

Electrochemistry - I

The branch of chemistry which deals with the study of relationship b/w electrical energy, chemical energy and interconversion of these energy is called electrochemistry?

Electrical conductance -

All substance do not conduct electrical current. The substance which allow the process of electrical current is called conductors.

The best conductors are metal such as Ag, Cu, Fe etc. On the other hand the substance which do not allow the process of electric current are called non-conductors or insulators.

Some common example of insulator are gold, wood, plastic, rubber etc.

The electrode connected to positive terminal attracts the negative ions is called anode.

The other electrode connected to (-) end of battery attract positive ion is called cathode.

Types of conductors -

The conductors are mainly two type -

(i) Metallic conductor

(ii) Electrolytic conductor

Metallic conductivity -

These are metallic substances which allow the process of current without undergoing any chemical change.

Example - Ag, Cu, Al, NO etc.

Electrolytic conductors -

These are the conductors like aqueous solution of acids, base and salt in which the flow of electric current is accompanied by chemical decomposition are known as electrolytic conductors.

Example - NaCl, KCl, HCl, CuSO₄ etc.

Difference b/w metallic conductor and electrolytic conductors -

Metallic Conductor

- It is carried out of by the movement of e⁻.
- Ohm's law is followed.
- Resistance increase with increase of temperature.
- Metallic conductor do not follow Faraday's law.

Electrolytic Conductor

- It is carried out of by the movement of ions.
- Ohm's law is followed.
- Resistance decrease with increase of temperature.

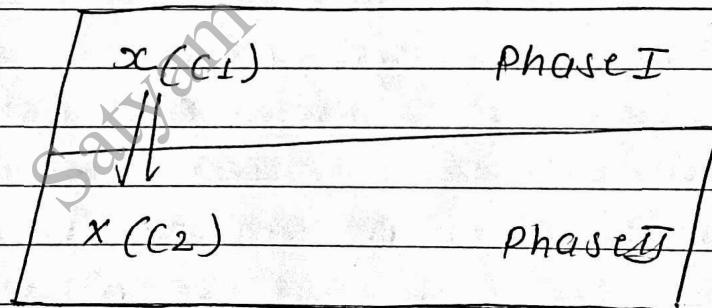
① Nernst distribution law-

Nernst in 1891 studied the distribution of a large number of solutes between two immiscible solvents and generalised the result in the form of a law. This is called Nernst's distribution law or simply distribution law or partition law.

The Nernst distribution law

may be stated as follows -

"A solute distributes itself between two immiscible solvents it contact with each other in such away that the ratio of the concentration of the same molecules spp in the two solvents is always constant at constant temperature irrespective of the amount of solute."



Mathematically,

$$\frac{\text{conc of solute (x) in phase I}}{\text{conc of solute (x) in phase II}} = K$$

$$\frac{c_1}{c_2} = K$$

when K is a constant called distribution coefficient or :

② Relation b/w ΔH and ΔE -

We know that

$$\Delta H = \Delta E + P\Delta V \quad \text{--- (1)}$$

$$\Delta H = H_P - H_R$$

Product -

Reactant - Product

$$P_{R'} - nRRT = P_{V_P} = nPRT$$

$$P_{V_P} - P_{R'} = nPRT - nRRT$$

$$P(V_P - V_R) = RT(nP - nR)$$

$$PV = RT(n)$$

$$PV = nRT$$

Putting the value of $P\Delta V$ in equ (1)

$$\boxed{\Delta H = \Delta E + n(g)RT}$$

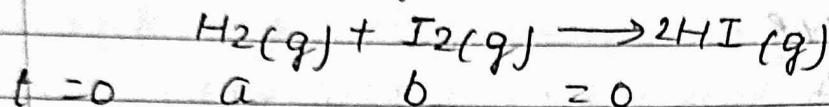
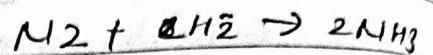
③

law of mass action for the synthesis of HI -

Goldsberg and Cragg put the formula law connected to the effect of conc of reactant and the rate of reaction is known as law of mass action.

Those reaction in which total no of moles of reactant and product remain the same as a result of chemical reaction i.e. $\Delta n = 0$

Formation of HI-



$$t=0 \quad a \quad b \quad = 0$$

$$t=t \quad (a-x) \quad (b-x) \quad = 2x$$

Let (a) mole of H_2 and (b) mole of I_2 is taken in a vessel volume (V) at equilibrium. x mole of H_2 and x mole of I_2 reacts to form two mole of HI.

Molar conc. of equilibrium

$$[H_2] = \frac{(a-x)}{V} M/l$$

$$[I_2] = \frac{(b-x)}{V} M/l$$

$$[2HI] = \frac{2x}{V}$$

$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$K = \frac{(2x/V)^2}{(a-x/V)(b-x/V)}$$

$$K_C = \frac{4x^2/V^2}{(a-x)(b-x)}$$

$$K_C = \frac{4x^2}{(a-x)(b-x)}$$

(4) Prove $\Delta G^\circ = -RT \ln K_p$ — Raoult's equation / isochore

The effect of temp. on chemical equilibrium can be determined by using thermodynamics.

5 The relation for the reaction isotherms when the reactant and products are gases and also in their standard state is represented by —

$$\Delta G^\circ = -RT \ln K_p \quad (I)$$

Differentiating eqn (I) w.r.t T at constant P

$$T \left[\frac{d(\Delta G^\circ)}{dt} \right]_P = -R \ln K_p - RT \left[\frac{d(\ln K_p)}{dt} \right]_P \quad (II)$$

Multiplying eqn (II) with T

$$T^2 \left[\frac{d(\Delta G^\circ)}{dt} \right]_P = -RT \ln K_p - RT^2 \left[\frac{d(\ln K_p)}{dt} \right]_P \quad (III)$$

From eqn (I) and (III)

$$T \left[\frac{d(\Delta G^\circ)}{dt} \right]_P = \Delta G^\circ - RT^2 \left[\frac{d(\ln K_p)}{dt} \right]_P \quad (IV)$$

From Gibbs' heat of energy

$$\Delta G^\circ = \Delta H^\circ + T \left[\frac{d(\Delta G^\circ)}{dT} \right]_P \quad (V)$$

From eqn (V) and (IV) we get

$$\frac{\Delta h^\circ}{RT^2} = \left[\frac{d(\ln k_p)}{dT} \right]_P$$

(5)

The clapeyron - clausius equation

The clapeyron - equation for liquid - vapour equilibrium may be written as follows -

$$\frac{dp}{dT} = \frac{\Delta H_v}{T_b(V_g - V_l)}$$

In this equilibrium, V_l (molar volume of the liquid state) may be neglected in comparison to V_g (molar volume of the gaseous state). Thus the above equ can be written as

$$\frac{dp}{dT} = \frac{\Delta H_v}{TV_g} \quad \text{--- (1)}$$

Here T_b is the normal boiling point of the liquid.

If the vapour obeys the ideal gas eqn then

$$V_g = \frac{RT}{P}$$

substituting the value of V_g in eqn (1) we get

$$\frac{dp}{dT} = \frac{\Delta H_v P}{RT^2}$$

$$\frac{L}{P} \cdot \frac{dp}{dT} = \frac{\Delta H_v}{RT^2}$$

$$\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT^2}$$

This eqn is known as Clapeyron-Clausius eqn.

Application of Clapeyron-Clausius Equation

I) Calculation of latent heat of vapourisation

If the vapour pressure of a liquid at temp T_1 & T_2 are P_1 & P_2 respectively, the molar heat of vapourisation ΔH_v can be calculated by substituting these values in Clapeyron-Clausius equation.

Similarly latent heat of fusion can be calculated if the vapour pressure at two different temp of a solid in equilibrium with its liquid phase are known.

II) Calculation of freezing point or boiling point

If the freezing point or the boiling point of a liquid at one pressure is known, it is possible to calculate it at another pressure with the help of Clapeyron-Clausius equation.

III) Calculation of vapour pressure

The vapour pressure of a liquid at a given temperature can be calculated if the vapour pressure at another and heat of vapourisation are known.

$$(x_1) \times (x_2) - [T-8] [+\alpha] = \alpha$$

$$(x_1) \quad [8\alpha]$$

$$\frac{8\alpha}{(x_1)} = \alpha$$

(6)

Ostwald's dilution law -

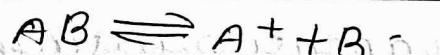
According to Arrhenius theory of electrolytic dissociation, the molecule of an electrolyte in aqueous solution undergoes dissociation to give positive and negative ions and setup a dynamic equilibrium between ion and unionised molecule. Ostwald applied the law of mass action to such processes and suggested a law known as Ostwald's dilution law. This may be stated as follows -

"At constant temp,

the degree of dissociation of weak electrolyte is directly proportional to the square root of dilution or inversely proportional to the square root of its concentration."

Derivation -

Let's consider an aqueous solution of a weak electrolyte AB whose conc. is c g/mole per litre and it's degree of dissociation is α . At equilibrium, concentration of various spp can be written as -



c 0 0 Initial conc.

$c(1-\alpha)$ $c\alpha$ $c\alpha$ Equilibrium conc.

Applying law of mass action we get -

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)}$$

$$K = \frac{c\alpha^2}{(1-\alpha)} \quad \text{--- } ①$$

equ ① is mathematical representation of Ostwald's dilution law : K is constant called dissociation constant of electrolyte AB. At constant temp , it has a constant value.

But for weak electrolyte , α is very small

$$\alpha \ll 1$$

thus equ ① may written as -

$$K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} = \sqrt{KV} \quad \text{--- (ii)}$$

V = dilution which inversely proportional to conc - from equ ① we get

$$\alpha \propto \frac{1}{\sqrt{C}}$$

$$\boxed{\alpha \propto \sqrt{V}}$$

or

⑥ Arrhenius theory of Electrolytic Dissociation -

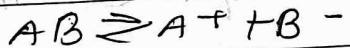
Arrhenius passed the electric current through the aqu solution of different electrolytes and conclude that the conductivity of solution was due to the presence of ions. In 1884 he put forward his theory which is known as Arrhenius theory of electrolytic dissociation

Postulates - The main postulate of Arrhenius theory
as follows-

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① Neutral electrolyte molecule, when dissolved in H₂O split up into two types of charged particles which were called ions and this process was called ionisation. (i) cation and (ii) anion

Now-a-days the theory assumes that the ions are present in solid electrolytes. These ions are held together by electrostatic forces of attraction. When dissolved in H₂O, these neutral molecules dissociate to give cation and anions. Thus,



$$K = \frac{[A^+][B^-]}{[AB]}$$

⑦ Debye-Hückel - On sagai theory of strong electrolytes-

P. Debye and E. Hückel (1923) put forward the modern theory of strong electrolytes considering the electrostatic force b/w the ions. This theory is known as Debye-Hückel theory of ionic attraction. The treatment was later modified by L. Onsager (1927). This theory is based on the following assumption:-

1- The strong electrolyte is completely ionised at all dilution & x-ray analysis of ionic solids of these electrolytes has shown that there is very small amount of un-ionised substance also present.

- II- The ratio $\frac{1}{r}$ does not correctly give the degree of dissociation α for strong electrolytes but only the conductance variation.
- III- The value of $\frac{1}{r}$ is much less than even at almost complete ionisation.

(8) Gibb's phase rule-

The phase rule is important generalisation dealing with the behaviour of heterogeneous system. With the application of phase rule it is possible to predict easily by means of a diagram the effect of change in pressure, temp and conc on a heterogeneous system in equilibrium. Willard Gibbs (1876) put forward a rule which is known as Gibb's phase rule. This rule may be stated as follows -

In a heterogeneous system in equilibrium then, the sum of the number of degrees of freedom and number of phases is equal to the number of components plus two

Mathematically,

$$F + P = C + 2$$

$$P = C - F + 2$$

F = no of degrees of freedom

C = no of component

P = no of phases.

Phase diagram of consist of the following part -

- (I) Three stable curves OA, OB and OC
- (II) One metastable curve OA
- (III) Triple point O
- (IV) Area AOC, BOC and AOB.

- (D) curves

Curve OA -

It is vapour pressure curve f_{H_2O} . It represents the equilibrium b/w liquid H_2O and vapour at different temp. The vapour pressure at triple point is P_{triple} .

Section E

~~Relation for entropy as a function v and T -~~

Entropy is a state function and its value depend upon the volume, pressure and temperature since temperature is take a one of the variable and second variable may be pressure and volume. Thus variables are either volume and temp or pressure and temperature.

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From definition of entropy -

$$ds = \frac{Q}{T} \quad \textcircled{1}$$

15

From 1st law of T.D

$$dQ = dE + PdV \quad \textcircled{2}$$

we know that

$$PV = RT$$

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$$P = \frac{RT}{V}$$

Again - $dE = crdT$

25

putting the value of P & dE in eqn $\textcircled{1}$

$$ds = \frac{dE + PdV}{T}$$

30

$$ds = \frac{crdT + \frac{RTdV}{V}}{T}$$

$$ds = cv \frac{dT}{T} + R \frac{dv}{v}$$

Integrating above equ with units s_1 to s_2 -
 T_1 to T_2 and v_1 to v_2

$$\int_{s_1}^{s_2} ds = cv \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}$$

$$[s]_{s_1}^{s_2} = cv [\log T]_{T_1}^{T_2} + R [\log v]_{v_1}^{v_2}$$

$$s_2 - s_1 = cv [\log T_2 - \log T_1] + R [\log v_2 - \log v_1]$$

$$ds = cv \log \frac{T_2}{T_1} + R \log \frac{v_2}{v_1}$$

$$ds = \cancel{cv} \cdot 2 \cdot 303 \cdot cv \log_{10} \frac{T_2}{T_1} + 2 \cdot 303 \cdot R \log_{10} \frac{v_2}{v_1}$$

For n moles of gas

$$ds = 2 \cdot 303 ncv \log_{10} \frac{T_2}{T_1} + 2 \cdot 303 nR \log \frac{v_2}{v_1}$$

$$\frac{P_A}{P_B} = \frac{36}{75} = \frac{12}{25}$$

$$A + B = 40$$

$$B = 40 - A$$

Prove that $C_p - C_v = R$

According to heat capacity at constant volume

$$C_V = \frac{dE}{dT} \quad (1)$$

According to heat capacity at constant pressure

$$C_P = \frac{dH}{dT} \quad (2)$$

From enthalpy definition

$$H = E + PV \quad (3)$$

Differentiate above equation with respect to T

$$dH = dE + PV$$

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{\partial}{\partial T} PV$$

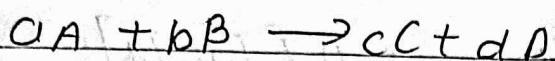
$$\frac{dH}{dT} = \frac{dE}{dT} + R \frac{d}{dT}$$

$$C_P = C_V + R$$

$$[C_P - C_V = R]$$

Hence the difference b/w heat capacity at constant pressure and volume is always equal to gas constant.

~~Kirchoff's equ. at constant pressure~~



$$\Delta H = \sum H_p - \sum H_i$$

Differentiating with respect to T at constant pressure.

$$\frac{d(\Delta H)}{dT} = \left[c \left(\frac{dH_C}{dT} \right)_P + d \left(\frac{dH_D}{dT} \right)_P \right] - \left[a \left(\frac{dH_A}{dT} \right)_P + b \left(\frac{dH_B}{dT} \right)_P \right] \quad (1)$$

$$\left[c \left(\frac{dH_C}{dT} \right)_P + d \left(\frac{dH_D}{dT} \right)_P \right] = (CP)_P$$

$$\left[a \left(\frac{dH_A}{dT} \right)_P + b \left(\frac{dH_B}{dT} \right)_P \right] = (CP)_R$$

From equation (1) we have

$$\frac{d(\Delta H)}{dT} = (CP)_P - (CP)_R$$

$$\frac{d(\Delta H)}{dT} = \Delta CP$$

$$d(\Delta H) \approx \Delta CP dT$$

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \Delta CP \int_{T_1}^{T_2} dT$$

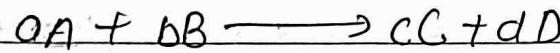
$$[\Delta H]_{\Delta H_1}^{\Delta H_2} = \Delta CP [T]_{T_1}^{T_2}$$

$$\Delta H_2 - \Delta H_1 = \Delta CP [T_2 - T_1]$$

$$(\Delta H_2)_{T_2} - (\Delta H)_{T_1} = \Delta CP [T_2 - T_1]$$

$$\Delta CP = \left[\frac{(\Delta H)_{T_2} - (\Delta H)_{T_1}}{[T_2 - T_1]} \right]$$

~~Kirchoff equ at constant volume -~~



$$\Delta E = \Sigma E_P - \Sigma E_R$$

Differentiating w.r.t T at constant volume

$$\frac{d(\Delta E)}{dt} = \left[c \left(\frac{dE_C}{dT} \right)_V + d \left(\frac{dE_D}{dT} \right)_V \right] - \left[a \left(\frac{dE_A}{dT} \right)_V + b \right.$$

$$\left. \left(\frac{dE_B}{dT} \right)_V \right]$$

$$\left[c \left(\frac{dE_C}{dT} \right)_V + d \left(\frac{dE_D}{dT} \right)_V \right] = CC_P$$

$$\left[a \left(\frac{dE_A}{dT} \right)_V + b \left(\frac{dE_B}{dT} \right)_V \right] = CV_P$$

From equ ① we have

$$\frac{d(\Delta E)}{dt} = CC_P - CV_P$$

$$\frac{d(\Delta E)}{dt} = \Delta C_V$$

$$d(\Delta E) = \Delta C_V dT$$

$$\int_{\Delta E_1}^{\Delta E_2} d(\Delta E) = \Delta C_V \int_{T_1}^{T_2} dT$$

$$[\Delta E]_{\Delta E_1}^{\Delta E_2} = \Delta C_V [T]_{T_1}^{T_2}$$

$$\Delta E_2 - \Delta E_1 = \Delta C_V [T_2 - T_1]$$

$$(\Delta E)_{T_2} - (\Delta E)_{T_1} = \Delta C_V (T_2 - T_1)$$

$$\Delta C_V = \frac{[(\Delta H)_{T_2} - (\Delta H)_{T_1}]}{[T_2 - T_1]}$$

Gibb's Helmholtz Equation -

There are two equ which were derived by Gibb's and Helmholtz. This equ are known as gibb's Helmholtz equation.

One equ can be expressed in term of change of free energy (ΔG) and enthalpy (ΔH) while the other can be expressed in term of change of work function (ΔA) and internal energy (ΔU)

(a) In term of change of free energy and enthalpy -

We know that

$$G = H - TS$$

$$G = E + PV - TS \quad \left\{ H = E + PV \right\}$$

differentiate above equ w.r.t T we get

$$G = E + PV - TS \quad \text{sdT} - TdS$$

$$\Delta G = dE + PDV - VdP - FdS \quad \text{sdT}$$

$$\Delta G = dq + VdP - FdS - \text{sdT} \quad \left\{ \text{from 1st law of TDS} \right.$$

$$\Delta G = dq + VdP - (dT) - \text{sdT} \quad \left\{ \because TdS \geq dq \right\}$$

$$\Delta G = VdP - \text{sdT}$$

At constant pressure

$$dP = 0$$

$$\Delta G = VdP - \text{sdT}$$

$$\Delta G = 0 - \text{sdT}$$

$$\Delta G = -\text{sdT}$$

for initial state

$$\Delta G_1 = -s_1 dT \quad \textcircled{1}$$

for final state

$$\Delta G_2 = -s_2 dT \quad \textcircled{11}$$

change

$$\Delta G_2 - \Delta G_1 = \alpha(s_2 dT) - (-s_1 dT)$$

$$\alpha(\Delta G) = -(s_2 - s_1) dT$$

$$d(\Delta G) = -\alpha s dT$$

$$\left(\frac{d(\Delta G)}{dT} \right)_P = -\alpha s \quad \textcircled{11}$$

we know that

$$\Delta G = \Delta H - T\Delta S \quad \textcircled{11}$$

Putting the value of ΔS in eqn $\textcircled{11}$ we get

$$\delta G = \partial H + T \left(\frac{\partial (\delta G)}{\partial T} \right)_P$$

⑥ In terms of change of free energy function and internal energy we know that

$$A = E - TS \quad \text{--- (I)}$$

for initial state

$$A_1 = E_1 - TS_1 \quad \text{--- (II)}$$

for final state -

$$A_2 = E_2 - TS_2 \quad \text{--- (III)}$$

for change -

$$A_2 - A_1 = (E_2 - TS_2) - (E_1 - TS_1)$$

$$\Delta A = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \quad \text{--- (IV)}$$

From equ (I)

$$A = E - TS$$

differentiating equ w.r.t T

$$\Delta E = E = TS$$

$$\Delta A = \Delta E + T\Delta S - SdT \quad \text{--- (V)}$$

From 1st law of T.D

$$dq = dE + PdV$$

thus IInd law of T.D

$$dq = TdS$$

$$TdS = dE + PdV$$

Putting the value of TdS in equ (V)

$$dA = dE - TdS - SdT$$

$$dA = dE - (dE + PdV) - SdT$$

$$dA = -PdV - SdT$$

At constant volume

$$dV = 0$$

$$dA = -PdV - SdT$$

$$dA = 0 - SdT = 1B.$$

$$dA = - SdT$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S}$$

for initial state -

$$\left(\frac{\partial A_1}{\partial T}\right)_V = -S_1 \rightarrow (VI)$$

for final state -

$$\left(\frac{\partial A_2}{\partial T}\right)_V = -S_2 \rightarrow (VII)$$

for change -

$$\left(\frac{\partial A_2}{\partial T}\right) - \left(\frac{\partial A_1}{\partial T}\right) = -S_2 - S_1$$

$$\left(\frac{\partial \Delta A}{\partial T}\right) = -S \rightarrow (VIII)$$

We know that

$$\frac{\Delta A - \Delta E}{T} = -S \rightarrow (IX)$$

$$\frac{\partial A - \partial E}{T} = \left(\frac{\partial (\partial A)}{\partial T} \right)_V$$

$$\partial A = \partial E + T \left(\frac{\partial (\partial A)}{\partial T} \right)_V$$

Short question -

①

Degree of Freedom (F) -

The term degree of

Freedom may be defined as follows -
The minimum number of independent variables
temp, pressure and conc which must be
specified so that the ~~the~~ remaining
variables are fixed automatically and the
system is completely defined. It is
denoted by F.

②

Henry's law -

The relation b/w pressure
and solubility of a gas in a particular
solvent was proposed by William Henry in
the form of law known as Henry's law. It
may be stated as follows -

"The mass of a gas
dissolved in a solvent at constant temp is
proportional to the pressure of the gas
in equilibrium with the solution."

Mathematically

$$m \propto p$$

$$m = k_p$$

m_1 = mass of gas dissolved in unit volume
of solvent

P = Pressure of the gas

k_2 = Henry's constant

Raoult's Law -

F. Raoult's law studied the vapour pressure of binary solution of volatile liquid e.g. benzene and toluene at constant temp and gave a law which is known as Raoult's law. According to this law:-

"At constant temp the partial pressure of any volatile component of solution is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution."

Math -

$$P_A = x_A \cdot P_A^{\circ}$$

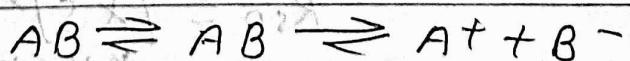
$$P_B = x_B \cdot P_B^{\circ}$$

Common Ion Effect -

The reduction of degree of dissociation of a salt by the addition of a common ion is called common ion effect.

Solubility Product -

Suppose a saturated solution of sparingly soluble salt AB . In solution the following equilibrium.



Applying law of mass action

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$K_x [AB] = [A^+] [B^-]$$

Since active mass of a solid is constant at constant temp., the value of $[AB]$ will be constant at constant temp. Thus the above eqn may be written as

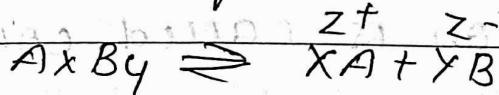
$$K_x \text{constant} \Rightarrow [A^+] [B^-]$$

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

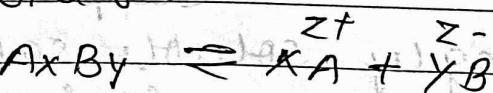
K_{sp} is solubility product of AB . It may be defined as -

The product of the conc. of ions in a saturated solution at a given temp. is constant. It has a constant value at a particular temp.

Now let's consider a general salt $A_x B_y$ which is in equilibrium in such a



If solubility of salt is s mole/litre, the concentration will be



$$K_{sp} = [X^z]^x \times [Y^z]^y$$

$$K_{sp} = X^z \cdot Y^y \cdot s$$

This is general eqn of calculate solubility product of salt.

Electronic theory of valency -

Compound	Formula	Electronic Formu l.
Sodium chloride	NaCl	Na^+ $(\ddot{\text{Cl}})$
Magnesium chloride	MgCl ₂	$[\ddot{\text{Cl}}]$ Mg^{2+} $[\ddot{\text{Cl}}]$
Calcium oxide	CaO	$[\text{Ca}]^{+2}$ $[\ddot{\text{O}}]^{-2}$

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Compound	Formula	Structural Formulas	Electronic Formulas
Hydrogen			
Oxygen			
Nitrogen			
Chlorine			
Water			
carbon dioxide oxide			
carbondioxide			
Ammonia			
Methane			
Ethene			
Ethylene			
Acetylene			
Hydrogen sulphide			
Hydrochloride			
Phosphene			
Silicic oxide			
Nitric acid			

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