

Use of Free Energy in Chemical Equilibrium

Thermodynamics :- The branch of science which deals with the study of quantitative relationships between heat and other form of energy.

When the study is confined to chemical changes only, is known as Chemical Thermodynamics.

System :- The part of universe which is under consideration is known as system.

Surroundings :- The remaining portion of universe which is open called surroundings.

$$\text{Universe} = \text{System} + \text{Surroundings}$$

Energy :- Energy is the essential requirement of life.
Energy is defined as the ability or capacity of the body to do work under given set of conditions.

It is Expressed in KiloCalories.

Laws of Thermodynamics

- ① Zeroth Law of Thermodynamics :-
If two systems A and B are in equilibrium then the third system C will be automatically in equilibrium

$$A \rightleftharpoons B \rightleftharpoons C$$

- ② First Law of Thermodynamics :- Energy can neither be created nor be destroyed but can be transferred from one form to another form.

ways to represent Energy
Pressure Volume Work

There are two types of work done

- ① Work is done by the system
When the work is done by the system, i.e. gas there is

~~Compression~~ Expansion process
 where dV = change in volume = +ve
 and work done = w will be -ve
 $w =$ -negative.

$dW = - PdV$ (work of expansion)
 Total work done when gas expands
 from initial volume (V_1) to final (V_2)

$$W = - \int_{V_1}^{V_2} PdV \quad \text{--- (1)}$$

$PV = nRT$ (Ideal gas equation)

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$W = -nRT [\ln]_{V_1}^{V_2}$$

$$W = -nRT [\ln V_2 - \ln V_1]$$

$$W = -nRT \ln \frac{V_2}{V_1}$$

By converting \ln to \log_{10} , we have
eq.

$$W = -2.303 nRT \log \frac{V_2}{V_1}$$

Acc to Boyle's Law

$PV = \text{Constant}$ (at constant Temp.)

$$P_1 V_1 = P_2 V_2$$

$$\boxed{\frac{P_1}{P_2} = \frac{V_2}{V_1}}$$

Equation ① becomes

$$W = -2.303 nRT \log \frac{P_1}{P_2}$$

② Work is done on the system
i.e. Compression occurs.

$$dv = -ve$$

$$W = +ve$$

$$W = 2.303 nRT \log \frac{P_1}{P_2}$$

Work of Compression

Internal Energy :-

Internal energy of a substance is the heat absorbed or evolved at constant volume. Internal energy is a state function.

Internal energy may be associated with different types of energies such as

$$E_{\text{internal}} = E_{\text{rotational}} + E_{\text{translation}} + E_{\text{vibrational}} + E_{\text{nuclear}} + E_{\text{electronic}} + E_{\text{molecular interaction}}$$

Internal energy of a system

depends on the state of system (state variables like P, V, T) not on the path which it follows.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$= E_{\text{products}} - E_{\text{reactants}}$$

Acc. to first law of thermodynamics

$$\frac{\Delta U}{\Delta t} = q + w$$

$$\Delta E$$

Heat Enthalpy:- (H)

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Heat change of a system is equal to the heat absorbed or evolved by the system at constant pressure.

At constant ~~temp~~ pressure:- there may be a change in the volume.

$$H = E + PV \quad \text{--- (1)}$$

where H is the enthalpy and it is the sum of internal energy and product of pressure and volume.

Enthalpy is a state function so

$$\Delta H = H_P - H_R$$

Equation (1) becomes

$$\Delta H = \Delta E + P\Delta V + V\Delta P$$

At constant pressure, $\Delta P = 0$ --- (2)

Equation (2) becomes

$$\Delta H = \Delta E + P\Delta V \quad \text{--- (3)}$$

Now acc. to first law of thermodynamics

$$\Delta E = q + w \quad \text{--- (4)}$$

Putting value in equation (3)

$$\Delta H = q + w + P\Delta V$$

Now the work done by the system⁷

$$W = -P\Delta V$$

$$\Delta H = Q - P\Delta V + P\Delta V$$

$$\Delta H = Q_p$$

— (5) Q_p = heat change at constant pressure

Hence in case of internal energy where change occurs at constant volume equation (5) becomes

$$\Delta E = Q_v$$
 — (6)

Relationship b/w Heat of Reaction at Constant Pressure (ΔH) and ΔE (Constant Volume)

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta H = \Delta E + P(V_2 - V_1)$$

$$\Delta H = \Delta E + PV_2 - PV_1$$

$$PV_1 = n_1 RT$$

$$PV_2 = n_2 RT$$

$$\Delta H = \Delta E + (n_2 RT - n_1 RT)$$

$$\Delta H = \Delta E + (n_2 - n_1) RT$$

$$\Delta H = \Delta E + \Delta n_g RT$$

$$\Delta n_g = n_2 - n_1$$

difference b/w no of moles of the gaseous products and gaseous reactants.

$$\Delta p = \Delta v + \Delta n_g RT$$

When $\Delta n_g = 0$

$$\Delta H = \Delta E$$

$$\Delta n_g = -ve$$

$$\Delta H < \Delta E$$

$$\Delta n_g = +ve$$

$$\Delta H > \Delta E$$

Conditions at which $\Delta H = \Delta E$

(i) $\Delta n = 0$



$$\Delta n_g = 2 - (1+1) = 0$$

(ii) $\Delta v = 0$

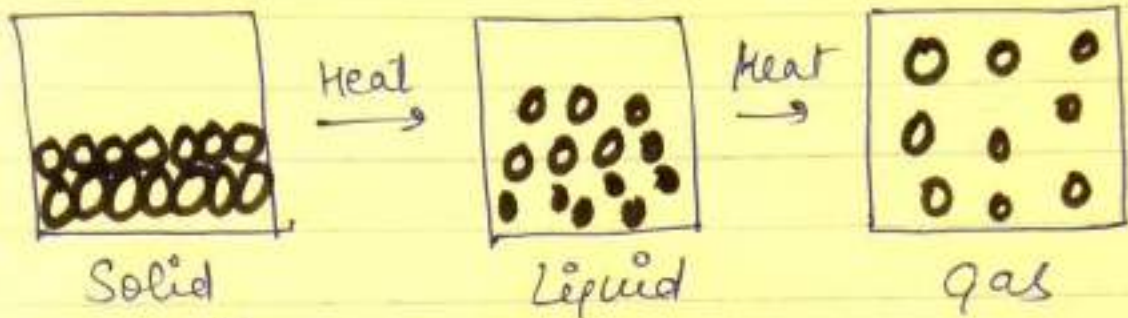
$$\Delta H = \Delta E$$

(iii) when there is no gaseous reactants or products $\Delta n = 0$

Entropy :-

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is defined as the property of a system which measures the randomness, or the amount of disorder of a system.



Degree of Randomness

Gas γ liquid γ Solid

The greater the randomness greater is the entropy.

Entropy is a state function. So change in its value is given by

$$\Delta S = S_2 - S_1 = \sum \text{Products} - \sum \text{Reactants}$$

When a system absorbs heat, the molecules start moving faster because of increase in KE. Hence disorder increase. More heat will get absorbed.

Change in entropy is the ratio of heat (q) and Temperature.

$$\Delta S = \frac{Q_{\text{reversible}}}{T}$$

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units of entropy $\rightarrow \text{J K}^{-1} / \text{mol}^{-1}$

Total change in the entropy of a system is always zero.

$$\Delta S = 0$$

Entropy change during phase transformation

1) Entropy of Fusion :- It is the change in entropy when 1 mole of a solid substance changes in to liquid form at the melting point.

$$\begin{aligned}\Delta S_{\text{fusion}} &= S_{\text{liquid}} - S_{\text{solid}} \\ &= \frac{\Delta_{\text{fus.}} H}{T_m}\end{aligned}$$

$\Delta_{\text{fus.}} S$ = entropy of fusion

S_{liquid} \rightarrow molar entropy of the liquid

S_{solid} \rightarrow molar entropy of solid

$\Delta_{\text{fus.}} H$ = Enthalpy of fusion

T_m = melting point

2.) Entropy of Vaporisation ($\Delta_{\text{vap.}} S$)

It is the entropy change when 1 mole of liquid changes in to vapor at its boiling temp.

$$\Delta_{\text{vap.}} S = S_{\text{vap}} - S_{\text{liquid}} = \frac{\Delta_{\text{vap.}} H}{T_b}$$

3) Entropy of Sublimation :- Entropy change when 1 mole of solid changes into vapours at a particular temp.

$$\Delta_{\text{sub.}} S = S_{\text{vap.}} - S_{\text{solid}} = \frac{\Delta_{\text{sub.}} H}{T}$$

2nd law of Thermodynamics :-

For every spontaneous process there is always change in entropy. (+ve)

$$\Delta S_{\text{universe}} = \Delta S_{\text{(system)}} + \Delta S_{\text{(surrounding)}}$$

If ΔS_{total} is negative, process is spontaneous

If ΔS_{total} is zero, the process is in equilibrium.

3rd law of Thermodynamics :-

It states that "The Entropy of a pure perfectly crystalline substance is zero at absolute zero (0K) of temp."

Now by applying third law of thermodynamics¹² absolute entropy of solids can be calculated at a temperature T can be calculated as

$$S_T = \int_{T=0}^{T=T} C_p \frac{dT}{T} = \left[C_p (d \ln T) \right]_0^T$$

4) Entropy of transition:- Entropy change when one mole of a solid changes from one crystalline state in to other at transition temp.

$$\Delta S = \frac{\Delta H_t}{T_t}$$

ΔH_t = molar heat T_t of transition

Physical Significance of Entropy

Entropy has been regarded as a measure of disorder or randomness of a system. Thus when a system goes from an orderly state to a disordered system, entropy increases. When water is in solid form, less randomness is there.

In liquid state, randomness increases and more randomness in vapours.

In a school when all classes are being held, all the students are sitting (means ordered system). As soon as the bell rings, students come out and get mixed up and hence an disordered system occurs.

Entropy change in a reversible process

Consider an example of isothermal expansion (Reversible) of an ideal gas. The gas absorbs Q_{rev} heat at temp. T . The change in entropy is

$$\Delta S_{system} = \frac{Q_{rev}}{T}$$

Since expansion is reversible, system is in equilibrium with its surroundings at all times during the expansion. Hence surrounding lose an energy.

$$\Delta S_{surrounding} = - \frac{Q_{rev}}{T}$$

$\Delta S = \Delta S_{sys} + \Delta S_{surrounding} = 0$
 Change in entropy of a universe is 0 for a reversible process.

Entropy as a Criterion for Spontaneity

$\Delta S_{sys} + \Delta S_{surrounding} = 0$ for Reversible
 $\Delta S_{sys} + \Delta S_{surrounding} > 0$ for irreversible
 $\Delta S_{sys} + \Delta S_{surrounding} < 0$

Entropy Change in Irreversible

When any part of the process is irreversible as whole process is irreversible. Heat lost by the surrounding is Q_{rev} . Change in entropy is given as

$\Delta S_{surrounding} = - \frac{Q_{rev}}{T}$

Hence $\Delta S_{sys} = \frac{Q_{rev}}{T} - \Delta S_{surrounding}$

$\Delta S = \Delta S_{system} - \Delta S_{surrounding}$

$\Delta S = \frac{Q_{rev}}{T} - \frac{Q_{irreversible}}{T}$

$Q_{rev} < Q_{irrev}$ $\Delta S > 0$

For irreversible there is net increase in entropy

Gibb's Free Energy 15

There is another thermodynamic quantity that helps in predicting the spontaneous nature of a process.

Earlier it was called as Gibbs free energy but now it is Gibbs energy or Gibbs function. It is denoted by G .

"Gibbs Free energy of a system is a measure of its capacity for doing useful work"

or
 It is the thermodynamic quantity of a system the decrease in whose value is equal to the maximum possible useful work that can be obtained from the system

$G = H - TS$

H = Heat Content T = absolute temp and S is the entropy

Change in Gibbs energy

$\Delta G = \Delta H - T \Delta S$ — (1)

$G_2 - G_1 = H_2 - H_1 - T[S_2 - S_1]$

Eq (1) is called as

Gibb's - Helmholtz equation

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad \text{--- (2)}$$

For Isothermal (Temperature is constant) $T_1 = T_2$ if $V_2 > V_1$, $\Delta S = +ve$
 $(\Delta S)_T = R \ln \frac{V_2}{V_1} = -R \ln \frac{P_2}{P_1} = R \ln \frac{P_1}{P_2}$
flow out @ and @ V_1

For Isobaric (Pressure is constant)
 $(\Delta S)_P = C_p \ln \frac{T_2}{T_1}$ (increase in temp results in increase in entropy)
flow @

For Isochoric (Volume is constant)
 $(\Delta S)_V = C_v \ln \frac{T_2}{T_1}$ (volume increase in temp then increase in entropy)

Cell Potential or EMF of a Cell

An electrochemical cell consists of two electrodes i.e. two half cells

First electrode have higher electrode potential than second electrode.

→ As a result of potential difference, electrons flow from higher potential electrode to lower potential electrode.

E°_{cell} = Standard EMF of a cell

$E^{\circ}_{\text{cathode}}$ = Standard reduction potential on Cathode

E°_{anode} = Standard reduction potential on Anode

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Gibb's free energy and EMF of a cell

When a cell reaction takes place, electrical energy is produced. The electrical work done by the cell is the decrease in free energy.

Electrical work done = Decrease in free energy

if $\Delta G = -ve$ work is done by the system
 $\Delta G = +ve$ work is done on the system

hence

Electric work done = Electrical energy produced = Quantity of electricity flowing \times EMF

$$\Delta G = \text{quantity of electricity produced} \times E_{\text{cell}}$$

$$\Delta G = n F E_{\text{cell}}$$

For one mole of electrons transferred³⁾ in cell reaction, quantity of electricity that flows through the cell is **one Faraday**
 $1F = 96500 \text{ Coulombs}$

So if n moles are transferred, then quantity of electricity flows is nF

$$\text{Electrical work done} = nF E_{\text{cell}}$$

Hence $-\Delta G^{\circ} = nF E_{\text{cell}}^{\circ}$ (For Standard)

Criteria of Spontaneity in terms of EMF

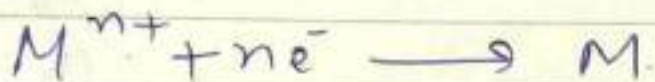
- ① if $\Delta G < 0$ or EMF > 0 reaction will be spontaneous
- ② if $\Delta G = 0$ or EMF $= 0$ reaction will be in equilibrium
- ③ if $-\Delta G > 0$ or EMF < 0 reaction will be non spontaneous.

Calculation of equilibrium constant K_c from ΔG°

Nernst Equation

(Concentration Dependence of electrode potential)
 Electrode potential is said to be standard electrode potential when it is carried under standard conditions i.e. 1 M conc. and 298 K temperature.

For General reaction



in thermodynamics, free energy (ΔG) in general reaction

$$\Delta G = \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

$$\Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ$$

Equation ① becomes

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

$$R = \text{gas constant} = 8.314 \text{ J K}^{-1}$$

$$T = \text{Temperature} = 298$$

$$E^\circ = \text{Standard EMF of a Cell (1 M at 298 K)}$$

$$E = \text{EMF of the Cell}$$

$$F = 96500$$

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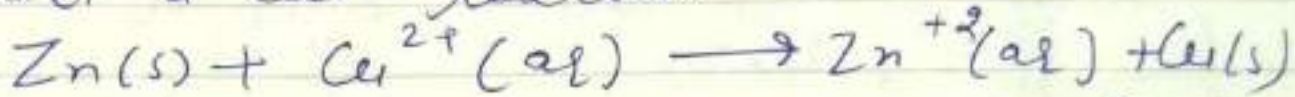
So eq (2) becomes $E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$ (3)

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]} \quad (4)$$

$$E = E^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{1}{[M^{n+}]}$$

Nernst equation in terms of EMF of a cell

Consider a cell reaction



In general



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \frac{[L]^l [M]^m}{[A]^a [B]^b}$$

From (3)

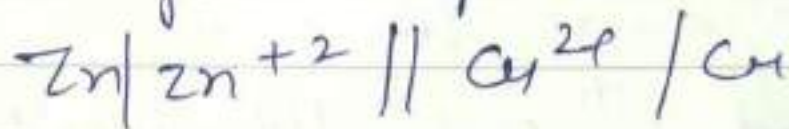
$$E_{\text{Cathode}} = E_{\text{Cu}^{2+}/\text{Cu}}^\circ - \frac{RT}{2F} \ln \frac{[\text{Cu}]}{[\text{Cu}^{2+}]} \quad (4)$$

$$E_{\text{Anode}} = E_{\text{Zn}^{2+}/\text{Zn}}^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}]}{[\text{Zn}^{2+}]} \quad (5)$$

Nernst equation

Applications of Nernst equation

- ① Calculation of the EMF of a cell
consider for Exp the cell



Applying Nernst equation

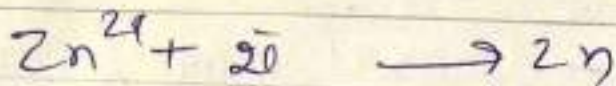
(40)

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

no. of e^{-} involved is 2.

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{Zn^{2+}}{Cu^{2+}}$$

(ii) Calculation of the single electrode potential



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

$$E^{\circ} - \frac{RT}{nF} \ln \frac{1}{Zn^{2+}}$$

$$E^{\circ} + \frac{RT}{nF} \ln [Zn^{2+}]$$

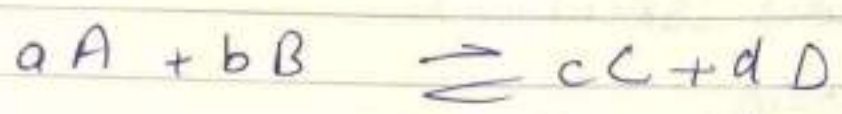
$$E^{\circ} + \frac{0.0591}{n} \log [Zn^{2+}]$$

where E and E° are the single e^{-} potential

Generally it is

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

(vii) Calculation of equilibrium constant
At the equilibrium there is no potential difference b/w the two electrodes and EMF of the cell = 0



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

At equilibrium $E_{cell} = 0$

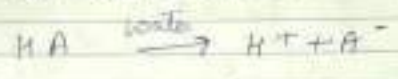
$$0 = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{cell}^{\circ} = \frac{0.0591}{n} \log K_c$$

K_c = equilibrium constant

Arrhenius Concept of Acids and Bases

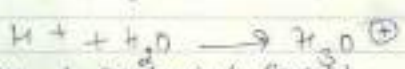
① Acids: - acid may be defined as a substance which gives hydrogen ion in aqueous solution



② Base - base may be defined as a substance which gives hydroxyl ion in aqueous solution



acc to Arrhenius hydrogen ion is free proton which has very small size and high charge density. It is strongly attracted by the negative end of water.



Limitations of Arrhenius Concept

There are such substances which do not

have OH ion but still they are bases like NH_3 , CaO

Bronsted-Lowry Concept of Acids and Bases

An acid is a substance which has a tendency to donate a proton

and base is a substance which has a tendency to accept a proton



Features of B/L Concept

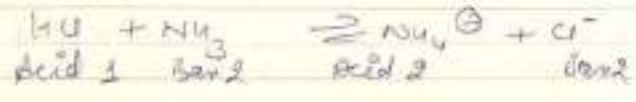
- ① It involves proton transfer theory of acids and bases
- ② Ions are also capable of acting as acids and bases



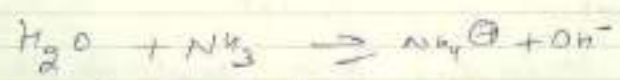
③ for an acid to act as a donor there must be an acceptor to accept protons



④ whenever acid-base pairs meet another pair of acid-base will get formed



⑤ Amphiprotic compounds - certain molecules at some time exhibit as acid or base

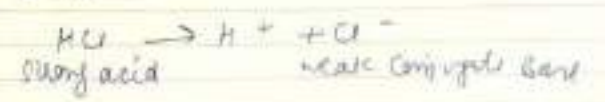


⑥ water has a dual character



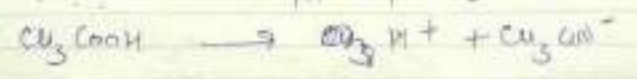
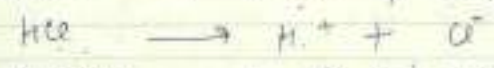
① all Brønsted acids are Arrhenius but Arrhenius bases are not Brønsted bases

Conjugate acid base pair

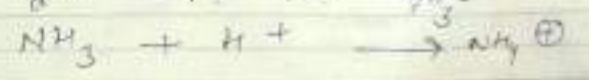
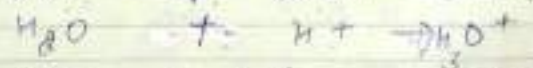


Conjugate Acid - Base Pair

Acid \rightarrow Proton + Conjugate base



Base + Proton \rightarrow Conjugate acid



In general

Strong acid + Strong base = Conjugate acid + Conjugate base

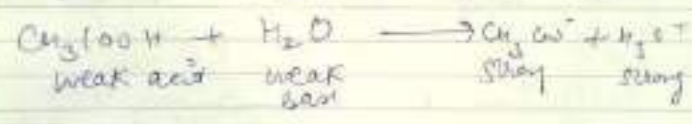
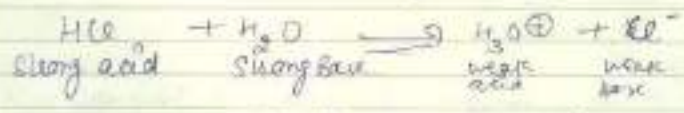


Polyprotic acid :-

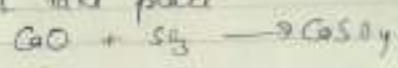
which have more than two protons
 H_2SO_4 dibasic - give two protons
 H_3PO_4 tribasic - gives three protons

Relative Strengths of Acids and Bases

Strong acid have weak conjugate base
Weak acid have strong conjugate base



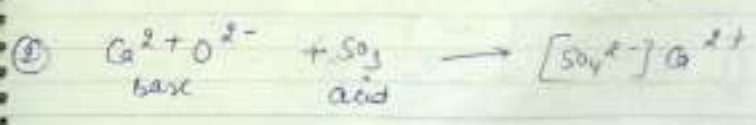
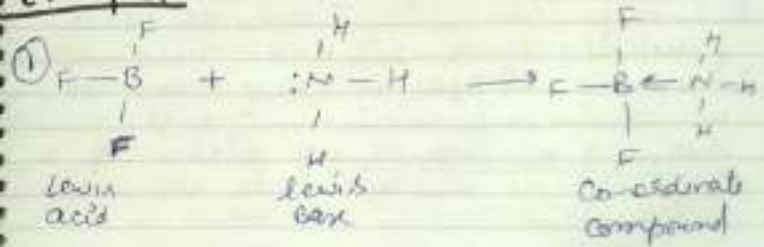
Limitation :- fails to explain those acid base reactions in which no proton transfer take place



Lewis Concept of Acids and Bases

Lewis acid is a substance which can accept a pair of electrons (electron acceptor)
Lewis base is a substance which can donate a pair of electrons (electron donor)

Examples



Solubility Equilibria

- Electrolytes usually undergo dissociation to form charged species when they are dissolved in a suitable solvent.
- These charged species are known as ions.
- Extent of dissociation is different in different cases.

Strong Electrolytes: - Electrolytes which undergo complete dissociation to ions.
Exp NaCl, HCl

Weak Electrolytes: - which do not undergo complete dissociation.
Exp CH_3COOH

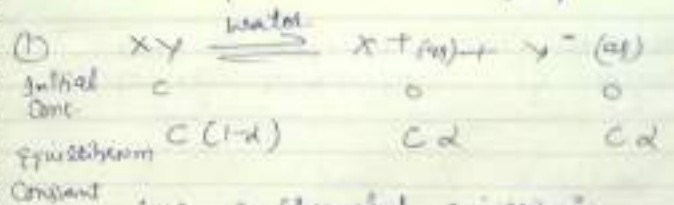
In case of weak electrolytes, an equilibrium is established b/w the ions in solution and undissociated ions. Known as "Ionic Equilibrium".

The fraction of ions which get ionised at equilibrium state is known as degree of dissociation or ionisation.

$$\alpha = \frac{\text{No. of dissociated molecules}}{\text{Total no. of molecules}}$$

Exp ① Equilibria involving soluble ionic compounds such as weak acid and weak base.

② Equilibria involving sparingly soluble ionic compounds: Solubility product



Constant law of chemical equilibrium

$$K_c = \frac{[\text{X}^m][\text{Y}^n]}{[\text{XY}]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha} \quad K_c = \text{dissociation constant}$$

$\alpha \rightarrow 1$
 $1-\alpha$ can be taken as 1

$$K_c = \frac{C\alpha^2}{1}$$

$$K_c = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_c}{C}} \quad \alpha \propto \frac{1}{\sqrt{C}}$$

More the conc. decrease in the degree of dissociation or vice versa.

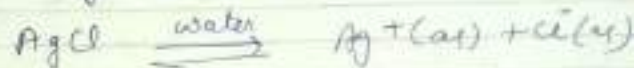
② Solubility Product

All electrolytes dissolve in water

Substances like AgCl , BaSO_4 sparingly soluble in water

Equilibrium is set up b/w the undissociated molecules and total molecules

Ex: AgCl dissolves in water



Applying law of mass action

$$K_c = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]_{\text{solid}}[\text{water}]}$$

$$K_c \times \text{water} = [\text{Ag}^+][\text{Cl}^-]$$

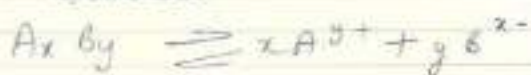
$$K_c \times K = [\text{Ag}^+][\text{Cl}^-]$$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

K_{sp} = Solubility product

In General



$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

where A^{y+} B^{x-} denote the $+$ ve and $-$ ve ions

Solubility product of a salt at a given temp is defined as the product of conc. of its ions, in a saturated solution, each concentration term raised to a power equal to the no. of times each ion occurs in the equation of a dissociation of a salt

Application :- (1) Calculation of solubility. Knowing the K_{sp} of a salt, its solubility can be calculated.

(ii) Predicting the precipitation of Reaction

- 1) A precipitate is formed if its ionic product is greater than K_{sp}
 $K_c > K_{sp}$
- 2) A solution is just saturated if $K_c(\text{ionic product}) = K_{sp}$
- 3) A solution is just unsaturated if $K_c < K_{sp}$

Solubility Product	Ionic product
(1) It is a product of the conc. of the ion of an electrolyte each conc. raised to power in a saturated sol.	It is the product of the conc. of ions of an electrolyte each conc. raised to the appropriate in any soln.
(2) Applicable to saturated solutions only	Applicable to all types
(3) It has constant value for an electrolyte at constant concentration	It has variable value by changing the concentration

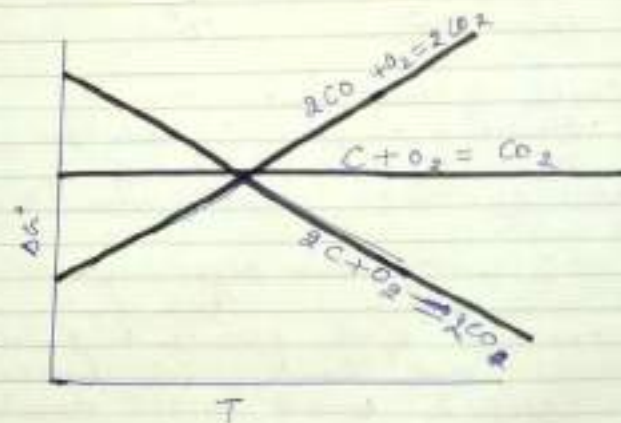
Ellingham Diagram

- It is used to evaluate the ease of reduction of metal oxides and sulfides for the metallurgy of different metals.
- This diagram was first invented by H. Ellingham in 1944.
- An Ellingham Diagram is a graph showing the variation of ΔG° with temperature showing the oxidation of metals.
- It is used to predict the equilibrium temperature between a metal, its oxide, and oxygen.

$$\Delta G = \Delta H - T\Delta S$$

Ellingham Diagram shows in graphical form which thermodynamic feasibility of a reaction depends upon Gibbs free energy. Ellingham diagram plots the Gibbs free energy change (ΔG) for each

oxidation reaction as a function of temperature. To compare the different reactions, all values of ΔG refer to the reaction of the same quantity of oxygen, is chosen as one mole of O_2 at 1 atm pressure.



Ellingham diagram for metal giving free energy formation of metal oxides and corresponding O_2 at equilibrium.