for the purification of Ti and Zr metals is called *Van Arkel method* while that used for the purification of Ni metal is called *Mond's process.* These processes have been discussed under the extraction of these metals at their proper places.

(*vii*) **Zone refining method.** The method of zone refining (also called **fractional crystallization** method) is used to obtain metals of very high purity. It is based on the principle that when impure molten metal begins to solidify, the pure substance crystallises while impurities remain in the liquid. In actual practice the process is carried in an apparatus shown in Fig. 14.3. An impure metal rod is surrounded by a circular heater over a small portion. Here the substance melts. The heater is slowly moved along the rod. As the heater moves along the rod, the pure metal crystallizes out of the melt while the impurities pass into the adjacent molten zone. The process is repeated several times when the impurities are completely swept into one end of the rod which is finally discarded. Semiconductors, silicon, germanium and gallium are purified by this method. This process is carried in an inert atmosphere to prevent oxidation of the metal.

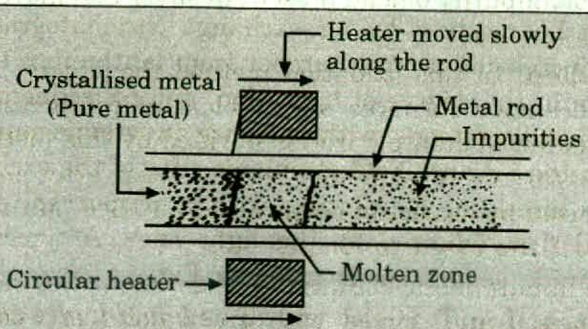


Fig. 14.3. Zone refining apparatus.

(*viii*) **Chromatography method.** The principle of separation or purification by chromatography is that the various components in a mixture are differentially adsorbed on a suitable adsorbent. In column chromatography, an adsorbent like alumina (Al_2O_3) is packed in a glass column. The mixture to be separated or purified (taken in a solvent) is poured on the top of the column. The components are then eluted out stepwise by a suitable eluant (solvent). The weakly adsorbed component is eluted out first followed by more strongly adsorbed components (Fig. 14.4).

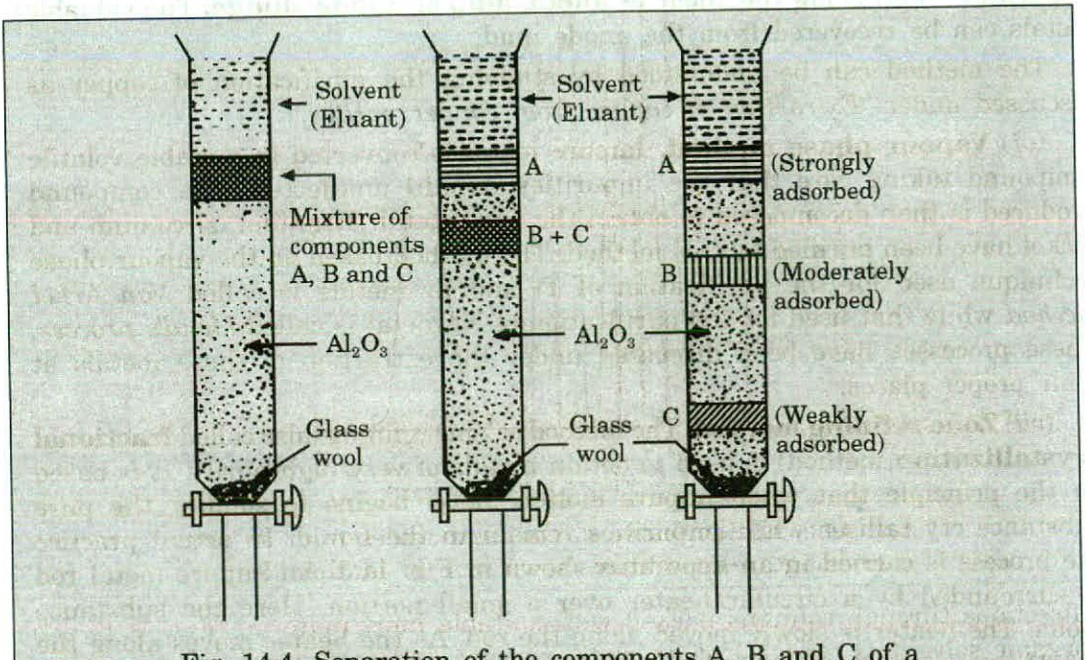


Fig. 14.4. Separation of the components A, B and C of a mixture by column chromatography.

Similarly, in ion-exchange chromatography an ion-exchanger (insoluble organic or inorganic solid containing cationic or anionic groups) capable of undergoing exchange reactions with other ions present in solution is used.

Lanthanides can be resolved by ion-exchange chromatography. Their ionic radii *decrease* with increasing atomic number from lanthanum to lutetium. This gives rise to *increase* in the degree of hydration, and consequent *increase* in the hydrated radii of lanthanide ions with increase in atomic number. Thus, the tendency with which the ions are held at anionic sites of the exchanger *decreases* from lanthanum to lutetium. By eluting with a proper solvent, the heavier members are eluted first followed by the light ones. A typical elution curve depicting the lanthanide separation is given in Fig. 14.5.

(*ix*) **Solvent extraction.** It is also known as *liquid-liquid counter extraction* method. In this method, the metal solution (usually in water) is treated with a suitable solvent (usually an organic liquid) which is immiscible with the metal solution but acts as a better solvent for the metal. In the continuous process of counter extraction, the metal solution and the solvent are made to flow in opposite

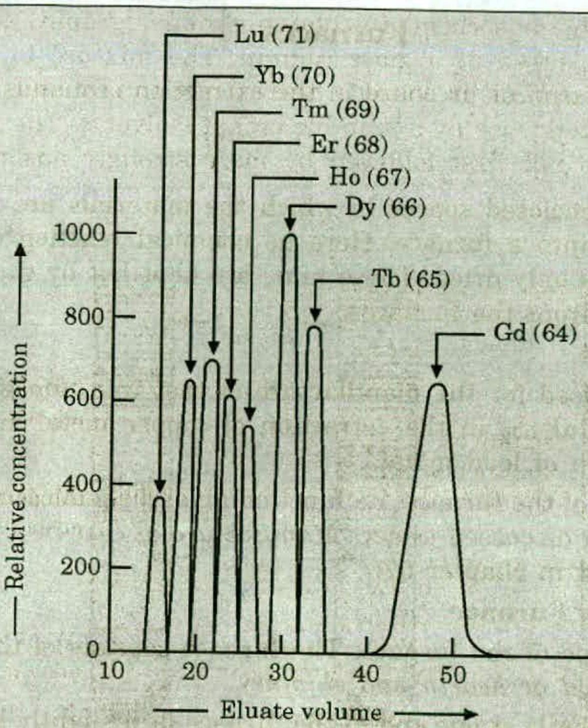


Fig. 14.5. Elution curve of the lanthanides from an ion exchange resin column (separation of lanthanides).

directions through columns packed with suitable inert material (Fig. 14.6). The organic solvent is stripped of its metal content and recycled.

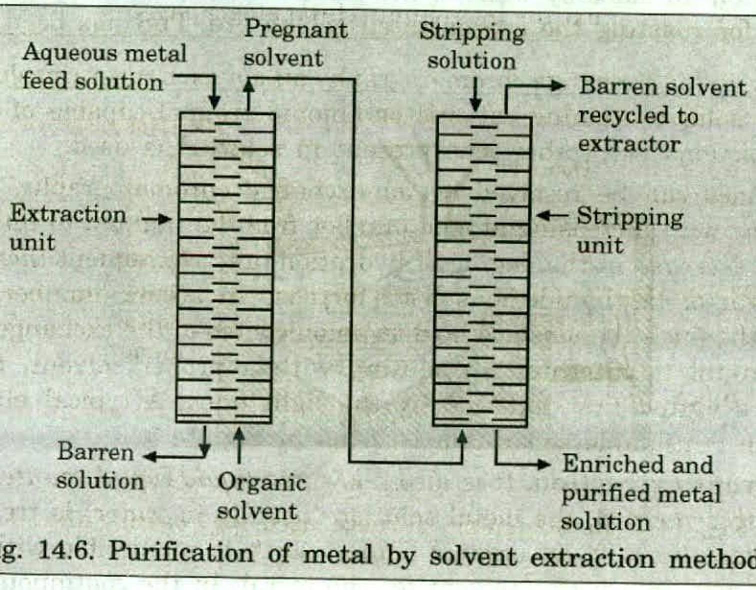


Fig. 14.6. Purification of metal by solvent extraction method.

Uranium and plutonium are purified and separated from each other and from other fission products by this method.

Furnaces

Several types of furnaces are used in the extraction of metals. Some of them are discussed below :

1. Kilns

These are large enclosed spaces in which the materials are mixed together before they are put into a furnace. Here no chemical reaction or fusion takes place. Here the ore is only dried. These kilns are kept hot by waste gases or by waste fuel obtained from the furnaces.

2. Blast Furnace

This furnace is used for the manufacture of cast iron, for smelting roasted copper pyrites ore, $CuFeS_2$ in the extraction of copper metal and for smelting PbO in the extraction of lead metal.

The construction of the furnace, its functioning and chemical reactions taking place in it have been discussed under *"Manufacture of cast iron from haematite ore, Fe_2O_3"* discussed in chapter 52.

3. Reverberatory Furnace

It is a special type of the furnace. The furnace consists of three main parts namely *fire place, bed or hearth* and *chimney.*

The fire place is built at one end of the furnace at a slightly lower level than that of the hearth and is closed at the bottom by fire-bars on which the fuel is placed and burnt. It is covered by a low roof which is made slanting and connects towards the other end with the chimney (flue). The hot gases (waste gases) from the fire place are reflected by the concave ceiling over the hearth. The furnace is surrounded on all sides by walls of fire-bricks. The sketch of a reverberatory furnace used for roasting the concentrated gelana ore, PbS has been shown in Fig. 14.7.

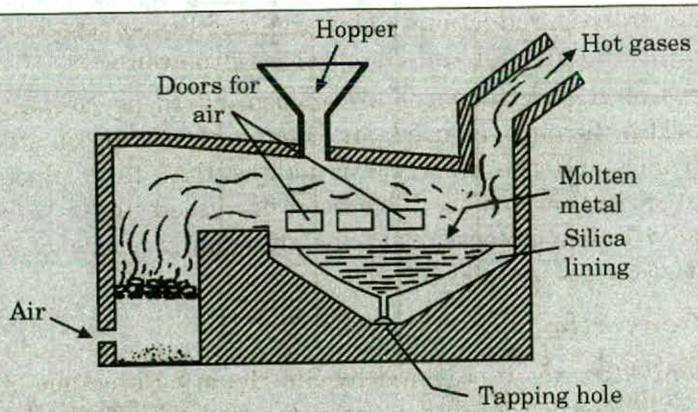


Fig. 14.7. Reverberatory furnace used for roasting the concentrated gelena ore, PbS.

Functioning of the furnace. The charge is placed on the hearth and the fuel is placed on the fire-place. Air enters from the fire-place through the iron grates and waste gases (hot gases) escape out of chimney. There are doors on one side of the furnace for introducing the charge and tap holes on the other side to remove the charge.

In this furnace the ore is not heated directly by the flames of the furnace, but by hot gases which are produced in the fire place. This furnace has been used for smelting (reducing) and roasting the ore. The reduction of the ore is done by the use of some reducing agent like anthracite coal (as in case of tin) while the oxidation is done by means of air. This furnace has been used (*i*) for *reducing* (*smelting*) the roasted tin stone, SnO_2 (an ore of tin) to molten tin metal by the use of anthracite coal (*ii*) for *roasting* the concentrated galena ore, PbS (an ore of Pb) to convert it into PbO and $PbSO_4$ by means of air (*iii*) for *roasting* the concentrated copper pyrites ore, $CuFeS_2$ (an ore of Cu) to convert it into Cu_2O and FeO by means of air.

4. Open-hearth Furnace or Regenerative Furnace

This furnace is like a reverberatory furnace with the dish in the shape of a large oval dish. This furnace works on the regenerative principle of heat economy and hence the name regenerative furnace. It is used for the manufacture of steel from cast iron and the process used is called *open-hearth process* or *Siemen-Martin's process*. Its different parts, functioning and chemical reactions that take place in the furnace during the manufacture of steel have been discussed under "*Manufacture of Steel*" in chapter 46.

5. Electric Furnaces

Electric furnaces are very useful where very high temperatures are required. Further, it is an important advantage of using electric furnaces that the temperatures can be easily controlled by simple regulation of power supply to the furnace or the position of the electrodes etc. These furnaces are particularly useful for the electrolytic reductions. The applicability of electric furnaces is dependent on the availability of the cheap electric power.

Different types of electric furnaces are in use. Of these Heroult's furnace is commonly used. This furnace is used for the manufacture of steel. Different parts of this furnace and the chemical reactions that take place during the manufacture of steel in this furnace have been discussed under "*Manufacture of Steel*" in chapter 46. The process used for the manufacture of steel by this furnace is called *electrical process*.

6. Bessemer's Convertor

Bessemer's convertor was discovered by Sir Henery Bessemer of England in 1856. It is a pear-shaped vessel and is used for the manufacture of steel from cast iron. The construction of the convertor and the reactions that take place in it during the manufacture of steel have been discussed under "*Extraction of Steel*" in chapter 46.

Question with Answers

Q.1 What are Ellingham diagrams ? Discuss their uses and limitations in pyrometallurgy.

Ans : What are Ellingham diagrams ?

We know that the standard free energy change of the formation ($\Delta_f G^\circ$ or ΔG_f°) of metal oxides (solid) is negative. The plots of ($\Delta_f G^\circ$) per mole of O_2 against absolute temperature (T) are called Ellingham diagrams for the formation of metal oxides. These diagrams for the formation of some metal oxides are given in Fig 14.5.

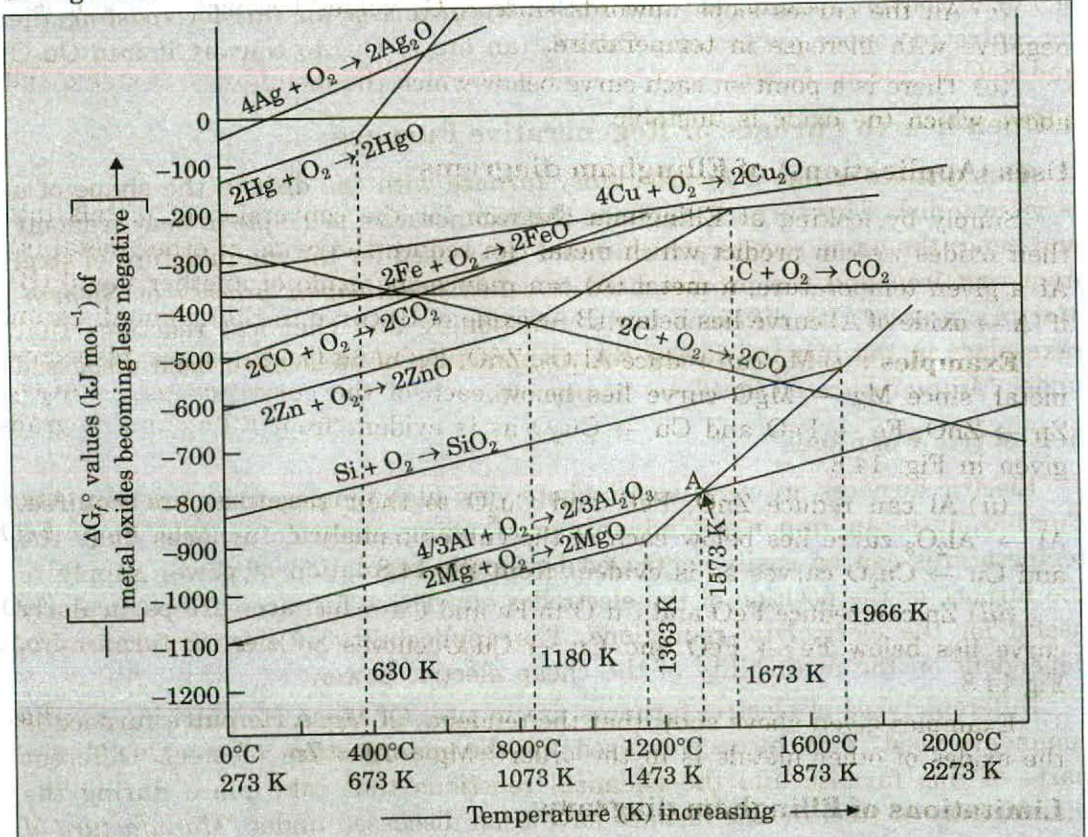


Fig. 14.8. Ellingham diagram : Plot of (ΔG°_f) Vs T for the formation of oxides of some metals

Ellingham diagrams can also be drawn for the conversion of metals to metal sulphides or metal halides using one mole of sulphur or halogen.

Characteristics of Ellingham Diagrams

Following points may be noted from Ellingham diagrams given in Fig 14.8.

(*i*) Each plot in a straight line.

(*ii*) Due to the decrease in entropy (ΔS is negative) during oxide formation reaction, the value of $\Delta_f G^\circ$ increases or becomes less negative with the increase of temperature. In other words curves have positive slopes. However, when some change in phase (*e.g.* solid → liquid, liquid → gas) takes place, abrupt change in the positive slope of the curve also takes place. For example :

(*a*) In Zn → ZnO curve, at the b.pt. of Zn (= 1180K) there is an abrupt increase in the positive slope of the curve.

(*b*) An abrupt increase in the positive slope takes place in Mg → MgO curve at the b.pt. of Mg (= 1363K)

(*iii*) For the oxidation reaction like $C(s) + O_2(g) \rightarrow CO_2(g)$ for which $\Delta S = 0$, the slope of $C \rightarrow CO_2$ curve is zero and hence this curve is parallel to the temperature axis.

(*iv*) All the curves slope upwords since $\Delta_f G^\circ$ values becomes less and less negative with increase in temperature.

(*v*) There is a point on each curve below which the metal oxide is stable and above which the oxide is unstable.

Uses (Applications) of Ellingham diagrams

Simply by looking at Ellingham diagram for the conversion of metals into their oxides we can predict which metal can reduce the oxide of other metal (*s*). At a given temperature, a metal (A) can reduce the oxide of another metal (B), if (A → oxide of A) curve lies below (B → oxide of B) curve in Ellingham diagram.

Examples : (*i*) Mg can reduce Al_2O_3, ZnO, FeO and Cu_2O to their respective metal, since Mg → MgO curve lies below each of the curves *viz* $Al \rightarrow Al_2O_3$, Zn → ZnO, Fe → FeO and $Cu \rightarrow Cu_2O$ as is evident from Ellingham diagram given in Fig. 14.8.

(*ii*) Al can reduce ZnO, FeO and Cu_2O to their respective metals, since $Al \rightarrow Al_2O_3$ curve lies below each of the curves namely Zn → ZnO, Fe → FeO and $Cu \rightarrow Cu_2O$ curves as is evident from Fig.14.8.

(*iii*) Zn can reduce FeO and Cu_2O to Fe and Cu respectively, since Zn → ZnO curve lies below Fe → FeO and $Cu \rightarrow Cu_2O$ curves both as is evident from Fig.14.8.

Examples given above show that the tendency of Mg, Al, Zn and Fe to reduce the oxides of other metals is in the order : Mg > Al > Zn > Fe > Cu.

Limitations of Ellingham diagrams

(*i*) Ellingham diagrams simply suggest whether the reduction of metal oxide by a given RA (*e.g.* other metal, C or CO) is posiible or not. These diagrams donot tell anything about the rate at which the reduction reactions take place.

(*ii*) These diagrams are based on the assumption that the reactants and products are in equilibirium. But this is not always true because the reactants/products may be solid.

Q.2 Give the principle involved in choosing a reducing agent for reducing metal oxide to metal.

Ans : The chemical principle involved in the reduction of a metal oxide to metal by another metal can be understood by considering the following redox reaction.

$$\underset{\substack{\text{Metal A}\\ \text{(RA)}}}{\text{A}} + \underset{\substack{\text{Oxide of}\\ \text{metal B}}}{\text{BO}} \longrightarrow \underset{\substack{\text{Metal}\\ \text{B}}}{\text{B}} + \underset{\substack{\text{Oxide of}\\ \text{metal A}}}{\text{AO}}$$

This is a redox reaction in which metal A reduces the oxide of metal B (BO) to B and is itself oxidised to its oxide (AO). Thus metal A acts as a RA. Metal A (RA) reduces BO to B since the value of ΔG_f° for (A → AO) is more negative than the value of ΔG_f° for (B → BO). Hence the value of ΔG_r° of the above reaction becomes negative. [*i.e.* $\Delta G_r^\circ = \Delta G_f^\circ (\text{AO}) - \Delta G_f^\circ (\text{BO})$].

From the above discussion we can conclude that any metal having higher negative value of ΔG_f° for its oxide will reduce the oxide of another metal with lower negative value of ΔG_f° for its oxide. Without making the calculation of ΔG_r° for the redox reaction, we can predict the feasibility of the reaction simply by looking at Ellingham diagram. If we look at Ellingham diagram, we find that a metal (A) can reduce the oxide (BO) of another metal B, if A → AO curve lies below B → BO curve.

Above principle can be understood in a better way by considering the following examples :

(*i*) **Reduction of FeO and Fe_2O_3 to Fe by Al.** The reduction of FeO and Fe_2O_3 to Fe by Al can be represented as :

$$\underset{\text{RA}}{2\text{Al}} + 3\,\text{FeO} \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{Fe}$$

$$\underset{\text{RA}}{2\text{Al}} + \text{Fe}_2\text{O}_3 \xrightarrow{\Delta} 2\text{Al}_2\text{O}_3 + 2\text{Fe}$$

In Ellingham diagram (Fig. 14.8), since $Al \rightarrow Al_2O_3$ curve lies below Fe → FeO and $Fe \rightarrow Fe_2O_3$ curves (not shown in diagram), Al can reduce FeO and Fe_2O_3 both to Fe and Al is oxidised to Al_2O_3.

(*ii*) **Reduction of Al_2O_3 to Al by Fe**. The reduction Al_2O_3 to Al by Fe can be shown as :

$2\,Fe + Al_2O_3 \rightarrow Fe_2O_3 + Al$

In Ellingham diagram (Fig. 14.8.), since Fe → FeO curve lies above $Al \rightarrow Al_2O_3$ curve, Fe cannot reduce Al_2O_3 to Al, *i.e.* the above redox reaction is not feasable.

(*iii*) **Reduction of FeO to Fe by cabon or CO.** The reduction of FeO to Fe by C and CO be shown as :

$$\text{FeO} \rightarrow \underset{\text{RA}}{\text{C}} \rightarrow \text{Fe} + \text{CO}$$

$$\text{FeO} + \underset{\text{RA}}{\text{CO}} \rightarrow \text{Fe} + \text{CO}_2$$

Ellingham diagram shows that :

(*a*) Above 1073K, since C → CO curve lies below Fe → FeO curve, (See Fig. 14.9) C is able to reduce FeO to Fe.

$$FeO + C \xrightarrow{< 1073K} Fe + CO$$

(*b*) Below 1073K, since $CO \rightarrow CO_2$ curve lies below $Fe \rightarrow FeO$ curve (Fig. 14.9), CO is able to reduce FeO to Fe. Thus :

$$FeO + CO \xrightarrow{< 1073K} Fe + CO_2.$$

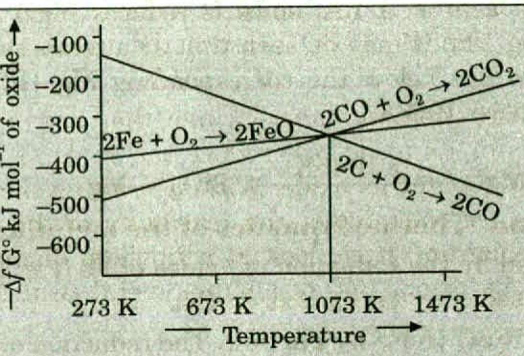


Fig. 14.9 Ellingham diagram for formation of FeO from Fe, CO from C and CO_2 from CO

Q.3 With the help of Ellingham diagram predict whether.

(*i*) Fe can reduce Al_2O_3 to Al and ZnO to Zn.

(*ii*) CO can reduce ZnO to Zn.

Ans : (*i*) $\underset{\text{RA}}{3Fe} + Al_2O_3 \rightarrow 3FeO + 2Al$

$\underset{\text{RA}}{Fe} + ZnO \rightarrow FeO + Zn$

Ellingham diagram given in Fig. 14.8 shows that since $Fe \rightarrow FeO$ curve lies above $Al \rightarrow Al_2O_3$ curve, Fe cannot reduce Al_2O_3 to Al. Similarly $Fe \rightarrow FeO$ curve lies above $Zn \rightarrow ZnO$ curve, Fe cannot reduce ZnO to Zn. Thus Fe cannot reduce any of the given oxides.

(*ii*) $\underset{\text{RA}}{CO} + ZnO \rightarrow Zn + CO_2$

Since $CO \rightarrow CO_2$ curve lies above $Zn \rightarrow ZnO$ curve, CO is not able to reduce ZnO to Zn.

Q.4 Metion the temperature at which :

(*i*) Mg can reduce SiO_2 to Si.

(*ii*) Si can reduce MgO to Mg.

Ans : (*i*) The reduction of SiO_2 to Si by Mg can be shown as :

$$\underset{\text{RA}}{2Mg} + SiO_2 \rightarrow 2MgO + Si$$

In this reaction Mg acts as a RA, since it reduces SiO_2 to Si and itself oxidised to MgO. Ellingham diagram given in Fig. 14.8 shows that at a temerature below 1966K, since $Mg \rightarrow MgO$ curve lies below the corresponding $Si \rightarrow SiO_2$ curve, Mg can reduce SiO_2 to Si below 1966 K.

$$2Mg + SiO_2 \xrightarrow{< 1966K} 2MgO + Si$$

(*ii*) The reduction of MgO to Mg by Si can be shown as :

$$\underset{RA}{Si} + 2MgO \rightarrow SiO_2 + 2Mg$$

In this reaction Si acts as a RA, since it reduces MgO to Mg and is itself oxidised to SiO_2. In Fig 14.8 it may be seen that at a temperatrure above 1966K, since Si → SiO_2 curve lies below the corresponding Mg → MgO curve, Si can reduce MgO to Mg above 1966K.

$$Si + MgO \xrightarrow{> 1966K} SiO_2 + Mg$$

Q.5 Write a note on "Thermodynamics of the metallurgy of iron".

Ans : Fe is obtained by the reduction of oxides of Fe (*e.g.* FeO, Fe_2O_3, Fe_3O_4). The reducing agent used may be carbon or CO.

(*i*) **Reduction of FeO to Fe by carbon.** The reduction of FeO to Fe by C can be shown by the following reaction. In this reaction C is oxidised to CO.

$$FeO + \underset{RA}{C} \longrightarrow Fe\ CO$$

From Fig. 14.9, it may be seen that C → CO and Fe → FeO curves cross each other at a temperature of 1073 K. Thus above this temperature, since C → CO curve lies below Fe → FeO curve, C is able to reduce FeO to Fe at a temperature higher than 1073K.

$$FeO + C \xrightarrow{> 1073K} Fe + CO$$

(*ii*) **Reduction of Fe_2O_3 (heamatite) and Fe_3O_4 to Fe by CO.** The reduction of Fe_2O_3 and Fe_3O_4 by CO can be shown by the following reactions. In these reactions CO is oxidised to CO_2 and both iron oxides are converted into FeO.

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

FeO obtained as above gets reduced to Fe by CO.

$$FeO + CO \rightarrow Fe + CO_2$$

It may be seen from Fig. 14.9 that at a temperature below 1073K, since CO → CO_2 curve lies below Fe → FeO curve, oxides of Fe (FeO, Fe_2O_3, Fe_3O_4) can be reduced to Fe by CO. Thus :

$$FeO + CO \xrightarrow{< 1073K} Fe + CO_2$$

Q.6 The values of free energy of formation of MgO(*s*) and CO(*g*) at 1273K and 2273K are given as : (*a*) At 1273K : MgO(*s*) = –914 KJmol^{-1}, CO(*g*) = – 439 KJmol^{-1} (*b*) At 2273K : MgO(*s*) = –314 KJmol^{-1}, CO(*g*) = – 628 KJmol^{-1}. On the basis of these data predict at which temperature carbon can reduce MgO(*s*) to Mg(*s*).

Ans : (*a*) **At 1273K.** Reduction of MgO(*s*) to Mg(*s*) by carbon(*s*) can be shown as :

$$MgO(s) + C(s) \longrightarrow Mg(s) + CO(g).$$

The value of free energy of the above reaction (ΔG_r) is given by :

$$\begin{aligned}\Delta G_r &= \Sigma\Delta G_f\ (\text{Products}) - \Sigma\Delta G_f\ (\text{Reactants})\\ &= [\Delta G_f\ (Mg) + \Delta G_f(CO)] - [\Delta G_f(MgO) + \Delta G_f(C)]\\ &= [0 + (-439)] - [-914 + 0]\\ &= -439 + 914 = +502\ \text{KJmol}^{-1}\end{aligned}$$

Since the value of ΔG_r is positive, the reduction of $MgO(s)$ to $Mg(s)$ by carbon is not feasible at 1273K.

(*b*) **At 2273K.** Reduction of $MgO(s)$ to $Mg(s)$ by $C(s)$ can be shown by the same equation as given above. In this case ΔG_r is given by :

$$\begin{aligned}\Delta G_r &= \Sigma\Delta G_f\ (\text{Products}) - \Sigma\Delta G_f\ (\text{Reactants})\\ &= [\Delta G_f\ (Mg) + \Delta G_f(CO)] - [\Delta G_f(MgO) + \Delta G_f(C)]\\ &= [0 + (-628)] - [-314 + 0]\\ &= -628 + 314 = -314\ \text{KJmol}^{-1}\end{aligned}$$

Since the value of ΔG_r is negative, the reduction of $MgO(s)$ to $Mg(s)$ by carbon is feasible at 2273K.

Q.7 The value of $\Delta_f G^\circ$ for the formation of Cr_2O_3 is –540 KJmol^{-1} and that of Al_2O_3 is –827 KJmol^{-1}. Is the reduction of Cr_2O_3 possible with Al ?

Ans : The reduction of Cr_2O_3 with Al can be represented by the equation :

$$Cr_2O_3(s) + 2Al(s) \xrightarrow{\Delta} 2Cr\ (s) + Al_2O_3(s)$$

The above reaction is feasible, if the value of $\Delta_r G^\circ$ for this reaction is negative. Now let us calculate the value of $\Delta_r G^\circ$ for the above reaction.

$$\begin{aligned}\Delta_r G^\circ &= \Sigma\Delta_f\ G^\circ\ (\text{Products}) - \Sigma\Delta_f\ G^\circ\ (\text{Reactants})\\ &= [\Delta_f G^\circ\ (Al_2O_3) + 2\times\Delta_f G^\circ\ (Cr)] - [\Delta_f G^\circ\ (Cr_2O_3) + 2\times\Delta_f G^\circ\ (Al)]\\ &= [-827 + 2\times 0] - [-540 + 2\times 0]\\ &= -827 + 540 = -287\ \text{KJmol}^{-1}\end{aligned}$$

Since the value of $\Delta_r G^\circ$ is negative (= –287 KJmol^{-1}), the above reaction is feasible, *i.e.* the reduction of Cr_2O_3 by Al is possible.

Q.8 With the help of the following oxidation reactions predict whether :

(*i*) Zn can be oxidised by CO.

(*ii*) ZnO can be reduced by graphite

$$Zn(s) + \frac{1}{2}O_2(g) \rightarrow ZnO(s),\ \Delta G^\circ = -360\ \text{KJmol}^{-1}$$

$$C(gr) + \frac{1}{2}O_2(g) \rightarrow CO(g),\quad \Delta G^\circ = -460\ \text{KJmol}^{-1}$$

Ans : (*i*) Oxidation of Zn to ZnO by CO can be shown as :

$$Zn(s) + CO(g) \rightarrow ZnO(s) + C(s)$$

The value of ΔG_r° for this reaction is given by :

$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ\ (ZnO) - \Delta G_f^\circ\ (CO)\\ &= -360 - (-460) = +100\ \text{KJmol}^{-1}\end{aligned}$$

Since the value of ΔG_r° is positive, Zn cannot be oxidised to ZnO by CO.

(*ii*) The reduction of ZnO by graphite, C(*gr*) can be represented by the equation

$$ZnO\ (s) + C(gr) \rightarrow Zn(s) + CO(g)$$

$$\Delta G_r^\circ = \Delta G_f^\circ\ (CO) - \Delta G_f^\circ\ (ZnO)$$

$$= -460 - (-360) = -100\ KJmol^{-1}$$

Since the value of ΔG_r° is negative, the reduction of ZnO by carbon is feasible.

Q.9 A mineral consists of PbS and ZnS. NaCN is used as a depressant in preventing ZnS from forming the froth. How does NaCN act as a depressant ?

Ans : When a mineral consisting of PbS and ZnS is concentrated by froth flotatation method, NaCN is used as a depressant. NaCN reacts with ZnS to form a complex, $Na_2\ [Zn(CN)_4]$

$$\underset{\text{Depressant}}{4NaCN} + ZnS\ (\text{Present in mineral}) \rightarrow Na_2\ [Zn(CN)_4] + Na_2S$$

Due to the conversion of ZnS into $Na_2\ [Zn\ (CN)_4]$, this sulphide ore is prevented from forming froth under these conditions, only *PbS* forms froth with air bubbles and can be separated from ZnS ore.

Q.10 Justify the statement : "The extraction of gold by leaching with NaCN in presence of O_2 involves both oxidation and reduction".

Ans : During the leaching process, Au is first oxidised to Au^+ by O_2 *of the air* which then combines with CN^- ions to form the soluble complex, sodium dicyanoaurate (I).

$$\underset{\substack{\text{Gold} \\ (\textit{Impure})}}{4Au(s)} + 8NaCN\ (aq) + 2H_2O\ (l) + O_2 \longrightarrow \underset{\substack{\text{Sod. dicyanoaurate (I)} \\ (\textit{Soluble complex})}}{4Na\ [Au(CN)_2]\ (aq)} + 4NaOH\ (aq)$$

Gold is then extracted from this complex by displacement method using a more electropositive zinc metal. In this reaction, Zn acts as a reducing agent. It reduces Au^+ to Au while it itself gets oxidized to Zn^{2+} which combines with CN^- ions to form soluble complex, sodium tetracyanozincate (II).

$$2Na\ [Au(CN)_2]\ (aq) + Zn(s) \rightarrow \underset{\substack{\text{Gold} \\ (\textit{Pure})}}{2Au(s)} + \underset{\text{Sod. tetracyanozincate (II)}}{Na_2\ [Zn\ (CN)_4]\ (aq)}$$

Q.11 Out of the following metals select the metals which are extracted by carbon-reduction process and which are extracted by electrolytic reduction process. Na, K, Mg, Ca, Al, Pb, Fe.

Ans : Since Na, K, Mg, Ca and Al are highly electropositive metals, these metals are obtained by the electrolytic reduction of their fused oxide (*e.g* MgO, Al_2O_3), hydroxide (e.g., NaOH, KOH) and chloride (e.g. NaCl, KCl, $MgCl_2$, $CaCl_2$). In this process the oxide, hydroxide and chiloride is reduced to the metal which is collected at cathode.

Since Pb and Fe are less electroposive metals, these are obtained by reducing their oxides with carbon (carbon-reduction process) or CO.

$$PbO + C \rightarrow Pb + CO, \quad PbO + CO \rightarrow Pb + CO_2$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO, \quad Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

Q.12 Name the following : (*i*) Two metals that never occur in native state (*ii*) Two metals that always occur both in native and in combined states (*iii*) Two metals which always occur naturally in an uncombined state (*iv*) Two metals which are manufactured by the electrolysis of their fused salts (*v*) Two metals that are used for the reduction in metallurgical process (*vi*) Two metals that can be obtained by the electrolytic reduction of aqueous solution of their salts. (I.I.T. 1976, Roorkee 1988)

Ans : (*i*) Since Na and K are highly reactive metals, they are never found in nature in the native (free or uncombined) state. These metals are found in nature in the form of their ores (combined state).

(*ii*) Cu and Ag are the metals which are found in nature both in the native (metallic condition) and combined state. In the combined state, Cu is found in the form of its sulphide ores (*e.g.* $CuFeS_2$, Cu_2S, Cu_3FeS_3), oxide ores (Cu_2O) and basic carbonate ores [*e.g.* $CuCO_3$. Cu $(OH)_2$, $2CuCO_3$, $Cu(OH)_2$] while Ag is found in the form of its sulphide ore (*e.g.* Ag_2S etc) and halide ores (*e.g.* AgCl).

(*iii*) Au and Pt are the metals which are found in nature only in the free or native or uncombined state. These are usualy found associated with rock or alluvial materials like clay, sand etc.

(*iv*) Na and Ca are the metals that are obtained by the electrolysis of their fused chlorides viz NaCl and $CaCl_2$. In the electrolysis of NaCl, some amount of $CaCl_2$ and KF is also added to fused NaCl. The addition of $CaCl_2$ and KF reduces the fusion temperature from 800°C to 600°C and the conductivity of the electrolyte (NaCl) is increased. In the electrolysis of $CaCl_2$ some amount of CaF_2 is also added to it. In both the cases the metal (i.e. Na and Ca) is deposited on cathode.

(*v*) Al and Mg are the two metals which are used for the reduction of metallic salts to the metals. For example :

$$TiCl_4 + 2Mg \longrightarrow Ti + 2MgCl_2$$

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

Al and Mg act as reducing agents.

(*vi*) Cu and Ag are the metals that can be obtained by the electrolytic reduction of aqueous solution of their salts.

Cu is obtained by electrolysing $CuSO_4$ solution using Cu sheet as cathode and lead sheet as anode. $CuSO_4$ is reduced to Cu which is collected on cathode.

Ag can be obtained by electrolysing $AgNO_3$ solution containing 10% HNO_3. Impure Ag is made anode and pure Ag is made cathode. On electrolysing the solution, Ag gets deposited on cathode.

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

$$NO_3^- + Ag \rightarrow AgNO_3 + e^- \text{ (\textit{At anode})}$$

$$Ag^+ + e^- \rightarrow Ag \text{ (\textit{At cathode})}$$

In this way Ag is transferred from anode to cathode. The impurity of Cu present in $AgNO_3$ goes into solution as $Cu(NO_3)_2$ and that of Au gets collected below the anode as anodic mud.

Q.13 Explain the following :

(i) Below 673K, CO is a better RA for reducing metal oxides but above this temerature carbon is a better RA.

Ans : When carbon (C) reduces a metal oxide (MO), it is oxidised to CO or CO_2

$$C + MO \rightarrow M + CO$$

$$C + 2MO \rightarrow 2M + CO_2$$

When CO reduces a metal oxide (MO), it gets oxidised to CO_2

$$CO + MO \rightarrow M + CO_2$$

Above redox reaction show that C is oxidised to CO or CO_2 and CO is oxidised to CO_2.

$$\begin{array}{llcl} (i) & 2C(s) + \quad O_2(g) & \longrightarrow & 2CO(g) \\ & \qquad\quad 1 \text{ volume} & & 2 \text{ volumes} \\ (ii) & C(s) \ + \quad O_2(g) & \longrightarrow & CO_2(g) \\ & \qquad\quad 1 \text{ volume} & & 1 \text{ volume} \\ (iii) & \underbrace{2CO(g) + O_2(g)}_{3 \text{ volumes}} & \longrightarrow & 2CO_2(g) \\ & & & 2 \text{ volumes} \end{array}$$

In reaction (*i*), since 2 volumes of CO(g) are produced by 1 volume of $O_2(g)$, (increase in volume), ΔS for this reaction is positive and hence the value of $\Delta G°_f$ (C → CO) becomes more negative as temperature increases ($\because \Delta H°_f = \Delta H - T\Delta S$). Consequently, C → CO line in Ellingham diagram given in Fig.14.10. slopes downwards.

In reaction (*ii*), since the value of $CO_2(g)$ produced is the same as that of $O_2(g)$ used, ΔS for this reaction is very small and hence the value of $\Delta G_f°$ for ($C \rightarrow CO_2$) does not change with tempreature. Consequantly, $C \rightarrow CO_2$ line is almost horizontal (*i.e.* parallel to the temperature axis) (See Fig. 14.10)

In reaction (*iii*), Since 2 volumes of CO_2 are produced by 3 volumes of the reactants, ΔS for this reaction is negative and hence the value of ($CO \rightarrow CO_2$) is more positive as the temperature increases. Consequently $CO \rightarrow CO_2$ line slopes upwards as shown in Fig. 14.10. C → CO, $C \rightarrow CO_2$ and $CO \rightarrow CO_2$ lines cross at 673K. Below this tempreature, C and CO both can reduce metal oxides (MO) to metals (M) and C/CO are oxidised to CO_2. Now since CO is more easily oxidised to CO_2 than C is oxidised to CO_2, below 673K CO reduces

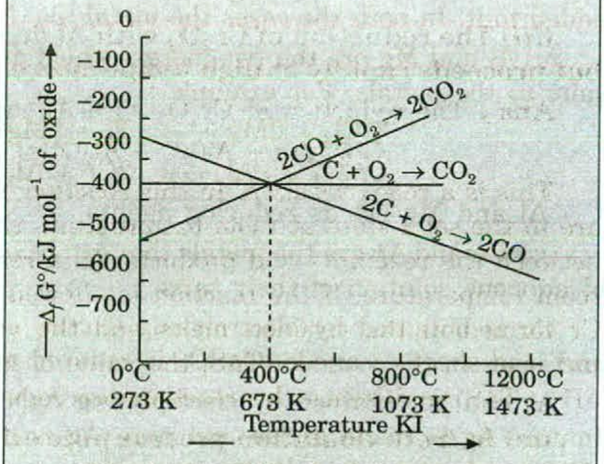


Fig. 14.10. Ellingham diagram for the formation of CO from C, CO_2 from C and CO_2 from CO

metal oxides more effectively than carbon, *i.e.* below 673K CO is a better RA than C for reducing metal oxides (MO) to metals (M).

$$CO + MO \xrightarrow{< 673K} M + CO_2$$

Above 673K, since CO is more stable than C, its oxidation to CO_2 is more difficult than the oxidation of C to CO_2. Thus above 673K, C is more easily oxidised to CO_2 than CO is oxidised to CO_2. As a result, carbon (C) is a better RA than CO for reducing MO to M at a tempreature higher than 673K.

$$C + 2MO \xrightarrow{>673K} 2M + CO_2$$

(*ii*) Below 1573K Mg can reduce Al_2O_3 to Al but above this temperature Al can reduce MgO to Mg.

Ans : If we look at Ellingham diagram given in Fig. 14.8, we find that $Mg \rightarrow MgO$ and $Al \rightarrow Al_2O_3$ curves intersect at a temperature of 1573K (Point A). Since below this temperature, $Mg \rightarrow MgO$ curve lies below $Al \rightarrow Al_2O_3$ curve, Mg can reduce Al_2O_3 to Al below 1573K *i.e.* the following reaction is feasible at a temperature below 1573K

$$Mg + Al_2O_3 \xrightarrow{< 1573K} Al + MgO$$

Above 1573K, since $Al \rightarrow Al_2O_3$ curve lies below $Mg \rightarrow MgO$ curve, Al can reduce MgO to Mg, *i.e.* the following reaction is feasible at a tempreatuer higher than 1573K.

$$2Al + 3MgO \xrightarrow{>1573K} Al_2O_3 + 3Mg$$

(*iii*) The reduction of Cr_2O_3 with Al does not occur at room temperature but proceeds rapidly at high temperature.

Ans : The reduction of Cr_2O_3 with Al can be shown as :

$$Cr_2O_3(s) + Al(s) \rightarrow Al_2O_3(s) + 2Cr(s)$$

This is a redox reaction. In this reaction, since all the reactants and products are in the solid state at room tempreature, there does not exits any equilibiriam between the reactants and products. As a result, this reaction does not occur at room temperature. If the reaction is allowed to take place at high temperature, Cr formed in the reaction melts and the value of $T\Delta S$ increases. Due to the increases in the value of $T\Delta S$, the value of $\Delta G°_r$ becomes more negative ($\Delta G_r° = \Delta H - T\Delta S$) and hence the reaction proceeds rapidly.

(*iv*) In froth floatation process pine oil and cresols/aniline are added to the suspension of ore in water.

Ans : The addition of pine oil enhances the non-wetability of the ore particles in water, *i.e.* ore particles are preferentially wetted by pine oil. As a result, ore particles become lighter and hence rise to the surface along with the froth. The addition of cresols/aniline stabilise the froth. Thus pine oil is used as a collector and aniline is used as froth stabiliser.

(*v*) Out of C and CO, C is a better reducing agent for reducing Zn to ZnO.

Ans : The reduction of ZnO to Zn by C and CO can be shown as :

$$\underset{\text{RA}}{ZnO + C} \longrightarrow Zn + CO$$

$$\underset{\text{RA}}{ZnO + CO} \longrightarrow Zn + CO_2$$

If we look at Ellingham diagram givenin Fig. 14.8 , we find that since $CO \rightarrow CO_2$ curve lies above $Zn \rightarrow ZnO$ curve, CO cannot reduce ZnO to Zn. On the other hand, at a temperature of 1673K, since $C \rightarrow CO$ curve lies below $Zn \rightarrow ZnO$ curve, C can reduce ZnO to Zn. Thus out of C and CO, C is a better RA than CO for reducing ZnO.

(*vi*) The reduction of a metal oxide to metal is easier, if the metal formed is in the liquid state.

Ans : We know that entropy of a metal in liquid state is higher than that of the same metal in solid state ($S_{\text{liquid}} > S_{\text{solid}}$). Thus when the metal formed is in the liquid state, and the metal oxide being reduced is in the solid state, the value of entropy change (ΔS) for the reduction reaction is more on the positive side.

Now since the value of $T\Delta S$ increases and that of ΔH remains the same, the value of ΔG_r° for the reduction reaction becomes on the negative side ($\Delta G_r^\circ = \Delta H - T\Delta S$) and hence reduction becomes easier.

(*vii*) In the extraction of metals from their sulphide ores, the sulphide ores are first converted into metal oxides and then these metal oxides are reduced to metal by suitable RA.

Ans : If a metal sulphide ore (*e.g.* Cu_2S) is directly reduced to metal (Cu) by carbon or H_2, C and H_2 are oxidised to CS_2 and H_2S respectively.

$$2Cu_2S + \underset{\text{RA}}{C} \longrightarrow 4Cu + CS_2$$

$$Cu_2S + \underset{\text{RA}}{H_2} \longrightarrow 2Cu + H_2S$$

These reactions would be feasible, if ΔG_f° of CS_2 and H_2S both are greater than that of Cu_2S. In fact, the value ΔG_f° of CS_2 and H_2S both are smaller than that of Cu_2S. Hence above reactions are not feasible, *i.e.* metal sulphides cannot be reduced by C or H_2

When oxide ore (Cu_2O) is reduced by C, C is oxidised to CO

$$Cu_2O(s) + \underset{\text{RA}}{C\,(s)} \longrightarrow 2Cu(s) + CO(g)$$

Now since, in Ellingham diagram, (Fig. 14.8) $C \rightarrow CO$ curve lies below $C \rightarrow Cu_2O$ curve, C can reduce Cu_2O to Cu.

(*viii*) Copper can be extracted by hydrometallyrgy but Zn cannot.

Ans : Hydrometallurgy is a process in which the ore of the metal is dissolved in a suitable solvent (leaching process) to get soluble compound of the metal. The solution of the compound contains the metal as ions. Metal is obtained from this solution by displacing it by a more reactive or more electropositive metal, *i.e.* the metal acting as displacing metal should have lower E° value than the metal being displaced. Cu is extracted from low grade ores. The ore is leached with an acid in presence of air when Cu metal goes into soultion as Cu^{2+} ions.

$$2Cu\ (s) + 2H_2SO_4\ (aq) + O_2(g) \longrightarrow 2CuSO_4\ (aq) + 2H_2O\ (l)$$

$$or\quad Cu\ (s) + 2H^+\ (aq) + \frac{1}{2}O_2\ (g) \longrightarrow Cu^{2+}\ (aq) + H_2O\ (l)$$

Cu^{2+} ions present in solution are displaced by a metal having lower E° value than $E^o_{Cu^{2+}/Cu}$ (= + 0.34V). Since Fe has lower value of E° ($E^o_{Fe^{2+}/Fe}$ = – 0.44V) than $E^o_{Cu^{2+}/Cu}$ (= + 0.34V), this metal is used for displacing Cu metal from the solution of Cu^{2+} ions.

$$Fe\ (\text{Displacing metal}) + Cu^{2+}\ (\text{Metal being displaced}) \longrightarrow Cu + Fe^{2+}$$

We know that $E^o_{Zn^{2+}/Zn} = -0.76V$. Since Al, Mg, Ca, K etc have lower E° values ($E^o_{Al^{3+}/Al} = -1.66V$, $E^o_{Mg^{2+}/Mg} = -2.37V$, $E^o_{Ca^{2+}/Ca} = -2.87V$, $E^o_{K^+/K} = -2.93V$), these metals should be able to displace Zn from the solution of Zn^{2+} ions. But these metals react with H_2O to give their hydroxides and H_2 (*e.g.* $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$), these are not able to displace Zn from the solution having Zn^{2+} ions.

Above discussion shows that Zn cannot be extracted from its ore by hydrometallurgy process but Cu can be.

(*ix*) In nature, Cu, Ag, Zn, Hg and Pb occur as sulphides and not as oxides.

Ans : The cations of Cu, Ag, Zn and Hg *viz* Cu^+, Ag^+, Zn^{2+} and Hg^{2+} have pseudo inert gas configuration, $(n-1)\ s^2\, p^6\, d^{10}$ and the cation of Pb (Pb^{2+}) has inert pair configuration, $4f^{14}\ 5d^{10}\ 6s^2$.

Due to these configurations these cations can easily polarise the bigger S^{2-} ion than the smaller O^{2-} ion. As a result, sulphides of these metals are more stable than their oxides. Consequently, these metals prefer to occur as sulphides and not as oxides in nature.

(*x*) For the recovery of Ag from $[Ag\ (CN)_2]^-$ ion this ion is reduced with Zn and not with Cu.

Ans : E° values of Zn and Cu are $E^o_{Zn^{2+}/Zn} = -0.76V$ and $E^o_{Cu^{2+}/Cu} = +0.34V$. Since $E^o_{Zn^{2+}/Zn} < E^o_{Cu^{2+}/Cu}$, Zn is stronger RA than Cu. Hence $[Ag\ (CN)_2]^-$ ion is reduced with Zn and not with Cu.

$$\underset{(Ag\,=\,+1)}{[2Ag\ (CN)_2]^-} + \underset{\substack{(Zn\,=\,0)\\(RA)}}{Zn} \longrightarrow \underset{(Ag\,=\,0)}{2Ag} + \underset{(Zn\,=\,+2)}{[Zn\ (CN)_4]^{2-}}$$

Another reasons is that Zn is cheaper than Cu.

(*xi*) In the metallurgy of Cu, partial roasting of the sulphide ore of the metal is done.

Ans : In the metallurgy of Cu, copper pyrites ore ($CuFeS_2$) is roasted (oxidation) in a reverberatory furnace when the ore is converted into a mixture of Cu_2S and FeS.

$$2CuFeS_2 + O_2 \xrightarrow{\text{Roasting}} Cu_2S + 2FeS + SO_2$$

Now Cu_2S formed as above is oxidised (roasting) to Cu_2O which combines with the unroasted Cu_2S and forms Cu metal by the self reduction of Cu_2O and Cu_2S.

$$2Cu_2S + 3O_2 \xrightarrow{\text{Partial roasting}} 2Cu_2O + 2SO_2$$

$$\begin{array}{llcll} 2\,Cu_2O & + \; Cu_2S \text{ (unroasted)} & \longrightarrow & 6Cu + SO_2 & \\ (Cu = +1, & (Cu = +1, & & Cu = 0 & (S = +4, \\ O = -2) & S = -2) & & O = -2) & \end{array}$$

Thus it is due to partial roasting (oxidation) of Cu_2S that self reduction of Cu_2O and Cu_2S takes place.

(*xii*) In the metallurgy of Cu, chalcocite ore (Cu_2S) is roasted and not calcined.

Ans : Calcination is a process in which an ore (generally carbonate or hydroxide ore) is heated strongly to convert it into oxide while roasting is a process in which an ore (generally sulphide ore) is heated strongly in the excess of air to convert it into oxide. Since chalcocite is a sulphide ore, it is roasted and not calcined.

(*xiii*) Al cannot be obtained by smelting Al_2O_3.

Ans : We know that smelting is a process in which the oxide of the metal is reduced to metal by heating the oxide with carbon. Since Al has great affinity for O_2, Al_2O_3 is a very stable compound. Al cannot be obtained by heating Al_2O_3 with carbon (smelting), since when Al_2O_3 is heated with carbon, Al_4C_3 (not Al) is obtained.

$$2\,Al_2O_3 + 6C \rightarrow Al_4C_3 + 6\,CO$$

(*xiv*) Graphite is used as an anode but not diamond.

Ans : Graphite is a good conductor of electricity due to the presence of free electrons within its layers which help to conduct electricity. Diamond, on the other hand, is a bad conductor of electricity since no free electrons are present in its structure. Consequently diamond is not used as an anode.

(*xv*) Metals usually do not occur in nature as nitrates.

Ans : Nitrates of all metals are soluble in water. Therefore, if metal nitrates were present in the crust of earth, these would be slowely and gradually washed by rain water into the sea. It is because of this reason that metals usually do not occur in nature as nitrates.

University Questions

1. (*a*) Explain briefly the principle involved in the following : (*i*) Electrolytic refining of metals (*ii*) Van Arkel process (*iii*) Concentration of sulphide ores.

(*b*) How does calcination differ from roasting? Illustrate using suitable examples. (*Delhi 99*)

2. Describe in short the methods for the extraction and isolation of metals from sulphide and oxide ores. (*Kanpur 2000*)
3. Write notes on : Roasting, Calcination, Smelting and Refining of metals. (*Kumaon 2000, Delhi 2002, Lucknow 2002*)
4. Discuss briefly cyanide process used for the extraction of metals from their ores. [*Gauhati (General) 2000*]
5. The extraction of a metal from its ore is essentially a reduction process represented by :

$$M^n + ne^- \longrightarrow M$$

6. Comment on the above statement and discuss various types of reducing agents employed for the purpose. (*Lucknow 2001*)
7. (*i*) Mention the advantages of powder metallurgy.
   (*ii*) Briefly discuss any two methods used in the refining of metals.
   (*iii*) What is the role of flux in metallurgy ?
   (*iv*) What is the reducing agent employed in the production of tungsten ? Give reason. (*Bangalore 2001*)
8. What different techniques are employed for the purification or refining of a metal ? (*Delhi 2003*)
9. Describe Van Arkel process (Vapour phase process). (*Banglore 2004*)
10. Write in brief the general principles involved in the extraction of metals from their ores. (*Purvanchal 2007*)
11. Explain "Roastring" with examples. (*Meerut 2009*)

CHAPTER

15

Various Reactive Forms and Isotopes of Hydrogen

Various Reactive Forms of Hydrogen

Following are the reactive forms of hydrogen :

1. Nascent Hydrogen

If hydrogen gas is bubbled through acidified potassium permanganate, colour is not discharged. To the same if we add some zinc pieces, tiny bubbles of hydrogen are found to rise and potassium permanganate is decolorised. Hydrogen produced *in situ* in the second case is more active and is called **nascent hydrogen** (*newly born*).

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 \quad + \quad \underset{\text{Nascent hydrogen}}{+ 2H}$$

$$2KMnO_4 + 3H_2SO_4 + 10H \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$$

Ferric chloride solution (*yellow*) is decolorised by adding zinc pieces and hydrochloric acid. This is also due to reduction of ferric chloride to ferrous chloride (*faint green solution*) by nascent hydrogen.

$$FeCl_3 + H \longrightarrow FeCl_2 + HCl$$

Nascent hydrogen produced from Zn and dil. H_2SO_4 can reduce $KClO_3$ to KCl and $AsCl_3$ to AsH_3.

$$KClO_3 + 6H \longrightarrow KCl + 3H_2O$$

$$AsCl_3 + 6H \longrightarrow AsH_3 + 3HCl$$

Preparation of Nascent Hydrogen. Nascent hydrogen can be prepared by the following methods :

(*i*) *By the action of Zn on* H_2SO_4

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

(*ii*) *By the action of water on sodium amalgam.*

$$Na + H_2O \longrightarrow NaOH + H$$

(*iii*) *A mixture of Sn and conc. HCl or Fe and water acidified with a little of HCl also gives nascent hydrogen which is used for reducing aromatic compounds.*

$$Sn + 2HCl \longrightarrow SnCl_2 + 2H$$

(*iv*) *Metallic sodium and abolute alcohol also gives nascent hydrogen.*

$$Na + C_2H_5OH \longrightarrow C_2H_5ONa + H$$

(*v*) *By the action of NaOH on Zn or Al*

$$Zn + 2NaOH \longrightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + 2H$$

Theories to Explain the Reactivity of Nascent Hydrogen. ***(i) Atomic Hydrogen Theory.*** In one of the explanations it was suggested that nascent hydrogen at the moment of its liberation exists as single atoms while in ordinary hydrogen these atoms have combined to form molecule, H_2. Its activity is due to its atomic state. Single atoms of nascent hydrogen are ready to react. On the other hand, some work is required to be done on molecules of ordinary hydrogen to split them into single atoms before they can react.

This theory fails to account for a number of facts such as the different degrees of reactivity of nascent hydrogen from different reagents. For example, nascent hydrogen from zinc and dilute sulphuric acid can reduce chlorates to chlorides but one from sodium amalgam and water cannot.

(ii) Energy theory. In another explanation, it is believed that difference in the degrees of activity of nascent hydrogen obtained from different sources is due to different amounts of energy associated with it. Some of the energy liberated as a result of chemical reaction appears as heat energy while the rest becomes associated with hydrogen.

(iii) Internal pressure Theory. In another suggested explanation, hydrogen at the moment of its production is believed to be in the form of very minute bubbles with great internal pressure on account of their small size. It has been shown experimentally that activity of ordinary hydrogen can be increased by applying great pressure.

(iv) Theory of association of energy. Recently, an attempt has been made to explain its activity on the basis of association of energy when electrons are transferred from metals of low electronegativity to H^+ ions in order to change its valency from +1 to zero.

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^-$$

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + e^-$$

$$\mathrm{Al} \longrightarrow \mathrm{Al}^{3+} + 3e^-$$

The hydrogen in solution accepts these electrons :

$$\mathrm{H}^+ + e^- \longrightarrow \mathrm{H}$$

As the energy liberated in the transfer of electrons is different for different reactions, the reducing capacity of various reactions producing nascent hydrogen would be different.

2. Adsorbed or Occluded Hydrogen

Some metals (*e.g.*, Pd, Pt, Au, Fe, Ni) can adsorb under certain conditions relatively large volumes of hydrogen. For example, Graham (1867) found that one volume of palladium adsorbs 935 volumes of hydrogen while cooling from red heat. The gas thus adsorbed by metals is given off when the metal is heated especially under reduced pressure.

The phenomenon was termed **occlusion** or **adsorption** by Grahm. The gas so adsorbed by the metal is termed **occluded** or **adsorbed hydrogen.**

Occluded hydrogen is more active and a stronger reducing agent than ordinary hydrogen. For example :

(*i*) It reduces ferrous salts,

(*ii*) It combines with chlorine and iodine even in the dark.

(*iii*) It precipitates mercury from mercuric chloride.

Theories to Explain the Nature of Occluded Hydrogen. Different views have been put forward from time-to-time to explain the nature of occluded hydrogen. For example :

(*i*) Formerly it was believed that occluded hydrogen forms a chemical compound with the metal.

(*ii*) Holt, Edgar and Firth (1913) suggested that a part of occluded hydrogen is present as a condensed layer on the surface (adsorption) while the rest of it dissolves in the interior of the metal.

(*iii*) According to Gillespie and Hall (1926) there was evidence for the existence of two immiscible solid solutions. They thought that one of these might be a compound, Pd_2H.

(*iv*) At present it is believed that occluded hydrogen gives an *interstitial compound* in which hydrogen occupies the holes in the crystal lattice of the metal.

3. Active Hydrogen

When ordinary hydrogen at room temperature is subjected to the action of silent electric discharge at an electrical pressure more than 30,000 volts, it changes into an active variety of hydrogen. This is called **active hydrogen.**

Active hydrogen is very reactive as shown by the reactions given below :

(*i*) It combines directly with lead or sulphur to form hydrides. The combination occurs at the room temperature.

(*ii*) It reduces cupric and ferric oxides to corresponding metals even in the cold.

Theories to Explain the Nature of Active Hydrogen. Nature of active hydrogen is not clearly understood. Two views put forward are :

(*i*) It consists of molecules H_3 (*cf.* formula of ozone, O_3 which is produced by passing silent electric discharge through ordinary oxygen).

(*ii*) It is atomic hydrogen.

Neither of these explanations has been universally accepted. Active hydrogen is at present regarded merely as an active form of ordinary hydrogen, H_2 (*cf.* active nitrogen).

4. Atomic Hydrogen

In 1922, Langmuir showed that when molecular hydrogen in contact with a tungsten or platinum wire was heated by an electric current at low pressure, it is dissociated into atomic hydrogen. The dissociation of molecular hydrogen into atomic hydrogen is an endothermic reaction.

$$\underset{\text{Molecular hydrogen}}{H_2} \longrightarrow \underbrace{H + H}_{\text{Atomic hydrogen}} - 103.7 \text{ K.cals}$$

The atomic hydrogen so produced was found to be more reactive than ordinary, nascent and adsorbed hydrogen.

Preparation of Atomic Hydrogen. (*i*) *By High temperature dissociation method.* This method is based on the observation made by *Langmuir* who showed that wires of W, Pt and Pd heated to temperature of 1000–2000°C in molecular hydrogen, at pressure of 0.01 mm or less, produce atomic hydrogen, by absorbing a large amount of energy. This method consists in blowing a current of hydrogen across an arc (20 amp. at 300—800 volts) struck between tungsten electrodes in an atmosphere of hydrogen. The degree of dissociation of molecular hydrogen into atomic hydrogen at different temperatures is as shown below :

Temperature (°K)	*Dissociation (%)*
1000	0.00000371
2000	0.122
3000	9.03
4000	62.50
5000	94.69

(*ii*) *By discharge Tube method.* *Wood* in 1922 showed that active hydrogen is formed when a glow discharge is passed through hydrogen at a pressure of 0.1 to 1.0 mm.

(*a*) *Bonhoeffer's Method*. Bonhoeffer designed an apparatus for the production of atomic hydrogen by Wood's method and for studying its effect on various substances. The apparatus contains a S-shaped discharge tube, 2 metres long and about 2 centimetres in diameter fitted with two cylindrical electrodes of sheet aluminium. It is connected with a U-tube on one side and to a trap bulb through an experimental tube on the other side. A very slow current of hydrogen is introduced into the U-tube which is surrounded by liquid air to remove water vapour from it. A pressure (0.1 to 1 mm) is maintained in the discharge tube where the gas is subjected to an electric discharge of 3000 to 500 volts when atomic hydrogen is formed. The action of atomic hydrogen on various substances is studied by introducing them in the current of atomic hydrogen coming out of the discharge tube (See Fig. 15.4).

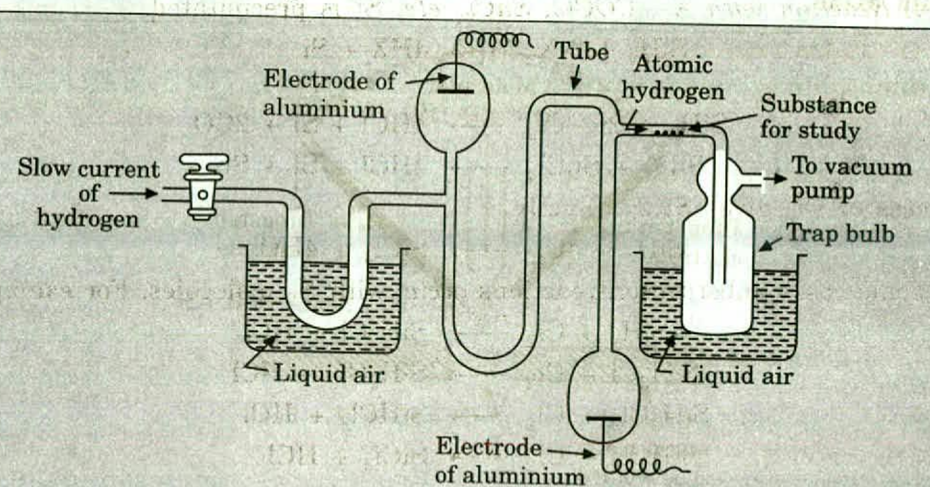


Fig. 15.4. Bonhoeffer's apparatus for the production of atomic hydrogen.

(*b*) *Harteck's Method*. It is a modification of Bonhoeffer's method. In this method a mixture of hydrogen and neon is fed into the discharge tube at pressures upto 20 mm. The presence of neon facilitates the dissociation of hydrogen into atoms.

(*iii*) *By Photochemical Method* (Cario and Frank–1922). Ordinary hydrogen mixed with mercury vapour is subjected to the resonance radiation of a mercury arc. The method gives larger yields of atomic hydrogen and at comparatively higher pressure (upto 0.5 atmosphere).

Properties of Atomic Hydrogen. (*i*) *Stability*. The life period of atomic hydrogen is only 1/3rd of a second but can be extended under special circumstances to 10 seconds.

(*ii*) *Recombination of atomic hydrogen to give molecular hydrogen.* Atomic hydrogen is extremely unstable (Life period = $\frac{1}{3}$ second) and quickly recombines to give molecular hydrogen. Metals like Pt, Pd etc. accelerate this recombination.

$$H + H \rightleftharpoons H_2 + 103.7 \text{ K.cals}$$

This exothermic reaction is used in *Atomic Hydrogen Welding Torch* which is employed for welding the cracked metals like Mn, Cr, W etc. In atomic hydrogen welding torch when molecular hydrogen is passed through an electric arc struck between two tungsten electrodes, the hydrogen molecules absorb heat and are split into atomic hydrogen.

$$\underset{\text{Molecular hydrogen}}{H_2} + \text{Heat} \longrightarrow \underbrace{H + H}_{\text{Atomic hydrogen}}$$

Just beyond the arc these atoms recombine to form H_2 molecules and evolve the heat which they previously absorbed.

$$\underbrace{H + H}_{\text{Atomic hydrogen}} \longrightarrow \underset{\text{Molecular hydrogen}}{H_2} + \text{Heat}$$

This heat plus the heat of burning hydrogen creates a high temperature (= 5000°C). This heat is used for welding the cracked metals. (See Fig. 16.5) and for melting some of the most refractory materials such as tungsten, tantalum and thorium oxide.

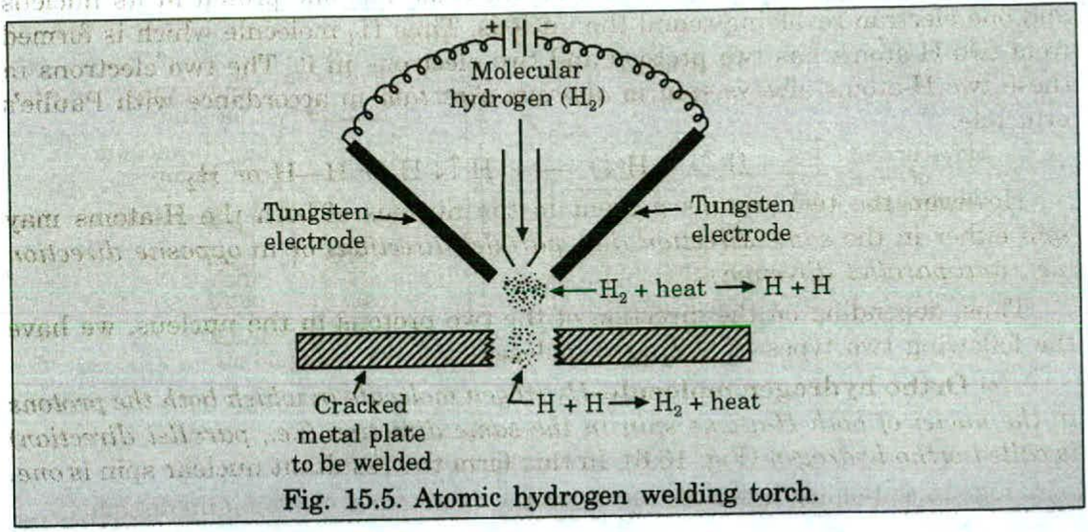


Fig. 15.5. Atomic hydrogen welding torch.

(iii) Formation of hydrides. It combines with metals (*e.g.*, Na, K, Li) and non-metals (*e.g.*, S, P, As, Sb) to give hydrides.

$$S + 2H \longrightarrow H_2S$$
$$Li + H \longrightarrow LiH$$
$$P + 3H \longrightarrow PH_3$$
$$As + 3H \longrightarrow AsH_3$$
$$Sb + 3H \longrightarrow SbH_3$$

(iv) Reducing action. It is an extremely powerful reducing agent and reduces oxides, chlorides and sulphides of Cu, Ag, Hg etc. to metal.

$$HgO + 2H \longrightarrow Hg + H_2O$$

(v) Combination with oxygen. It combines with oxygen to give hydrogen peroxide.

$$2H + O_2 \longrightarrow H_2O_2$$

(vi) Luminiscent effect. A mixture of atomic hydrogen and vapour of alkali metals or mercury gives characteristic glows.

(vii) Combination with organic compounds. It reduces unsaturated organic compounds to saturated compounds, *e.g.* C_2H_4 is converted into C_2H_6 and oleic acid changes into stearic acid.

$$\underset{\text{Ethylene}}{C_2H_4} + 2H \longrightarrow \underset{\text{Ethane}}{C_2H_6}$$

$$\underset{\text{Oleic acid}}{C_{17}H_{33}COOH} + 2H \longrightarrow \underset{\text{Stearic acid}}{C_{17}H_{35}COOH}$$

Uses of Atomic Hydrogen. Atomic hydrogen is used for the production of atomic hydrogen welding torch which is employed for welding and cutting metals as already described under *Properties of atomic hydrogen.*

5. Ortho and Para Hydrogen Molecules

Definition. We know that a hydrogen molecule is composed of two hydrogen atoms. Each of these two H-atoms of H_2 molecule has one proton in its nucleus and one electron revolving round the nucleus. Thus H_2 molecule which is formed from two H-atoms has two protons and two electrons in it. The two electrons in these two H-atoms always spin in *opposite direction* in accordance with Paulie's principle.

$$H(\uparrow) + H(\downarrow) \longrightarrow H \uparrow\downarrow H \text{ or } H{-}H \text{ or } H_2$$

However, the two protons present in the nucleus of both the H-atoms may spin either in the *same direction* (*i.e.*, *parallel direction*) or in *opposite direction* (*i.e.*, *anti-parallel direction*).

Thus, depending on the direction of the two protons in the nucleus, we have the following two types of hydrogen molecule :

(*i*) **Ortho hydrogen molecule.** *Hydrogen molecule in which both the protons in the nuclei of both H-atoms spin in the same direction (i.e., parallel direction) is called ortho hydrogen* (Fig. 16.6). In this form the resultant nuclear spin is *one*.

(*ii*) **Para hydrogen molecule.** *Hydrogen molecule in which both the protons in the nuclei of both H-atoms spin in opposite direction (i.e., antiparallel direction) is called para hydrogen* (Fig. 16.6). In this form the resultant nuclear spin is zero.

Note that the two electrons in ortho as well as in para hydrogen molecule *always spin in the opposite direction*, otherwise it will not be possible to get stable hydrogen molecule.

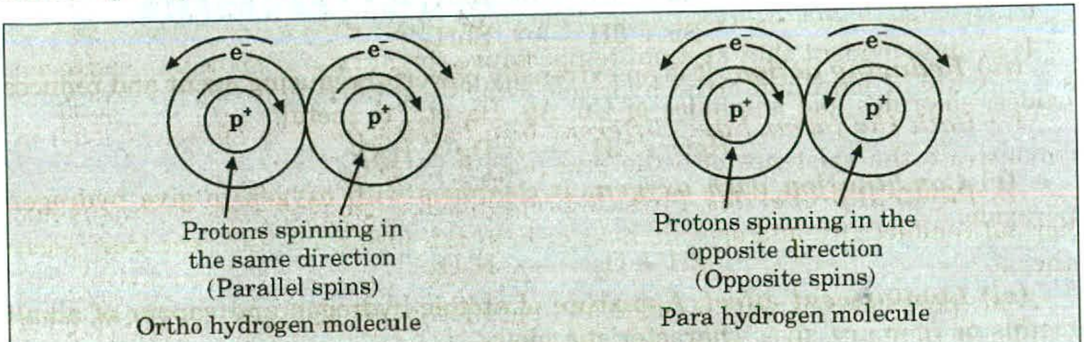


Fig. 15.6. Ortho and para hydrogen molecules. Here P^+ indicates proton.

In 1929, Bonhoeffer and Harteck were also able to show the existence of ortho and para hydrogens from spectral studies.

Differences Between Ortho and Para Hydrogen Molecules.

(i) Internal molecular energy. Mecke discovered in 1934 that the two forms differ in their internal molecular energy. This difference is due to the fact that in case of ortho hydrogen molecule, the spins of the two protons, being in the same direction, increase the molecular energy of ortho form. The resultant spin of ortho hydrogen molecule is *one*.

On the other hand, in case of para hydrogen molecule, the spins of the two protons, being in the opposite direction, neutralise (*i.e.* cancel) each other and thus make the resultant spin equal to *zero*. This neutralisation of spins decreases the molecular energy of para hydrogen molecule.

Thus we see that *para form has lower internal energy than the ortho form.*

(ii) Stability. The ortho form is more stable than the para form and hence the latter (*i.e.*, para form) has a tendency to change to the ortho form.

(iii) Effect of temperature on the relative proportions of the two forms in ordinary hydrogen. It has been shown that the relative proportion of ortho and para hydrogens (*i.e.*, ortho-para ratio) present in ordinary molecular hydrogen is dependent on temperature. *At absolute zero* molecular hydrogen consists *only of para form* (*i.e.*, ratio of para and ortho forms = 1 : 0) which has lower internal energy. *As the temperature increases, the proportion of ortho form increases and that of para form decreases. At the temperature of liquefaction of air, the ratio of para and ortho forms is 1 : 1, while at room temp. and even at elevated temperatures this ratio is 1 : 3. Thus :*

Temperature	*% of para H_2*	*% of ortho H_2*	*Ratio (para : ortho)*
Absolute zero	100%	Nil	1 : 0
Temperature of liquefaction of air	50%	50%	1 : 1
Room temp. and even at elevated temperatures	25%	75%	1 : 3

It is quite evident that at room temperature the ordinary molecular hydrogen is a mixture of para and ortho hydrogen which are present in 1 : 3 ratio.

(*iv*) *Both the forms have different band spectrum.* This fact was used to demonstrate the existence of ortho and para hydrogens.

(*v*) *Physical properties.* Physical properties like melting point, boiling point, thermal conductivity and specific heat of both the forms are different from each other.

Some physical constants of ortho and para forms are given below. Ortho form is difficult to obtain in a pure state and as such its constants are left blank.

	Ortho form	*Para form*
Boiling point at 760 mm	—	20.26°C
Vapour pressure at 20–39° A :	751 mm (Extrapolated)	737 mm
Triple point	—	13.83°C

Due to the neutralisation of nuclear spins, the magnetic moment of para hydrogen is zero while that of ortho form, as extrapolated from the data for known ortho-para mixture, is approximately twice the momentum of a proton.

The appreciable difference in the thermal conductivities of the two forms has been used to estimate the percentage of ortho and para forms in a given sample of hydrogen.

Although the physical properties of the two forms are different, their chemical properties are similar, because both the forms have same covalent bonding.

Separation of the two Forms from Ordinary Hydrogen : Preparation of Pure Para Hydrogen.

(*i*) We know that ordinary molecular hydrogen at room temperature consists of para and ortho hydrogens in 1 : 3 ratio. In order to separate para form from the ordinary hydrogen, the ordinary hydrogen is passed through a tube packed with activated charcoal and cooled in liquid air or liquid hydrogen for about four hours. The para form thus obtained is pumped off and is about 99.5% pure. It can be stored for a week in glass vessels at room temperature without appreciable change into ortho form.

(*ii*) The two forms can be separated from each other by gas chromatography.

Conversion of Para Hydrogen into Ortho Hydrogen.

Ortho hydrogen is more stable than the para form and the latter has a tendency to change to the ortho form. This process is accelerated under certain conditions and it is possible to convert the para form into ortho.

(*i*) *By heating it to 800°C or above.*

(*ii*) *By passing an electric discharge through it.*

(*iii*) *By treatment with catalysts like plantinum.*

(*iv*) *By mixing it with paramagnetic molecules like oxygen or nitrogen peroxide.*

(*v*) *By mixing with atomic hydrogen.* It was shown by Geib and Herteck that when atomic hydrogen collides with para hydrogen molecule, the para hydrogen molecule is converted into ortho molecule as depicted below in Fig. 15.7.

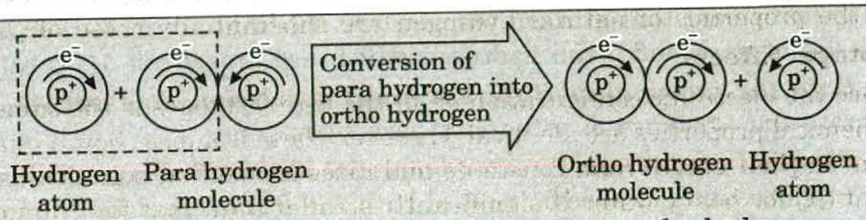


Fig. 15.7. Conversion of para hydrogen into ortho hydrogen

Isotopes of Hydrogen

It has been established by means of mass spectrograph that hydrogen has *three* isotopes with mass number 1, 2 and 3. These isotopes are discussed below :

(*i*) Hydrogen or Protium (${}_1^1\text{H}$ or H). It is represented as ${}_1\text{H}^1$ in which the numbers 1 and 1 indicate the atomic number and mass number (*i.e.* atomic mass or atomic weight) of this isotope. Its exact mass number is, however, 1.0081. Its nucleus consists of one proton and no neutron. It has one electron in 1*s* energy level.

(*ii*) Heavy Hydrogen or Deuterium (${}_1^2\text{H}$ or ${}_1^2\text{D}$). Its actual mass number is 2.0147. Its nucleus consists of one proton and one neutron. It has also one electron in 1s energy level.

(*iii*) Tritium (${}_1^3\text{H}$ or ${}_1^3\text{T}$). Its mass number is 3.0170. Its nucleus consists of one proton and two neutrons. It has one electron in 1*s* energy level.

Some of the properties of these isotopes are given Table 16.1.

Table 15.1. Some properties of the three isotopes of hydrogen

Property	Ordinary hydrogen or protium	Heavy hydrogen or deuterium	Tritium
Symbol	${}_1^1\text{H}$ or H	${}_1^2\text{H}$ or ${}_1^2\text{D}$	${}_1^3\text{H}$ or ${}_1^3\text{T}$
Atomic number	1	1	1
Mass number (*i.e.* atomic mass or atomic weight)	1.0081	2.0147	3.0170
Atomicity	2	2	2
Molecular formula	H_2	D_2	T_2
No. of protons in the nucleus	1	1	1
No. of neutrons in the nucleus	Nil	1	2
No. of electrons	1	1	1
Relative abundance of their diatomic molecules in ordinary hydrogen	99.984%	0.0156%	10^{-15}%
Stability	Stable	Stable	Radioactive and hence unstable
Electronic configuration	$1s^1$	$1s^1$	$1s^1$

Structure of Isotopes

The structure of three isotopes of hydrogen has already been discussed.

It has been estimated that a sample of ordinary hydrogen contains 99.994% of H_2 and 0.0156% of D_2. 10^{17} molecules of ordinary hydrogen contain only one molecule of tritium. The cause of the presence of tritium in ordinary hydrogen in traces only is that the nucleus of tritium is radioactive and hence unstable.

Since the quantities of D_2 and T_2 present in natural hydrogen are exceedingly small, the properties of natural hydrogen are substantially those of protium.

Isotope Effects

Since the electronic configuration of all the three isotopes is the same *viz.* $1s^1$, their chemical properties are identical. However, these isotopes show a quantitative different in their equilibrium constants and rates of reaction, *e.g.* the dissociation constant (K) for heavy water is significantly smaller than that for ordinary water.

$$H_2O \rightleftharpoons H^+ + OH^- ;\ K = 1.0 \times 10^{-10}$$

$$D_2O \rightleftharpoons D^+ + OD^- ;\ K = 0.2 \times 10^{-14}$$

The difference in the masses of isotopes of hydrogen have marked effects on the rates of chemical reactions *e.g.*

(*i*) A bond to a protium atom can be broken as much as 18 times faster than that to a deuterium atom. Thus protium reacts with Cl_2 13.4 times faster than deuterium does.

(*ii*) The addition of H_2 to ethylenic compounds takes place two times faster than with deuterium at the same temperature.

(*iii*) Protium is more rapidly adsorbed on the surfaces than deuterium.

The above examples show that the reactions with deuterium are slower than those with protium. These differences in the rates of chemical reaction are due to the difference in the masses of deuterium and protium.

Such differences in properties which are due to the difference in masses of the isotopes are termed **isotope effects.**

Now let us discuss these isotopes in detail.

1. Ordinary Hydrogen or Protium ($_1^1H$ or H)

It is ordinary hydrogen whose nucleus consists of one proton and one electron is revolving in 1*s* orbital round it.

2. Heavy Hydrogen or Deuterium ($_1^2$(H or $_1^2$)D)

Discovery. The credit of the discovery of heavy hydrogen goes to *Urey* who was awarded a Nobel Prize in 1934 for this discovery.

In 1931 *Birge* and *Manzel* reported that the atomic weight of hydrogen as determined by mass spectrograph was 1.0076 while that determined by chemical methods such as displacement of hydrogen from H_2SO_4 by Zn metal, was 1.0078. In order to explain this discrepency in atomic weights, they suggested that ordinary hydrogen contains a very small proportion of an isotope of mass 2.

About the same time, *Allison* and *his coworkers* also reported that ordinary hydrogen is a mixture of two isotopes of hydrogen. The heavier isotope has mass 2 and is present in the ratio of 1 part in about 5000 parts.

Encouraged by the clues and the calculations shown above *Urey, Brickwedde* and *Murphy* evaporated 4 litres of liquid hydrogen under reduced pressure and at a temperature of freezing hydrogen. On concentrating the residue thus obtained, they examined the spectrum and found that it contained very faint lines. They assumed that the faint lines were due the heavy isotopes of hydrogen with atomic weight 2. Afterwards the masses of light and heavy isotopes of hydrogen were more accurately determined as 1.0081 and 2.0147 respectively. They named this heavier isotope as **deuterium** and gave the symbol **D** to it.

Preparation. Deuterium is prepared by the following methods :

(*i*) By separating deuterium from the mixture of protium and deuterium. Water is decomposed by metals to give a gas which consists of varying amounts of H_2, HD and D_2. Since hydrogen, being lighter than deuterium, is liberated faster than deuterium from water, the first few fractions of the gas are richer in hydrogen while the last fractions contain greater proportion of deuterium. The final fraction of the gas is collected and as electric discharge is passed through it, whereby the atoms of hydrogen and deuterium combine to give a mixture containing H_2 and D_2 molecules. On electrolysis HD also gives H_2 and D_2 molecules.

Now from the mixture of H_2 and D_2, we can separate D_2. The methods used for the separation of D_2 from the mixture are given below :

(*a*) *Diffusion process.* The separation of deuterium from the mixture of deuterium and protium (*i.e.* hydrogen) can be effected by the diffusion process. This *process makes the use of difference in the rates of diffusion of the two isotopes, viz.* protium ($_1H^1$) and deuterium ($_1D^2$). Since protium is lighter, it diffuses more readily than deuterium. Although this method is slow and tedious, yet it gives spectroscopically pure deuterium, *i.e.*, the spectrum of deuterium obtained by this method shows no trace of ordinary hydrogen.

The process is carried out under reduced pressure since lower the pressure, the greater is the efficiency of the process.

The apparatus used in this process consists of a number of porous diffusion units which are called *Hertz diffusion units* (This method is due to Hertz) and are placed in series as shown in Fig. 15.8. The apparatus is called *Hertz apparatus.* Each unit contains a porous membrane shown by dotted portion in the figure and is connected with mercury diffusion pump (P_1, P_2, P_3......). With the help of these diffusion pumps the mixture of the two isotopes is allowed to circulate into the diffusion units at the reduced pressure.

As the mixture of the two isotopes is allowed to pass into the diffusion units under reduced pressure, say, from left to right, with the help of mercury diffusion pumps, the lighter isotope *viz.* protium diffuses faster and its proportion increases on the right side, *i.e.* it is collected in the right reservoir (placed on the right). On the other hand, the heavier isotope *viz.* deuterium is left behind and is collected into the left reservoir (placed on the left). This process is repeated a number of times to get pure deuterium.

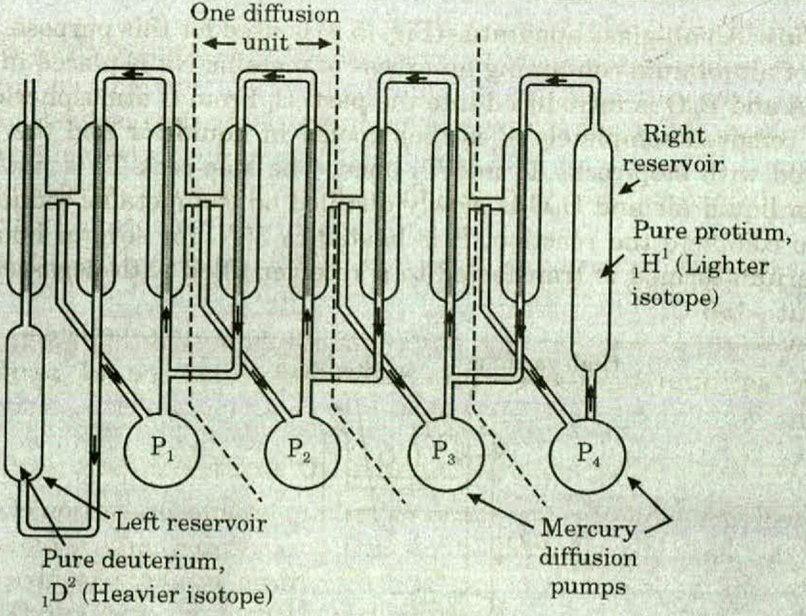


Fig. 15.8. Hertz apparatus for the separation of deuterium from the mixture of protium and deuterium.

(*b*) *Fractional distillation of liquid hydrogen isotopes process.* The mixture of the two isotopes is first of all liquefied by cooling and compression. The liquid so obtained is then slowly distilled under reduced pressure and at the temperature of freezing hydrogen. On concentrating the residue, enriched deuterium is obtained from which pure deuterium can be obtained by the fractional diffusion process as discussed in (*a*).

(*c*) *Adsorption on charcoal process.* This method is based on the fact that protium gets adsorbed on the surface of coconut charcoal more rapidly than deuterium. Thus when a mixture of protium and deuterium is kept in contact with coconut charcoal at the temperature of liquid air for a few hours, most of protium gets adsorbed on the surface of the charcoal while deuterium is collected.

(*ii*) From heavy water. Ordinary water contains about 1 part in 6000 parts of what is known as *heavy water*, the molecule of which consists of two heavy hydrogen atoms and one oxygen atom (D_2O). Heavy water is obtained by the electrolysis of an aqueous alkali solution, between nicked electrodes, 20 litres of the solution yielding about 0.5 c.c. of pure heavy water. Deuterium can be obtained from this heavy water, D_2O by using any of the following methods :

(*a*) *By the action of sodium on D_2O.* Fairly pure sample of heavy hydrogen may be obtained by the action of sodium on heavy water

$$2D_2O + 2Na \longrightarrow \underset{\text{Sod. deutroxide}}{2NaOD} + D_2$$

The drawback of this method is that a part of deuterium is lost as NaOD. This method is used when a comparatively small quantity (upto 1 lit) of deuterium is required.

Procedure. An all-glass apparatus (Fig. 15.9) is used for this purpose. A crucible (U) made of aluminium containing an excess of metallic Na is placed in the lower part, B of A and D_2O is introduced into the part, C. From C atmospheric moisture should be removed completely. C is then cooled in liquid air and the apparatus is evacuated with stop-cocks T_1 and T_2 open. The stop-cock T_2 is now closed, B is cooled in liquid air and D_2O is slowly distilled on the metallic sodium. Finally in order to complete the reaction, B is heated to 35°C for several hours. At the end, deuterium formed is transferred to a receiver filled with degassed charcoal and kept at –196°C.

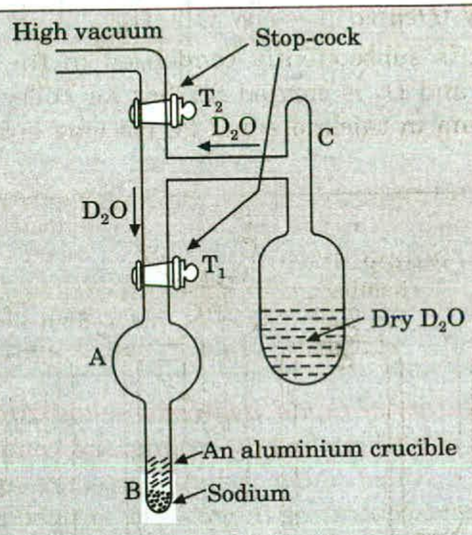


Fig. 15.9. Preparation of deuterium by the action sodium on D_2O.

(*b*) *By the action of magnesium on D_2O.* When large quantities of deuterium are required, reaction between Mg and D_2O has been found to be more suitable.

$$D_2O + Mg \longrightarrow D_2 + MgO$$

Procedure. In this method, D_2O is slowly evaporated from a Pyrex flask that has been previously evacuated to 10^{-4} mm. The vapour passes up a reaction column, set up vertically on the top of the flask. The column is charged with magnesium shavings and is heated to about 500° by means of a furnace. The gas of deuterium produced is very pure and the yield is quantitative.

(*c*) *By the action of uranium on D_2O.* This method not only gives deuterium but also gives us a method for its storage as *uranium deuteride*, UD_3. UD_3 when heated gives D_2 of high purity. The reactions are :

(*i*) Preparation of D_2 : $2D_2O + U \longrightarrow UO_2 + 2D_2$.

(*ii*) Storage of UD_3 : $3D_2 + 2U \longrightarrow 2UD_3$.

(*iii*) Decomposition of UD_3 : $2UD_3 \longrightarrow 3D_2 + 2U$.

With the help of reaction (*iii*) we can get D_2 in any desired quantity.

(*d*) *By the decomposition of D_2O by heated tungsten filament.* This method has been given by *Forkas* and *Farkas* and is useful when small volumes of D_2 are required. The apparatus consists of a decomposition chamber provided with a tungsten filament (*See* Fig. 15.10).

One side of the chamber is connected with a small receiver containing heavy water and the other to a pump. Before beginning the experiment the apparatus is heated to about 1000°C and the tungsten filament to 2000°C as to remove the whole of the absorbed water. The whole apparatus is connected to a high vacuum pump during this preliminary treatment. The receiver containing heavy water is heated and vapours of D_2O so obtained are led to the decomposition chamber where they are decomposed to D_2 by the electrically heated tungsten filament.

D_2O (*Vapours*) + 2W (*Heated*) $\longrightarrow$ $W_2O + D_2$

W_2O is volatile and is subsequently condensed in the U-tube following the decomposition chamber and D_2 is carried further for collection. It is stated that a wire of tungsten 0.2 mm in thickness and 20 cm long ordinarily gives 80 ml of D_2O.

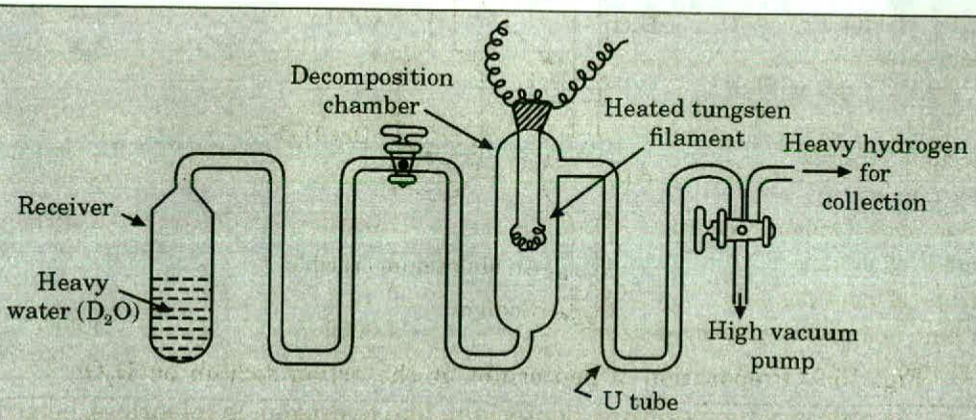


Fig. 15.10. Preparation of heavy hydrogen by the decomposition of heavy water (D_2O) by heated tungsten filament.

(*e*) *By the decomposition of D_2O by heated Zn turnings.* When D_2 is required in large quantities, D_2O is decomposed by heated Zn turnings to get D_2.

Zn (*Heated*) + D_2O (*Vapours*) $\longrightarrow$ ZnO + D_2

(*f*) *By the electrolysis of D_2O.* D_2 can also be prepared by electrolysing pure D_2O acidified with 35% deuteriumsulphuric acid (D_2SO_4) in a specially designed all-glass apparatus. The apparatus is evacuated before electrolysis and a low current of 5 amperes is passed between platinum electrodes when D_2 is set free at the cathode and O_2 at the anode.

$$2D_2O \longrightarrow \underset{\text{(At cathode)}}{2D_2} + \underset{\text{(At anode)}}{O_2}$$

Deuterium obtained by this method may contain small quantities of O_2 and D_2O vapour. It is purified by heating it over platinised asbestos, followed by drying with liquid air. The yield at 5 amp. is reported to be 2 litres per hour.

Physical Properties. (*i*) *Physical constants*. Physical properties of deuterium are some what different from those of ordinary hydrogen. Some of the physical constants of the two isotopes are given in Table 16.2.

Table 15.2. Physical constant of ordinary (protium) and heavy (deuterium) hydrogen.

Property	Ordinary hydrogen (Protium, H_2)	Heavy hydrogen (Deuterium, D_2)
Symbol	H	D
Boiling point (°C)	–252.6	–249.5
Melting point (°C) (Freezing point)	–259.1	–254.5
Triple point (°C)	–259.1	–254.3
Latent heat of fusion (cal/mole)	28.0	52.3
Heat of dissociation (cal/mole)	104,500	14,900
Heat of vaporisation at triple point (cal/g. mole)	219.7	308
Molecular volume of solid (c.c.)	26.15	23.17
Density of liquid at 25°C	1.0000	1.0076
Vapour pressure at –259.1°C (mm of Hg)	5.4	5.8
Atomicity	2	2
Molecular formula	H_2	D_2
Mass number	1	2
Atomic mass (Atomic weight)	1.0081	2.0015
Number of protons	1	1
Number of neutrons	0	1
Per cent abundance of their diatomic molecules	1.0000	1.0076

(*ii*) At ordinary temperature, deuterium, like hydrogen, is colourless, odourless and tasteless with atomicity equal to two, *i.e.*, deuterium is *diatomic* and hence its molecular formula is written as D_2. Its density is twice that of hydrogen.

(*iii*) It is insoluble in water and bad conductor of heat and electricity.

(*iv*) *Ortho and para forms of deuterium*. The deuterium molecule also, like hydrogen is a mixture of ortho and para forms. At ordinary temperature. It consists of 2 parts of ortho and 1 part of para and this composition is retained even at higher temperatures. At low temperature, it is only ortho form which predominates while in normal hydrogen the para form predominates at ordinary temperature.

Chemical Properties. The chemical properties of deuterium are similar to those of hydrogen, the only difference being that deuterium reacts more slowly and less completely as compared to hydrogen. Some of the chemical properties of deuterium are given below :

(*i*) **Occlusion.** Deuterium is occluded by metallic surfaces more slowly than hydrogen.

(*ii*) **Action of oxygen.** It is combustible and burns in oxygen at 560°C to form heavy water

$$2D_2 + O_2 \longrightarrow 2D_2O \text{ (\textit{Heavy water})}$$

(*iii*) **Action of water.** It reacts with water vapour at 200–400°C in presence of zinc oxide or alumina to form a mixture of deuterium oxide and hydrogen.

$$H_2O + D_2 \rightleftharpoons D_2O + H_2$$

(*iv*) **Action of halogens.** It combines with halogens to form deuterium halides.

$$D_2 + Cl_2 \xrightarrow{\text{In light}} 2DCl \text{ (\textit{Deuterium chloride})}$$

$$D_2 + Br_2 \xrightarrow{\text{On heating}} 2DBr \text{ (\textit{Deuterium bromide})}$$

$$D_2 + F_2 \xrightarrow[\text{dark}]{\text{In cold and}} 2DF \text{ (\textit{Deuterium fluoride})}$$

(*v*) **Combination with nitrogen.** Deuterium combines with nitrogen in the presence of a catalyst to form deutero-ammonia or heavy ammonia.

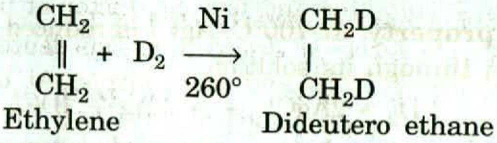
$$3D_2 + N_2 \longrightarrow 2ND_3$$

(*vi*) **Combination with metals.** It combines with alkali metals at 300°C to form deutrides which closely resemble metallic hydrides in their chemical properties.

$$2Na + D_2 \longrightarrow 2NaD \text{ (Sodium \textit{deuteride})}$$

$$NaD + H_2O \longrightarrow NaOH + HD$$

(*vii*) **Reaction with unsaturated hydrocarbons.** Deuterium gives addition reactions with unsaturated hydrocarbons. The reaction, however, is slower as compared with addition reaction with hydrogen.



$$\underset{\text{Ethylene}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}} + D_2 \xrightarrow[260^\circ]{\text{Ni}} \underset{\text{Dideutero ethane}}{\begin{matrix} CH_2D \\ | \\ CH_2D \end{matrix}}$$

(*viii*) **Exchange reactions.** Under suitable conditions, it is possible for deuterium to take the place of hydrogen in some compounds, *e.g.*, at high temperature deuterium reacts with H_2, NH_3, H_2O and CH_4 and slowly exchanges hydrogen atoms of these molecules. The exchange of hydrogen by deuterium may take place partially or completely.

$$2NH_3 + 3D_2 \rightleftharpoons \underset{\substack{\text{Deuterium} \\ \text{ammonia}}}{2ND_3} + 3H_2$$

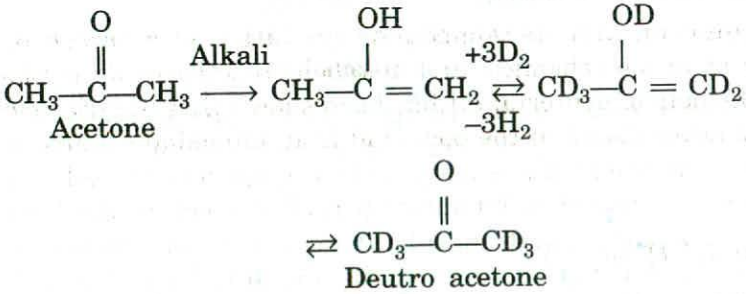
$$H_2O + D_2 \rightleftharpoons \underset{\substack{\text{Deuterium}\\ \text{oxide}}}{D_2O} + H_2$$

$$CH_4 + 2D_2 \longrightarrow \underset{\substack{\text{Deuterium}\\ \text{methane}}}{CD_4} + 2H_2$$

Some exchange reactions take place in presence of hydrogenation catalyst such as finely divided nickel, palladium or platinum black.

$$C_6H_6 + 3D_2 \underset{\text{black}}{\overset{\text{Platinum}}{\rightleftharpoons}} \underset{\substack{\text{Deutero}\\ \text{benzene}}}{C_6D_6} + 3H_2$$

Exchange reactions occur with great readiness when they involve ions in solutions, *e.g.*, in alkaline solution both acetone and acetyl acetone exchange all of their hydrogen atoms for deuterium because of their ionisation.



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{\text{Alkali}} CH_3-\overset{\overset{OH}{|}}{C}=CH_2 \underset{-3H_2}{\overset{+3D_2}{\rightleftharpoons}} CD_3-\overset{\overset{OD}{|}}{C}=CD_2$$

$$\rightleftharpoons \underset{\text{Deutro acetone}}{CD_3-\overset{\overset{O}{\|}}{C}-CD_3}$$

Similarly, acetylene undergoes deuterium exchange in alkaline solution because of the weakly acidic character of C—H bond in acetylene.

$$C_2H_2 \overset{\text{Alkali}}{\rightleftharpoons} \underset{\substack{\text{Deutero}\\ \text{acetylene}}}{C_2D_2} + H_2$$

(*ix*) **Reducing property.** At 700°C, AgCl is reduced to metallic silver, when deuterium is passed through its solution.

$$D_2 + 2AgCl \longrightarrow 2Ag + 2DCl$$

Uses. (*i*) It has been found as a source of *deutrons* which are capable of initiating several nuclear transformations through the formation of compound nucleus at relatively low energies. Some of nuclear transformations produced by deutrons are given below :

(*a*) (*D*, α) *reactions* :

$${}_3Li^6 + {}_1D^2 \longrightarrow [{}_4Be^8] \longrightarrow {}_2He^4 + {}_2He^4$$

$${}_8O^{16} + {}_1D^2 \longrightarrow [{}_9F^{18}] \longrightarrow {}_7N^{14} + {}_2He^4$$

(*b*) (*D, p*) *reactions* :

$$_{15}P^{31} + {}_1D^2 \longrightarrow [_{16}S^{33}] \longrightarrow {}_{15}P^{32} + {}_1H^1$$

$$_{11}Na^{22} + {}_1D^2 \longrightarrow [_{12}Mg^{32}] \longrightarrow {}_{11}Na^{24} + {}_1H^1$$

(*c*) (*D, n*) *reactions* :

$$_6C^{12} + {}_1D^2 \longrightarrow [_7N^{14}] \longrightarrow {}_7N^{13} + {}_0n^1$$

$$_1T^3 \text{ (or } {}_1H^3) + {}_1D^2 \longrightarrow [_2He^5] \longrightarrow {}_2He^4 + {}_0n^1 + \text{energy}$$

The energy liberated is used in hydrogen bomb.

(*d*) (*D, T*) *reactions* :

$$_3Li^7 + {}_1D^2 \longrightarrow [_4Be^9] \longrightarrow {}_3Li^6 + {}_1T^3$$

$$_{15}P^{31} + {}_1D^2 \longrightarrow [_{16}S^{33}] \longrightarrow {}_{15}P^{30} + {}_1T^3$$

(*ii*) It is used in the preparation of hydrogen bomb.

(*iii*) It has been used in the preparation of deuterium compounds which are very useful, *e.g.*, D_2O is used as a *moderator* in nuclear reactors to slow down the speed of fast moving neutrons.

(*iv*) Deuterium and its compounds are used as a *tracer* in the study of mechanism of various chemical and metabolic reactions taking place in the body, *e.g.*, with the help of deuterium it has been shown that butyric acid (a component of butter) is never stored in the body and is an immediate source of energy which at once gets consumed while stearic acid (a component of lard) is not used up at once and hence is useful in building up reverse stock in the body.

3. Tritium ($_1{}^3$(H or $^3{}_1$T)

Occurrence. It is an extremely rare isotope of hydrogen. It has been established that 10^{17} molecules of ordinary hydrogen contain only traces of tritium, *i.e.*, only $10^{-15}\%$ of ordinary hydrogen is tritium. The cause of the presence of tritium in ordinary hydrogen only in traces is that the nucleus of tritium is radioactive and hence unstable. Evidently it is very difficult to separate tritium from ordinary hydrogen. 10^{17} parts of ordinary water contain about 7 parts of tritium.

In nature, the traces of tritium are present. These are formed continuously in the upper atmosphere by the action of neutrons (produced by the action of cosmic radiations on the atmospheric gases) on atmospheric nitrogen.

$$_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{12} + {}_1T^3$$

Preparation. (*i*) *Oliphant, Harteek* and *Rutherford* (1934) obtained tritium by bombarding compounds such as D_3PO_4, ND_4Cl, $(ND)_2SO_4$ etc., with high energy deuterons.

$$\underset{\text{Deuterium}}{_1D^2} + \underset{\text{Deuteron}}{_1D^2} \longrightarrow \underset{\text{Tritium}}{_1T^3} + {}_1H^1$$

This is the first method of its preparation which led to its discovery.

(*ii*) *By the nuclear reactions produced by deutrons.*

$${}_4\text{Be}^9 + {}_1\text{D}^2 \longrightarrow {}_4\text{Be}^8 + {}_1\text{T}^3$$

$${}_6\text{Li}^7 + {}_1\text{D}^2 \longrightarrow [{}_4\text{Be}^9] \longrightarrow {}_3\text{Li}^6 + {}_1\text{T}^3$$

$${}_{47}\text{Ag}^{109} + {}_1\text{D}^2 \longrightarrow [{}_{48}\text{Cd}^{111}] \longrightarrow {}_{47}\text{Ag}^{108} + {}_1\text{T}^3$$

$${}_{15}\text{P}^{31} + {}_1\text{D}^2 \longrightarrow [{}_{16}\text{S}^{33}] \longrightarrow {}_{15}\text{P}^{30} + {}_1\text{T}^3$$

(*iii*) *By neutron bombardment of boron and nitrogen* (*i.e.*, neutron bombarding against saturated aqueous solution of boric acid and ammonium nitrate) :

$${}_5\text{B}^{11} + {}_0n^1 \longrightarrow [{}_5\text{B}^{12}] \longrightarrow {}_4\text{Be}^9 + {}_1\text{T}^3$$

$${}_7\text{N}^{14} + {}_0n^1 \longrightarrow [{}_7\text{N}^{15}] \longrightarrow {}_6\text{C}^{12} + {}_1\text{T}^3$$

(*iv*) *By slow neutron bombardment of lithium* :

$${}_3\text{Li}^6 + {}_0n^1 \longrightarrow {}_1\text{T}^3 + {}_2\text{He}^4$$

This is probably the best method of obtaining tritium.

Properties. (*i*) Because of the unfavourable neutron-to-proton ratio, tritium is a radioactive isotope with its half-life period of 12.4 years. It emits low energy β-particles and is changed into a lighter isotope of helium, ${}_2\text{He}^3$.

$${}_1\text{T}^3 \longrightarrow {}_2\text{He}^3 + \underset{\beta\text{-particle}}{{}_{-1}\text{e}^0}$$

The radioactive decay of tritium is the source of the traces of ${}_2\text{He}^3$ in the atmosphere.

(*ii*) Some of its physical constants are given below :

Boiling point = –248.1°C; Melting point (Tripole point) = –252.4°C; Heat of sublimation at triple point = 393.0 cals/mole; Heat of vaporisation at normal boiling point = 333 cals/mole; Vapour pressure at the triple point = 162.00 mm.

(*iii*) Its atomicity is 2 and hence its molecular formula is T_2.

(*iv*) Its chemistry is very nearly identical with that of hydrogen. However, reactions with tritium are still slower than those with deuterium.

(*v*) *Action of H_2.* It combines with H_2 on heating (300–400°C) to form tritium hydride, HT.

$$H_2 + T_2 \longrightarrow 2HT$$

HT reacts with HCl to give tritium chloride, TCl.

$$HT + HCl \longrightarrow TCl + H_2$$

(*vi*) *Action of O_2.* When burnt in O_2, it forms tritium oxide, T_2O.

$$2T_2 + O_2 \longrightarrow 2T_2O$$

Uses. (*i*) It has the possibility of use as an artificial radioactive tracer in chemistry, medicine and biology.

(*ii*) It is used in nuclear fusion reactions such as :

$${}_1\text{D}^2 + {}_1\text{H}^3 \longrightarrow {}_2\text{He}^4 + {}_0n^1 + \text{Energy}$$

In this reaction huge amount of energy is liberated which is used in hydrogen bomb.

(*iii*) It is a source of tritons which are used in several nuclear transformations. For example :

(*a*) (T, p) *reactions* :

$${}_{27}\mathrm{Co}^{59} + {}_{1}\mathrm{T}^{3} \longrightarrow {}_{27}\mathrm{Cu}^{64} + {}_{1}\mathrm{H}^{1} \text{ (or } {}_{1}\mathrm{p}^{1}\text{)}$$

(*b*) (T, D) *reactions* :

$${}_{3}\mathrm{Li}^{6} + {}_{1}\mathrm{T}^{3} \longrightarrow {}_{3}\mathrm{Li}^{7} + {}_{1}\mathrm{D}^{2}$$

$${}_{29}\mathrm{Cu}^{63} + {}_{1}\mathrm{T}^{3} \longrightarrow {}_{29}\mathrm{Cu}^{64} + {}_{1}\mathrm{D}^{2}$$

(*c*) (T, n) *reactions* :

$${}_{16}\mathrm{S}^{32} + {}_{1}\mathrm{T}^{3} \longrightarrow {}_{17}\mathrm{Cl}^{34} + {}_{0}n^{1}$$

(*d*) (T, α) *reactions* :

$${}_{3}\mathrm{Li}^{7} + {}_{1}\mathrm{T}^{3} \longrightarrow {}_{2}\mathrm{He}^{6} + {}_{2}\mathrm{He}^{4}$$

(*iv*) It is also of potential use in thermo-nuclear process.

(*v*) Tritium hydride, TH, is a very important compound of tritium. It is used in the preparation of a number of organic compounds containing this radioactive isotope.

Questions with Answers

Q.1 Explain the following :

(*a*) Hydrogen is not prepared by action of concentrated sulphuric acid on zinc.

Ans : Conc. H_2SO_4 reacts with zinc to form SO_2 rather than H_2

$$\mathrm{Zn} + 2\ \mathrm{H_2SO_4}\ \text{(Conc.)} \xrightarrow{\text{Heat}} \mathrm{ZnSO_4} + \mathrm{SO_2} + 2\mathrm{H_2O}$$

(*b*) A solution of ferric chloride is unaffected when hydrogen is bubbled through it, but gets reduced when zinc is added to the same acidified solution.

Ans : Ordinary H_2 is less reactive and hence it does not reduce acidified $FeCl_3$ solution. However, when zinc is added to acidified $FeCl_3$ solution, nascent hydrogen thus produced is associated with more energy. Consequently, it is more reactive and hence reduces acidified $FeCl_3$ solution.

$$\begin{array}{lcl} \mathrm{FeCl_3 + H_2} & \longrightarrow & \text{No reaction} \\ \mathrm{Zn + H_2SO_4} & \longrightarrow & \mathrm{ZnSO_4 + H_2^{*}}\ \textit{(nascent hydrogen)} \\ \mathrm{2FeCl_3 + H_2^{*}} & \longrightarrow & \mathrm{2FeCl_2 + 2HCl} \\ \textit{(Yellow)} & & \textit{(Green)} \end{array}$$

(*c*) Dihydrogen is not preferred in balloons these days ?

Ans : Dihydrogen is highly combustible and hence is likely to catch fire in presence of excess of air.

(*d*) Hydrogen is unreactive at room temperature.

Ans : Due to high enthlapy of H–H bond, hydrogen is quite unreactive at room tempreature. However, at high tempreatures or in presence of catalysts, it combines with many metals and non-metals to form hydrides.

(*e*) Hydrogen occurs in diatomic form rather than in monoatomic form under normal conditions ?

Ans : Hydrogen atom has only one electron and thus has one electron less than the stable inert gas configuration of helium. Therefore, to achieve stable inert gas configuration of helium, it shares its single electron with the electron of other hydrogen atom to form a stable diatomic molecule.

(*f*) Conc. H_2SO_4 cannot be used for drying H_2.

Ans : Conc. H_2SO_4, on absorbing H_2O from anoist H_2, produces so much heat that H_2 catches fire.

Q.2 Name one example of a reaction in which dihydrogen acts (*i*) as an oxidising agent and (*ii*) as a reducing agent.

Ans : (*i*) **As oxidising agent.** In the reaction of dihydrogen with metals to form metal hydrides, it acts as an oxidising agent.

$$\underset{(\text{Na} = 0)}{2\,\text{Na}(s)} + \underset{(\text{H} = 0)}{\text{H}_2(g)} \xrightarrow{\text{Heat}} \underset{(\text{Na} = +1,\ \text{H} = -1)}{2\,\text{Na}^+\,\text{H}^-(s)}$$

Here, Na has been oxidised to Na^+ while dihydrogen has been reduced to hydride (H^-) ion.

(*ii*) **As reducing agent.** In the reaction of heated cupric oxide with dihydrogen to form H_2O and copper metal, dihydrogen acts as a reducing agent.

$$\underset{(\text{Cu} = +2,\ \text{O} = -2)}{\text{CuO}\ (s)} + \underset{(\text{H} = 0)}{\text{H}_2\ (s)} \xrightarrow{\text{Heat}} \underset{(\text{Cu} = 0)}{\text{Cu}\ (s)} + \underset{(\text{H} = +1,\ \text{O} = -2)}{\text{H}_2\text{O}\ (g)}$$

Q.3 Write the names of isotopes of hydrogen. What is the mass ratio of these isotopes ?

Ans : Protium $^1_1$H, Deuterium $^2_1$H or D, Tritium $^3_1$H or T. The mass ratio of protium : deuterium : tritium = 1 : 2 : 3.

Q.4 Which istope of hydrogen (*i*) does not contain neturons (*ii*) contains equal number of protons and neutrons (*iii*) is radioactive.

Ans : (*i*) protium (*ii*) deuterium (*iii*) tritium.

Q.5 Name one compound each in which hydrogen exists in (*i*) + 1 (*ii*) –1 (*iii*) zero oxidation state.

Ans : (*i*) HCl or H_2O or NH_3 (*ii*) NaH or CaH_2 (*iii*) H_2.

Q.6 Give two advantages of using hydrogen over gasoline as a fuel.

Ans : High heat of combustion and no pollutants like SO_2, NO_2, CO_2, etc.

Q.7 Which isotope of hydrogen is used as a tracer in organic reactions.

Ans : Hydrogen has three isotopes, *viz*, H, D and T. Due to difference in masses, the rate constants of these isotopes with the same subtrate are different.

In other words, both D and T show isotope effect. But since T is not only radioactive but is also least abundant hydrogen isotope, D is used as a tracer to study the mechanism of organic reactions.

Q.8 How can the production of dihydrogen obtained from coal gasification be increased ?

Ans : The process of producing syngas or synthesis gas from coal is called coal gasification.

$$\underset{\text{Coal}}{C\,(s)} + \underset{\text{Steam}}{H_2O\,(g)} \xrightarrow[\text{Ni}]{1270\text{K}} \underbrace{CO\,(g) + H_2\,(g)}_{\text{Syngas}}$$

The production of hydrogen can be increased by reacting carbon monoxide of syngas with steam in presence of iron chromate as catalyst at 673K.

$$CO\,(g) + H_2O\,(g) \xrightarrow{FeCrO_4,\ 673\text{K}} CO_2\,(g) + H_2\,(g)$$

CO_2 thus produced is removed either by scrubbing with a solution of sodium arsenite or by passing the mixture through water under 30 atm. pressure when CO_2 dissolves leaving behind H_2 which is collected.

Q.9 How does H_2 react with Cl_2 ?

Ans : Dihydrogen reduces chlorine to Cl^- ion and itself gets oxidised to H^+ ions. An electron pair is then shared between these two species to form a cvalent molecule of hydrogen chloride.

$$\underset{(H = 0)}{H_2\,(g)} + \underset{(Cl = 0)}{Cl_2\,(g)} \longrightarrow \underset{(H = +1,\ Cl = -1)}{2\,HCl\,(g)}$$

Q.10 Complete the following reactions :

(*i*) $H_2\,(g) + M_mO_o\,(s) \xrightarrow{\Delta} \ldots$

(*ii*) $CO\,(g) + H_2\,(g) \xrightarrow{\Delta} \ldots$

Ans : (*i*) $oH_2\,(g) + M_mO_o\,(s) \xrightarrow{\Delta} mM\,(s) + oH_2O\,(l)$

(*ii*) $CO\,(g) + 2H_2\,(g) \xrightarrow[\text{Catalyst}]{\Delta} \underset{\text{Methanol}}{CH_3OH\,(l)}$

Q.11 What do you understand by the terms : (*i*) hydrogen economy (*ii*) hydrogenation (*iii*) syngas (*iv*) water-gas shift reaction and (*v*) fuel cell ?

Ans : (*i*) Hydrogen economy. The proposal to use hydrogen as a fuel in industry, power plants and possibly also in homes and motor vehicles is called hydrogen economy. The basic principle of hydrogen economy is the storage and transportation of energy in the form of liquid or gaseous dihydrogen.

(*ii*) Hydrogentation means addition of hydrogen across double and triple bonds to form saturated compounds. The vegetable oils such as soyabean oil, cotton seed oil, groundnut oil, are called polyunsaturated oils since they contain many C = C bonds. When these oils are exposed to air for prolonged periods, the double bonds present in them undergo oxidation, *i.e.* develop unpleasant taste. To avoid this, double bonds are hydrogenated. For this purpose, dihydrogen is bubbled through edible oils in presence of finely divided nickel at 473K when the oils are converted with solid fats.

$$\text{Vegetable oil} + H_2 \xrightarrow{\text{Ni, 473K}} \text{Vegetable Ghee}$$

This process is called hydrogenation or hardening of oils and is used in the manufacture of vegatable ghee like Dalda, Gagan, Rath, etc. from vegetable oils. It may, however, be noted that *hydrogenation reduces the number of double bonds but does not completely eliminate them.*

***(iii)* Syngas.** The mixtures of CO and H_2 are called synthesis gas or syngas. It is so named because it is used for the synthesis of methanol and a number of hydrocarbons. It can be produced by the reaction of steam on hydrocarbon or coke at high temperature in the presence of nickel as catalyst.

$$C_nH_{2n+2} + nH_2O \xrightarrow[\text{Ni}]{1270\text{K}} nCO + (2n + 1)\ H_2$$

e.g.

$$CH_4\ (g) + H_2O\ (g) \xrightarrow[\text{Ni}]{1270\text{K}} CO\ (g) + 3\ H_2\ (g)$$

These days syngas is produced from sewage saw dust, scarp wood, newspapers, etc. The process of producing syngas form coal is called '*coal gasification*'

$$C\ (s) + H_2O\ (g) \xrightarrow[\text{Ni}]{1270\text{K}} \underbrace{CO\ (g) + H_2\ (g)}_{\text{Syngas}}$$

***(iv)* Water-gas shift reaction.** The amount of hydrogen in the syngas can be increased by reacting CO of syngas with steam in the presence of iron chromate as catalyst

$$CO\ (g) + H_2O\ (g) \xrightarrow[FeCrO_4]{673\text{ K}} CO_2\ (g) + H_2\ (g)$$

This is called water-gas reaction.

***(v)* Fuel-cell.** Fuel cell is a device which converts the energy produced during the combustion of a fuel directly into electrical energy. Dihydrogen is used in hydrogen-oxygen fuel cells for generating electrical energy. It has many advantages over the conventional fossil fuels. It does not cause any pollution and releases more amount of energy per unit mass of fuel as compared to gasoline and other fuels.

Q.12 What is water gas ? How is it prepared ?

Ans : An equimolar mixture of CO and H_2 is called water gas. It is prepared by passing steam over red hot coke.

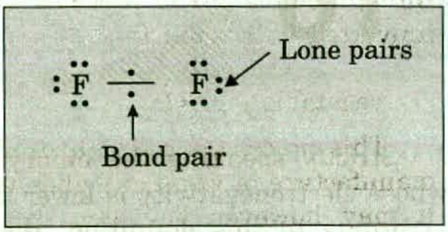
$$C\ (s) + \underset{\text{Steam}}{H_2O\ (g)} \xrightarrow{1270\text{ K}} \underbrace{CO\ (g) + H_2\ (g)}_{\text{Water gas}}$$

Q.13 Arrange H_2, D_2 and F_2 molecules in the increasing order of their bond dissociation enthalpy.

Ans : Due to greater nuclear mass, the bond pair in D–D bond is attracted more strongly than in H–H bond. Therefore, bond dissociation energy of D–D bond is higher than that of H–H bond.

However, due to repulsions between lone pairs of F and the bond pair (See Figure given in the margin), F–F bond dissociation enthaply is the minimum. Thus the bond dissociation enthalpy increases in the order :

$$F - F < H - H < D - D.$$



Q.14 In what respect do ortho and para hydrogen differ from each other ?

Ans : In H_2 molecule, the two electrons of two H-atoms spin in opposite direction (Paulie's exclusion principle) but the spin of two protons in the nucleus of two H-atoms spin in the same direction (parallel spins) in ortho hydrogen and in opposite direction (anti parallel spins) in para hydrogen. Thus ortho and para hydrogen differ in the direction in which the two protons present in the nucleus of two H-atoms spin.

University Questions

1. Justify the position of hydrogen in the periodic table. *(Meerut 89, Garhwal 88)*
2. Outline the manufacture of hydrogen by Lane's process. *(Kerala 80)*
3. What are the different forms of hydrogen? Give two properties and two uses of each. *(Raj. 83; GND 87; MD Rohtak 84)*
4. Write a short note on "ortho and para hydrogen". *(Meerut 80 S, 81, 81 S, 82, 83, 84, 88; Lucknow 80, 81; Kanpur 81; Bundelkhand 88; Rohilkhand 83, 84; Allahabad 87)*
5. (*a*) How is heavy hydrogen prepared by the electrolysis of heavy water and by chemical methods?
    (*b*) Write the uses of deuterium.
    (*c*) What is difference between ortho and para hydrogen?
    (*d*) What is nascent hydrogen? *(Himachal Pradesh 99)*
6. (*a*) How is atomic hydrogen prepared?
    (*b*) What are important uses of atomic hydrogen?
    (*c*) What happens when : (*i*) Deuterium combines with N_2 (*ii*) Tritium is burnt in air (*iii*) Deuterium is passed over heated alkali metal (*iv*) Atomic hydrogen is kept with molecular oxygen at 20° K.
    (*d*) What is the difference between ortho and para hydrogen? *(Himachal Pradesh 2000)*
7. Write a note on isotopes of hydrogen. *(Kanpur 2000)*