

## Expansion work

First law of thermodynamics: The internal energy of an isolated system is constant.

\* If 'W' is the work done on a system, 'q' for the energy transferred as heat to a system, then  $\Delta U$ , internal energy change is written as

$$\boxed{\Delta U = q + W} \quad (1)$$

This equation is the mathematical statement of the first law.  $\Delta U = 0$  ( $q = 0, W = 0$ ).

For infinitesimal change, if the work done on a system is ' $dW$ ' & the energy supplied to it as heat is ' $dq$ ', then

$$dU = dq + dW \quad (2)$$

### Expansion work or pressure-volume or mechanical work

Expansion work = Work required to move an object a distance  $dz$  against an opposing force of magnitude  $F$  is

$$dW = -F dz \quad (3)$$

As shown in fig ①, when a piston of area  $A$  moves out through a distance  $dz$ , it sweeps out a volume,  $dV = Adz$ .

The external pressure  $P_{ext}$  is equivalent to a weight pressing on the piston and the force opposing expansion is  $F = P_{ext} A$ .

When the system expands through a distance  $dz$  against an external pressure  $P_{ext}$ , the work done is  $dW = -P_{ext} Adz$

$$dW = -P_{ext} dV \quad (4)$$

Total work done when the volume changes from  $V_i$  to  $V_f$

$$W = - \int_{V_i}^{V_f} P_{ext} dV \quad (5)$$

For expansion  $- V_f > V_i$

for compression  $- V_i > V_f$

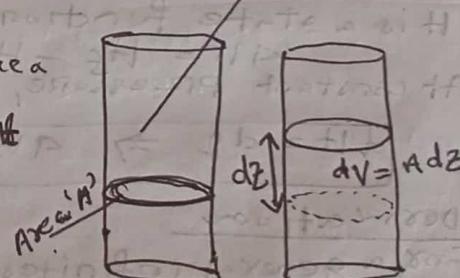


Fig ①

## Isothermal reversible expansion

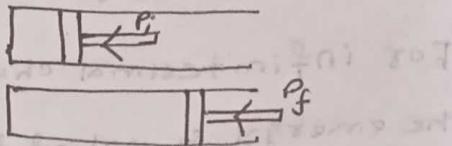
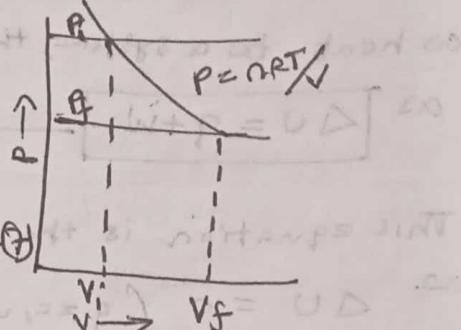
Let us consider the isothermal and reversible expansion of a perfect gas.  $pV = nRT \Rightarrow p = \frac{nRT}{V}$  (6)

The work of reversible isothermal expansion of a perfect gas from  $V_i$  to  $V_f$  at a temperature  $T$  is

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

For expansion  $W < 0$ . Work done by the system

For compression  $W > 0$ . Work done on the system



Enthalpy (H) Energy supplied as heat at constant pressure

The enthalpy (H) is defined as

$$H = U + PV \quad (8) \Rightarrow H = U + nRT$$

where  $P$  &  $V$  are the pressure & volume of the system.

H is a state function (depends on the initial & final states)

$\Delta H = H_f - H_i$   
At constant pressure, no additional work

$$dH = dU + d(PV) \Rightarrow dH = dq + PdV$$

$$dH = dq + dw$$

Derivation

For a general infinitesimal change in the state of the system,  $U$  changes to  $U + dU$ ,  $P$  changes to  $P + dP$ ,  $V$  changes to  $V + dV$ , then

$$H + dH = (U + dU) + (P + dP)(V + dV)$$

$$H + dH = U + dU + PV + PdV + VdU + VdP + \frac{dP}{dV}dV \quad \text{small} \\ dH = dU + PdV + VdP \quad \text{negligible}$$

$$dH = dq + dw + pdv + vdp \quad \left[ \begin{array}{l} dU = dq + dw \\ dw = -pdV \end{array} \right]$$

$$dH = dq - pdV + pdV + Vdp$$

$$dH = dq + Vdp$$

At constant  $dP = 0$

$$dH = dq$$

Entropy is a measure of the energy dispersed in a process.

\* The entropy of an isolated system increases in the course of a spontaneous change:  $\Delta S_{\text{total}} > 0$ .

Where  $S_{\text{total}}$  is the total entropy of the system & surroundings.

\* The change in entropy ( $\Delta S$ ) occurs as a result of a physical or chemical change (process).

\* It is the change in the extent to which entropy is dispersed on how much energy is transferred as heat.

\* Heat stimulates random motion in the surroundings.

$$\boxed{\Delta S = \frac{dq_{\text{rev}}}{T}}$$

- This is the thermodynamic definition of entropy.

For a measurable change between two states i & f.

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$$

### Entropy changes accompanying specific processes

(a) Expansion The entropy change when a perfect gas expands

isothermally from  $V_i$  to  $V_f$  is

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$\Delta S = nR \ln \frac{P_i}{P_f}$$

$$\Delta S_{\text{surv}} = \frac{dq_{\text{surv, rev}}}{T_{\text{surv}}} \quad \boxed{\Delta S = \frac{q_{\text{surv}}}{T_{\text{surv}}}}$$

(b) Phase transition

The degree of dispersal of matter and energy changes when a substance freezes or boils as a result of changes in the order with which molecules pack together and the extent to which energy is localized or dispersed.

\* At the transition temperature, any transfer of energy as heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium.  $q_p = \Delta_{\text{th}} H$

$$\boxed{\Delta S_{\text{ts}} = \frac{\Delta H_{\text{ts}}}{T_{\text{ts}}}}$$

#### Problems

① Calculate the entropy change of a perfect gas under isothermal expansion from  $V_i$  to  $V_f$ ?  
Given  $V_f = 2V_i$

② Find the enthalpy of vaporization of ethane from its boiling point,  $\sim 88.6^\circ\text{C}$ .

③ One mole of an ideal gas book expands reversibly from  $3 \times 10^{-2} \text{ m}^3$  to  $5 \times 10^{-2} \text{ m}^3$ . Calculate the entropy change of the gas?

### Third law of thermodynamics

Nernst heat theorem The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero,  $\Delta S \rightarrow 0$ ,  $T \rightarrow 0$ , provided all the substances involved are perfectly crystalline.

\* "The entropy of all perfect crystalline substances is zero at  $T = 0$ "

Gibbs free energy The energy available for a useful work from a system is known as Gibbs free energy.  $G_f = H_f - TS$

The change in free energy of the system is given by

$$\Delta G_f = \Delta H_f - T\Delta S, \quad \Delta G_f = \text{Work exp} \rightarrow \text{Maximum non expansion work.}$$

\*  $\Delta G_f < 0 \Rightarrow \Delta G_f = -ve = \text{spontaneous process}$

\*  $\Delta G_f > 0 \Rightarrow \Delta G_f = +ve = \text{Non spontaneous process}$

$\Delta G_f = 0 \Rightarrow \Delta G_f = 0 = \text{Equilibrium process.}$

Example How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mole of glucose molecule under standard conditions at  $37^\circ\text{C}$  (blood temperature). The standard entropy and enthalpy of the reaction are  $+182.4 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $-2808 \text{ kJ mol}^{-1}$  respectively.

Solution

$$\Delta G_f = \Delta H_f - T\Delta S$$

$$= -2808 \text{ kJ mol}^{-1} - (310 \text{ K}) \times (182.4 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Delta G_f = -2865 \text{ kJ mol}^{-1} \cancel{\text{expansion work}}$$

Variation of free energy change with temperature & pressure

$$h = U - TS \quad \text{--- (1)}$$

$$U = H + PV \quad \text{--- (2)}$$

From (1) & (2)

$$h = U + PV - TS \quad \text{--- (3)}$$

On differentiation

$$dh = dU + PV - TS - dT \quad \left[ dU = dq + dw \right] \quad \text{--- (4)}$$

If the work done is only due to expansion, then  $-dw = PdV$

$$dq = dU + PV$$

$$\left[ ds = \frac{dq}{T} \right]$$

$$\Rightarrow Tds = dU + PV \quad \text{--- (5)}$$

From (4) & (5)

$$dh = dU + PV + VdP - dU - PV - SdT$$

$$dh = VdP - SdT \quad \text{--- (6)}$$

At constant pressure,  $dP = 0$

$$\left( \frac{dh}{dT} \right)_P = -S \quad \text{--- (7)}$$

At constant temperature,  $dT = 0$

$$\left( \frac{dh}{dP} \right)_T = V \quad \text{--- (8)}$$

Free energy change,  $\Delta h$  is given by

$$\Delta h = h_2 - h_1 = \int_{P_1}^{P_2} VdP$$

For ideal gas  $|PV = nRT|$

$$\Delta h = nRT \int_{P_1}^{P_2} \frac{dp}{P} = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

Example: calculate the free energy change which occurs when 1 mole of an ideal gas expands reversibly and isothermally at  $37^\circ\text{C}$  from an initial volume of  $55 \text{ dm}^3$  to  $1000 \text{ dm}^3$ .

$$\text{Solution} \quad \Delta h = nRT \ln \left( \frac{V_1}{V_2} \right) = 1 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K}) \ln \left( \frac{55 \text{ dm}^3}{1000 \text{ dm}^3} \right)$$

$$= -7476.8 \text{ J mol}^{-1}$$

An electrochemical cell consists of two electrodes of metallic conductors in contact with an electrolyte an ionic character (which may be a solution, a liquid or a solid)

The various types or kinds of electrode are summarized as in table ①

<u>Electrode type</u>	<u>Designation</u>	<u>Redox couple</u>	<u>Half reaction</u>
Metal/metal ion	$M(s)/M^+(aq)$	$M^+/M$	$M^+(aq) + e^- \rightarrow M(s)$
Gas	$Pt(s)/X_2(g)/X^-(aq)$	$X^+/X_2$	$X^-(aq) + e^- \rightarrow \frac{1}{2}X(g)$
Metal/in soluble salt	$M(s)/MX(s)/X^-(aq)$	$MX/M, X^-$	$MX(s) + e^- \rightarrow M(s) + X^-(aq)$
Redox	$Pt(s)/M^+(aq), M^{2+}(aq)$	$M^{2+}/M^+$	$M^{2+}(aq) + e^- \rightarrow M^+(aq)$

\* Any "inert metal" shown as part of the specification is posed to act as a source or sink of electrons but takes no <sup>other</sup> part in the reaction other than acting as a catalyst for it.

\* If the electrolytes are different, the two compartments may be joined by a salt bridge which is a tube containing a concentrated electrolyte solution (KCl) that completes the electrical circuit and enables the cell to function.

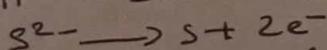
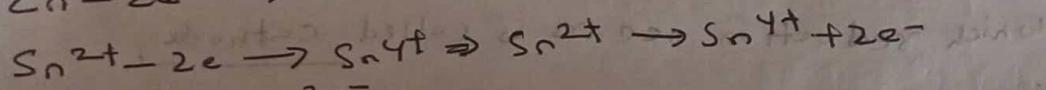
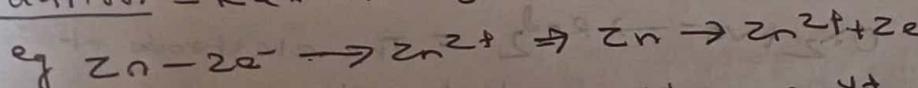
\* A galvanic cell is an electrochemical cell that produce electricity as a result of the spontaneous reaction occurring inside it.

\* An electrolytic cell is an electrochemical cell in which an non-spontaneous reaction is driven by an external source of current.

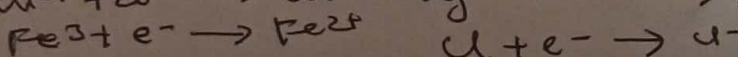
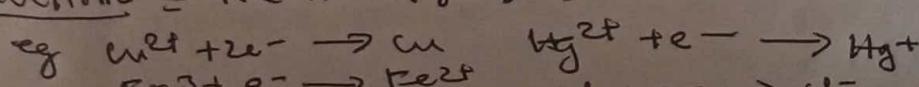
\* The difference in electrode potential which causes the current to flow the electrode at a higher potential to the electrode at lower potential is known as the cell potential or emf of the cell ( $emf = \text{electromotive force}$ ). It is measured by potentiometer.

Half reactions and electrodes

Oxidation = Removal of electron from a species.



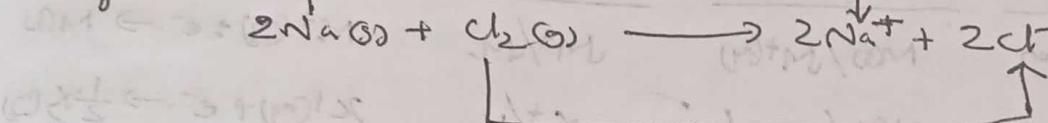
Reduction = Addition (gain) of electron from a species



Redox reaction Reaction in which there is a transfer of electrons from one species to another.

\* Redox reaction is the sum of oxidation half reaction in which electrons are lost and a reduction half reaction in which electrons are gained.

eg  $\text{2Na(s) + Cl}_2\text{(g)} \rightarrow \text{2Na}^+\text{(s) + 2Cl}^-\text{(s)}$  oxidation ( $2e^-$  lost)



Reducing agent or reductant = electron donor

eg  $\text{C, H}_2\text{S, HI etc}$

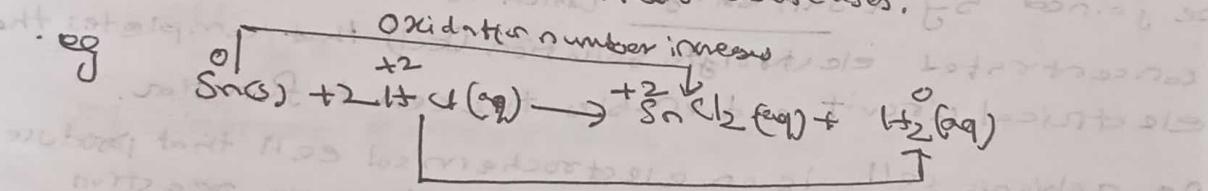
Oxidizing agent or oxidant = electron acceptor

eg  $\text{KMnO}_4, \text{K}_2\text{Cr}_2\text{O}_7, \text{HNO}_3$  etc

Redox reaction in terms of Oxidation number

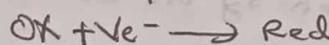
Oxidation = increased in oxidation number

Reduction = oxidation number decreases.



decrease in oxidation number

\* The reduced and oxidized species in a half reaction forms a redox couple.



\* The reduction and oxidation process responsible for the overall reaction in a cell are separated in space. oxidation takes place at one electrode and reduction takes place at the other.

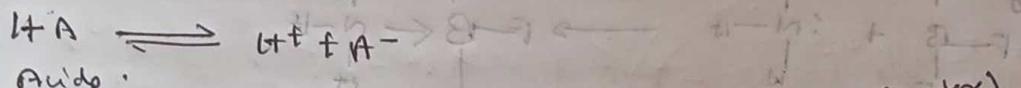
Oxidation  $\text{Red} \rightarrow \text{OX, } \text{Ve}^-$  = The electrode at which oxidation occurs is called anode.

Reduction  $\text{OX} + \text{Ve}^- \rightarrow \text{Red}$  = The electrode at which reduction occurs is called cathode.

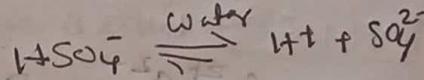
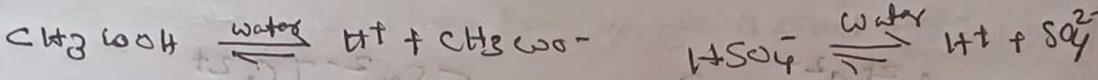
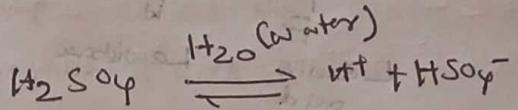
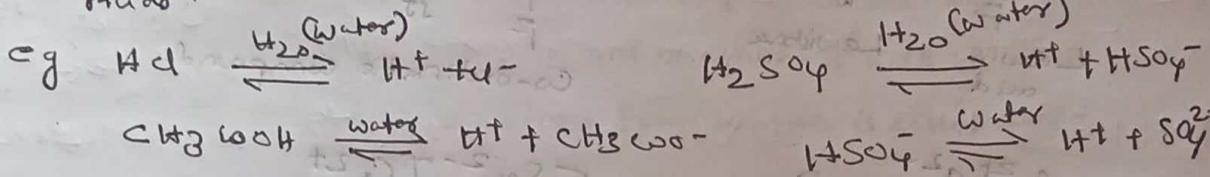
## Arrhenius concept of Acids and Bases

Based on the behaviour of electrolytes in solution, Arrhenius provided the concept of acids and bases.

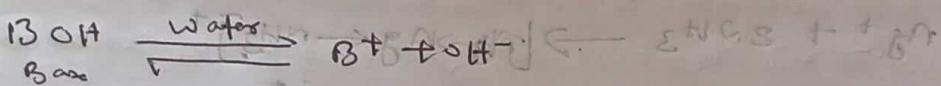
Acid Hydrogen containing substance which gives  $H^+$  ions in aqueous solution. The presence of ionisable hydrogen is an essential feature of all acids.



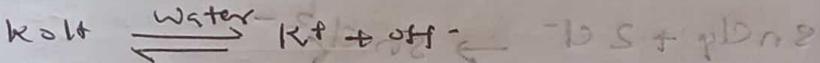
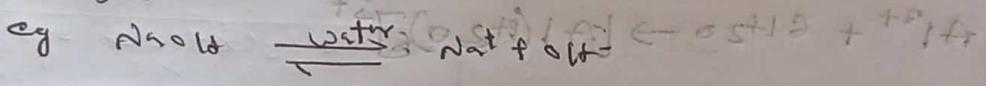
Acids



Bases A substance which contains one or more hydroxyl groups and furnishes hydroxyl ( $OH^-$ ) ions in aqueous solution.



Base



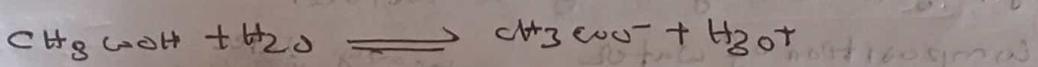
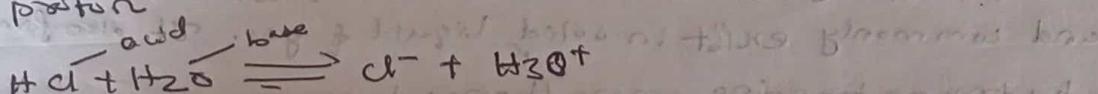
\* Nature of hydrogen ion in aqueous solution -  $H^+$  ion always exists in solution in the more stable form,  $H_3O^+$  known as hydronium ion.



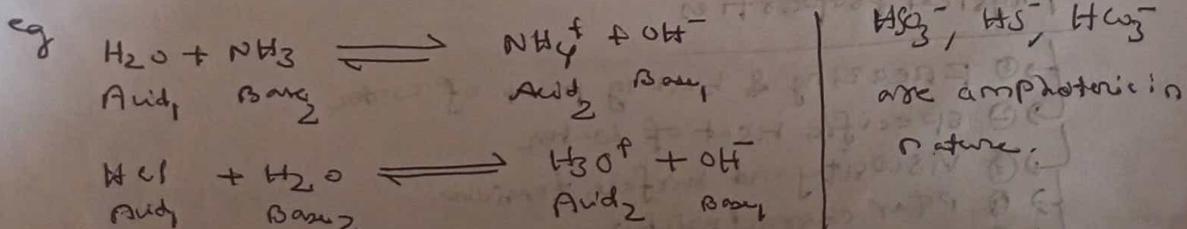
## Brønsted-Lowry concept of Acids and Bases

Acid - substance (molecular or ionic) which has tendency to donate a proton

Base - substance (molecular or ionic) which has tendency to accept a proton



Amphoteric compounds: Certain molecules and ions may exhibit both acidic or basic behaviour under the appropriate conditions. Such species are known as amphoteric.



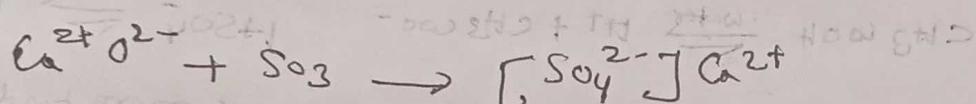
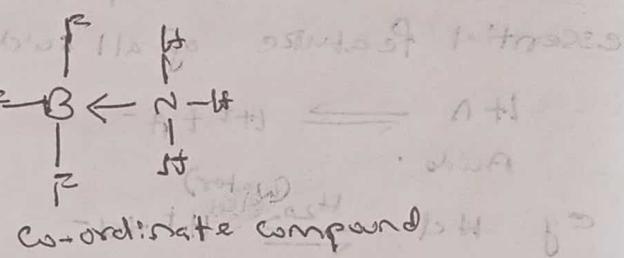
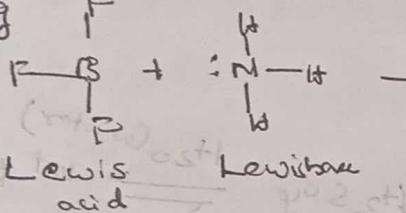
## Lewis concept of Acids and Bases

Acid - Base

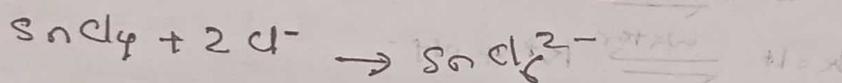
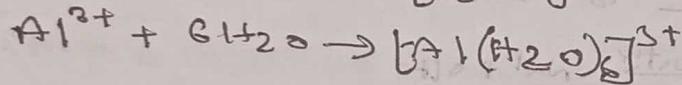
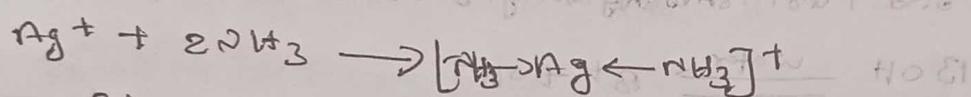
A substance which can accept an electron pair while a Base is a substance which can donate an electron pairs to form a coordinate bond.

\* Acid - Electron acceptor. Base Electron donor.

e.g F



Lewis base Lewis acid



## Water Chemistry

\* Water is God's greatest gift to mankind. Our body contains around 70% water. It is required in lesser for production of steam, which acts as a source of energy, as coolant in many power and chemical plants, in steel plant, paper mill, textile, ice and many other industries.

\* Water ( $\text{H}_2\text{O}$ ) is a polar inorganic compound. It is used as solvent. It is the most abundant substance on earth and commonly exist in solid, liquid & gas. It also form hydrogen bonding among themselves.

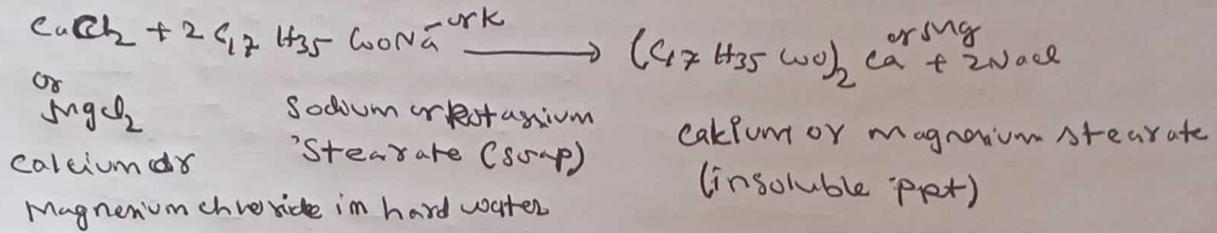
Composition of water Heavy water  $\text{D}_2\text{O}$

\*  $\text{H}_2\text{O}$  (99.78%),  $\text{D}_2\text{O}$  (0.02%) & other forms exists in traces only.  $\hookrightarrow$  Nuclear technology on  $\text{D}_2\text{O}$  is at moderate level.

## Physical properties

- ① Freezing & boiling point of water
- ② Specific heat of water
- ③ Viscosity and surface tension
- ④ Polar characteristics
- ⑤ Amphotropic nature

Hardness of water: Water which does not produce lather with soap solution but form a white precipitate is called hard water. It is due to the presence of dissolved salts in it. Soaps are sodium or potassium salts of higher fatty acids like stearic acid, oleic acid and palmitic acid.



\* Water which easily forms lather with soap is called soft water, such water does not contain calcium and magnesium salts in it.

\* The process of removing hardness from water is called softening of water.

Hydrogen bonding: The attractive force which binds covalently bonded hydrogen atom of one molecule with electronegative atom (F, O, N) of another molecule of the same substance is known as the hydrogen bond. e.g. ... H—F ... H—F—F—H—F ... .

Factors responsible for formation of hydrogen bond

④ High electronegativity - F > O > N

$\text{H}-\text{F} \cdots \text{H}-\text{F} \cdots \text{H}-\text{F} \cdots \text{H}-\text{F} \cdots$        $\text{O}-\text{H} \cdots \text{O}-\text{H} \cdots \text{O}-\text{H} \cdots \text{O}-\text{H} \cdots$        $\text{N}-\text{H} \cdots \text{N}-\text{H} \cdots \text{N}-\text{H} \cdots$   
 $2.9 \cdot 0.01 \text{ kJ mol}^{-1}$        $22 \cdot 0.01 \text{ kJ mol}^{-1}$        $17 \cdot 0.01 \text{ kJ mol}^{-1}$

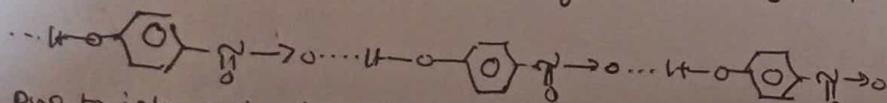
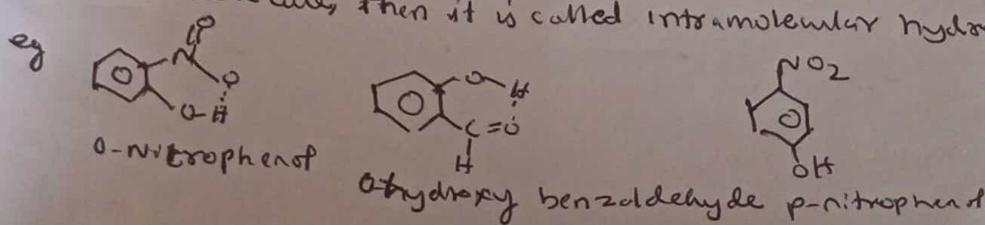
② Small size of the atom

$\text{HF}$  - hydrogen bond form,  $\text{H}-\text{Cl}$  and  $\text{H}_2\text{S}$  - no hydrogen bond form

## Types of hydrogen bonds

① Intermolecular hydrogen bond : The hydrogen bond formed between two or more molecules of the same or different substances is known as intermolecular hydrogen bonding. e.g.  $\text{H}_2\text{O}$ ,  $\text{HF}$ ,  $\text{N}_2\text{O}$  etc.

② Intramolecular hydrogen bond : When hydrogen bonding exists within the same molecule, then it is called intramolecular hydrogen bonding.  
e.g. 



Due to intermolecular H-bonding for p-nitrophenol, association of molecules takes place and thereby boiling point increases while o-nitrophenol, due to intramolecular H-bonding (Chelation) prevents association of molecules and therefore has low boiling point.

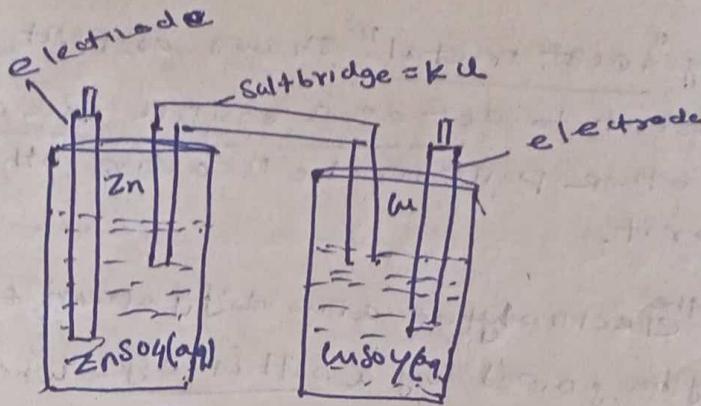
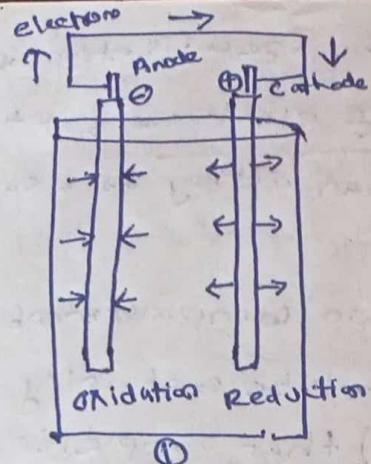
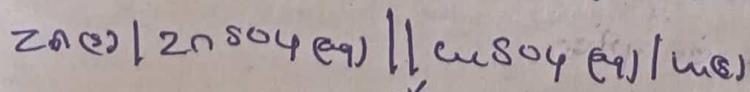
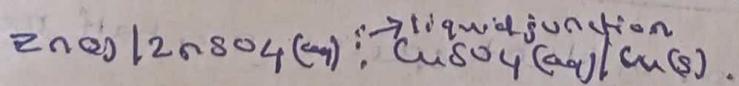
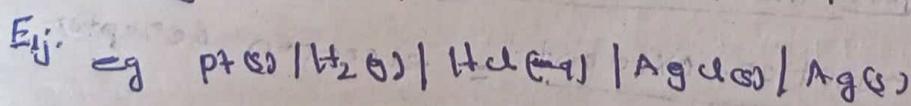


Fig ① When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation, the anode) and collected from another (the site of reduction, the cathode) and so there is a net flow of current which can be used to do work. (+) sign = electrons enter the cell  
 (-) sign = electrons leave the cell.

Fig ② The salt bridge, essentially an inverted U-tube full of concentrated salt solution has two opposing liquid junction potentials that almost cancel.

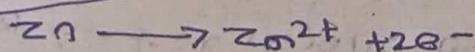
For Daniel cell redox couple at one electrode is  $\text{Cu}^{2+}/\text{Cu}$   
 & at the other is  $\text{Zn}^{2+}/\text{Zn}$ .

\* In a cell with two different electrolyte solutions in contact, as in the Daniel cell, there is an additional source of potential difference across the interface of the two electrolytes. This potential is called liquid junction potential.

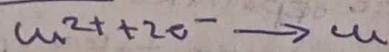


liquid junction potential has been eliminated.

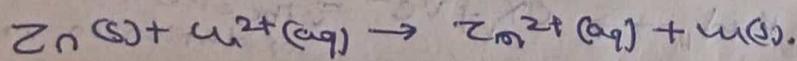
Oxidation



Reduction



The overall chemical reaction taking place in the cell is called cell reaction



\* Electrical energy in a Galvanic cell The electrical energy produced by a galvanic cell is given by the product of its electromotive force and the quantity of electricity which passes.

### Electrical energy and free energy change of the cell reaction

Suppose in a particular cell reaction,  $n$  is the number of electrons liberated at one electrode (or taken up at the other electrode). Then,  $n$  faradays ( $nF$ ) of electricity will be generated in the complete cell reaction.

$$\text{EMF} = E$$

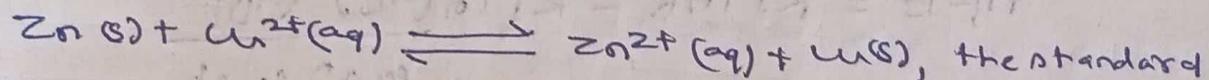
∴ Electrical energy produced by the cell =  $nFE$

Hence

$$-\Delta G_r = nFE$$

#### Example

For the Daniell cell involving the cell reaction



the standard free energies of formation of  $\text{Zn}(\text{s})$ ,  $\text{Cu}(\text{s})$ ,  $\text{Cu}^{2+}(\text{aq})$  &  $\text{Zn}^{2+}(\text{aq})$  are  $0$ ,  $0$ ,  $64.4 \text{ kJ mol}^{-1}$  and  $-154.0 \text{ kJ mol}^{-1}$  respectively. Find the standard EMF of the cell.

#### Solution

$$\Delta G^\circ = \Delta G_{fP}^\circ - \Delta G_{fR}^\circ = (-154.0 + 0) - (0 + 64.4 \text{ kJ}) \\ = -218.4 \text{ kJ}$$

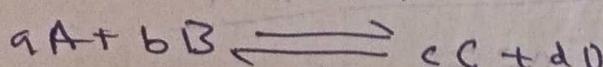
$$-\Delta G^\circ = nFE^\circ, n = 2$$

$$E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{-218.4 \text{ kJ mol}^{-1}}{2 \times 96485 \text{ C mol}^{-1}} = \frac{218400 \text{ V mol}}{2 \times 96485 \text{ C mol}^{-1}}$$

$$= 1.13 \text{ V}.$$

#### Electromotive force and Equilibrium constant of a cell reaction

Suppose the reaction occurring in a reversible cell is represented by the general equation



The decrease in free energy,  $-\Delta G_r$ , accompanying the process is given by  $-\Delta G_r = -\Delta G_r^\circ - RT \ln K - (1)$

where.

$$Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

If  $E$  is the EMF of the cell in volts and the cell reaction involves the passage of  $n$  faradays ( $10^6$  coulombs), the electrical energy produced by the cell is  $nFE$  volts coulombs i.e., joules.

$$nFE = -\Delta G^\circ - RT \ln Q \quad \text{--- (2)}$$

From Van't Hoff reaction isotherm

$$-\Delta G^\circ = RT \ln K \quad \text{--- (3)}$$

where  $K$  is the equilibrium constant of the cell reaction

Substituting  $Q$  & eqn (3) in (2) we get

$$nFE = RT \ln K - RT \ln \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

Replacing activities by concentrations and changing into

$$E = \frac{2.303 RT}{nF} \log K - \frac{2.303 RT}{nF} \log \frac{[e]^c [D]^d}{[A]^a [B]^b}$$

At  $25^\circ C$

$$\frac{2.303 RT}{nF} = \frac{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{96485 \text{ C mol}^{-1}}$$

$$= 0.0591 \text{ volt}$$

Hence,

$$E = \frac{0.0591}{n} \log K - \frac{0.0591}{n} \log \frac{[e]^c [D]^d}{[A]^a [B]^b}$$

Standard EMF & Equilibrium constant

$$-\Delta H^\circ = RT \ln K = nFE^\circ$$

$$\therefore \ln K = \frac{nFE^\circ}{RT} \Rightarrow \log K = \frac{nFE^\circ}{2.303 RT}$$

## Effect of concentration of electrolyte on cell potential

$$-\Delta G = -\Delta G^\circ - RT \ln Q$$

$$\eta FE = \eta F E^\circ - RT \ln Q \quad Q = \text{reaction quotient}$$

$$\Rightarrow E = E^\circ - \frac{RT}{nF} \ln Q \quad \text{of the cell reaction.}$$

$$= E^\circ - \frac{RT}{nF} \ln \frac{(a_C)^c (a_B)^d}{(a_A)^a (a_B)^b}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ at } 25^\circ C$$

This equation gives the effect of the concentration of reactants and products involved in the cell reaction on the EMF of the cell.

## Effect of electrolyte concentration on electrode potential. Nernst equation.

Let us consider an electrode consisting of a metal in contact with a solution of its own cations. As an example, we may consider a zinc rod in contact with a solution of zinc sulphate furnishing  $Zn^{2+}$  ion.



The decrease in free energy accompanying the electrode reaction is given by

$$\eta FE = \eta F E^\circ - RT \ln \left( \frac{a_{Zn}}{a_{Zn^{2+}}} \right)$$

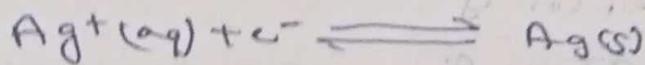
$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{Zn}}{a_{Zn^{2+}}}$$

$$= E^\circ - \frac{RT}{2F} \ln a_{Zn^{2+}} \quad [i.e., \text{for sol.}, a_1]$$

$$E = E^\circ - \frac{RT}{2F} \ln [Zn^{2+}]$$

Another example

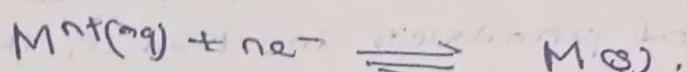
Half cell reaction



The electrode potential is given by

$$\begin{aligned} E &= E^\circ - \frac{RT}{F} \ln \frac{1}{[\text{Ag}^+]} \\ &= E^\circ + \frac{RT}{F} \ln [\text{Ag}^+] \end{aligned}$$

Hence, the general expression for the electrode potential of a metal M in contact with  $M^{n+}$  ions, involving the electrode reaction



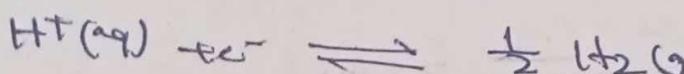
may be written as

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]} \quad \text{or}$$

$$= E^\circ + \frac{RT}{nF} \ln [\text{M}^{n+}]$$

$$\boxed{E = E^\circ + \frac{0.0591}{n} \log [\text{M}^{n+}]} \quad \text{Nernst Eqn.}$$

For hydrogen electrode

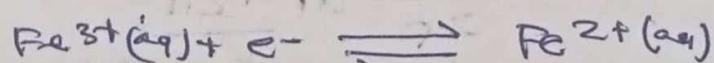


$$E = E^\circ - \frac{RT}{F} \ln \frac{1}{[\text{H}^+]} \quad \text{or}$$

$$= E^\circ + \frac{RT}{F} \ln [\text{H}^+]$$

$$\begin{aligned} E &= E^\circ - \frac{RT}{F} \frac{[\text{Red}]}{[\text{Ox}]} \\ &= E^\circ + \frac{RT}{F} \ln \frac{[\text{Ox}]}{[\text{Red}]} \end{aligned}$$

For  $\text{Fe}^{3+}/\text{Fe}^{2+}$  electrode



$$E = E^\circ - \frac{RT}{F} \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad \text{or}$$

$$= E^\circ + \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

## standard electrode potentials; Electrochemical series.

The potential of an electrode at a given temperature, depends upon the concentration of the ions in the surrounding solution. If the concentration of the ions is unity and the temperature is  $25^{\circ}\text{C}$ , the potential of the electrode is termed as the standard electrode potential.

The standard electrode potentials of a number of electrodes are given in Table ①. These values are said to be on hydrogen scale since in these determinations the potential of the standard hydrogen electrode, used as the reference electrode has been taken as zero.

Table ①. The electrochemical series of the metals.

### Least strongly reducing

Bismuth,  $\text{Bi}^{3+}$ ,  $\text{Bi}$   $E^\circ(\text{Vatb})$

Silver,  $\text{Ag}^+$ ,  $\text{Ag}$   $+1.80$

Copper,  $\text{Cu}^{2+}$ ,  $\text{Cu}$   $+0.80$

Hydrogen  $2\text{H}^+$ ,  $\text{H}_2(\text{g})$ , Pt  $0.00$

Ptad,  $\text{Pb}^{2+}$ ,  $\text{Pb}$   $-0.13$

Tin,  $\text{Sn}^{2+}$ ,  $\text{Sn}$   $-0.15$

Nickel  $\text{Ni}^{2+}$ ,  $\text{Ni}$   $-0.24$

Iron,  $\text{Fe}^{2+}$ ,  $\text{Fe}$   $-0.44$

Zinc,  $\text{Zn}^{2+}$ ,  $\text{Zn}$   $-0.74$

Chromium,  $\text{Cr}^{3+}$ ,  $\text{Cr}$   $-0.76$

Aluminum,  $\text{Al}^{3+}$ ,  $\text{Al}$   $-1.66$

Magnesium,  $\text{Mg}^{2+}$ ,  $\text{Mg}$   $-2.52$

Sodium,  $\text{Na}^+$ ,  $\text{Na}$   $-2.71$

Calcium,  $\text{Ca}^{2+}$ ,  $\text{Ca}$   $-2.87$

Potassium,  $\text{K}^+$ ,  $\text{K}$   $-2.92$

Lithium,  $\text{Li}^+$ ,  $\text{Li}$   $-3.04$

### Most strongly reducing

Table ① shows a part of the electrochemical series, the metallic elements (and hydrogen) arranged in the order of their reducing power as measured by their standard potentials in aqueous solution.

- \* A metal low in the series (with a lower standard potential) can reduce the ions of the metals with higher standard potentials.
- \* For example, zinc lies above magnesium in the electrochemical series, so zinc cannot reduce the magnesium ions in aqueous solution.
- \* Zinc can reduce hydrogen ions, because hydrogen lies higher in the series.

Fuel cells are galvanic cells in which chemical energy is directly converted into electrical energy.

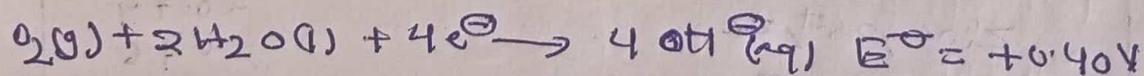
A fundamental and important example of a fuel cell is the hydrogen/oxygen cell such as the ones used in space missions (Fig.)

\* One of the electrolytes used is concentrated aqueous potassium hydroxide maintained at

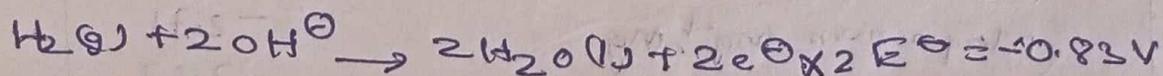
200°C and 20-40 atm.

\* The electrodes are porous nickel in the form of sheets of compressed powder.

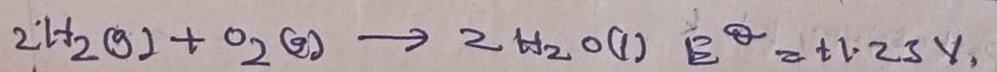
\* In cathode, reduction reaction occurs.



\* In anode, oxidation reaction occurs.

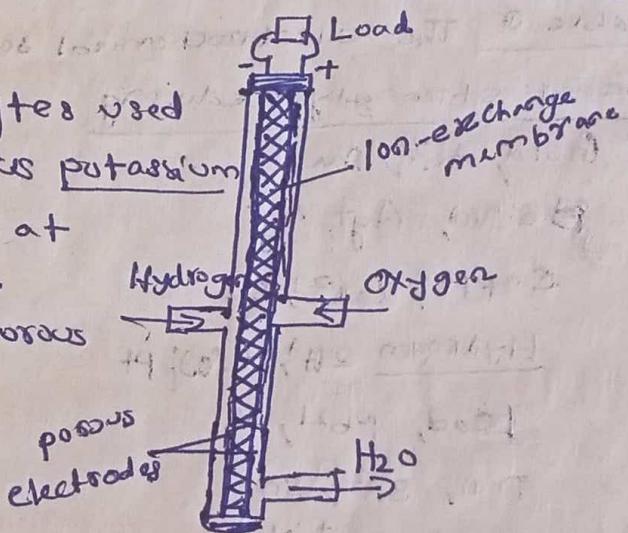
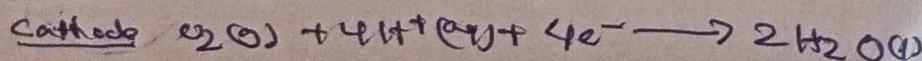
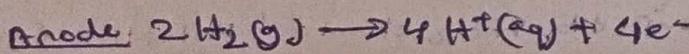


Overall reaction.



\* One type of highly developed fuel cell has phosphoric acid as the electrolyte and operates with hydrogen and air at about 200°C.

\* The hydrogen is obtained from natural gas.



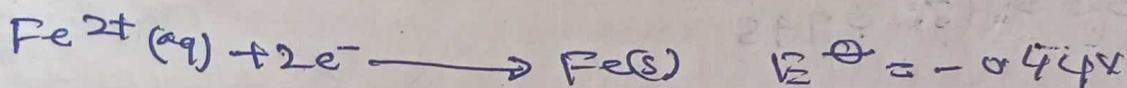
\* This fuel cell has shown promise for combined heat and power systems (CHP system). The power output of batteries of such cells has reached the order of 10 MW. Its efficiency can reach up to 80%.

\* Hydrogen gas is an attractive fuel, but it is difficult to store and dangerous to handle.

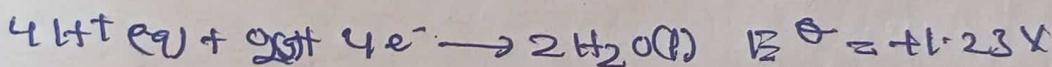
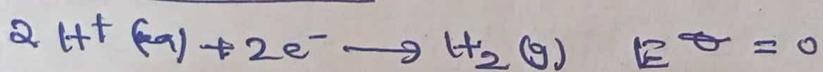
\* portable cells is to store the hydrogen in carbon

The process of slow destruction of metal due to chemical or electrochemical attack of the environment at their surfaces resulting in the formation of compounds such as oxides, carbonates, sulphides, sulphates etc. called corrosion, e.g.  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{FeCO}_3$ ,  $\text{Fe(OH)}_2$  etc.

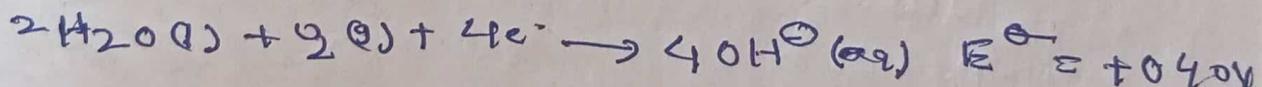
Corrosion A thermodynamic warning of the likelihood of corrosion is obtained by comparing the standard potentials of the metal reduction such as



In acidic solution



In basic solution



Because all three redox couples have standard potentials more positive than  $E^\ominus (\text{Fe}^{2+}/\text{Fe})$ , all three can drive the oxidation of iron to iron(II).

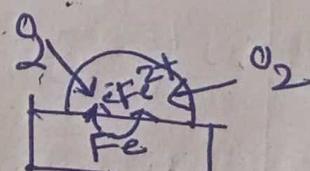


Fig: A simple version of the corrosion process is that of a droplet of water which is oxygen rich near its boundary with air. The oxidation of the iron takes place in the region away from the oxygen because the electrons are transported through the metal.

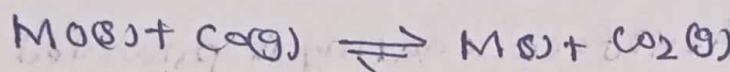
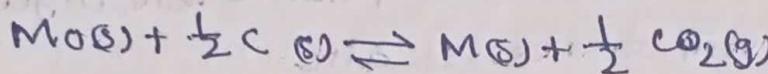
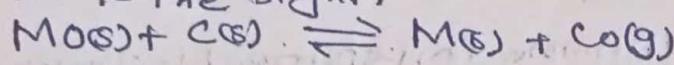
## protecting materials against corrosion

Several techniques for inhibiting corrosion are available. The rate of corrosion depends on the surface exposed.

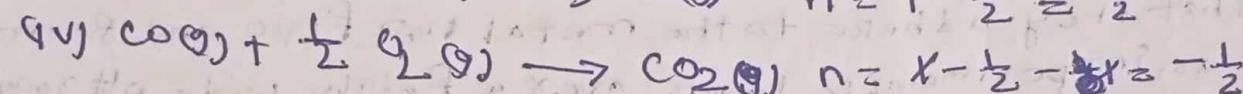
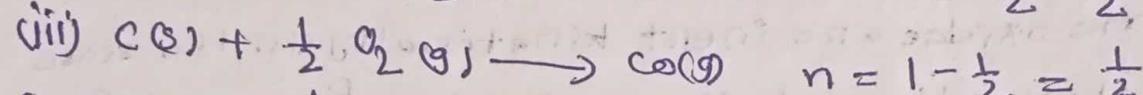
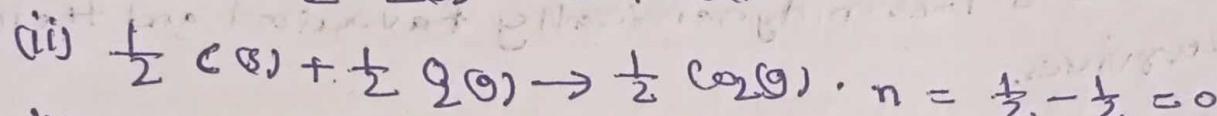
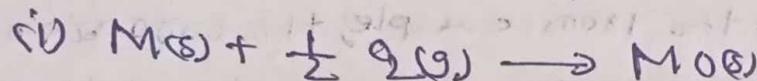
- \* Cover the surface with some impermeable layer, such as paint, which prevent access to air.
- \* Another form of surface coating is provided by galvanizing, the coating of an iron object with zinc. Since standard potential of latter is  $-0.76\text{ V}$  which is more negative than the iron couple, the corrosion of zinc is thermodynamically favoured and the iron survives.
- \* Some oxides are inert kinetically in the sense that they adhere to the metal surface and form an impermeable layer over a fairly wide pH range. This passivation or kinetic protection can be seen as a way of decreasing the exchange currents by sealing the surface. Thus aluminium is inert in air even though its standard potential is strongly negative ( $-1.66\text{ V}$ ).
- \* Another method of protection is to change the electric potential of the object by pumping in electrons that can be used to satisfy the demands of the oxygen reduction involving the oxidation of the metal. In cathodic protection, the object is connected to a metal with a more negative standard potential (such as magnesium,  $-2.86\text{ V}$ ). The magnesium acts as a sacrificial anode, supplying its own electrons to the iron and becoming oxidized to  $\text{Mg}^{2+}$  in the process.

## The extraction of metal from their oxides

Metals can be obtained from their oxides by reduction with carbon or carbon monoxide if any of the equilibria lie to the right.



These equilibria can be discussed in terms of the thermodynamic functions for the reactions



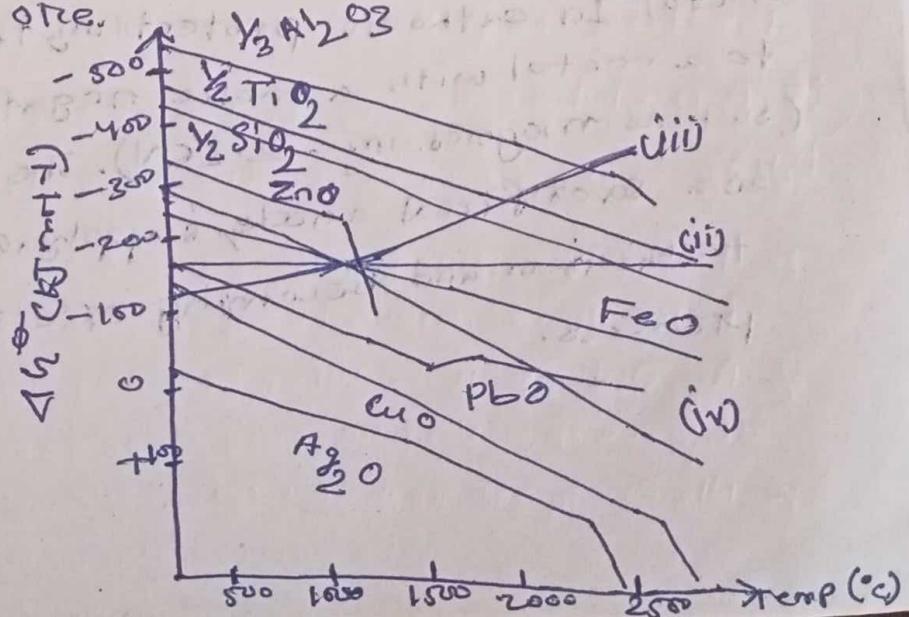
\* The temperature dependences of the standard Gibbs free energies of reaction (i) - (iv) depend on the reaction entropy through

$$\frac{d\Delta G^\circ}{dT} = -\Delta S^\circ$$

$$[\Delta H = \Delta H + \Delta S]$$

$$\left[ \frac{d\Delta H}{dT} = \alpha - \Delta S \right]$$

\* Ellingham diagram represents the  $\Delta G^\circ$  vs T. such diagrams help in predicting the feasibility of thermal reduction of an ore.



- (ii) The amount of gas is constant, so entropy change is small and  $\Delta H^\circ$  changes only slightly with temperature.
- (iii) There is a net increase in the amount of gas the standard reaction entropy is ~~large~~ large and positive. Therefore  $\Delta H^\circ$  decreases sharply with increasing temperature.
- (iv) There is a net decrease in the amount of gas,  $\Delta H^\circ$  increases sharply with increasing temperature.

These results are summarized with diagram (Fig) which is called an Ellingham diagram.

\* The standard reaction entropy is similar for all metals because in each case gaseous oxygen is eliminated and a compact, solid oxide is formed. As a result, the temperature dependence of the standard Gibbs energy of oxidation should be similar for all metals as is shown by the similar slopes of the lines in the diagram.

\* The kinks at high temperature correspond to the evaporation of the metals. Less pronounced kinks occur at the melting temperatures of the metals and the oxides.

\* The equilibrium lies to the right if  $\Delta H^\circ < 0$ . This is the case when the line for reaction (i) lies below (is more positive than) the line for one of the reactions (ii) to (v).

\* A metal oxide is reduced by any carbon reaction lying above it, because the overall reaction  $\Delta H^\circ < 0$ .

\* For example,  $MgO$  can be reduced to  $Mg$  at any temperature above room temperature.

\*  $Ag_2O$  decomposes when heated at above  $200^\circ C$  even in the absence of carbon, because Gibbs free energy (i) becomes positive.

\*  $Al_2O_3$  is not reduced by carbon until the temperature has been raised to above  $2000^\circ C$ .