Chemical Equilibrium

Introduction :

Equilibrium is a state in which there are no observable changes as time goes by. When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to from product molecules while product molecules react to yield reactant molecules. This dynamic situation is the subject of this chapter. Here we will discuss different types of equilibrium reactions, the meaning of the equilibrium constant and its relationship to the rate constant and factors that can effect a system at equilibrium.

Section (A) : Properties of equilibrium, active mass

Types of chemical reactions

The reaction which proceed in one direction only

(a) Precipitation reactions e.g.

$NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl^-$

(b) Neutralization reactions e.g.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(s) + H_2O$

(c) Reactions in open vessels with one of the gaseous product

Reactions which proceed in both the direction. These are possible only in closed vessel e.g.

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

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Types of chemical reactions

	Irreversible reaction		Reversible reaction
1	The reaction which proceeds in one direction (forward direction) only.	1	The reaction which proceed in both the direction under the same set of experimental conditions.
2	Reactants are almost completely converted into products. Products do not react to form reactants again.	2	Reactants form products and products also react to form reactants in backward direction. These are possible in closed vessels .
3	Do not attain equilibrium state.	3	Attain the equilibrium state and never go to completion.
4	Such reactions are represented by single arrow {$\rightarrow$}	4	Represented by double arrow ($\rightleftharpoons$) or ($\rightleftarrows$)
5	Examples –	5	Examples :–
(a)	Precipitation reactions e.g. $NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl\downarrow$	(a)	Homogeneous reactions- only one phase is present (i) Gaseous phase– $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b)	Neutralization reactions e.g $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$		$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ [Birkland eyde process (HNO_3)] $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Haber's process)
(c)	$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$		(ii) Liquid phase $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
(d)	**Reactions in open vessel:** Even a reversible reaction will become irreversible if it is carried out in open vessel. Ex. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ Open vessel	(b)	**Heterogeneous reactions:** More than one phases are present $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ Closed vessel

State of Chemical equilibrium :

State of equilibrium means the balance of driving forces i.e. the factors taking the reaction in forward direction and the backword direction are balancing each other.

The equilibrium state represents a compromise between two opposing tendencies.

- Tendency to minimise energy.
- Molecules try to maximise entropy.

In a reversible reaction like :

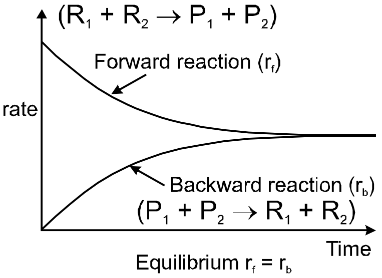
$$\underbrace{R_1+R_2}_{\text{Reactants}} \rightleftharpoons \underbrace{P_1+P_2}_{\text{Products}}$$

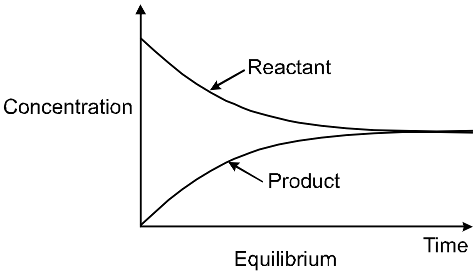
Initially only reactants are present. R_1 and R_2 combine to form P_1 and P_2. As soon as P_1 and P_2 are formed**,** they start the backward reaction. As concentrations of R_1 and R_2 decrease rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when both the rates become equal. Such a state is known as “Chemical Equilibrium” or “state of Equilibrium”.

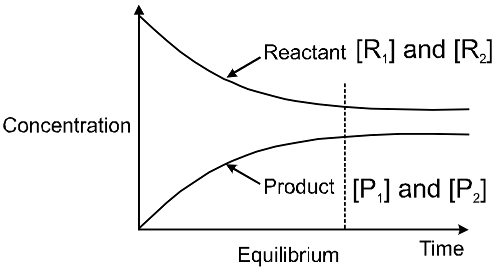
At equilibrium :

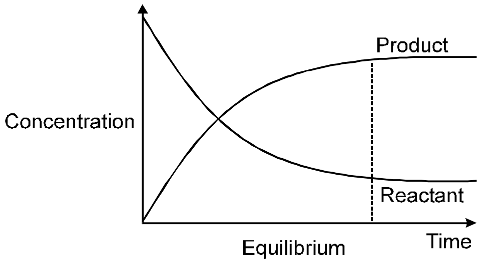
(i) Rate of forward reaction (r_f) = rate of backward reaction (r_b) (dynamic nature)

(ii) All measurable parameters become constant with respect to time.









Types of equilibria on the basis of process

Physical Equilibrium

Equilibrium in physical process is called physical equilibrium.

For example phase changes like

$H_2O(l) \rightleftharpoons H_2O(g)$;

Solvation like

$NaCl(s) \overset{H_2O}{\underset{\text{excess}}{\rightleftharpoons}} NaCl(aq)$

Chemical Equilibrium

Equilibrium in chemical process is called chemical equilibrium.

For example

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

Types of equilibria on basis of physical state

Homogeneous equilibrium

One phase in the system

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

Heterogeneous equilibrium

More than one phase are present in system

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH + O_2(g)$

Characteristics of chemical equilibrium :

- The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved in both directions.
- Equilibrium is dynamic in nature.
  It means that at microscopic level reaction has not stopped. It appears that no change is occuring but both the opposing reactions are proceeding at the same rate. So there is no net change.Thus equilibrium is not static in nature.
- A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative

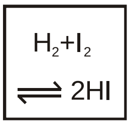
concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.

- Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc.which may be suitable in a given reaction.
- At equilibrium, free energy change $\Delta G = 0$
- Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc.(Le chateliers Principle).
- System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

Solved Examples

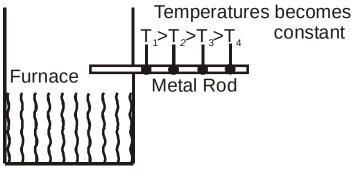
Ex-1. (1) Consider the following cases–

(I)

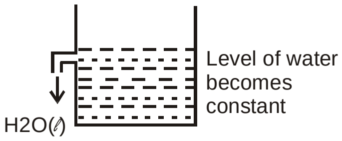


Equilibrium state has been attained

(II)



(III)



The nature of flow of energy in case (I) is same as that in–

(A) II (B) III (C) II and III (D) None

Sol. (D) None, because in II and III, the flow of energy or matter is taking place only in one direction. While in equilibrium state, the flow of energy takes place in both directions equally. Thus (I) is a dynamic equilibrium while states in II and III are called steady state (static equilibrium).

Law of mass action : [By Guldberg and Waage]

Rate at which a substance reacts $\propto$ [Active Mass of the substance]

Active Mass = Molar concentration i.e. Moles/Litres

$$= \frac{\text{Wt of substance (gram)}}{\text{Molar wt.} \times \text{Vol.(Litre)}}$$

It is represented in square brackets i.e. [ ] e.g. [A], $[N_2]$ etc.

Note: Active masses are dimensionless quantities but for our purposes we generally take them with dimensions of molarity, partical pressure, etc.

The rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients.

Ex. $aA + bB \longrightarrow$ products

Rate of reaction α $[A]^a\,[B]^b$

Rate = k $[A]^a\,[B]^b$, where k is the rate constant of the reaction.

Section (B & C) : Homogeneous equilibrium: K_C in gaseous system & K_P in gaseous system

Equilibrium constant (K) :

For a general reaction

$$aA + bB \rightleftharpoons cC + dD,$$

Forward reaction rate $r_f = k_f\,[A]^a\,[B]^b$,

Backward reaction rate $r_b = k_b\,[C]^c[D]^d$,

At equilibrium $r_f = r_b$

$$k_f\,[A]^a_{eq}\,[B]^b_{eq} = k_b\,[C]^c_{eq}\,[D]^d_{eq}$$

The concentrations of reactants & products at equilibrium are related by

$$\frac{k_f}{k_b} = K_C = \frac{[C]^c_{eq}\,[D]^d_{eq}}{[A]^a_{eq}\,[B]^b_{eq}}$$

❍ **K_c** is a constant and is called the **equilibrium constant in terms of concentration.** where <u>all the concentrations are at equilibrium </u>and are expressed in moles/litre.

e.g. $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2(g)$ ⇒ $K_C = \dfrac{[PCl_3]_{eq}\;[Cl_2]_{eq}}{[PCl_5]_{eq}}$

e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ⇒ $K_C = \dfrac{[NH_3]^2_{eq}}{[N_2]\;[H_2]^3_{eq}}$

e.g. $\dfrac{1}{2}H_2(g) + \dfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$ ⇒ $K_c = \dfrac{[HI]'_{eq}}{[H_2]^{1/2}_{eq}\,[I_2]^{1/2}_{eq}}$

❍ **K_P → Equilibrium constant in terms of partial pressure.** It is defined for the equilibrium reaction which contains at least one gaseous component.

e.g. $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$

$$K_P = \frac{[P_C]^c_{eq}\;[P_D]^d_{eq}}{[P_A]^a_{eq}\;[P_B]^b_{eq}}$$

Where various pressures are the partial pressures of various gases substances.

Section (D) : Relation between K_P and K_C

❍ **Relation between K_p & K_C**

$PV = nRT$ or, $P = \dfrac{n}{V}RT$

$P = CRT$ where $C = \dfrac{n}{V}$ = (moles per litre)

$P_C = [C]\,RT$; $P_D = [D]\,RT$; $P_A = [A]\,RT$; $P_B = [B]\,RT$

⇒ $K_P = \dfrac{[C]^c(RT)^c[D]^d(RT)^d}{[A]^a(RT)^a[B]^b(RT)^b} = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$

$K_p = K_c(RT)^{\Delta n}$

Where $\Delta n_g = (c + d) - (a + b)$, calculation of Δn involves only gaseous components.

⇒ Δn_g = sum of the number of moles of gaseous products – sum of the number of moles of gaseous reactants. <u>Δn_g can be positive, negative, zero or even fraction.</u>

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$\Delta n_g = 1$ (because there is only one gas component in the products and no gas component in the reaction)

⇒ $K_p = K_c.(RT)$

Unit of Equilibrium contants :

- Unit of K_p is $(atm)^{\Delta n}$
- Unit of K_c is $(mole/Lit)^{\Delta n} = (conc.)^{\Delta n}$

Note : ❍ In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.

❍ **For pure solids and pure liquids, although they have their own active masses but they remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.**

e.g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_C = [\,CO_2]$, $K_P = P_{CO_2}$

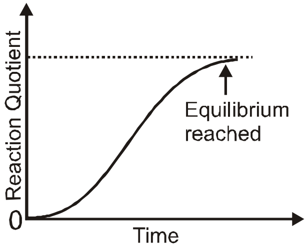
Section (E) : Reaction quotient and Its applications

- **Predicting the direction of the reaction**

  Reaction Quotient (Q)

  At each point in a reaction, we can write a ratio of concentration terms having the same form as the equilibrium constant expression. This ratio is called the reaction quotient denoted by symbol Q.
  It helps in predicting the direction of a reaction.

  The expression $Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ <u>at any time during reaction</u> is called reaction quotient.The concentrations [C], [D], [A], [B] are not necessarily at equilibrium.



- *The reaction quotient is a variable quantity with time.*
- *It helps in predicting the direction of a reaction.*

  ❍ if $Q > K_c$ reaction will proceed in backward direction until equilibrium in reached.
  ❍ if $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
  ❍ if $Q = K_c$ Reaction is at equilibrium.

  eg. $2A(g) + B(g) \rightleftharpoons C(g) + D(g)$

  Q_C = Reaction quotient in terms of concentration

  $$Q_C = \frac{[C][D]}{[A]^2[B]}$$

  $$K_C = \frac{[C]_{eq}[D]_{eq}}{[A]^2_{eq}[B]_{eq}}$$ [Here all the conc. are at equilibrium]

Solved Examples

Ex-2. For the reaction $NOBr\,(g) \rightleftharpoons NO(g) + \frac{1}{2}Br_2\,(g)$

$K_P = 0.15$ atm at 90°C. If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will Br_2 be consumed or formed ?

Sol. $Q_P = \frac{[P_{Br_2}]^{1/2}[P_{NO}]}{[P_{NOBr}]} = \frac{[0.2]^{1/2}\,[0.4]}{[0.50]} = 0.36$

$K_P = 0.15$

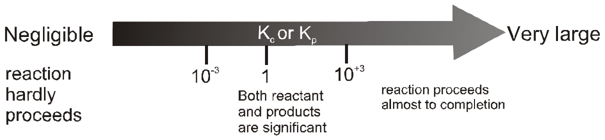
$\therefore \quad Q_P > K_P$

Hence, reaction will shift in backward direction $\therefore$ Br_2 will be consumed

---

- **Predicting the extent of the reaction**

  $$K = \frac{[\text{Product}]_{eq}}{[\text{Reactant}]_{eq}}$$



Case-I: If K is large ($K > 10^3$) then product concentration is very very larger than the reactant ([Product] >>[Reactant]) Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

Case-II : If K is very small ($K < 10^{-3}$)
[Product] << [Reactant]
Hence concentration of Product can be neglected as compared to the reactant.
In this case, the reaction is reactant favourable.

Solved Examples

Ex-3. The K_P values for three reactions are 10^{-5}, 20 and 300 then what will be the correct order of the percentage composition of the products.

Sol. Since K_p order is $10^{-5} < 20 < 300$ so the percentage composition of products will be greatest for $K_p = 300$.

Section (F) : Properties of equilibrium Constant

- Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached
- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- **K depends on the stoichiometry of the reaction.**
  - If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 . K_2$

		Equation constant
	$A(g) \rightleftharpoons B(g)$	K_1
	$B(g) \rightleftharpoons C(g)$	K_2
On adding	$A(g) \rightleftharpoons C(g)$	$K = K_1 . K_2$

  - If the reaction having eq. constant K_1 is reversed then resulting equation has eq. constant $\frac{1}{K_1}$

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

On reversing, $C(g) + D(g) \rightleftharpoons A(g) + B(g) \quad K = \frac{1}{K_1}$

  - If a chemical reaction having equilibrium constant K_1 is multiplied by a factor n then the resulting equation has equilibrium constant $K = (K_1)^n$, n can be fraction

eg. $D_2(g) \rightleftharpoons 2A(g) \qquad K_1$

Multiplying by $\left(\frac{1}{2}\right)$, $\quad \frac{1}{2}D_2 \rightleftharpoons A \qquad K = (K_1)^{1/2} = \sqrt{K_1}$

- **Equilibrium constant is dependent only on the temperature.**
  It means K_p and K_c will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.
  - However if temperature is changed,

$$\log\frac{k_2}{k_1} = \frac{\Delta H}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] ; \quad \Delta H = \text{Enthalpy of reaction}$$

If $T_2 > T_1$ then $K_2 > K_1$ provided ΔH = +ve (endothermic reaction)
$K_2 < K_1$ if ΔH = –ve (exothermic reaction)
In the above equation, the unit of R and $\Delta H/T$ should be same.

Section (G) : Homogenuous Equilibrium (liquid system)

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.

$$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Solved Examples

Ex-4. In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at T°C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterfied. Calculate the equilibrium constant of this reaction.

Sol.

$$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$$

Initial	1	1	0	1
At equilibrium	1 – x	1 – x	x	1 + x
	1 – 0.543	1 – 0.543	0.543	1 + 0.543

$$(54.3\% \text{ of 1 mole} = \frac{1 \times 54.3}{100} = 0.543 \text{ mole})$$

Hence given x = 0.543 mole

Applying law of mass action : $K_C = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$

❍ **EQUATION INVOLVING IONS :**

Equilibrium involving ions always take place in aquous medium. In case of expression of K_C concentration of ion is taken.

Ex. $Ag^+(aq.) + Cl^-(aq.) \rightleftharpoons AgCl(s)$ $K_c = \frac{1}{[Ag^+][Cl^-]}$

Section (H) : Heterogenuous equilibrium

For pure solid and pure liquid, active mass is taken to be unity i.e. 1 as they remain constant throughout the reaction :

- $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

  $K_P = (P_{CO_2})_{eq}$, $K_C = [CO_2\ (g)]_{eq}$

  $$[CaCO_3(s)] = \frac{\text{moles}}{\text{volume}} = \frac{W_{CaCO_3}}{\frac{M_{CaCO_3}}{V}} = \frac{\text{density}\ CaCO_3}{M_{CaCO_3}} = \text{constant}$$

  $$K = \frac{[CaO(s)]_{eq}\ [CO_2(g)]_{eq}}{[CaCO_3(s)]_{eq}}$$

  $$\frac{K.[CaCO_3(s)]_{eq}}{[CaO(s)]_{eq}} = [CO_2(g)]_{eq}$$

  $K_C = [CO_2(g)]_{eq}$

- $H_2O(\ell) \rightleftharpoons H_2O(g)_{eq}$

  $K_P = (P_{H_2O(g)})_{eq}$, $K_C = [H_2O\ (g)]_{eq}$

[For pure solid and pure liquid active mass is taken as unity i.e. = 1]

Section (I) : Degree of dissociation (α) and vapour density

It is the fraction of one mole dissociated into the products. (Defined for one mole of substance)

So, α = no. of moles dissociated / initial no. of moles taken
= fraction of moles dissociated out of 1 mole.

Note : % dissociation = α × 100

Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5 dissociated then $\alpha = \frac{2}{5} = 0.4$

Let a gas A_n dissociates to give n moles of A as follows-

	$A_n(g)$	$\rightleftharpoons$ $nA(g)$	
t = 0	a	0	
$t = t_{eq}$	a – x	n.x	$\alpha = \frac{x}{a} \Rightarrow x = a\alpha.$
	a – a α = a(1–α)	n a α	

Total no. of moles = a – a α + n a α = [1 + (n – 1) α] a

Significance of n

$$n = \frac{\text{sum of stoichiometric coefficient of product}}{\text{sum of coefficient of reactants}}$$

(i) for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $(n = 2)$

(ii) for $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $\left(n = \frac{3}{2} + \frac{1}{2} = 2\right)$

(iii) for $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $(n = 1)$

Solved Examples

Ex-5. Calculate the degree of dissociation and K_p for the following reaction.

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$
t = 0	a	0	0
t = t	a –x	x	x

Since for a mole, x moles are dissociated

Sol. ∴ For 1 mole, $\frac{x}{a}$ moles = α are dissociated

∴ $x = a\,\alpha$

		$PCl_5(g) \rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$
∴ At	$t = t_{eq}$	$a - a\alpha$	$a\alpha$	$a\alpha$

Total no. of moles at equilibrium = $a + a\alpha = a(1 + \alpha)$

$$P_{PCl_5} = \frac{a(1-\alpha)\,P}{a(1+\alpha)}, \quad P_{PCl_3} = \frac{a\,\alpha\ .\,P}{a\,(1+\alpha)}, \quad P_{Cl_2} = \frac{a\,\alpha}{a\,(1+\alpha)}\,.P$$

$$K_P = \frac{\left\{\left(\frac{\alpha P}{1+\alpha}\right)\right\}^2}{\left(\frac{1-\alpha}{1+\alpha}\right)P} \qquad K_P = \frac{\alpha^2\,.\,P}{1-\alpha^2} \text{ (Remember)}$$

Observed molecular weight and Observed Vapour Density of the mixture

Observed molecular weight of $A_n(g)$ = $\frac{\text{molecular weight of } A_n(g)}{\text{total no. of moles at equilibrium}} = \frac{a.M_{th}}{a(1+(n-1)\alpha)}$

∴ $M_{obs} = \frac{M_{th}}{[1+(n-1)\alpha]}$

where M_{th} = theoritical molecular weight (n = atomicity)

$M_{mixture} = \frac{M_{A_n}}{[1+(n-1)\alpha]}$, M_{A_n} = Molar mass of gas A_n

Vapour density (V.D). : Density of the gas divided by density of hydrogen under same temp & pressure is called vapour density.

❍ D = vapour density without dissociation = $\frac{M_{A_n}}{2}$

d = vapour density of mixture = observed v.d. = $\frac{M_{mix}}{2}$

$$\frac{D}{d} = 1 + (n-1)\,\alpha$$

∴ $\alpha = \frac{D-d}{(n-1)\times d} = \frac{M_T - M_o}{(n-1)M_0}$

Where M_T = The oritical molecular wt., M_0 = observed molecular wt. or molecular wt. of the mixture at equilibrium.

Note : It is not applicable for n = 1 eg. Dissociation of HI & NO (as the total number of don't change during the dissociation.)

Solved Examples

Ex-6. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 33°C calculate the no. of moles of NO_2 if 100g of N_2O_4 were taken initially.

Sol. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$M_{mix} = 2 \times 38.3 = 76.6$

$M_{mix} = \dfrac{M_{th}}{1+\alpha} = \dfrac{92}{1+\alpha} \quad \Rightarrow \quad \alpha = 0.2$

$$\begin{array}{lll} & N_2O_4 & \rightleftharpoons \; 2NO_2 \\ t = 0 & a & \quad 0 \\ t = t & a - a\alpha & \quad 2a\alpha \end{array}$$

no. of moles of $NO_2 = 2a\alpha = \dfrac{2 \times 100 \times 0.2}{92} = 0.435$

Section (J) : Thermodyanamics of equilibrium

For a general reaction, $mA + nB \rightleftharpoons pC + qD$, ΔG is given by-

$$\mathbf{\Delta G = \Delta G^o + 2.303\ RT\ \log_{10}Q}$$

where ΔG = Gibb's Free energy change

ΔG^o = Standard Gibb's Free energy change

Q = reaction quotient

Since, at equlibrium, Q = K

Here K is thermodynamic equilibrium constant replacing K_c or K_p

$K = \dfrac{(a_C)^p\,(a_D)^q}{(a_A)^m\,(a_B)^n}$; Here a_X denotes the activity of X.

In fact, 'a_x' is the ratio of the activity of substance at equilibrium and its activity in standard condition. That is why it is unitless and K is also unitless.

Note : (i) Themodynamic equilibrium constant is unitless since activity is unitless.
(ii) For pure solids & pure liquids, activity is unity.
(iii) For gases (ideal behaviour), the activity is its partial pressure (in atm).
(iv) For components in solution, activity is molar concentration.

At equilibrium, $\Delta G = 0$

$\Rightarrow \quad \Delta G^o = -\,2.303\ RT\ \log_{10}K$

Now since, $\Delta G^o = \Delta H^o - T\Delta S^o$

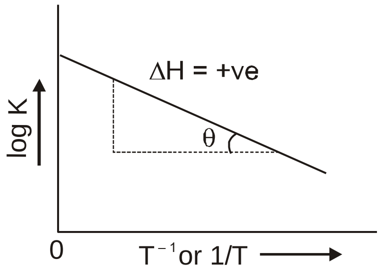
where ΔH^o = Standard enthalpy change of the reaction

ΔS° = Standard entropy change

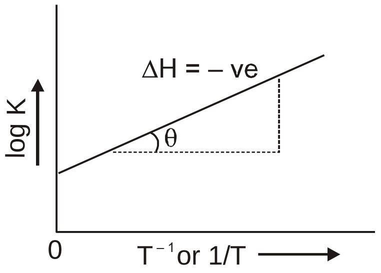
$\Rightarrow \quad -\,2.303\ RT\ \log_{10}K = \Delta H^o - T\Delta S^o$

$\Rightarrow \quad \log_{10}K = -\,\dfrac{\Delta H^o}{2.303} \cdot \dfrac{1}{RT} + \dfrac{\Delta S^o}{2.303R}$

If plot of ln k vs $\dfrac{1}{T}$ is plotted then it is a straight line with slope = $-\dfrac{\Delta H^o}{R}$ and intercept = $\dfrac{\Delta S^o}{R}$



Endothermic reaction



Exothermic reaction

Slope = $\dfrac{-\Delta H^o}{2.303R}$ = $\tan\theta$, y intercept = $\dfrac{\Delta S^o}{2.303R}$

If at temperature T_1, equilibrium constant is K_1 and at T_2, it is K_2 then ;

$$\log_{10}K_1 = \frac{-\Delta H^o}{2.303R} \cdot \frac{1}{T_1} + \frac{\Delta S^o}{2.303R} \qquad \text{........... (i)}$$

$$\log_{10}K_2 = \frac{-\Delta H^o}{2.303R} \cdot \frac{1}{T_2} + \frac{\Delta S^o}{2.303R} \qquad \text{........... (ii)}$$

[Assuming ΔH^o and ΔS^o remains constant in this temperature range.]

Subtract eq. (ii) from (i) we get **Vant Hoff equation-**

$$\log\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^o}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Note : ❍ ΔH should be substituted with sign.

❍ Unit of $\Delta H/T$ and gas constant R should be same.

❍ For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature

❍ For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

Condition for spontaneity : $\Delta G < 0$ for spontaneous process or reaction.

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

$\Rightarrow \quad \Delta H - T\Delta S < 0 \qquad \Rightarrow \qquad T > \Delta H/\Delta S$

* $\Delta G > 0$ for non-spontaneous process or reaction.

* $\Delta G = 0$ for equilibrium.

Solved Examples

Ex-7. Variation of equilibrium constant K with temperature T is given by van't Hoff equation,

$$\log K = \log A - \frac{\Delta H^o}{2.303\ RT}$$

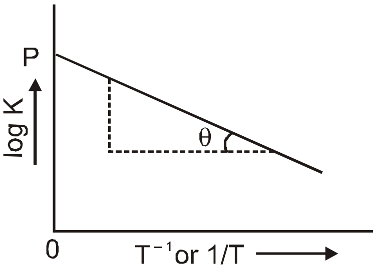
A graph between log K and T^{-1} was a straight line as shown in the figure and having $\theta = \tan^{-1}(0.5)$ and OP = 10. Calculate :

(a) $\Delta H°$ (standard heat of reaction) when T = 300 K,

(b) A (pre-exponential factor),

(c) Equilibrium constant K, at 300 K,

(d) K at 900 K if $\Delta H°$ is independent of temperature.



Sol. (a) $\log_{10} K = \log_{10} A - \dfrac{\Delta H^o}{2.303\ RT}$

It is an equation of a straight line of the type y = c + mx

Slope 'm' = $\tan\theta = \dfrac{\Delta H°}{2.303\ R}$

$0.5 = \dfrac{\Delta H^o}{2.303 \times 8.314} \qquad \Rightarrow \qquad \Delta H° = 9.574\ \text{J mol}^{-1}$

(b) Intercept 'c' = $\log_{10} A = 10 \qquad \therefore \qquad A = 10^{10}$

(c) $\log K = 10 - \dfrac{9.574}{2.303 \times 8.314 \times 298} \quad \Rightarrow \quad K = 9.96 \times 10^9$

(d) $\log\left(\dfrac{K_2}{K_1}\right) = \dfrac{\Delta H}{2.303R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\}$

$$\log\frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314}\left\{\frac{1}{298} - \frac{1}{798}\right\}$$

On solving $\quad K_2 = 9.98 \times 10^9$

Ans. (a) 9.574 J mol^{-1} ; (b) A = 10^{10} ; (c) 9.96 ×10^9 ; (d) 9.98 × 10^9

Section (K) : Le-chatelier's principle

Le Chatelier's Principle:

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

- **Effect of concentration :** If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g. In the following example.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

[reactant] ↑ Forward shift

[Product] ↑ Backward shift

- If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction.
- If concentration of product is increased then reaction shifts in the backward direction

Note : The addition of any solid component does not affect the equilibrium.

- **Effect of volume :**
  - If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
  - If volume is increased then, for

$\Delta n_g > 0$ reaction will shift in the forward direction

$\Delta n_g < 0$ reaction will shift in the backward direction

$\Delta n_g = 0$ reaction will not shift. eg. $H_2(g) + I_2(g)$ $2HI(g) \rightleftharpoons$ (No effect)

Explanation :

(i) $\Delta n_g > 0$, eg. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_C = \frac{\frac{(n_{Cl_2})}{V} \times \frac{(n_{PCl_3})}{V}}{\frac{(n_{PCl_5})}{V}} \quad \Rightarrow \quad Q_C \propto \frac{1}{V} \text{ for } \Delta n_g > 0 \qquad [(n) = \text{moles}]$$

On incerasing V, Q_C, decreases.

Now, for $Q_C < K_C$ reaction will shift in forward direction.

Thus, if, Volume ↑ Q_C ↓ (Forward shift)

Volume ↓ Q_C ↑ (Backward shift)

(ii) $\Delta n_g < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_C = \frac{\left\{\frac{(n_{NH_3})}{V}\right\}^2}{\left\{\frac{(n_{N_2})}{V}\right\}\left\{\frac{(n_{H_2})}{V}\right\}^3} \quad \Rightarrow \quad Q_C \propto V^2 \qquad \text{for } \Delta n_g < 0$$

V ↑ Q_C ↑ (Backward shift) ; V ↓ Q_C ↓ (Forward shift)

- **Effect of pressure :**

On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.

□ P ∝ no. of moles

(i) For $\Delta n_g = 0 \rightarrow$ No. effects

(ii) For $\Delta n_g > 0$, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_p = \frac{(X_{PCl_3}P).(X_{Cl_2}P)}{(X_{PCl_5}.P)} \quad \Rightarrow \quad Q_P \propto P \qquad [(\ ) = \text{mole fraction}]$$

P ↓; Q_P ↓; (Forward shift)

P ↑; Q_P ↑; (Backward shift)

(iii) For $\Delta n < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_P = \frac{\left[(X_{NH_3})P\right]^2}{[(X_{N_2}).P][(X_{H_2})P]^3} \quad \Rightarrow \quad Q_P \propto \frac{1}{P^2}$$

$P\uparrow$; $Q_P\downarrow$; (Forward shift) ; $P\downarrow$; $Q_P\uparrow$; (Backward shift)

- **Effect of catalyst :**
  Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the <u>equilibrium will be attained faster</u> i.e time taken to reach the equilibrium is less.

- **Effect of inert gas addition :**
  (a) At constant volume : Inert gas addition has no effect at constant volume
  (b) At constant pressure : If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed
    (i) $\Delta n_g > 0$, reaction will shift in the forward direction
    (ii) $\Delta n_g < 0$, reaction will shift in the backward direction
    (iii) $\Delta n_g = 0$, no effect

- **Effect of temperature :**
  (i) Exothermic reaction : The reaction in which heat is evolved

  $A(g) + B(g) \rightleftharpoons C(g) + D(g) + \text{Heat} \qquad \Delta H = -\text{ve}$

  eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

  $T\uparrow \Rightarrow$ K' will decrease

  $$\log\frac{K_1}{K_2} = \frac{\Delta H^o}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ (from vant' hoff equation)

  $$\log\frac{K_1}{K_2} < 0 \Rightarrow \log K_1 - \log K_2 > 0 \Rightarrow \log K_1 > \log K_2 \Rightarrow K_1 > K_2$$

  Reaction will shift in backward direction.

  $T\downarrow \Rightarrow$ K will increases.

  Reaction will shift in forward direction.

  (ii) Endothermic reaction : energy consumed.

  $A(g) + B(g) \rightleftharpoons C(g) + D(g) - \text{Heat} \qquad \therefore \Delta H = +\text{ve}$

  $T\uparrow \Rightarrow K\uparrow \Rightarrow$ Forward ; $T\downarrow \Rightarrow K\downarrow \Rightarrow$ Backward

Application of le chatelier's principle : Practical equilibrium situations :

Section (L) : Vapour pressure and Relative Humidity

- It is the pressure exerted by the vapours over it's liquid when it is in equilibrium with the liquid. Vapour pressure of water is also called **aqueous tension.**

  H_2O (□) $\rightleftharpoons H_2O(g)$; $K_P = P_{H_2O}$ = **constant at fixed temperature**

  Hence V.P. of liquid is independent of pressure, volume and concentration change.
  e.g. at 25°C, vapour pressure of water ≈ 24 mm of Hg

  Relative Humidity = $\dfrac{\text{Partial pressure of } H_2O \text{ vapours}}{\text{Vapour pressure of } H_2O \text{ at that temp.}}$

- **Formation of diamond :**

  $$\underset{\substack{\downarrow \\ \text{Density Low} \\ \text{Volume High}}}{C\text{ (graphite)}} \rightleftharpoons \underset{\substack{\downarrow \\ \text{Density High} \\ \text{Volume Low}}}{C\text{ (diamond)}} - \text{Heat}; \qquad \Delta H = +\text{ve}$$

  Formation of diamond is favourable at high pressure and high temperature

- **Melting of ice :**

$H_2O\,(s) \rightleftharpoons H_2O$ (□); $\Delta H = +$ ve

↓ ↓

Density Low Density High
Volume High Volume Low

Melting of ice is favourable at high temperature and high pressure.

- **Boiling of water :**

H_2O(□) $\rightleftharpoons H_2O(g)$

↓ ↓

Density High Density Low
Volume Low Volume High

On incerasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward.
Hence, on incerasing pressure, the boiling point increases.

- **Formation of ammonia by Haber's process :**

$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2NH_3\,(g) \quad \Delta H = -\,22.4$ Kcal/mol.

(i) The reaction will shift in the forward direction at low temperature, but at very low temperature the rate of reaction becomes very low; thus moderate temperature is used for this reaction.
(ii) At high pressure, reaction will shift in forward direction to form more product.

- **Manufacturing of SO_3 by contact process**

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 45.2$ kcal

High pressure (1.5 to 1.7 atm), Low temperature (500°C), higher quantity of SO_2 and O_2 are favourable conditions for the formation of SO_3.

- **Manufacturing of NO by Birkeland–Eyde process**

$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) - 43.2$ kcal

  - ❍ No effect on change of pressure
  - ❍ High temperature (1200°C to 2000°C), High concentration of N_2 and O_2 are favourable condition for the formation of NO.

Solved Examples

***Ex*-8.** The equilibrium constant of the reaction at 25°C

$$CuSO_4.5H_2O\,(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$$

is 1.084×10^{-4} atm^2. Find out under what conditions of relative humidity, $CuSO_4.5H_2O$ will start loosing its water of crystallization according to above reaction. (Vapour pressure of water at 25°C is 24 mm of Hg).

Sol. $K_P = \left(P_{H_2O}\right)^2$ so $P_{H_2O} = \sqrt{1.084 \times 10^{-4}} = 1.041 \times 10^{-2}$ atm $\approx$ 8 mm of Hg

❍ If in a room, pressure of water is greater than 8 mm of Hg then $CuSO_4.3H_2O$ will absorb water from air and will form $CuSO_4.5H_2O$ & will keep absorbing until partial pressure of H_2O becomes 8 mm of Hg.

❍ If $P_{H_2O} < 8$ mm of Hg then $CuSO_4.5H_2O$ will loose water of crystallization and reaction will move in forward direction.

i.e. If relative humidity $< \dfrac{8}{24} < 33.33\%$ then $CuSO_4.5H_2O$ will loose water of crystallization.

Section (M) : Simultaneous equilibria

If in any container there are two or more equilibria existing simultaneously involving one or more than one common species. Then in both/all equilibrium the concentration of common species is the total concentration of that species due to all the equilibria under consideration.

e.g.

$$\begin{array}{llll} & A(s) \rightleftharpoons & X(g) & + \ Y(g) \\ t = 0 & a & 0 & 0 \\ t = t_{eq} & a - t & t & t + u \end{array}$$

$$\begin{array}{lll} B(s) \rightleftharpoons & Z(g) & + \ Y(g) \\ b & 0 & 0 \\ b - u & u & u + t \end{array}$$

$K_{C_1} = t\,(u + t)$

$K_{C_2} = (u + t)\,u$

Solved Examples

Ex-9. 102 g of solid NH_4HS is taken in the 2L evacuated flask at 57°C. Following two equilibrium exist simultaneously

$$NH_4HS\ (s) \rightleftharpoons NH_3\,(g) + H_2S\ (g) \qquad ; \qquad NH_3\,(g) \rightleftharpoons \frac{1}{2} N_2\,(g) + \frac{3}{2} H_2\,(g)$$

one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of H_2 was found at the equilibrium then find the equilibrium concentration of all the species and K_C for both the reaction.

Sol. Moles of $NH_4HS = \frac{102}{51} = 2$

$$\begin{array}{llll} NH_4HS\ (s) \rightleftharpoons & NH_3\,(g) & + \ H_2S\ (g) & K_{C_1} \\ 2 & 0 & 0 & \\ 1 & 1 - x & 1 & \end{array}$$

$$\begin{array}{llll} NH_3\,(g) \rightleftharpoons & \frac{1}{2} N_2\,(g) & + \ \frac{3}{2} H_2\,(g) & K_{C_2} \\ 1 - x & \frac{x}{2} & \frac{3x}{2} & \end{array}$$

Given that moles of $H_2 = \frac{3x}{2} = 0.75 \quad \Rightarrow \quad x = \frac{1}{2}$

$$K_{C_1} = \frac{1}{2}\frac{(1-x)}{2} = \frac{1}{8} \qquad \text{[Since V = 2 L]}$$

$$K_{C_2} = \frac{\left(\frac{3x}{4}\right)^{3/2}\left(\frac{x}{4}\right)^{½}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2}\left(\frac{1}{8}\right)^{½}}{\frac{1}{4}} = (3)^{3/2}\,\frac{1}{64} \times \frac{4}{1} = \frac{(3)^{3/2}}{16}$$

SUMMARY

Chemical equilibrium is a dynamic state in which the concentration of reactants and products remain constant because the rates of the forward and the reverse reaction are equal. For the general reaction

$$a\,A(g) + b\,B\,(g) \rightleftharpoons c\,C(g) + d\,D(g)$$

concentrations in the equilibrium mixture are related by the equilibrium equation :

$$K_C = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}}$$

The ratio on the right side of the equation is called the equilibrium constant expression. The equilibrium constant K_c is the number obtained when equilibrium concentrations (in mol/L) are substituted into the equilibrium constant expression. The value of K_c varies with temperature and depends upon the form of the balanced chemical equation.

The equilibrium constant K_p can be used for gas phase reactions. It is defined in the same way as K_c except that the equilibrium constant expression contains partial pressures (in atmospheres) instead of molar concentrations. The constants K_p and K_c are related by the equation,

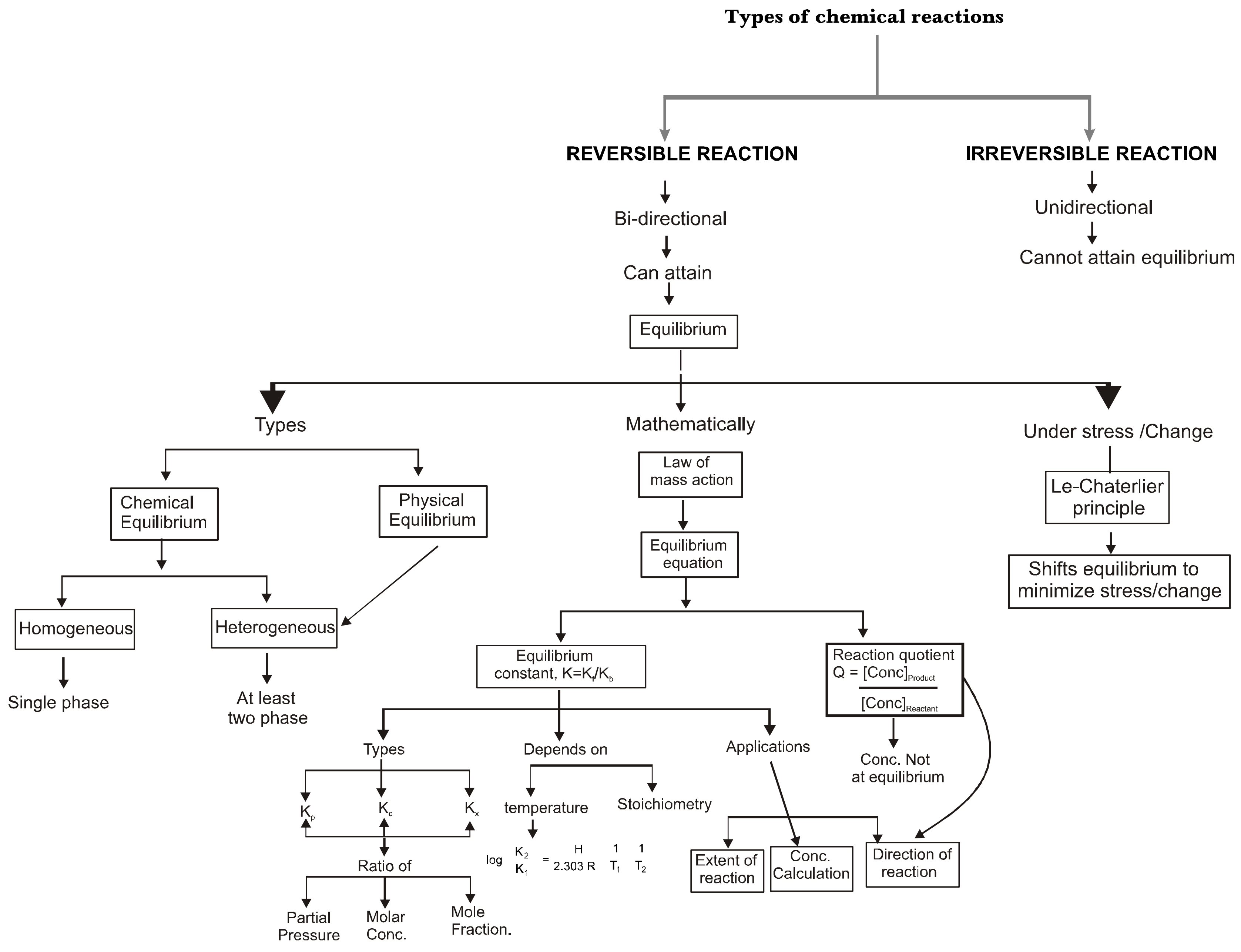
$K_p = K_c\ (RT)^{\Delta ng}$, where $\Delta n_g = (c + d) - (a + b)$.

Homogeneous equilibrium are those in which all reactants and products are in a single phase; heterogeneous equilibria are those in which reactants and products for heterogeneous equilibrium does not include concentrations of pure solids or pure liquids.

The value of the equilibrium constant for a reaction makes it possible to judge the extent of reaction, predict the direction of reaction, and calculate equilibrium concentrations (or partial pressures) from initial concentration (or partial pressures) . The farther the reaction proceed towards completion, the larger the value of K_c. The direction of a reaction not at equilibrium depends on the relative values of K_c and the reaction quotient Q_c which is defined in the same way as K_c except that the concentrations in the equilibrium constant expression are not necessarily equilibrium concentrations. If $Q_c < K_c$, net reaction goes from left to right to attain equilibrium; if $Q_c = K_c$, the system is at equilibrium.

The composition of an equilibrium mixture can be altered by changes in concentration, pressure (volume), or temperature. The qualitative effect of these changes is predicted by Le Chatelier's principle, which says that if a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. Temperature changes affect equilibrium concentrations because K_c is temperature-dependent. As the temperature increases, K_c for an exothermic reaction decreases, and K_c for an endothermic reaction increases.

A catalyst increases the rate at which chemical equilibrium is reached, but it does not affect the equilibrium constant or the equilibrium concentration. The equilibrium constant for a single-step reaction equals the ratio of the rate constants for the forward and reverse reactions : $K_c = k_f / k_b$.


Types of chemical reactions
REVERSIBLE REACTION
IRREVERSIBLE REACTION
Bi-directional
Can attain
Equilibrium
Unidirectional
Cannot attain equilibrium
Types
Mathematically
Under stress /Change
Chemical Equilibrium
Physical Equilibrium
Homogeneous
Heterogeneous
Single phase
At least two phase
Law of mass action
Equilibrium equation
Equilibrium constant, $K=K_f/K_b$
Reaction quotient $Q = \frac{[Conc]_{Product}}{[Conc]_{Reactant}}$
Conc. Not at equilibrium
Types
Depends on
Applications
K_p
K_c
K_x
Ratio of
Partial Pressure
Molar Conc.
Mole Fraction.
temperature
Stoichiometry
$\log {K_2 \atop K_1} = {H \atop 2.303\,R}\ {1 \atop T_1}\ {1 \atop T_2}$
Extent of reaction
Conc. Calculation
Direction of reaction
Le-Chaterlier principle
Shifts equilibrium to minimize stress/change

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. An example of a reversible reaction is :

(A) $Pb(NO_3)_2(aq) + 2NaI(aq) \rightleftharpoons PbI_2(s) + 2NaNO_3(aq)$

(B) $AgNO_3(aq) + HCl(aq) \rightleftharpoons AgCl(s) + HNO_3(aq)$

(C) $2Na(s) + H_2O(\ell) \rightleftharpoons 2NaOH\ (aq) + H_2(g)$

(D) $KNO_3(aq) + NaCl(aq) \rightleftharpoons KCl(aq) + NaNO_3(aq)$

Ans. **(D)**

Sol. Precipitation reactions, acid base reactions and reactions in which gases are liberated and are taking place in open container will be irreversible reactions.

2. For the reaction, $A + B \rightleftharpoons 3C$, if 'a' mol/litre of each 'A' & 'B' are taken initially then at equilibrium the incorrect relation is :

(A) $[A] - [B] = 0$ (B) $3[B] + [C] = 3a$ (C) $3[A] + [C] = 3a$ (D) $[A] + [B] = 3[C]$

Ans. **(D)**

Sol. At equilibrium :

$$[A] = [B]$$

$$[A] + \frac{1}{3}[C] = a$$

3. The equilibrium constant for the decomposition of water $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ is given by :

(α = degree of dissociation of $H_2O(g)$; p = Total equilibrium pressure)

(A) $K = \dfrac{\alpha^2 p^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$ (B) $K = \dfrac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(C) $K = \dfrac{\alpha^3 p^{1/2}}{\sqrt{2}}$ (D) $K = \dfrac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

Ans. **(B)**

Sol : $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$

$1 \quad 0 \quad 0$

$1-\alpha \quad \alpha \quad \alpha/2$

Total moles at equilibrium = $1 - \alpha + \alpha + \alpha/2 = 1 + \alpha/2$

Let the total pressure at equilibrium be = p

So, $p_{H_2O} = \dfrac{1-\alpha}{1+\alpha/2} \times p$

$p_{H_2} = \dfrac{\alpha}{1+\alpha/2} \times p$

$p_{O_2} = \dfrac{\alpha/2}{1+\alpha/2} \times p$

So $K_p = \dfrac{(p_{O_2})^{1/2}(p_{H_2})}{(p_{H_2O})}$

4. The reaction quotient Q for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is given by $Q = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed in backward direction, when:

(A) $Q = K_c$ (B) $Q < K_c$ (C) $Q > K_c$ (D) $Q = 0$

Ans. **(C)**

Sol. When Q > K, reaction will favour backward direction and when Q < K, it will favour forward direction.

5. 0.96 g of HI were heated to attain equilibrium $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$. The reaction mixture on titration requires 15.7 mL of N/10 hypo solution. Calculate degree of dissociation of HI.

Ans. 20.9%

Sol. meq of $I_2 = \frac{w_{I_2}}{127} \times 1000 = 1.57$

$w_{I_2} = \frac{127 \times 1.57}{1000}$ $n_{I_2} = \frac{1.57}{2000}$

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

$a - a\alpha$ $\frac{a\alpha}{2}$ $\frac{a\alpha}{2}$ $\frac{0.96}{256} \times \alpha = \frac{1.57}{2000}$

$\alpha = 0.209$ **Ans.**

6. Would 1% CO_2 by volume in air be sufficient to prevent any loss in weight when M_2CO_3 is heated at 120ºC ?

$M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g)$

$K_p = 0.0095$ atm at 120ºC. How long would the partial pressure of CO_2 have to be to promote this reaction at 120ºC ?

Ans. (No reactions)

Sol. For, $M_2CO_3(g)\ (s) \rightleftharpoons M_2O\ (s) + CO_2\ (g)$

∵ CO_2 is 1% in air ; ∴ $P'_{CO_2} = \frac{1}{100} \times P_{air} = \frac{1}{100} \times 1$ atm. = 0.01 atm.

Also for equilibrium $K_P = P'_{CO_2} = 0.0095$ atm.

∵ Given, $P'_{CO_2} = 0.01$ atm.

Since decomposition is carried out in presence of P'_{CO_2} of 0.01 atm and $K_P = 0.0095$ atm, thus, practically no decomposition of M_2CO_3. Thus, 1% CO_2 is sufficient to prevent any loss in weight.

If at all reaction is desired, the P'_{CO_2} must be lesser than 0.0095 atm as P'_{CO_2} at equilibrium cannot be more than 0.0095 atm.

Altrernate solution :

For $M_2CO_3\ (s) \rightleftharpoons M_2O\ (s) + CO_2\ (g)$

$$\left(\frac{1}{100} + P\right)$$

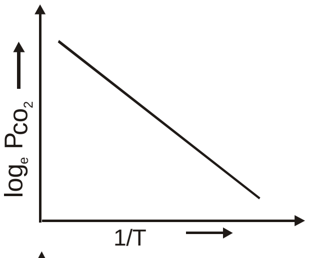
∵ $K_P = P'_{CO_2}$ and the pressure of CO_2 already present in 1/100 atm. Let the decomposition of M_2CO_3 produces the CO_2 of pressure P, then

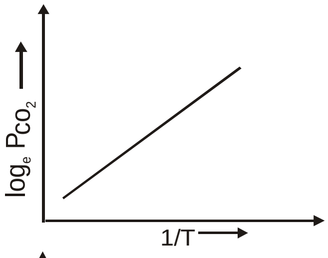
∴ $K_P = \frac{1}{100} + P$ or $0.0095 = P + 001$ or $P = -0.0005$.

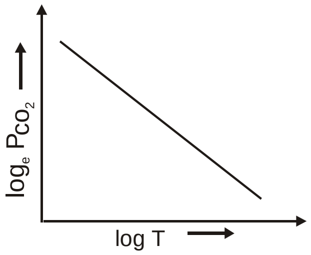
The value of pressure comes negative and thus, it may be concluded that M_2CO_3 will not dissociate in pressure of CO_2 of pressure 0.01 atm.

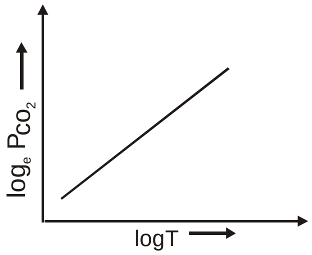
7. For the chemical equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

ΔH_f^o can be determined from which one of the following plots ?

(A) 

(B) 

(C) 

(D) 

Sol. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_p = P_{CO_2}$$

$$\log K_p = \log A - \frac{\Delta H_r^0}{2.303RT}$$

$$\log P_{CO_2} = \log A - \frac{\Delta H_r^\circ}{2.303}\frac{1}{RT} \qquad \text{......... (i)}$$

Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.

So, Ans. (A).

8. In a container of constant volume at a particular temparature N_2 and H_2 are mixed in the molar ratio of 9:13. The following two equilibria are found to be coexisting in the container

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$$

The total equilibrium pressure is found to be 3.5 atm while partial pressure of $NH_3(g)$ and $H_2(g)$ are 0.5 atm and 1 atm respectively. Calculate of equilibrium constants of the two reactions given above.

Sol. Let the initial partial pressures of N_2 and H_2 be 9P and 13 P respectively

$$\begin{array}{lclcl} N_2\,(g) & + & 3H_2\,(g) & \rightleftharpoons & 2NH_3\,(g) \\ 9P - y - x & & 13P - 3x - 2y & & 2x \end{array}$$

$$\begin{array}{lclcl} N_2\,(g) & + & 2H_2\,(g) & \rightleftharpoons & N_2H_4\,(g) \\ 9P - y - x & & 13P - 3x - 2y & & y \end{array}$$

Total pressure $= P_{N_2} + P_{H_2} + P_{NH_3} + P_{N_2H_4} = 3.5$ atm

$= (9P - x - y) + (13\,P - 3x - 2y) + 2x + y = 3.5$ atm ...(1)

$P_{NH_3} = 2x = 0.5$ atm ...(2)

$P_{H_2} = (13P - 3x - 2y) = 1$ atm ...(3)

from (1) $\Rightarrow$ $(9P - x - y) + 1\text{ atm} + 0.5 + y = 3.5$

$\Rightarrow$ $(9P - x) = 2$ atm

so $9P = 2.25$

$P = 0.25$ atm

from (3) equation $2y = 1.5$

$y = 0.75$ atm

so $P_{N_2} = 9P - x - y = 1.25$ atm

$P_{H_2} = 1$ atm

$P_{NH_3} = 0.5$ atm

$P_{N_2H_4} = 0.75$ atm

So, $$K_{P_1} = \frac{P_{NH_3}^2}{P_{H_2}^3\,.\,P_{N_2}} = \frac{0.5 \times 0.5}{1 \times 1 \times 1 \times 1.25} = 0.2\text{ atm}^{-2}$$

$$K_{P_2} = \frac{P_{N_2H_4}}{P_{N_2}.P_{H_2}^2} = \frac{0.75}{1 \times 1 \times 1.25} = 0.6\text{ atm}^{-2}$$