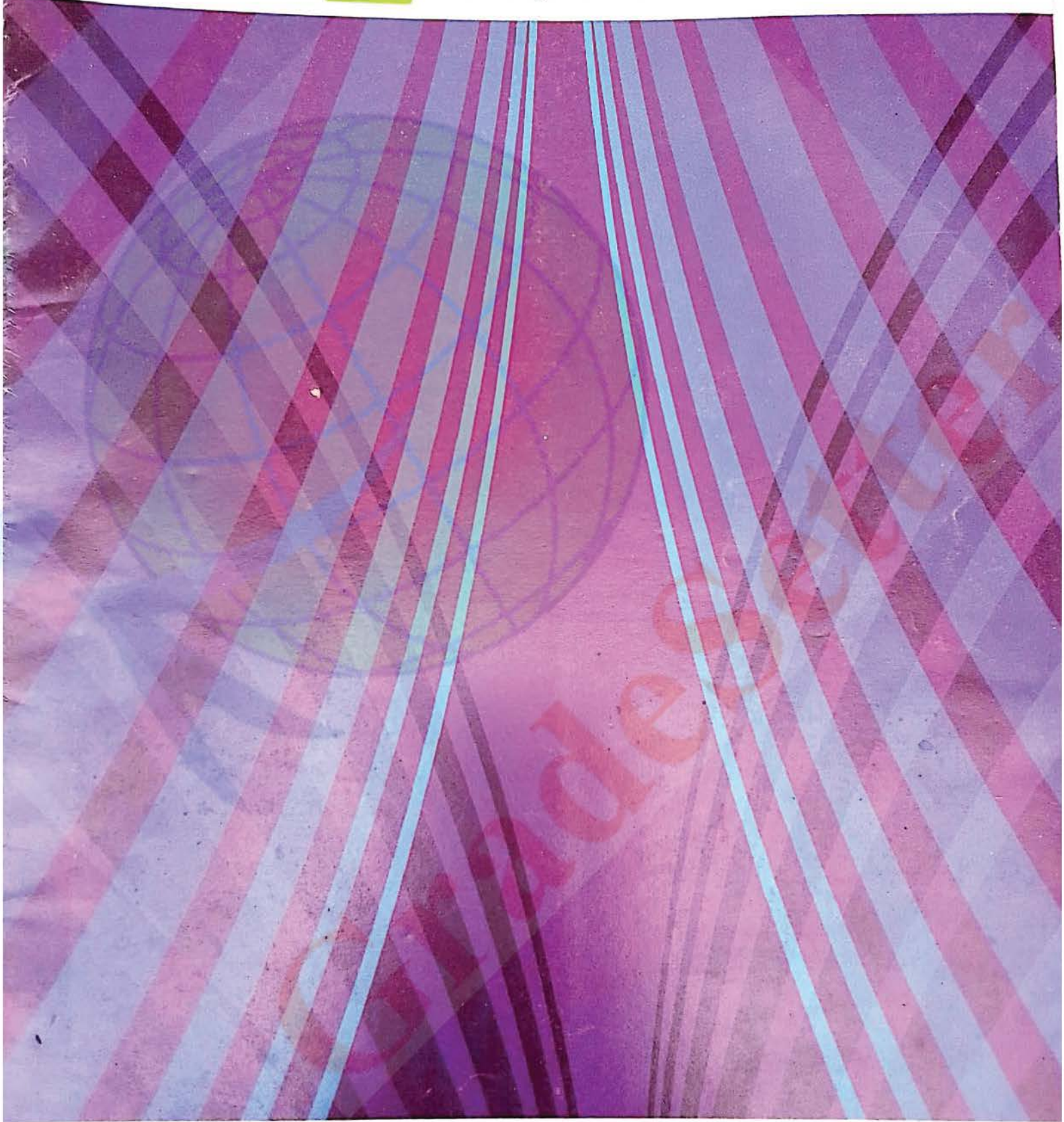




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CHEMISTRY

CHEMICAL EQUILIBRIUM

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JEE (Main) Syllabus

Meaning of equilibrium, concept of dynamic equilibrium. Equilibria involving physical processes: Solid -liquid, liquid-gas and solid-gas equilibria, Henry's law, general characteristics of equilibrium involving physical processes. Equilibria involving chemical processes: Law of chemical equilibrium, equilibrium constants (K_p and K_c) and their significance, significance of ΔG and ΔG° in chemical equilibria, factors affecting equilibrium concentration, pressure, temperature, effect of catalyst; Le-Chatelier's principle.

JEE (Advanced) Syllabus

Law of mass action; Equilibrium constant, Le Chatelier's principle (effect of concentration, temperature and pressure); Significance of ΔG and ΔG° in chemical equilibrium.

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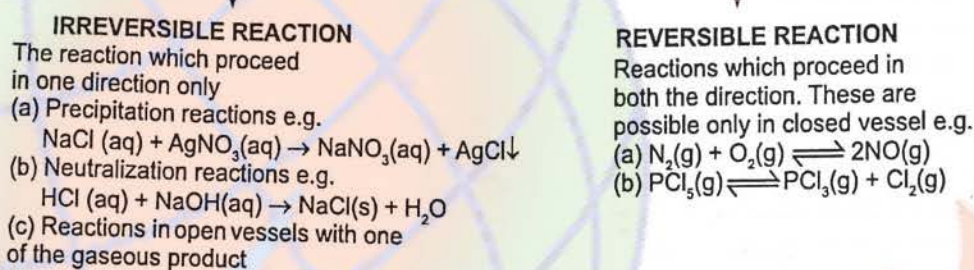
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Chemical Equilibrium

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 form 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



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 (\rightleftharpoons)
5 Examples -	5 Examples :-
(a) Precipitation reactions e.g. $\text{NaCl(aq)} + \text{AgNO}_3\text{(aq)} \rightarrow \text{NaNO}_3\text{(aq)} + \text{AgCl}\downarrow$	(a) Homogeneous reactions- only one phase is present
(b) Neutralization reactions e.g. $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}$	(i) Gaseous phase-
(c) $2\text{KClO}_3\text{(s)} \xrightarrow{\Delta} 2\text{KCl(s)} + 3\text{O}_2\text{(g)}$	$\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$
(d) Reactions in open vessel :- Even a reversible reaction will become irreversible if it is carried out in open vessel. Ex.	$\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$ [Birkland eyde process (HNO_3)]
$\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$	$\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$ (Haber's process)
$\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$ Open vessel	(ii) Liquid phase
	$\text{CH}_3\text{COOH(l)} + \text{C}_2\text{H}_5\text{OH(l)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5\text{(l)} + \text{H}_2\text{O(l)}$
	Heterogeneous reactions- More than one phases are present
	$\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$
	(b) $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$ 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 backward 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.

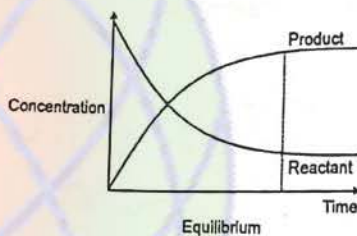
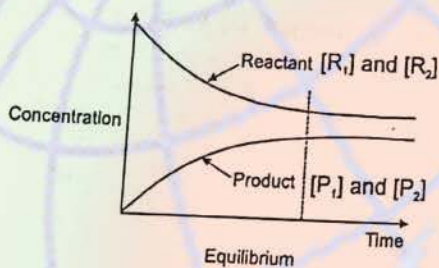
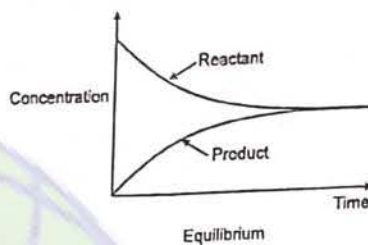
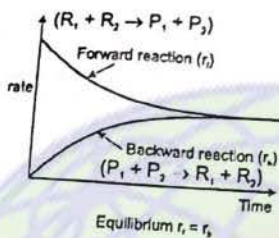
In a reversible reaction like-



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.



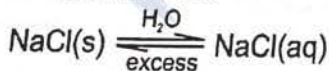
Types of equilibria on the basis of process

Physical Equilibrium

Equilibrium in physical process is called physical equilibrium.

For example phase changes like
 $H_2O(l) \rightleftharpoons H_2O(g)$;

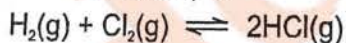
Solvation like



Chemical Equilibrium

Equilibrium in chemical process is called chemical equilibrium.

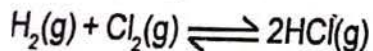
For example



Types of equilibria on basis of physical state

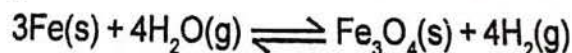
Homogeneous equilibrium

When all reactants and products are in same phase



Heterogeneous equilibrium

When more than one phase are present





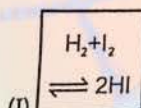
Chemical Equilibrium

Characteristics of chemical equilibrium :

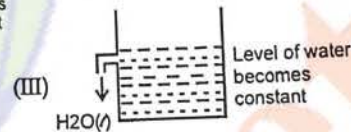
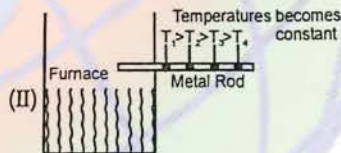
- The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved from both direction.
- Equilibrium is dynamic in nature.
It means that reaction has not stopped. It appears that no change is occurring but But both the opposing 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 :



Equilibrium state has been attained



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], [N₂] etc.

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



Rate of reaction $\propto [A]^a [B]^b$

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

where k is the rate constant of the reaction.

Solved Examples

Ex.2 Four vessel each of volume $V = 10$ Litres 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)?

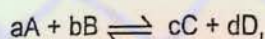
Sol. (1) $\Rightarrow [\text{CH}_4] = \frac{16}{16 \times 10} = 0.1 \text{ M}$ (2) $\Rightarrow [\text{H}_2\text{O}] = \frac{18}{18 \times 10} = 0.1 \text{ M}$

(3) $\Rightarrow [\text{Cl}_2] = \frac{35.5}{71 \times 10} = 0.05 \text{ M}$ (4) $\Rightarrow [\text{CO}_2] = \frac{44}{44 \times 10} = 0.1 \text{ M}$

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

Equilibrium constant (K) :

For a general reaction



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

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

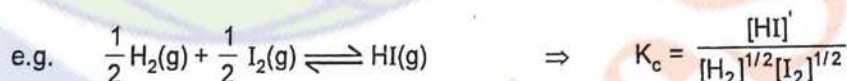
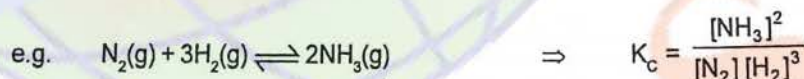
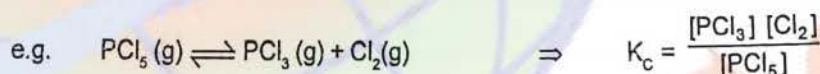
At equilibrium $r_f = r_b$

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

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.



Solved Examples

Ex.3 In a reaction $A(\text{g}) + B(\text{g}) \rightleftharpoons C(\text{g}) + D(\text{g})$, 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



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

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

Chemical Equilibrium

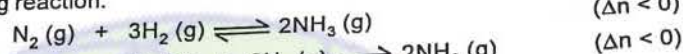
- $K_p \rightarrow$ Equilibrium constant in terms of partial pressure. It is defined for the equilibrium reaction which contains at least one gaseous component.
e.g. $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

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

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

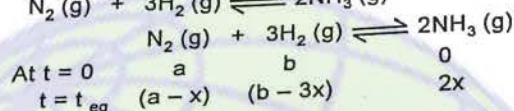
Solved Examples

- 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.



(P, T, V given)

Sol.



($\Delta n < 0$)

(P, T, V given)

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

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

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

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

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

$$K_p = \frac{4x^2 \cdot P^2}{(a+b-2x)^2} \cdot \frac{1}{P^4 \cdot \frac{(a-x)(b-3x)^3}{(a+b-2x)^4}} = \frac{(a+b-2x)^2 \cdot 4x^2}{P^2(a-x)(b-3x)^3}$$

- Relation between K_p & K_c

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

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

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

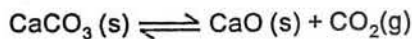
$$\Rightarrow K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

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



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

$\Rightarrow \Delta n = \text{sum of the number of moles of gaseous products} - \text{sum of the number of moles of gaseous reactants. } \Delta n \text{ can be positive, negative, zero or even fraction.}$



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

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

Unit of Equilibrium constants :

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

- 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.



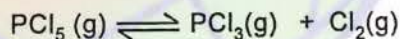
$$K_c = [\text{CO}_2], \quad K_p = P_{\text{CO}_2}$$

Solved Examples

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



Sol.



At	$t = 0$	a	0	0
At	$t = t_{\text{eq}}$	$(a - x)$	x	x

$$[\text{PCl}_5] = \frac{a-x}{V}, \quad [\text{PCl}_3] = \frac{x}{V}, \quad [\text{Cl}_2] = \frac{x}{V}$$

$$K_c = \frac{\left(\frac{x}{V}\right)^2}{\left(\frac{a-x}{V}\right)}$$

Total no. of moles = $a - x + x + x = a + x$

$$[P_{\text{PCl}_5}] = \frac{(a-x)P}{a+x}, \quad [P_{\text{PCl}_3}] = \frac{x \cdot P}{a+x}, \quad [P_{\text{Cl}_2}] = \frac{x \cdot P}{a+x}$$

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

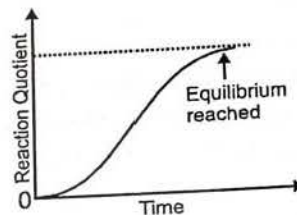
● **Predicting the direction of the reaction**

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.

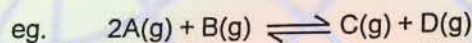
The expression $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ at any time during reaction

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



Q_c = Reaction quotient in terms of concentration

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

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

Solved Examples

Ex.6 For the reaction $NOBr(g) \rightleftharpoons NO(g) + \frac{1}{2} Br_2(g)$

$K_p = 0.15$ atm at $90^\circ C$. 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. $Q_p = \frac{[P_{Br_2}]^{1/2} [P_{NO}]}{[P_{NOBr}]} = \frac{[0.2]^{1/2} [0.4]}{[0.50]} = 0.36$

$K_p = 0.15$

$\therefore Q_p > K_p$

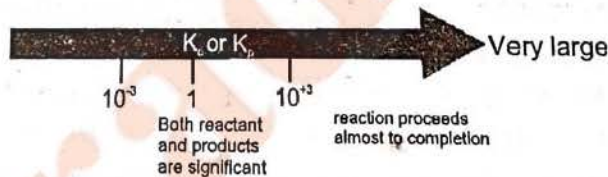
Hence, reaction will shift in backward direction

$\therefore Br_2$ will be consumed

● **Predicting the extent of the reaction**

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

Negligible
reaction
hardly
proceeds



Case-I : If K is large ($K > 10^3$) then product concentration is very very larger than the reactant ($[Product] \gg [Reactant]$)
 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 ($K < 10^{-3}$)

$[Product] \ll [Reactant]$

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.

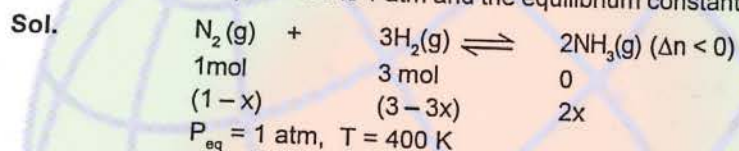
Sol. Since K_p order is $10^{-5} < 20 < 300$ so the percentage composition of products will be greatest for $K_p = 300$.

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 $\frac{4}{27}$



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

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

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

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

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

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

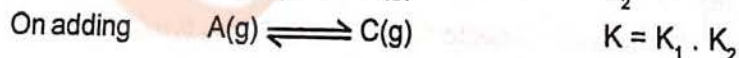
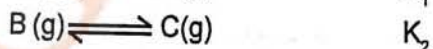
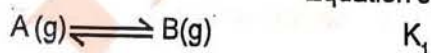
$$\therefore [NH_3] = 0.38 \times 2 = 0.76$$

Characteristics of equilibrium constant & factors affecting it :

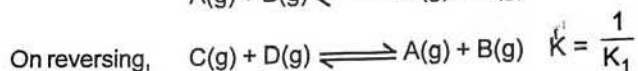
- Equilibrium constant does not depend upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached
- The equilibrium constant does not give any idea about time taken to attain equilibrium.
- **K depends on the stoichiometry of the reaction.**

○ If two chemical reactions at equilibrium having equilibrium constants K_1 and K_2 are added then the resulting equation has equilibrium constant $K = K_1 \cdot K_2$

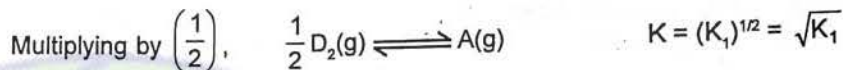
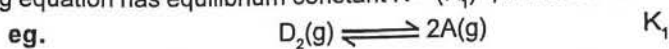
Equation constant



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



- 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



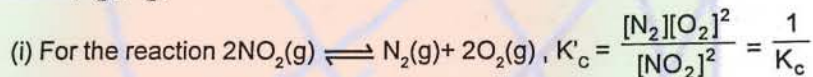
Solved Examples

Ex.9 The value of K_c for the reaction, $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ at a certain temperature is 400. calculate the value of equilibrium constant for.

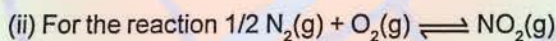


Sol. Equilibrium constant (K_c) for the reaction $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ is

$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 400$$



$$K'_c = \frac{1}{400} = 0.0025 \text{ mole litre}^{-1}$$



$$K''_c = \frac{[NO_2]}{[N_2]^{1/2}[O_2]} = \sqrt{K_c} \Rightarrow K''_c = \sqrt{400} = 20 \text{ litre}^{-1/2} \text{ mole}^{-1/2}$$

- **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,

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

If $T_2 > T_1$ then $K_2 > K_1$ provided $\Delta H = +ve$ (endothermic reaction)

$K_2 < K_1$ if $\Delta H = -ve$ (exothermic reaction)

In the above equation, the unit of R and $\Delta H/T$ should be same.

- **Relation between equilibrium constant & standard free energy change.**

$$\Delta G^\circ = -2.303 RT \log K$$

Where ΔG° = standard free energy change

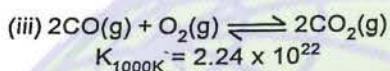
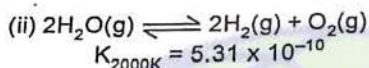
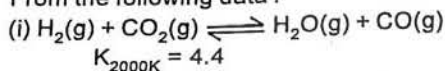
T = Absolute temperature,

R = universal gas constant.

Chemical Equilibrium

Solved Examples

Ex.10 From the following data :



State whether the reaction (iii) is exothermic or endothermic?

Sol. Equation (iii) = - [2 × (i) + (ii)]

$$\therefore K_{2000 (iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$\therefore T \uparrow K \downarrow \Rightarrow$ reaction is exothermic.

Homogeneous liquid system : Formation of ethyl acetate :

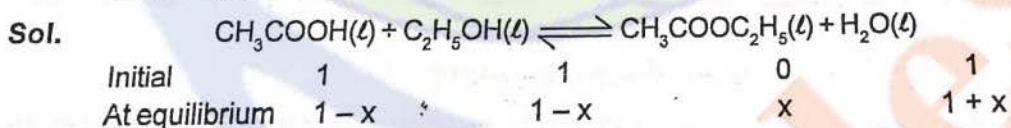
The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.



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

Solved Examples

Ex.11 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 esterified. Calculate the equilibrium constant of this reaction.



1 - 0.543, 1 - 0.543, 0.543, 1 + 0.543

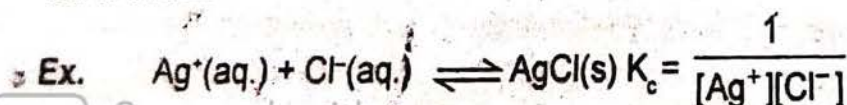
(54.3% of 1 mole = $\frac{1 \times 54.3}{100} = 0.543$ mole)

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 aqueous medium . In case of expression of K_c concentration of ion is taken.

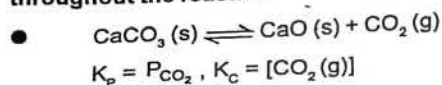




Chemical Equilibrium

Heterogenous Equilibrium :

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

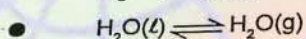


$$[\text{CaCO}_3(\text{s})] = \frac{\text{moles}}{\text{volume}} = \frac{W_{\text{CaCO}_3}}{M_{\text{CaCO}_3} \cdot V} = \frac{\text{density CaCO}_3}{M_{\text{CaCO}_3}} = \text{constant}$$

$$K = \frac{[\text{CaO}(\text{s})][\text{CO}_2(\text{g})]}{[\text{CaCO}_3(\text{s})]}$$

$$\frac{K \cdot [\text{CaCO}_3(\text{s})]}{[\text{CaO}(\text{s})]} = [\text{CO}_2(\text{g})]$$

$$K_c = [\text{CO}_2(\text{g})]$$



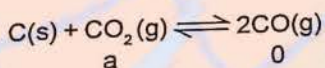
$$K_p = P_{\text{H}_2\text{O}(\text{g})}, K_c = [\text{H}_2\text{O}(\text{g})]$$

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

Solved Examples

Ex.12 In a reaction $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts. Calculate K_p .

Sol.



$$t = 0 \quad \begin{array}{ccc} & a & 0 \\ t = t_{\text{eq}} & a - \frac{a}{2} & 2 \frac{a}{2} \end{array}$$

$$P_{\text{eq}} = 12 \text{ atm}$$

$$X_{\text{CO}_2} = \frac{1}{3}, X_{\text{CO}} = \frac{2}{3}$$

$$P_{\text{CO}_2} = \frac{1}{3} \times 12 = 4$$

$$P_{\text{CO}} = \frac{2}{3} \times 12 = 8$$

$$\therefore K_p = \frac{8 \times 8}{4} = 16$$

Degree of Dissociation (α) :

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

So, $\alpha = \frac{\text{no. of moles dissociated}}{\text{initial no. of moles taken}}$
= fraction of moles dissociated out of 1 mole.

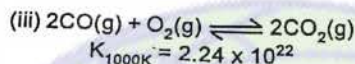
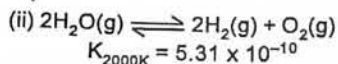
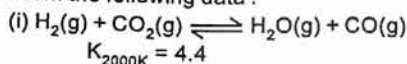
Note : % dissociation = $\alpha \times 100$

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



Solved Examples

Ex.10 From the following data :



State whether the reaction (iii) is exothermic or endothermic?

Sol. Equation (iii) = - [2 × (i) + (ii)]

$$\therefore K_{2000K} \text{ (iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

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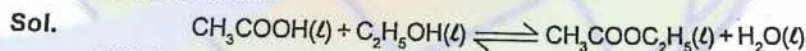
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Solved Examples

Ex.11 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 esterified. Calculate the equilibrium constant of this reaction.



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

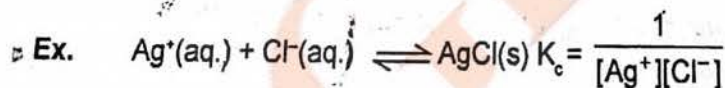
$$(54.3\% \text{ of } 1 \text{ mole}) = \frac{1 \times 54.3}{100} = 0.543 \text{ mole}$$

Hence given x = 0.543 mole
 Applying law of mass action :

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$$

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



throughout the reaction
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 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

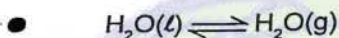
$$K_p = P_{\text{CO}_2}, K_c = [\text{CO}_2(\text{g})]$$

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$$K_c = [\text{CO}_2(\text{g})]$$



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