CHEMICAL EQUILIBRIUM

Preface

The study of Chemical Equilibrium tells us about types of reactions, reactants & products.In this chapter we will learn about definition of equilibrium & chemical equilibrium, law of mass action & active mass. Different equilibrium constants, Le-Chatelier principle etc.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope better understanding of the chapter and to have better grasping level in the class.

Total number of questions in **Chemical Equilibrium** are :

(i)	In Chapter Examples	....	14
(ii)	Solved Examples	....	15
	Total no. of questions	....	**29**

1. REACTION

The transformation of one substance into another is known as reaction.

2. REACTANT

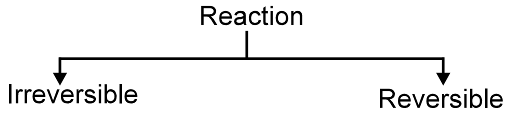
The substances used at initial stage of reaction are known as reactant.

3. PRODUCT

The substances formed at final stage of reaction are known as product.

4. TYPES OF REACTIONS ON THE BASIS OF DIRECTION

On the basis of the direction, reactions are of two types.



4.1 Irreversible reactions :

The chemical reactions in which the products formed do not combine to give back the reactants are known as irreversible reaction.

A. Properties of irreversible reactions –

(a) Reactions in which reactant react to form product only.

(b) Reactions proceed in one single direction.

(c) Always proceed to completion.

(d) Always carried out in open vessel.

(e) In these type of reactions, If product are gaseous in state, then they can escape from reacting site. If they are solid in state they will precipitate.

B. Some examples of irreversible reactions are as follows –

(a) All thermal decomposition in open vessel.

(b) All the neutralisation reaction of strong acid and strong base.

(c) All precipitation reactions.

(d) All gaseous reactions in open vessel.

4.2 Reversible reactions :

The reactions in which the products can react with one another to give back the reactants again under suitable conditions called as reversible reaction.

A. Properties of reversible reactions –

(a) In these type of reactions, reactant react to form product and product further react to form reactant.

(b) Reactions proceed in both directions.

(c) These type of reactions never get completed.

(d) Always carried out in closed vessel.

B. Some examples of reversible reactions are as follows –

(a) All thermal dissociation in closed vessel.

$$CaCO_3 \overset{\Delta}{\rightleftharpoons} CaO + CO_2$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(b) All types of salt hydrolysis except strong acid strong base salt.

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

Salt of weak base
\+
strong acid

(c) All gaseous reactions in closed vessel.

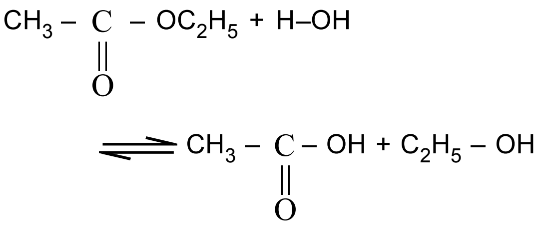
$$N_2 + O_2 \rightleftharpoons 2NO$$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$2\,SO_3 \rightleftharpoons 2SO_2 + O_2$$

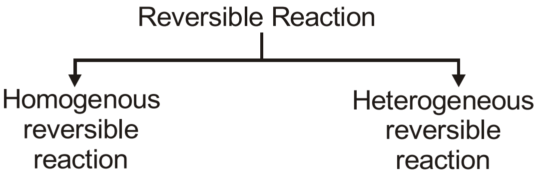
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(d) All the reactions of organic hydrolysis.



$$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + H\text{–}OH \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-OH + C_2H_5-OH$$

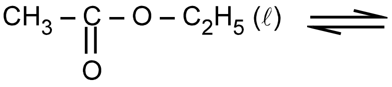
Reversible reactions are also of two type-



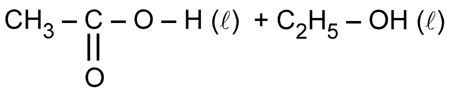
4.2.1 Homogenous reversible reactions :

If in the reversible reactions physical state of all reactants and products are same, it is known as called as homogenous reversible reaction.

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



$$CH_3-\underset{\underset{O}{\|}}{C}-O-C_2H_5(\ell) \rightleftharpoons$$



$$CH_3-\underset{\underset{O}{\|}}{C}-O-H\,(\ell) + C_2H_5-OH\,(\ell)$$

$$\text{Graphite (s)} \rightleftharpoons \text{Diamond (s)}$$

$$S_{Rh.}\,(s) \rightleftharpoons S_{mono.}\,(s)$$

4.2.2 Heterogenous reversible reaction :

If in the reversible reaction, physical state of reactant and product are different, it is known as heterogeneous reversible reaction.

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

$$FeO(g) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

$$Fe(s) + H_2O\,(\ell) \rightleftharpoons Fe\,(OH)_2(s) + H_2(g)$$

$$FeCl_3(s) + 3H_2O\,(\ell) \rightleftharpoons Fe(OH)_3(s) + 3HCl\,(\ell)$$

$$H_2O\,(\ell) \rightleftharpoons H_2O\,(g)$$

5. CHEMICAL EQUILIBRIUM

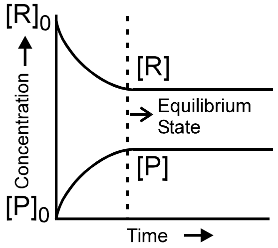
- **(a)** State of reversible reaction at which rate of forward reaction becomes equal to the rate of backward reaction is called chemical equilibrium.
- **(b)** State where rate of formation of product is equal to the rate of dissociation of reactant is known as chemical equilibrium.
- **(c)** State of reversible reaction in which the concentration of reactant and concentration of product remain unchanged but not necessarily equal,is called chemical equilibrium.
- **(d)** State where exchange of energy becomes zero is also called as chemical equilibrium.

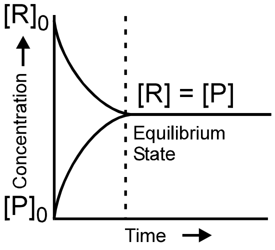
5.1 Characteristics of chemical equilibrium :

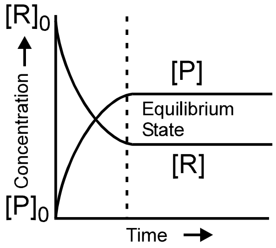
- **(a)** It is a dynamic equilibrium i.e. at this stage of reaction takes place in both the directions of same speed although appears to be stopped.
- **(b)** On the stage of equilibrium the reaction proceeds both the side.
- **(c)** At the state of equilibrium, both reactants and products are present and their concentration do not change with respect to time.
- **(d)** The state of equilibrium is not effected by the presence of catalyst : It only helps to attain the equilibrium state in less or more time.
- **(e)** Change in pressure, temperature or concentration favours one of the reactions and thus shifts the equilibrium point in one direction.
- **(f)** Change in free energy is equal to zero at the state of equilibrium ($\Delta G = 0$).

5.2 Graphical representation of chemical equilibrium –

$$R \rightleftharpoons P$$







6. LAW OF MASS ACTION

- **(a)** This law was given by **Guldberg** and **Waage**.
- **(b)** According to this law, the rate of dissociation of reactant and the rate of formation of product is directly proportional to active mass of itself at constant temperature.

$$A + B \longrightarrow C + D$$

$$\frac{-dA}{dt} \propto [A]$$

$$\frac{-dB}{dt} \propto [B]$$

$$\frac{dC}{dt} \propto [C]$$

$$\frac{dD}{dt} \propto [D]$$

While, the rate of a chemical reaction is directly proportional to the product of active masses of reactants.

$$r \propto [A]\,[B]$$

$$r = K\,[A]\,[B]$$

6.1 Active Mass or activity or effective concentration or molar concentration –

(a) It is the molecular concentration of a substance i.e. the no. of gram moles per litre.

(b) It is represented by enclosing its formula in square brackets ([ ]) of a substance.

Active mass = Molar concentration =

$$\frac{\text{No. of moles}}{\text{volume (in litres)}} = \frac{\text{No. of grams of substance}}{\text{Mol. wt.} \times \text{volume (in litre)}}$$

Note : The active mass of solids is one.

eg. What is the active mass of 4 gm H_2 in 2 litre volume ?

$$[H_2] = \frac{4}{2 \times 2} = 1$$

eg. What is the active mass of 14 gm N_2 in 2 litre volume ?

$$[N_2] = \frac{14}{28 \times 2} = \frac{1}{4}$$

eg. What is the active mass of 14 gm N_2 in $\frac{1}{2}$ litre volume ?

$$[N_2] = \frac{14}{28 \times \frac{1}{2}} = \frac{14 \times 2}{28} = 1$$

Note: –Law of mass action is applicable only for reversible reaction.

6.2 Mathematical Expression of law of mass action :

At the constant temperature, let us consider the following reversible reaction.

$$A + B \rightleftharpoons C + D$$

According to law of mass action -

Rate of forward reaction

$$r_f \propto [A]\,[B] \text{ or } r_f = K_1\,[A]\,[B]$$

where K_1 is the rate constant of the forward reaction.

Rate of backward reaction

$$r_b \propto [C]\,[D] \quad \text{or} \quad r_b = K_2\,[C]\,[D]$$

where K_2 is the rate constant of the backward reaction.

At equilibrium :

Rate of forward reaction = Rate of backward reaction

$$K_1\,[A]\,[B] = K_2\,[C]\,[D]$$

or $$\frac{K_1}{K_2} = \frac{[C][D]}{[A][B]}$$

or $$\boxed{K = \frac{[C]\,[D]}{[A]\,[B]}}$$

Here, k is equilibrium constant of given reversible reaction.

6.3 Applications of law of mass action : –

6.3.1 Formation of Nitric Oxide : ($\Delta n = 0$)

A. Calculation of K_C : –

Suppose the initial concentration of N_2 and O_2 is a and b respectively. x is the degree of dissociation.

	N_2 +	O_2 $\rightleftharpoons$	$2NO$
Initial concentration	a	b	0
moles at equilibrium	(a–x)	(b–x)	2x
Active mass (mol l^{-1})	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$

Here, V is the volume of container in litre.

According to the law of mass action

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

Substituting the values in the above equation

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

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

B. Calculation of K_P :

All the things being same as above, except pressure. Let P atmosphere is the pressure at equilibrium.

$$N_2 + O_2 \rightleftharpoons 2\,NO$$

Initial concentration	a	b	0
moles at equilibrium	(a–x)	(b–x)	2x

Total no. of moles = (a–x) + (b–x) + 2x = (a+b)

Now, the partial pressure of the above three species can be calculated as below-

$$P_{N_2} = \frac{(a-x)P}{(a+b)}$$

$$P_{O_2} = \frac{(b-x)P}{(a+b)}$$

$$P_{NO} = \frac{(2x)P}{(a+b)}$$

According to the law of mass action

$$K_P = \frac{[P_{NO}]^2}{[P_{N_2}][P_{O_2}]}$$

substituting the value of P_{NO}, P_{N_2}, P_{O_2} in the above equation of K_P -

$$K_P = \frac{\left[\frac{(2x)P}{(a+b)}\right]^2}{\left[\frac{(a-x)P}{(a+b)}\right]\left[\frac{(b-x)P}{(a+b)}\right]}$$

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

6.3.2 Thermal Dissociation of Phosphorus Penta-chloride- ($\Delta n > 0$)

A. Calculation of K_C - Suppose one mole of PCl_5 is take in a closed container of V litre. Further at equilibrium x mol of it dissociated

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial concentration	1	0	0
moles at equilibrium	(1–x)	x	x
Active mass (mol l^{-1})	$\frac{1-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

According to law of mass action

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Substituting the values in the above equation.

$$K_C = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{1-x}{v}\right)}$$

$$\boxed{K_C = \frac{x^2}{(1-x)\,v}}$$

The formula of K_C has V in the denominator, hence the equilibrium will be affected by V of the reaction container.

If $x << 1$ then $1 - x \approx 1$

So, $K_C = \frac{x^2}{v}$

$x^2 = K_C \,.V$

$x^2 \propto V$

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

If we increase the volume, the dissociation x is also increased.

B. Calculation of K_P -

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

initial concentration	1	0	0
moles at equilibrium	1–x	x	x

Total no. of moles at equilibrium,

(1 – x) + x + x = (1 + x) moles

According to law of mass action

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

At equilibrium $P_{PCl_3} = \frac{x \times P}{(1+x)}$

$$P_{Cl_2} = \frac{x \times P}{(1+x)}$$

$$P_{PCl_5} = \frac{(1-x)P}{(1+x)}$$

Substituting the values in the above equation of K_P -

$$K_P = \frac{\left(\frac{x \times P}{1+x}\right)\left(\frac{x \times P}{1+x}\right)}{\frac{(1-x) \times P}{(1+x)}}$$

$$K_P = \frac{x^2 P}{1-x^2}$$

The equation of K_P is not independent of pressure.

suppose, $x << 1$ then $1 - x^2 \approx 1$

$$K_P = x^2 P$$

$$x^2 = \frac{K_P}{P}$$

$$x^2 \propto \frac{1}{P}$$

$$\boxed{x \propto \frac{1}{\sqrt{P}}}$$

The degree of dissociation of PCl_5 is inversely proportional to the square root of pressure so, decrease of pressure increases dissociation of PCl_5.

6.3.3 Formation of Ammonia – ($\Delta n < 0$)

A. Calculation of K_C : –

	N_2	+ $3H_2 \rightleftharpoons$	$2NH_3$
Initial concentration	1	3	0
moles at equilibrium	(1–x)	(3–3x)	2x
Active mass (mol l^{-1})	$\left(\frac{1-x}{v}\right)$	$\left(\frac{3-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$

According to law of mass action

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting the values in the above equation-

$$K_C = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{1-x}{v}\right)\left(\frac{3-3x}{v}\right)^3}$$

$$K_C = \frac{4x^2v^2}{(1-x)(3-3x)^3}$$

$$\boxed{K_C = \frac{4x^2v^2}{27(1-x)^4}}$$

The formula of K_C has V in the denominator, hence the equilibrium will be affected by V of the reaction container.

Dependence If, $x << 1$ then, $(1 - x)^4 = 1$

$$K_C = \frac{4x^2v^2}{27}$$

$$x^2 = \frac{K_C}{V^2}$$

$$x^2 \propto \frac{1}{V^2}$$

$$\boxed{x \propto \frac{1}{V}}$$

If we increase the volume of the container the degree of dissociation x is decreased.

B. Calculation of K_P :

	N_2	+ $3H_2 \rightleftharpoons$	$2NH_3$
Initial concentration	1	3	0
moles at equilibrium	(1 – x)	(3 – 3x)	2x

Total number of moles at equilibrium

$= (1 - x) + (3 - 3x) + 2x = (4 - 2x)$

According to the law of mass action

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3}$$

At equilibrium $P_{NH_3} = \frac{(2x).P}{(4-2x)}$

$$P_{N_2} = \frac{(1-x).P}{(4-2x)}$$

$$P_{H_2} = \frac{(3-3x).P}{(4-2x)}$$

Substituting the values in the above equation of K_P.

$$K_P = \frac{\left(\frac{2x}{4-2x}.P\right)^2}{\left(\frac{1-x}{4-2x}.P\right)\left(\frac{3-3x}{4-2x}.P\right)^3}$$

$$K_P = \frac{4x^2(4-2x)^2}{(1-x)^3(3-3x)^2P^2}$$

$$\boxed{K_P = \frac{16x^2(2-x)^2}{27(1-x)^4P^2}}$$

The equation of K_P is not independent of pressure suppose, $x << 1$ then,

$(1 - x)^4 = 1$ $(2 - x)^2 = 4$

$$K_P = \frac{64x^2}{27P^2}$$

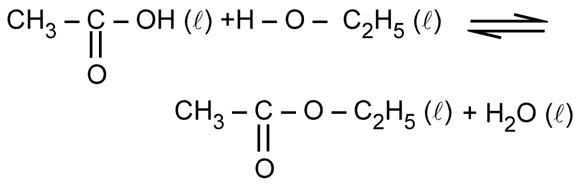
$$x^2 \propto P^2$$

$$\boxed{x \propto P}$$

If we increase the pressure the degree of dissociation x is also increased.

6.3.4 Liquid equilibrium (Ester formation) -

It is proposed by Bartholate and Gill. In this reaction all the reactants and products are in liquid state.



$$CH_3-\underset{\underset{O}{||}}{C}-OH\,(\ell) + H-O-C_2H_5\,(\ell) \rightleftharpoons CH_3-\underset{\underset{O}{||}}{C}-O-C_2H_5\,(\ell) + H_2O\,(\ell)$$

Initial concentration	a	b	0	0
Moles at equilibrium	(a – x)	(b – x)	x	x
Active mass (mole ℓ^{-1})	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

According to law of mass action

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

Substituting the values in the above equation

$$K_C = \frac{\left(\frac{x}{v}\right)\times\left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

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

Note : The value of K_P is equal to unity in liquid and solid equilibrium.

Examples based on Law of Mass Action

Ex.1 In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the concentration of H_2, I_2 and HI at equilibrium are 8.0, 3.0 and 28.0 moles per litre respectively. What will be the equilibrium constant –

(A) 30.61 (B) 32.66

(C) 29.40 (D) 20.90 **Ans. [B]**

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

Applying law of mass action –

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

Given $[H_2] = 8.0$ mol L^{-1}

$[I_2] = 3.0$ mol L^{-1}

$[HI] = 28.0$ mol L^{-1}

So, $K_C = \frac{(28.0)^2}{(8.0)\times(3.0)}$ = **32.86**

Ex.2 For a gas reaction, $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere, respectively. The total pressure of the entire system is 2.8 atmosphere. What will be the value of K_P if all the concentration are given in atmosphere ? What will be the value of K_P if all the concentration are given in atmosphere –

(A) 32 atm^{-2} (B) 20 atm^{-2}

(C) 50 atm^{-2} (D) 80 atm^{-2}

Ans. [C]

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

Partial pressures

0.8 atm 0.4 atm [2.8 – (0.8 + 0.4) = 1.6]

Applying law of mass action –

$$K_P = \frac{(P_{NH_3})^2}{(P_{N_2})\,(P_{H_2})^3}$$

$$= \frac{1.6 \times 1.6}{0.8 \times 0.4 \times 0.4 \times 0.4}$$

K_P = **50 atm^{-2}**

Ex.3 One mole of nitrogen and three moles of hydrogen are mixed in a 4 litre container. If 0.25 percent of nitrogen is converted to ammonia by the following reaction -

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

What will be the equilibrium constant (K_C) in concentration units ? What will be the value of K for the following equilibrium –

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g).$$

(A) 1.49×10^{-5} lit mol^{-1}

(B) 2.22×10^{-10} lit^2 mol^{-2}

(C) 3.86×10^{-3} lit mol^{-1}

(D) Question is incomplete **Ans. [C]**

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

At equilibrium $(1 - x)$ $(3 - 3x)$ $2x$

$(x = 0.0025)$

Active masses $\frac{(1-0.0025)}{4}$ $\frac{(3-0.0075)}{4}$ $\frac{0.0050}{4}$

Applying law of mass action,

$$K_C = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{\left(\frac{0.0050}{4}\right)^2}{\left(\frac{0.9975}{4}\right)\left(\frac{2.9925}{4}\right)^3}$$

$$= 1.49 \times 10^{-5} \text{ lit}^2 \text{ mol}^{-2}$$

K_C for the reaction,

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$$

is equal to $\sqrt{K_C}$,

$$K = \sqrt{K_C} = \sqrt{1.49 \times 10^{-5}}$$

$$= \mathbf{3.86 \times 10^{-3} \text{ lit mol}^{-1}}$$

Ex.4 When ethanol and acetic acid were mixed together in equilimolecular proportion 66.6% are converted into ethyl acetate. Calculate K_C. Also calculate quantity of ester produced if one mole of acetic acid is treated with 0.5 mole and 4 mole of alcohol respectively.

(A) 4, 0.93, 0.43 (B) 0.93, 4, 0.43

(C) 0.43, 0.93, 4 (D) 4, 0.43, 0.93

Ans. [D]

Sol.

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
1	1	0	0
1 – 0.666	1 – 0.666	0.666	0.666

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

$$= \frac{[0.666]\,[0.666]}{[0.333]\,[0.333]} = \mathbf{4}$$

(a) Let x moles of ester is formed from 1 mole of acid and 0.5 mole of alcohol, then

$$K_C = \frac{x^2}{(1-x)(0.5-x)} \frac{x^2}{(1-x)(0.5-x)} = 4$$

$x = \mathbf{0.43}$

(b) $K_C = \frac{x^2}{(1-x)(4-x)}$

or $4 = \frac{x^2}{(1-x)(4-x)}$

$x = \mathbf{0.93}$

Ex.5 One mole of ammonium carbamate dissociate as shown below at 500 K.

$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

If the pressure exerted by the released gases is 3.0 atm, the value of K_P is -

(A) 7 atm (B) 3 atm (C) 4 atm (D) 8 atm

Ans. [C]

Sol. Applying the law of chemical equilibrium, we get

$$K_P = (P_{NH_3})^2\,(P_{CO_2})$$

Since total pressure is 3 atm, the partial pressures of NH_3 (g) and CO_2(g) are

$$[P_{NH_3}] = 3 \times \frac{2}{3} = 2 \text{ atm}$$

$$[P_{CO_2}] = 3 \times \frac{1}{3} = 1 \text{ atm}$$

$$K_P = [2.0]^2\,[1.0] = \mathbf{4.0 \text{ atm}}$$

Ex.6 Iron filling and water were placed in a 5 litre tank and sealed. The tank was heated to 1273 K. Upon analysis the tank was found to contain 1.10 gram of hydrogen and 42.5 gm of water vapour. If the reaction in the tank is represented by

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

the equilibrium constant will be -

(A) 2.949×10^3 (B) 6.490×10^3

(C) 4.940×10^3 (D) 3.200×10^3

Ans. [A]

Sol. In the reaction,

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

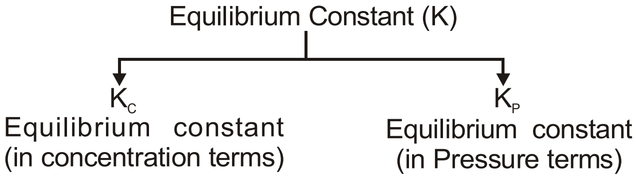
$4H_2O(g)$	$4H_2(g)$
42.5 gm	1.10 gm
42.5/18	1.10/2
= 2.36 moles	= 0.55 moles

Now, $K_C = \frac{[H_2]^4}{[H_2O]^4} = \frac{[0.55/5]^4}{[2.36/5]^4}$

$$K_C = \frac{(0.55)^4}{(2.36)^4} = \mathbf{2.949 \times 10^3}$$

7. TYPES OF EQUILIBRIUM CONSTANT

Equilibrium constant (K) is also of two types



7.1 Equilibrium concentration constant (K_c) :

If we use the term concentration in given reaction with the equilibrium constant (K) is called equilibrium concentration constant (K_c).

$$K = K_c = \frac{[C][D]}{[A][B]}$$

7.2 Equilibrium Pressure constant (K_p) :

It we use the term pressure in given reaction with the equilibrium constant (K) is called equilibrium pressure constant (K_P).

$$K_p = \frac{p_C \times p_D}{p_A \times p_B}$$

where p_A = Partial pressure of A
p_B = Partial pressure of B
p_C = Partial pressure of C
p_D = Partial pressure of D

Partial pressure of a gas given by the following formula.

$$p = \frac{\text{No. of mole of given gas at equilibrium}}{\text{Total no. of moles at equilibrium}} \times P$$

or p = mole fraction × P.

Here, P is the total pressure.

7.3 Factors which do not influence equilibrium constant :

(a) Concentration of reactants and products.
(b) Pressure and volume.
(c) Presence of catalyst.
(d) Addition of the inert gas at constant Pressure and volume.

7.4 Factors influence the equilibrium constant :

A. Mode of representation of chemical reaction.
B. Stoichiometry of reaction.
C. Temperature.

A. Mode of representation of reaction –

If we take reaction $2HI \rightleftharpoons H_2 + I_2$

Then, we write the value of equilibrium constant K_{C_1} for the above reaction as following.

$$K_{C_1} = \frac{[H_2][I_2]}{[HI]^2} \qquad \text{.......} \ (i)$$

Now, if we take reaction $H_2 + I_2 \rightleftharpoons 2HI$

Then, we write the value of equilibrium constant K_{C_2} for above reaction as following

$$K_{C_2} = \frac{[HI]^2}{[H_2][I_2]} = \frac{1}{K_{C_1}} \qquad \text{......} \ (ii)$$

B. Stoichiometry of the reaction –

Method of writing the equation of the reversible reaction is called as stoichiometry of the reaction.

Now, we consider the formation of HI(g) by the combination of H_2(g) and I_2(g).

$$H_2 + I_2 \overset{\Delta}{\rightleftharpoons} 2HI$$

The expression of its equilibrium constant is-

$$K_{C_1} = \frac{[HI]^2}{[H_2][I_2]}$$

If the equation of above reaction is written by following method –

$$\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g)$$

The expression for the equilibrium constant is –

$$K_{C_2} = \frac{[HI]}{[H_2]^{½}[I_2]^{½}}$$

on the basis of comparing both the equilibrium constant equation.

$$K_{C_2} = \sqrt{K_{C_1}} \quad \text{or} \quad (K_{C_1})^{1/2}$$

Result – When we divide a reaction by a factor 'n' in the equation, the value of new equilibrium constant is equal to the root of n of the previous equilibrium constant.

For Example – Suppose, the equilibrium constant for the following reaction.

$A + B \rightleftharpoons C + D$ is K_1 then for the reaction

$$\frac{1}{n} A + \frac{1}{n} B \rightleftharpoons \frac{1}{n} C + \frac{1}{n} D$$

the value of the equilibrium constant K_2 is equal to $n\sqrt{K_1}$ or $(K_1)^{1/n}$.

C Temperature – Increase in temperature favours the endothermic reaction and decrease in temperature favours the exothermic reaction for the forward reaction.

Means for exothermic reactions, the value of K_c and K_p decrease with rise in temperature while for endothermic reactions, the value of K_c and K_p increases with rise in temperature. This type of variation in equilibrium constant with temperature given by **Van't Hoff** equation as follows -

$$\log K_2 - \log K_1 = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\text{or} \quad \log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Where,

K_2 = equilibrium constant at temperature T_2

K_1 = equilibrium constant at temperature T_1

ΔH = Energy of reaction of constant temperature

R = Molar gas constant

According to the temperature, reaction are of three types.

(a) Athermic or Non-thermic reaction means $\Delta H = 0$

$$\log K_2 - \log K_1 = 0$$
$$\log K_2 = \log K_1$$

Result : – There is no effect of temperature on this type of reaction.

(b) Endothermic reaction $\Rightarrow \Delta H = (+)$ ve

$\log K_2 - \log K_1 = (+)$ ve,

means $K_2 > K_1$

Result : – On increase of temperature equilibrium constant will also increase for this type of reaction.

(c) Exothermic reaction $\Rightarrow \Delta H = (-)$ ve

$\log K_2 - \log K_1 = (-)$ ve,

means $K_2 < K_1$

Result– On the increase of temperature equilibrium constant will decreases for exothermic reaction.

7.5 Units of K_p and K_C–

Partial pressure are measured by the unit of atmospheres and therefore units of K_p will be $(\text{Atmospheres})^{\Delta n}$.

In the same way, the concentration is expressed in the term of moles per litre. Therefore, units of K_c will be $(\text{moles litre}^{-1})^{\Delta n}$.

Value of Δn	Units of K_p	Units of K_c
0	No Unit	No unit
> 0	$(\text{atm})^{\Delta n}$	$(\text{moles } l^{-1})^{\Delta n}$
< 0	$(\text{atm})^{\Delta n}$	$(\text{moles } l^{-1})^{\Delta n}$

7.6 Relation between K_p and K_C:

Let us consider the following reaction

$$n_1 A + n_2 B \rightleftharpoons m_1 C + m_2 D.$$

The value of K_c for the reaction is,

$$K_c = \frac{[C]^{m_1}[D]^{m_2}}{[A]^{n_1}[B]^{n_2}}$$

According to gas law $PV = nRT$

$$P = \left(\frac{n}{v}\right) RT \quad .... \text{(i)}$$

Here $\frac{n}{v} = \frac{\text{no. of moles}}{\text{lit.}} = [\ ]$ = Active mass

$$\because \quad K_P = \frac{(p_C)^{m_1}(p_D)^{m_2}}{(p_A)^{n_1}(p_B)^{n_2}}$$

on putting the value of 'p' in the formula of K_P by the equation . ..... (i)

$$K_P = \frac{([C]RT)^{m_1}([D]RT)^{m_2}}{([A]RT)^{n_1}([B]RT)^{n_2}}$$

$$K_P = \frac{[C]^{m_1}[D]^{m_2}\ (RT)^{m_1+m_2}}{[A]^{n_1}[B]^{n_2}\ (RT)^{n_1+n_2}}$$

$$K_P = K_C\ (RT)^{(m_1+m_2)-(n_1+n_2)}$$

$$K_P = K_C(RT)^{\Delta n}$$

$$[\Delta n = (m_1 + m_2) - (n_1 + n_2)]$$

Δn = number of moles of product – number of moles of reactant.

T = Absolute temperature.

Note : Δn only includes gaseous moles.

I. on the basis of Δn, the reactions are of three types.

(a) Reaction in which $\Delta n = 0$

$N_2 + O_2 \rightleftharpoons 2NO \quad \Delta n = 2 - 2 = 0$

By the relation of

$$K_P = K_C\ (RT)^{\Delta n} \qquad \because \ \Delta n = 0$$
$$K_P = K_C\ (RT)^0$$

So, $\boxed{K_P = K_C}$

(b) Reaction in which the value of Δn is negative-

$$2\,CO + O_2 \rightleftharpoons 2\,CO_2$$
$$\Delta n = 2 - 3 = -1$$

By the relation of $K_P = K_C\ (RT)^{\Delta n}$

$$K_P = K_C\ (RT)^{-1}$$

or $K_P = \frac{K_C}{RT}$ means $K_P \times RT = K_C$

So, $\boxed{K_C > K_P}$

(c) Reaction in which the value of Δn is positive–

$$2\ SO_3 \rightleftharpoons 2\ SO_2 + O_2$$

$$\Delta n = 3 - 2 = +1$$

By the relation of $K_P = K_C\ (RT)^{\Delta n}$

$$K_P = K_C\ (RT)^{+1}$$

$$\text{means } K_P = K_C \times RT$$

So, $\boxed{K_P > K_C}$

II. On the basis of the value of pressure, reactions are also of three types as follows-

(a) Reaction in which the value of $\Delta n = 0$

$$N_2 + O_2 \rightleftharpoons 2\ NO$$

$$\Delta n = 2 - 2 = 0$$

$$K_P = K_C\ (RT)^{\Delta n}$$

According to relationship

$K_P = K_C\ (RT)^0$ means $\boxed{K_P = K_C}$

In this type of reaction, there is no effect of pressure.

(b) Reaction in which the value of Δn is (+)ve.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$\Delta n = 2 - 1 = +1$$

In this type of reaction, when pressure is increases then the degree of dissociation decreases.

(c) Reaction in which the value of Δn is (–)ve.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\Delta n = 2 - 3 = -1$$

In this type of reaction, when the pressure is increases then the degree of dissociation is also increases.

Examples based on Equilibrium Constant

Ex.7 At 700 K, the equilibrium constant K_P, for the reaction

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

is 1.8×10^{-3} kPa. What is the numerical value of K_C for this reaction at the same temperature –

(1) 3.09×10^{-7} mole litre^{-1}

(2) 9.03×10^{-7} mole litre^{-1}

(3) 5.05×10^{-9} mole litre^{-1}

(4) 5.05×10^{-5} mole litre^{-1}

Ans. [A]

Sol. We know the relationship

$$K_P = K_C(RT)^{\Delta n}$$

Here $K_P = 1.80 \times 10^{-3}$

$$KP_a = \frac{1.8 \times 10^{-3}}{101.3} \text{ atm}$$

$$= 1.78 \times 10^{-5} \text{ atm}$$

$R = 0.0821$ litre atm K^{-1} mol^{-1}

$\Delta n = 3 - 2 = 1$

$T = 700$ K

$$K_C = \frac{K_P}{(RT)^{\Delta n}} = \frac{1.78 \times 10^{-5}}{0.0821 \times 70}$$

$$= \mathbf{3.09 \times 10^{-7}\ mole\ litre^{-1}}.$$

Ex.8 The value of K_C for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; is 0.50 at 400° C. What will be the value of K_P at 400°C when concentration are expressed in mole litre^{-1} and pressure in atmosphere–

(A) 1.64×10^{-4} (B) 2.80×10^{-6}

(C) 2.80×10^{-4} (D) 1.64×10^{-6}

Ans [A]

Sol. Applying the relationship

$$K_P = K_C(RT)^{\Delta n}$$

$K_P = 0.50$, $R = 0.82$ litre-atm deg^{-1} mol^{-1}

$T(400 + 273) = 673$ L $\Delta n = (2 - 4) = -2$

$$K_P = 0.5(0.082 \times 673)^{-2}$$

$$= 0.5(55.185)^{-2} = \mathbf{1.64 \times 10^{-4}}$$

Ex.9 The equilibrium constant for the reaction $H_2\ (g) + S\ (s) \rightleftharpoons H_2S\ (g)$; is 18.5 at 935 K and 9.25 at 1000 K respectively. The change in enthalpy of the reaction will be -

(A) zero

(B) + ve

(C) – ve

(D) cannot be predicted **Ans. [C]**

Sol. Since $(K_{eq})_2 < (K_{eq})_1$ while $T_2 > T_1$

$\therefore$ Reaction is exothermic

Hence, $\Delta H = -$ ve

Ex.10 The equilibrium constant K_C for the decomposition of PCl_5 is 0.0625 mole l^{-1} at 300°C. What will be the value of K_P –

Sol.
$$PCl_5\ (g) \rightleftharpoons PCl_3(g) + Cl_2\ (g)$$

$$\Delta n = 2 - 1 = 1$$

$$K_P = K_C(RT)^{\Delta n}$$

$$= 0.0625 \times (0.082 \times 573)^1$$

$$= \mathbf{2.936\ atm}$$

Ex.11 K_P for the reaction $A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$; is 0.05 atm. What will be its K_C at 1000 K in terms of R –

(A) $\frac{5 \times 10^{-5}}{R}$ (B) $\frac{R}{5 \times 10^{-5}}$

(C) 5×10^{-5} R (D) None of these

Ans. [A]

Sol. We know that

$$K_P = K_C (RT)^{\Delta n}$$

or, $K_c = \frac{K_P}{(RT)^{\Delta n}}$

Here $\Delta n = 4 - 3 = 1$

$T = 1000$ K, $K_P = 0.05$

$$K_C = \frac{0.05}{(R \times 1000)^1} = \frac{5 \times 10^{-5}}{R}$$

8. LE-CHATELIER'S PRINCIPLE

(a) According to this principle, if a system in equilibrium is subjected to a change of temperature, pressure or concentration, then the equilibrium shifts in a direction, as the effect of the changed condition is nullified.

(b) It explains the effect of changes in temperature, pressure and concentrations on various reactions in equilibrium.

A. Effect of change in temperature -

(a) If the temperature is raised, reaction will proceed in that direction in which the effect of raised heat can be destroyed so that the temperature on the system remains constant.

(b) Athermic or nonthermic reaction not affected by the change in temperature.

(i) Endothermic reaction –

$$A + B + \text{energy} \rightleftharpoons C + D$$

or, $A + B \rightleftharpoons C + D \quad \Delta H = (+)$ ve

Here, $K = \frac{[C][D]}{[A][B]}$

If we increase in temperature, the equilibrium shifts in forward direction of endothermic reaction which proceed with absorption of heat.

eg. $N_2 + O_2 + 43.2$ k. cal. $\rightleftharpoons 2NO$

or $N_2 + O_2 \rightleftharpoons 2NO \quad \Delta H = + 43.2$ kcal

(ii) Exothermic reaction : –

$$A + B \rightleftharpoons C + D + \text{energy}$$

or $A + B \rightleftharpoons C + D \quad \Delta H = (-)$ ve

If we increase in temperature, the equilibrium shifts in backward direction of exothermic reaction which proceed with evolution of heat.

eg. $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 23$ k cal

or $N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -23$ k cal

B. Effect of change in pressure :

According to **Le-Chatelier's** principle, if the pressure is increased, reaction will take place in that direction, which will bring about lowering of pressure or lowering in number of moles.

This implies that -

(i) Increase of pressure shifts the equilibrium in that direction where the number of moles decreases or $\Delta n < 0$.

eg. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\Delta n = 2 - 4 = -2 < 0$

(ii) Decrease of pressure shifts the equilibrium in that direction where the number of moles increase or $\Delta n > 0$.

eg. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$\Delta n = 2 - 1 = 1 > 0$

(iii) Change of pressure has no effect, if the number of moles of gaseous product remain same as the gaseous reactants i.e. $\Delta n = 0$

eg. $H_2 + I_2 \rightleftharpoons 2HI$

$\Delta n = 2 - 2 = 0$

$CO + H_2O \rightleftharpoons CO_2 + H_2$

$\Delta n = 2 - 2 = 0$

C. Effect of change in concentration :

If in any reversible reaction, concentration of the reactants is increased at equilibrium state, the equilibrium shifts in the forward direction, means more product are formed. It is due to the fact that increase in concentration of reactant increases the number of effective collisions between the reactant molecule.

Similarly, if the concentration of products is increased, then to maintain the equilibrium constant, concentration of reactant has to increase and backward reaction is favoured.

Thus, it implies as -

(i) Increase in the concentration of any reactants, the equilibrium shifts in the forward direction.

(ii) Increase in the concentration of products, the equilibrium shifts in the backward direction.

Note : addition or removal of gaseous species only can affect equilibrium position.

D. Effect of addition of catalyst :

There is no effect on equilibrium by the addition of catalyst. It is due to the fact that the catalyst increase the rate of forward and backward reaction equally i.e. the catalyst helps in acquiring the equilibrium state quickly.

E. Effect of addition of inert gas :

Addition of inert gas at constant pressure to the equilibrium system causes the under mentioned effect.

(i) For the equilibrium system where the $\Delta n > 0$, the addition of inert gas at constant pressure increases the total volume of the system and decreases the molar concentration of reactant and product and the dissociation of reactant increases.

eg. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) For the equilibrium system where $\Delta n < 0$, the addition of inert gas at constant pressure will shifts the equilibrium to the backward direction.

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

(iii) For the equilibrium system where $\Delta n = 0$, the addition of inert gas at constant pressure has no effect.

eg. $H_2(s) + I_2(g) \rightleftharpoons 2HI(s)$

(iv) The addition of inert gas at constant volume has no effect on the equilibrium system.

8.1 Application of Le chatelier principle on physical equilibria -

A. Melting of Ice :

$H_2\,O(s)$	$H_2O\,(\ell)$
Ice	water
more volume	less volume

Since, if we increase the pressure, the equilibrium will be shifted in the direction of less volume. Hence, the rise of pressure, more ice will melt into water i.e. melting point of ice is decreased by rise of pressure.

B. Vaporization of liquid -

$H_2\,O_{(\ell)}$	$\rightleftharpoons$	$H_2O_{(g)}$
water		vapour
less volume		more volume

Vaporization of a liquid is endothermic process in the nature i.e. the evaporation of a liquid into its vapour is completed by absorption of heat, so the rise of temperature will favour vaporization. On the other hand in this process, on increase of pressure the equilibrium will shift in the direction of less volume means water cannot be converted into vapour and boiling point increases.

C. Melting of Sulphur :

$\text{Sulphur}_{(s)}$	$\rightleftharpoons$	$\text{Sulphur}_{(\ell)}$
less volume		more volume

On increase in pressure, the equilibrium will shift towards less volume means solid is not converted into liquid and thus, melting point of sulphur increases.

9. CALCULATION OF DEGREE OF DISSOCIATION BY VAPOUR DENSITY MEASUREMENT

In those type of reactions in which there is a change in the number of moles after dissociation, the extent of dissociation can be determined by vapour density measurement.

Let us, consider the following reaction -

	$PCl_5 \rightleftharpoons$	PCl_3	$+\ Cl_2$
Initially	1	0	0
moles at equilibrium	$(1-\alpha)$	α	α

(Here 'α' is the degree of dissociation)

Total number of moles at equilibrium = $(1-\alpha) + \alpha + \alpha = (1+\alpha)$

Now, the V is the volume occupied by 1 mol of $PCl_5(s)$ which have vapour density is 'D' before dissociation and after dissociation is 'd'. So, under the same conditions, the volume occupied by $(1+\alpha)$ moles at equilibrium would be $(1+\alpha)$ V litre.

Since $\quad \text{Density} \propto \dfrac{1}{\text{Volume}}$

Therefore $\quad D \propto \dfrac{1}{V}$

$$d\ \alpha\ \frac{1}{(1+\alpha)V}$$

or $$\frac{D}{d} = \frac{\frac{1}{V}}{1/(1+\alpha)V} = (1+\alpha)$$

or $$\alpha = \frac{D}{d} - 1 = \frac{D-d}{d}$$

or $$\boxed{\alpha = \frac{D-d}{(n-1)d}}$$

Note: When one mole of a reactant on dissociation gives 'n' moles of gaseous products, the above equation takes in the form of

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

Examples based on Calculation of Degree of Dissociation by Density Measurement

Ex.12 The vapour density of N_2O_4 at a certain temperature is 30. The percentage dissociation of N_2O_4 at this temperature is-

(1) 55.5% (2) 60%

(3) 70% (4) 53.3% **Ans. [D]**

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

Mol. mass of N_2O_4 = (28 + 64) = 92

Vapour density, $D = \frac{92}{2} = 46$

Let the degree of dissociation be x.

Given,

Applying the relationship,

$$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$$

Degree of dissociation = **53.3%**

Ex.13 If PCl_5 is 80% dissociated at 523 K. Calculate the vapour density of the equilibrium mixture at 523 K –

(A) 75.9 (B) 57.9

(C) 97.5 (D) 95.7

Ans [B]

Sol. Vapour density of $PCl_5 = \frac{M.W. \text{ of } PCl_5}{2}$

$$= \frac{208.5}{2} = 104.25$$

Applying the formula,

$$0.8 = \frac{104.25 - d}{(2-1)d}$$

$$0.8\ d = 104.25 - d$$

$$1.8\ d = 104.25$$

$$d = \frac{104.25}{1.8} = \mathbf{57.9}$$

Ex.14 Ammonium carbamate when heated to 200ºC gives a mixture of vapours

$(NH_2COONH_4 \rightleftharpoons 2NH_3 + CO_2)$

with a vapour density 13.0. What is the degree of dissociation of ammonium carbamate –

(A) 1 (B) 2

(C) 3 (D) 4 **Ans. [A]**

Sol. Vapour density of ammonium carbamate before dissociation (D).

$$= \frac{\text{Mol. wt.}}{2} = \frac{78}{2} = 39$$

Vapour density after dissociation (d) = 13.0 (given)

Now, $$\alpha = \frac{D-d}{(n-1)d} = \frac{39-13}{(3-1)\times 13}$$

$$= \frac{26}{26} = 1 \quad \textbf{i.e.} \quad \alpha = 1$$

So, ammonium carbamate will be 100% dissociated.

SOLVED EXAMPLES

Ex.1 The volume of a closed reaction vessel in which the equilibrium :

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

sets is halved, Now -

(A) The rates of forward and backward reactions will remain the same.

(B) The equilibrium will not shift.

(C) The equilibrium will shift to the right.

(D) The rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

Ans. [D]

Sol. In the reaction

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

In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decrease in volume and so if the volume of the reaction vessel is halved the equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will increase i.e. double that of reverse reaction.

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

When 46g of I_2 and 1g of H_2 are heated at equilibrium at 450ºC, the equilibrium mixture contained 1.9g of I_2. How many moles of I_2 and HI are present at equilibrium –

(A) 0.0075 & 0.147 moles

(B) 0.0050 & 0.147 moles

(C) 0.0075 & 0.347 moles

(D) 0.0052 & 0.347 moles **Ans. [C]**

Sol. Moles of I_2 taken $= \frac{46}{254} = 0.181$

Moles of H_2 taken $= \frac{1}{2} = 0.5$

Moles of I_2 remaining $= \frac{1.9}{254} = 0.0075$

Moles of I_2 used = 0.181 – 0.0075 = 0.1735

Moles of H_2 used =0.1735

Moles of H_2 remaining 0.5 – 0.1735 = 0.3265

Moles of HI formed = 0.1735 × 2 = 0.347

At equilibrium

Moles of I_2 = 0.0075 moles

Moles of HI = 0.347 moles

Ex.3 A two litre flask contains 1.4 gm nitrogen and 1.0 gm hydrogen. The ratio of active mass of nitrogen and hydrogen would be -

(A) 1 : 3 (B) 1 : 5

(C) 1.4 : 1 (D) 1 : 10

Ans. [D]

Sol. $[N_2] = \frac{1.4}{28 \times 2}$, $[H_2] = \frac{1}{2 \times 2}$

$[N_2] : [H_2] = \frac{1}{40} : \frac{1}{4}$

= 1: 10

Ex.4 In the reaction :

$$A + B \rightleftharpoons C + D$$

the initial concentration of A is double the initial concentration of B. At equilibrium the concentration of B was found to be one third of the concentration of C. The value of equilibrium constant is –

(A) 1.8 (B) 1.008

(C) 0.0028 (D) 0.08

Ans. [A]

Sol.

A	+ B	$\rightleftharpoons$ C	+ D	
1	0.5	0	0	Initially
1-x	0.5-x	x	x	At equilibrium

According to question

(0.5 – x) = 1/3 x

or x = 1.5 – 3x

4x = 1.5

$x = \frac{1.5}{4} = 0.375$

$$K_C = \frac{x \times x}{(1-x)(0.5-x)}$$

$$= \frac{0.375 \times 0.375}{(1-0.375) \times (0.5-0.375)}$$

$$= \frac{0.375 \times 0.375}{0.625 \times 0.125}$$

= 1.8

Ex.5 The value of K_C for the reaction :
$A + 3B \rightleftharpoons 2C$ at 400°C . Calculate the value of K_P

(A) 1.64×10^{-4} (B) 1.64×10^{-6}

(C) 1.64×10^{-5} (D) 1.64×10^{-3}

Ans. [A]

Sol. $K_P = K_C\,[RT]^{\Delta n}$ $\Delta n = 2 - 4 = -2$

$T = 673K$, $K_C = 0.5$, $R = 0.082$ litre. atm.

$K_P = 0.5 \times (0.082 \times 673)^{-2}$

$= 1.64 \times 10^{-4}$ atm.

Ex.6 Two moles of ammonia was introduced in an evacuated vessel of 1 litre capacity. At high temperature the gas undergoes partial dissociation according to the equation :

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

At equilibrium the concentration of ammonia was found to be 1 mole. What is the value of 'K' ?

(A) $3/4 = 0.75\ mol^2\ \ell^{-2}$

(B) $3/2 = 1.5\ mol^2\ \ell^{-2}$

(B) $27/16 = 1.7\ mol^2\ \ell^{-2}$

(D) $27/64 = 0.42\ mol^2\ \ell^{-2}$ **Ans. [C]**

Sol. Let α be the degree of dissociation :
Hence we have :

$$\begin{array}{cccc} 2NH_3(g) & \rightleftharpoons & N_2(g) & + 3H_2(g) \\ 2 & & 0 & 0 \\ 2-2\alpha & & \alpha & 3\alpha \end{array}$$

At equilibrium : $[NH_3] = 2 - 2\alpha = 1$
or $\alpha = 1/2$

$$[N_2] = \frac{1}{2},\ [H_2] = \frac{3}{2},\ [NH_3] = 1$$

$$\because \quad K = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$= \frac{\frac{1}{2} \times \frac{3}{2} \times \frac{3}{2} \times \frac{3}{2}}{1 \times 1} = \frac{27}{16}$$

$= 1.7\ mol^2\ \ell^{-2}$

Ex.7 In a 2 litre flask, the reaction takes place as :

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

The equilibrium conc. of $[COCl_2]$ was found to be 0.4. If the excess of $COCl_2$ is added to the system, the equilibrium reestablishes and $[COCl_2]$ becomes 1.6. What is the equilibrium conc. of [CO] ?

(A) Half of the former value

(B) Thrice of the former value

(C) Remains unaltered

(D) Twice of the former value **Ans. [D]**

Sol. $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

$$\frac{[CO][Cl_2]}{[COCl_2]} = K_C$$

Let $[CO] = x$, then $[Cl_2] = x$

$$\therefore \quad \frac{x^2}{[COCl_2]} = K_C \text{ or } \frac{x^2}{0.4} = K_C$$

$$\text{Again } K_C = \frac{x^2}{0.4} = \frac{[CO][Cl_2]}{[COCl_2]}$$

$$\frac{x^2}{0.4} = \frac{[CO]^2}{1.6}\ ;\ \{[CO] = [Cl]\}$$

$x^2 \times 4 = [CO]^2$

$2x = [CO]$

Ex.8 4.0 gms of hydrogen react with 9.023×10^{23} molecules of chlorine to form HCl gas. The total pressure after the reaction was found to be 700 mm. The partial pressure of HCl will be –

(A) 3900 mm (B) 600 mm

(C) 700 mm (D) 350 mm

Ans. [B]

Sol.

$$\begin{array}{cccc} H_2 + & Cl_2 \rightleftharpoons & 2HCl & \\ \frac{4}{2} & \frac{9.023 \times 10^{23}}{6.02 \times 10^{23}} & 0 & \text{Initially} \\ 2 & \approx \frac{3}{2} & 0 & \text{Initially} \end{array}$$

3/2 moles of Cl_2 will react with 3/2 moles of H_2 to give $\frac{3}{2} \times 2 = 3.0$ moles of HCl. So the total number of moles in the reaction

$$= \left(2 - \frac{3}{2}\right) + 0 + 3 = 3.5$$

$$\text{Partial pressure of HCl} = \frac{3 \times 700}{3.5}$$

$= 600$ mm

Ex.9 The equilibrium constant 'K' for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 16. What would be value of equilibrium constant 'K' for the reaction :

$$NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$$

(A) 0.25 (B) 0.4
(C) 2 (D) 0.625 **Ans. [A]**

Sol. We know that : [New reaction = reverse of old reaction $\times \frac{1}{2}$]

$$K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{16}} = \frac{1}{4}$$

$$= 0.25$$

Ex.10 1.0 mole of $PCl_3(g)$ and 2.0 moles of Cl_2 (g) were placed in a 3 litre flask and heated to 400 K. When equilibrium was established , only 0.70 mole of PCl_3 (g) remained . What is the value of equilibrium constant for the reaction :

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ at 400 K ?

(A) 0.25 (B) 1.31
(C) 0.76 (D) 2.6 **Ans. [C]**

Sol.

	$PCl_3(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$PCl_5(g)$
Initial conc.	1.0	2.0	0
At equilibrium	0.7	1.7	0.3

$$K_C \; \frac{0.3/3}{0.7/3 \times 1.7/3} = \frac{0.3 \times 3}{0.7 \times 1.7} = 0.76$$

Ex.11 For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$,
The moles of each component PCl_5, PCl_3 and Cl_2 at equilibrium were found to be 2. If the total pressure is 3 atm. The K_P will be –

(A) 1 atm. (B) 2 atm.
(C) 3 atm. (D) 1.5 atm.

Ans. [A]

Sol. Total Moles = 2 + 2+ 2 = 6

$$P_{PCl_3} = \frac{2}{6} \times 3,\ P_{PCl_5} = \frac{2}{6} \times 3,\ P_{Cl_2} = \frac{2}{6} \times 3$$

$$K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{1 \times 1}{1} = 1 \text{ atmosphere.}$$

Ex.12 For the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

The value of equilibrium constant is 9.0. The degree of dissociation of HI will be –

(A) 2 (B) 2/5
(C) 5/2 (D) 1/2 **Ans. [B]**

Sol. Equilibrium constant of the reaction

$H_2 + I_2 \rightleftharpoons 2HI$ is 9.0

So the equilibrium constant for the dissociation of HI i.e. $2HI \rightleftharpoons H_2 + I_2$ will be 1/9.

$$\begin{array}{cccc} 2HI & \rightleftharpoons & H_2 & + \; I_2 \\ 1 & & 0 & 0 \\ 1-x & & \frac{x}{2} & \frac{x}{2} \end{array}$$

$$K_C = \frac{x}{2} \times \frac{x}{2} \quad \frac{1}{(1-x)} \times \frac{1}{(1-x)}$$

$$\frac{1}{9} = \frac{x^2}{2 \times 2(1-x)^2} ;$$

$$\frac{1}{3} = \frac{x}{2(1-x)}$$

or $2 - 2x = 3x$

$5x = 2$

$x = 2 / 5$

Ex.13 For the reaction $N_2 \rightleftharpoons 2NH_3$, $N_2 : H_2$ were taken in the ratio of 1 : 3 . Up to the point of equilibrium 50% each reactant has been reacted. If total pressure at equilibrium is P. The partial pressure of ammonia would be –

(A) P/3 (B) P/6
(C) P/4 (D) P/8 **Ans. [A]**

Sol.

	N_2 +	$3H_2$ $\rightleftharpoons$	$2NH_3$
Initially	1	3	0
At equilibrium	1-0.5	3-1.5	2 × 0.5

Total moles = (1 – 0.5) + (3 –1.5) + 1 = 3

$$;\ P_{NH_3} = \frac{1}{3}P$$

Ex.14 In a reaction vessel of 2 litre capacity 3 moles of N_2 reacts with 2 moles of O_2 to produce 1 mole of NO. What is the molar concentration of N_2 at equilibrium ?

(A) 1.25 (B) 1.50

(C) 0.75 (D) 2.0 **Ans. [A]**

Sol.

$$\begin{array}{ccccc} N_2 & + & O_2 & \rightleftharpoons & 2NO \\ 3 & & 2 & & 0 \\ 3\text{-}x & & 2\text{-}x & & 2x \end{array}$$

$\because$ $2x = 1 \; ; \; x = 0.5$

$$[N_2] = \frac{3-0.5}{2} = 1.25$$

Ex.15 HI was heated in a sealed tube at 440°C till the equilibrium was established. The dissociation of HI was found to be 22%. The equilibrium constant for dissociation is –

(A) 0.282 (B) 0.0786

(C) 0.0199 (D) 1.99

Ans. [C]

Sol. The equilibrium of the dissociation of

$$\begin{array}{ccccc} 2HI & \rightleftharpoons & H_2 & + & I_2 \\ 1 & & 0 & & 0 \\ 1-\frac{22}{100} & & \frac{22}{100\times 2} & & \frac{22}{100\times 2} \\ 0.78 & & 0.11 & & 0.11 \end{array}$$

$$K_C = \frac{0.11\times 0.11}{0.78\times 0.78} \approx 0.0199$$