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CHEMISTRY

Target : JEE (Main)

CHEMICAL EQUILIBRIUM

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 disrupt a system at equilibrium.

Types of chemical reactions

IRREVERSIBLE REACTION

The reaction which proceed in one direction only

(a) Precipitation reactions e.g.

$NaCl\ (aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl\downarrow$

(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

REVERSIBLE REACTION

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)]
(c)	$2KClO_3\ (s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$		$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Haber's process) (ii) Liquid phase $CH_3\ COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
(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.

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

In a reversible reaction like–

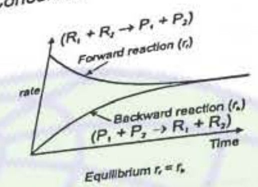
$$\underbrace{R_1 + R_2}_{\text{Reactants}} \rightleftharpoons \underbrace{P_1 + P_2}_{\text{Products}}$$

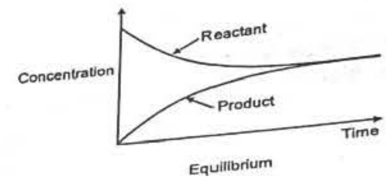
Initially only reactants are present. R_1 and R_2 combine to form P_1 and P_2. As soon as P_1 and P_2 are formed, they start the backward reaction. As concentrations of R_1 and R_2 decrease rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when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

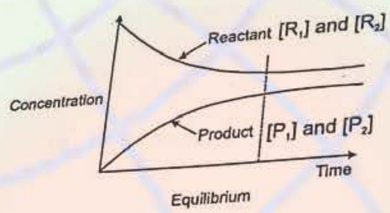
At equilibrium :

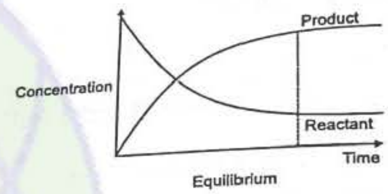
(i) Rate of forward reaction (r_f) = rate of backward reaction (r_b)

(ii) Concentration (mole/litre) of reactant and product remains 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

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

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

When all reactants and products are in same phase

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

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

Heterogeneous equilibrium

When more than one phase are present

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

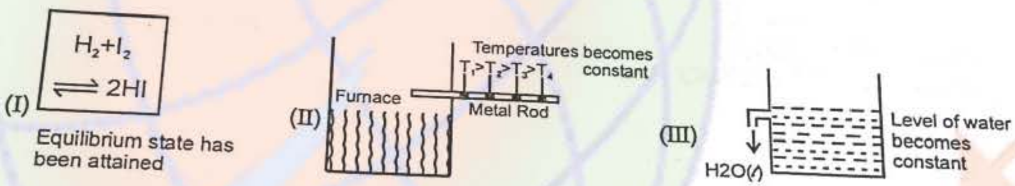
$$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH + O_2(g)$$

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 from both direction.
- Equilibrium is dynamic in nature.
  It means that reaction has not stopped. It appears that no change is occuring but 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 Consider the following cases :



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

(1) II (2) III (3) II and III (4) None

Sol. (4) 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]

$$\text{Active Mass} = \text{Molar concentration i.e. Moles/Litres} = \frac{\text{Wt of substance (gram)}}{\text{Molar wt.} \times \text{Vol.(Litre)}}$$

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

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 $\alpha\ [A]^a [B]^b$

Rate = $k\,[A]^a [B]^b$,

where k is the rate constant of the reaction.

Solved Examples

Ex.2 Four vessel each of volume V = 10 Lilres contains
(1) 16 g CH_4 (2) 18 g H_2O (3) 35.5 g Cl_2 (4) 44 g CO_2
Which container will contain same molar concentration and same active mass as that in (1)?

Sol. (1) $\Rightarrow [CH_4] = \frac{16}{16 \times 10} = 0.1$ M (2) $\Rightarrow [H_2O] = \frac{18}{18 \times 10} = 0.1$ M

(3) $\Rightarrow [Cl_2] = \frac{35.5}{71 \times 10} = 0.05$ M (4) $\Rightarrow [CO_2] = \frac{44}{44 \times 10} = 0.1$ M

Hence, (2) and (4) has same molar concentration as that in (1).

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 $r_f = r_b$

$k_f [A]^a [B]^b = k_b [C]^c [D]^d$

The concentrations of reactants & products at equilibrium are related by

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

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

e.g. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\Rightarrow$ $K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$

e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Rightarrow$ $K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$

e.g. $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$ $\Rightarrow$ $K_c = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$

Solved Examples

Ex.3 In a reaction A (g) + B (g) $\rightleftharpoons$ C (g)+ D(g) , A, B, are mixed in a vessel at temperature T. The initial concentration of A was twice the initial concentration of B. After the equilibrium is reached, concentration of C was thrice the concentration of B Calculate K_c.

Sol. Let concentration of B initially is 'a' mole/litre

	A	+ B	$\rightleftharpoons$ C	+ D	
					$\Rightarrow \Delta n = 0$
at t = 0	2a	a	0	0	
at t = t_{eq}	2a – x	a – x	x	x	

Given that

$x = 3(a - x)$ $\Rightarrow$ $x = \frac{3}{4}a$ $K_c = \frac{[C]\,[D]}{[A]\,[B]}$

$$K_c = \frac{x.x}{(2a-x)(a-x)} \Rightarrow K_c = \frac{\left(\frac{3a}{4}\right)^2}{\left(2a-\frac{3a}{4}\right)\left(a-\frac{3a}{4}\right)} \Rightarrow K_c = \frac{9}{5} = 1.8$$

- $K_p \rightarrow$ **Equilibrium constant in terms of partial pressure.** It is defined for the equilibrium reaction which contains at least one gaseous component.

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

$$K_p = \frac{[P_C]^c\ [P_D]^d}{[P_A]^a\ [P_B]^b}$$

where various pressures are the partial pressures of various gases substancs.

Solved Examples

Ex.4 Calculate the expression for K_c and K_p if initially a moles of N_2 and b moles of H_2 is taken for the following reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ($\Delta n < 0$) (P, T, V given)

Sol. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ($\Delta n < 0$) (P, T, V given)

	$N_2(g)$	$3H_2(g)$	$2NH_3(g)$
At t = 0	a	b	0
$t = t_{eq}$	$(a - x)$	$(b - 3x)$	$2x$

$$[N_2] = \frac{a-x}{V}, \quad [H_2] = \frac{b-3x}{V}, \quad [NH_3] = \frac{2x}{V}$$

$$K_C = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

Total no. of moles at equilibrium = a + b – 2x

$$[P_{N_2}] = \frac{(a-x)}{a+b-2x}\cdot P, \quad [P_{H_2}] = \frac{(b-3x)}{a+b-2x}\cdot P, \quad [P_{NH_3}] = \frac{(2x).P}{a+b-2x}$$

$$\therefore \quad K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{\left(\frac{2x}{a+b-2x}.P\right)^2}{\left[\left(\frac{a-x}{a+b-2x}\right).P\right]\left[\frac{(b-3x)P}{a+b-2x}\right]^3}$$

$$K_P = \frac{\frac{4x^2.P^2}{(a+b-2x)^2}}{P^4.\frac{(a-x)(b-3x)^3}{(a+b-2x)^4}} = \frac{(a+b-2x)^2.4x^2}{P^2(a-x)(b-3x)^3}$$

- **Relation between K_p & K_c**

$$PV = nRT \quad \text{or,} \quad P = \frac{n}{V}RT$$

$$P = CRT \text{ where } C = \frac{n}{v} = \text{(moles per litre)}$$

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

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

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

Where $\Delta n = (c + d) - (a + b)$, calc...

$\Rightarrow$ Δn = sum of the number of moles of gaseous pr... reactants. Δn can be positive, negative, zero or even fraction.

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

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

$\Rightarrow K_p = K_c.(RT)$

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

$K_c = [CO_2]$, $K_p = P_{CO_2}$

Solved Examples

Ex.5 Calculate k_p and K_c if initially a moles of PCl_5 is taken

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

Sol.

		$PCl_5\,(g)$	$\rightleftharpoons PCl_3(g)$	$+\ Cl_2(g)$
At	$t = 0$	a	0	0
At	$t = t_{eq}$	$(a - x)$	x	x

$$[PCl_5] = \frac{a-x}{V},\ [PCl_3] = \frac{x}{V},\quad [Cl_2] = \frac{x}{V}$$

$$K_C = \frac{\left(\frac{x}{v}\right)^2}{\left(\frac{a-x}{v}\right)}$$

Total no. of moles = a − x + x + x = a + x

$$[P_{PCl_5}] = \frac{(a-x)P}{a+x},\qquad [P_{PCl_3}] = \frac{x\,.\,P}{a+x},\qquad [P_{Cl_2}] = \frac{x\,.\,P}{a+x}$$

$$K_P = \frac{\left(\frac{xP}{a+x}\right)\cdot\left(\frac{xP}{a+x}\right)}{\left(\frac{a-x\,P}{a+x}\right)} = \frac{x^2P}{a^2-x^2}$$

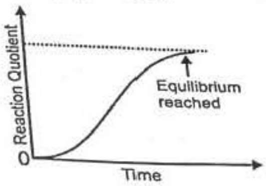
Applications of Equilibrium constant :

- **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 $Q = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ at any time during reaction 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

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

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

Solved Examples

Ex.6 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. $Q_P = \dfrac{[P_{Br_2}]^{1/2}[P_{NO}]}{[P_{NOBr}]} = \dfrac{[0.2]^{1/2}\,[0.4]}{[0.50]} = 0.36$

$K_P = 0.15$

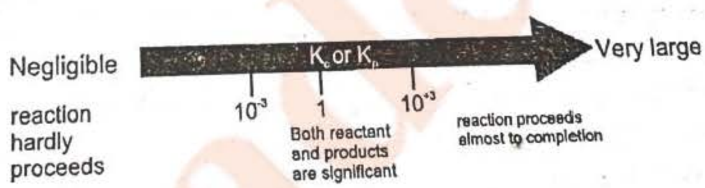
$\therefore$ $Q_P > K_P$

Hence, reaction will shift in backward direction

$\therefore$ Br_2 will be consumed

- **Predicting the extent of the reaction**

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



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.7 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 $K_p = 300$.

- **Calculating equilibrium concentrations**
  The concentration of various reactants and products can be calculated using the equilibrium constant and the initial concentrations.

Solved Examples

Ex.8 1 mole of N_2 and 3 moles of H_2 are placed in 1L vessel. Find the concentration of NH_3 at equilibrium, if equilibrium pressure is 1 atm and the equilibrium constant at 400K is $\frac{4}{27}$

Sol.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad (\Delta n < 0)$$

	$N_2(g)$	$3H_2(g)$	$2NH_3(g)$
	1mol	3 mol	0
	$(1-x)$	$(3-3x)$	$2x$

$P_{eq} = 1$ atm, $T = 400$ K

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x)^2}{(3-3x)^3(1-x)} = \frac{4}{27}$$

$$\frac{x^2}{(1-x)^4} = 1 \quad \Rightarrow \quad x = (1-x)^2 \quad \Rightarrow \quad x^2 - 3x + 1 = 0$$

$$\Rightarrow \quad x = \frac{3 \pm \sqrt{9-4}}{2} \quad \Rightarrow \quad x = \frac{3 \pm \sqrt{5}}{2}$$

$$x = \frac{3+2.24}{2} \text{ or } x = \frac{3-2.24}{2}$$

$$x = \frac{5.24}{2} = 2.62 \text{ or, } \quad x = \frac{0.76}{2}$$

$\Rightarrow$ $x = 0.38$ (since x cannot be greater than 1)

$\therefore$ $[NH_3] = 0.38 \times 2 = 0.76$

Characteristics of equilibrium constant & factors affecting it :

- 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	$A(g) \rightleftharpoons C(g)$	$K = K_1 . K_2$

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