Chemical Equilibrium

ANALYSIS OF REVERSIBLE CHEMICAL REACTIONS Section - 1

Chemical reactions in one sense can be divided into two categories : ***molecular chemical reactions*** *(involving molecules as reactants and products)* and ***ionic reactions*** *(involving ions along with molecules as reactants and products).*

In another sense, reactions can also be divided into two categories : ***Irreversible chemical reactions*** *(the reactions which proceed to completion and the products fail to recombine to give back reactants)* and ***reversible reactions*** *(the reactions which never go to completion and can occur in either direction, i.e., the products recombine to give back reactants).*

Analysis of reversible chemical processes is of great importance and interest. We divide their study in two parts :

(i) *Molecular (reversible) reactions* and

(ii) *Ionic (reversible) reactions.*

In chemical equilibrium, we will consider molecular reversible reactions, such as :

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

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

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

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

Each reversible reaction consists of one pair of reaction : One is *forward reaction* and other is *backward* or *reverse reaction* and these two are referred to as *two opposing chemical changes.*

At one stage during reversible reactions, two reactions, i.e., *forward* and *backward* reactions proceed at the same time with the same speed, the reaction is then said to be in *equilibrium***.** A *chemical equilibrium* is the state that exists when two opposing reactions, i.e., forward and backward reactions are proceeding at the same rate in a reversible reaction.

For a simple case : $A + B \rightleftharpoons C + D$

Initially, when A and B are mixed, they react. When they react, the rate of forward reaction decreases since the concentration of A and B decreases with time. As C and D are formed, they react to give back A and B. The rate of reaction between C and D increases with time as more C and D molecules are formed, more they collide and react. Eventually, the two reactions occur at the same rate and the system is at *equilibrium.*

To understand the concept more clearly, let us consider the manufacturing of NH_3 (ammonia) from N_2 and H_2. The reaction between $N_2(g)$ and $H_2(g)$ to form $NH_3(g)$ is a reversible reaction. Instead of " $\longrightarrow$ ", we use double arrow for a reversible reaction " $\rightleftharpoons$ " i.e., $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Forward Reaction : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ .... (i)

Backward Reaction : $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$ .... (ii)

Note :

- Regardless of whether we start with NH_3 or with pure hydrogen and nitrogen, the reaction does not go to completion.
- If we start with only H_2 and N_2, the reaction (ii) cannot at first occur because there is no NH_3. As the forward reaction proceeds, NH_3 forms and reaction (ii) starts.
- Initially, the rate of forward reaction is fast. But as the time goes on, rate of forward reaction decreases and the rate of reaction (ii) i.e., reverse reaction increases.
- Eventually, the rate at which NH_3 is being formed (*Forward Reaction*) becomes equal to the rate at which NH_3 is being decomposed (*Reverse Reaction*). This state is called as ***Chemical equilibrium***.
- Once the equilibrium is reached, relative concentrations of H_2, N_2 and NH_3 do not change as long as temperature remains constant.
- At equilibrium, both reactions, i.e., forward and backward continue to perform (but their rate is same) and such a state of equilibrium where both opposing forces balance each other and molecular activity still continues, is known as ***dynamic equilibrium***.
- In *dynamic chemical equilibrium*, molecular activity never ceases, at each instant some molecules are being formed and some are being broken ; only the rate of two forces is same.

At Equilibrium Stage (at a given temperature) :

(i) Rate of forward reaction = Rate of backward reaction

(ii) At no instant, any reaction (forward or backward) stops.

(iii) Relative concentrations of reactants and products do not change.

(iv) Any change i.e., external stress (*pressure, temperature or concentration*) causes disturbance in equilibrium state. The state of equilibrium being stable, is again reached by some adjustment.

Reaction Coefficients and Equilibrium Constant (Q and K)

In 1863, Guldberg and Waage (two Norwegian chemists) stated that, at constant temperature, the rate of chemical reaction is directly proportional to the product of active masses (raised to power their stoichiometric coefficients) of reactants present at any given time.

For a *reversible reaction* : $mA + nB \underset{k_b}{\overset{k_f}{\rightleftharpoons}} pC + qD$

Forward reaction. : $mA + nB \xrightarrow{k_f} pC + qD$

Rate of forward reaction $(r_f) \propto a_A^m\, a_B^n$ $\qquad a$: denotes activity (*active masses*)

$\Rightarrow \quad r_f = k_f\, a_A^m\, a_B^n$ $\qquad k_f$ = rate constant for forward reaction

Backward reaction : $pC + qD \xrightarrow{k_b} mA + nB$

Rate of backward reaction $(r_b) \propto a_C^p\, a_D^q$

$\Rightarrow \quad r_b = k_b\, a_C^p\, a_D^q$ $\qquad k_b$ = rate constant for backward reaction

For a reversible reaction, reaction coefficient (Q) is defined as $Q = \dfrac{a_C^p\, a_D^q}{a_A^m\, a_B^n}$

At equilibrium :

$r_f = r_b$ and Q is called as equilibrium constant (K_{eq}) at this stage

$$K_{eq} = \frac{k_f}{k_b} = \left[\frac{a_C^p \, a_D^q}{a_A^m \, a_B^n}\right]_{\text{at equilibrium}}$$

Note : **(i)** Activity is denoted by ***a***.

Activity of aqueous solution is expressed in concentration (mol/L)

Activity of gases is expressed in partial pressure (atm).

Activity of pure solids and liquids is unity, i.e., $a_{\text{solid}} = 1$ [for example $a_{\text{Fe}} = 1, a_{\text{water}} = 1$]

(ii) When activities are expressed in concentration (mol/L), then equilibrium constant K_{eq} is denoted as K_C.

$$K_C = \frac{[C]^p \, [D]^q}{[A]^m \, [B]^n}$$ where [ ] denotes concentration.

When activities are expressed in terms of partial pressure, then equilibrium constant K_{eq} is denoted as K_P.

$$K_P = \frac{(p_C)^p \, (p_D)^q}{(p_A)^m \, (p_B)^n}$$ p : partial pressure (= mole fraction × total pressure)

When activities are expressed in terms of mol fraction, then equilibrium constant K_{eq} is denoted as K_χ.

$$K_\chi = \frac{(\chi_C)^p \, (\chi_D)^q}{(\chi_A)^m \, (\chi_B)^n}$$ where χ denotes mol fraction.

(iii) K_{eq} changes only when the temperature changes. There is no effect of change in pressure or concentrations on the value of K_{eq}.

(iv) Analysis of a reversible system on the basis of activities of reacting species is done in terms of reaction coefficient (Q). First an expression for Q (or K_{eq} at equilibrium) is written properly and activity values are then substituted.

Comparing the value of Q with the standard value of K_{eq} (at a given T), one can comment on the status of reversible system by following the table given below:

$Q < K_{eq}$	It means equilibrium has not yet reached. The system is essentially moving to right *(forward direction)* increasing product concentrations and simultaneously decreasing reactant concentrations. One can say that forward reaction is dominant at this instant over backward reaction.
$Q = K_{eq}$	It means equilibrium has been established and concentrations of reactants and products will remain constant.
$Q > K_{eq}$	It means equilibrium has not yet established. The reaction must proceed to left (Reverse or backward direction), increasing reactant concentrations and simultaneously decreasing product concentrations.

Illustrating the concept :

Consider the reaction $SO_2Cl_2\,(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ *; at* 375°C, *the value of equilibrium constant for the reaction is* 0.0032. *It was observed that concentration of the three species is* 0.050 *mol/L each at a certain instant. Discuss what will happen in the reaction vessel ?*

SOLUTION :

In this question, concentration of three species, i.e., $SO_2Cl_2(g)$, $SO_2(g)$ and $Cl_2(g)$ each is given, but it is not mentioned that whether the system is at equilibrium or not. So first check it.

Find reaction coefficient for given equation.

$$Q = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{(0.05)(0.05)}{(0.05)} = 0.05$$

$\Rightarrow$ $Q \neq K_{eq}$, so system is not at equilibrium state.

As $Q > K_{eq}$, the concentrations must adjust till $Q = K_{eq}$ for equilibrium. This can happen only if reaction shifts backwards, and products recombine to give back reactants. Hence in the reaction vessel, the system will move backward so that it can achieve equilibrium state.

Writing K_{eq} for reversible reactions :

Homogenous Reactions : (Reactions in which all the reactants and products are in the same phase)

Here, we will discuss some important reversible reactions and explain how to approach while analysing the equilibrium state for those reactions.

Illustrating the concept :

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

Let '*a*' moles of H_2 and '*b*' moles of I_2 are taken initially and let at equilibrium '*x*' moles each of H_2 and I_2 are reacted at a total pressure of P atm.

We will write the expression for K_p for this reaction.

$$K_P = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} \qquad p_i = \text{Partial pressure}$$

Moles	H_2	I_2	HI
Initial	a	b	0
At equilibrium	$a-x$	$b-x$	$2x$

[for each mole of H_2 and I_2, 2 moles of HI are produced]

Total moles at equilibrium = $(a-x)+(b-x)+2x = (a+b)$ [Note : Consider only the gaseous moles]

$\Rightarrow$ $p_{HI} = mol\ fraction \times P$ $\Rightarrow$ $p_{HI} = \frac{2x}{a+b}P\ ;\ p_{H_2} = \frac{(a-x)}{a+b}P\ ;\ p_{I_2} = \frac{(b-x)}{a+b}P$

$$\Rightarrow \quad K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{\left(\frac{2x}{a+b}P\right)^2}{\left(\frac{a-x}{a+b}P\right)\left(\frac{b-x}{a+b}P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

Note : Try to write expression for K_C and observe.

Illustrating the concept :

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

Let '*a*' moles of NH_3 are given initially and let x moles of NH_3 are decomposed at equilibrium and V Lt be the capacity of vessel in which reaction is being studied. We will write an expression for K_c for this reaction. $K_c = \dfrac{[N_2][H_2]^3}{[NH_3]^2}$

Moles	NH_3	N_2	H_2
Initial	a	0	0
At equilibrium	$a-x$	$x/2$	$3x/2$

Concentrations (mol/L) at equilibrium

$$[NH_3] = \frac{(a-x)}{V}, [N_2] = \frac{x}{2V}, [H_2] = \frac{3x}{2V} \quad \Rightarrow \quad K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{\left(\frac{x}{2V}\right)\left(\frac{3x}{2V}\right)^3}{\left(\frac{a-x}{V}\right)^2} = \frac{27x^4}{16V^2(a-x)^2}$$

Note : Try to write expression for K_P.

Illustrating the concept :

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

If a moles of PCl_5 be put in a container of volume V Lt and at equilibrium 'x' moles of it were decomposed, find its K_p and K_c at equilibrium pressure of P atm.

$K_p = \dfrac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$ Find partial pressures of each component at equilibrium

Moles	PCl_5	PCl_3	Cl_2
Initial	a	0	0
At equilibrium	$a-x$	x	x

Total moles $(n_T) = (a-x) + x + x = a + x$

$$\Rightarrow \quad p_{PCl_5} = \frac{(a-x)}{(a+x)}P, \; p_{PCl_3} = p_{Cl_2} = \frac{x}{a+x}P$$

$$\Rightarrow \quad K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} \Rightarrow K_p = \frac{\left(\frac{x}{a+x}P\right)\left(\frac{x}{a+x}P\right)}{\left(\frac{a-x}{a+x}P\right)} \Rightarrow K_p = \frac{x^2 P}{\left(a^2 - x^2\right)}$$

For $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$, find molar concentrations of each component at equilibrium.

$$[PCl_5] = \frac{a-x}{V}; [PCl_3] = [Cl_2] = \frac{x}{V} \quad \Rightarrow \quad K_C = \frac{\left(\frac{x}{V}\right)^2}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

Illustrating the concept :

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

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

Note : $[H_2O] = 1$, as it is pure solvent. For reactions in aqueous medium, K_P has no meaning.

Heterogeneous Reactions : (Reactions involving reactants and products in more than one phase)

Illustrating the concept :

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

$$K_p = \frac{(p_{H_2})^4}{(p_{H_2O})^4}$$

Note : Activities of Fe(s) and Fe_3O_4(s) are equal to unity as both are pure solids.

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

$$K_p = p_{CO_2}$$

Note : Activities of $CaCO_3$ (s) and CaO (s) are equal to unity as both are pure solids.

- $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$$K_p = p_{NH_3} \cdot p_{H_2S}$$

Note : For heterogeneous reactions, generally K_p is written and the analysis is done in terms of partial pressure of components.

- If K_1 be the equilibrium constant for $A + B \rightleftharpoons C + D$, then

  Equilibrium constant for reverse reaction $C + D \rightleftharpoons A + B$ is $1/K_1$

  Equilibrium constant for $nA + nB \rightleftharpoons nC + nD$ is $(K_1)^n$, n can be fraction also (+ve only)
- If K_1 be equilibrium constant for $P \rightleftharpoons Q$ and K_2 be equilibrium constant for $R \rightleftharpoons S$

  then equilibrium constant for $P + R \rightleftharpoons Q + S$ is $K_1 . K_2$
- If K_1 be the equilibrium constant for $A \rightleftharpoons B$ and K_2 be the equilibrium constant for $C \rightleftharpoons D$

  then equilibrium constant for the reaction : $A - C \rightleftharpoons B - D$ i.e. $A + D \rightleftharpoons B + C$ is $\dfrac{K_1}{K_2}$

Relation between K_p, K_c and K_χ

For the equilibrium $mA + nB \rightleftharpoons pC + qD$

$$K_P = \frac{p_C^p\, p_D^q}{p_A^m\, p_B^n} \quad \text{and} \quad K_C = \frac{[C]^p[D]^q}{[A]^m[B]^n} \quad \text{and} \quad K_\chi = \frac{(\chi_C)^p(\chi_D)^q}{(\chi_A)^m(\chi_B)^n}$$

Use ideal gas equation : $pV = nRT \Rightarrow p = \frac{n}{V} RT = CRT$ (where $C \equiv [\ ]$ is the concentration)

Thus, $p_A = [A]\,RT$; $p_B = [B]\,RT$; $p_C = [C]\,RT$; $p_D = [D]\,RT$

Substituting the values of partial pressure in terms of concentration to get : $K_P = K_C (RT)^{\Delta n_g}$

Δn_g = number of moles of gaseous products – number of moles of gaseous reactants $= (p + q) - (m + n)$

[Note : Only gaseous moles have been considered since PV = nRT is applicable only for ideal gas]

Also, $K_P = \frac{p_C^p\, p_D^q}{p_A^m\, p_B^n} \Rightarrow K_P = \frac{(\chi_C P_T)^p (\chi_D P_T)^q}{(\chi_A P_T)^m (\chi_B P_T)^n} = (P_T)^{\Delta n_g} K_\chi$ (where P_T = Total Pressure)

Note : For $\Delta n_g = 0$, $K_P = K_C = K_\chi$

For example ;

(i) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (ii) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

Illustration - 1 *For a homogenous gaseous reaction $X(g) + 2Y(g) \rightleftharpoons Z(g)$, at 473 K, the value of K_c = 0.35 concentration units. When 2 moles of Y are mixed with 1 mole of X, at what pressure 60% of X is converted to Z ?*

SOLUTION :

Since pressure is to be calculated, so first find K_P using the relation between K_c and K_P.

$K_c = 0.35, R = 0.0821, T = 473, \Delta n_g = 1 - 3 = -2$

$$K_p = K_c (RT)^{\Delta ng} = 0.35 \times (0.0821 \times 473)^{-2}$$
$$= 2.32 \times 10^{-4}$$

[Note : V of flask is also not given. So, convert K_c to K_p]

The expression for K_p is : $K_p = \frac{p_Z}{p_X (p_Y)^2}$

Moles	X	Y	Z
Initial	1	2	0
At equilibrium	$1 - x$	$2 - 2x$	x

$\Rightarrow$ Total moles $(n_T) = 3 - 2x$

Let P = equilibrium pressure

$$\Rightarrow p_X = \frac{1-x}{3-2x} P,\ p_Y = \frac{2-2x}{3-2x} P,\ p_Z = \frac{x}{3-2x} P$$

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

$\Rightarrow x = 0.6$ (given)

$$K_p = \frac{0.6\,(3-1.2)^2}{P^2 (1-0.6)\,(2-1.2)^2} = 2.32 \times 10^{-4}$$

$\Rightarrow P^2 = (1.8 \times 10^2)^2 \Rightarrow P = 180$ atm

[Alternative approach : Solve for volume of flask using $K_C = \frac{[Z]}{[X]\,[Y]^2}$ and use PV = nRT to solve for P]

Illustration - 2 *Solid NH_4HS (s) (Ammonium hydrogen sulphate) dissociates to give $NH_3(g)$ and H_2S (g) and is allowed to attain equilibrium at 100°C. If the value of K_P for its dissociation is found to be 0.34, find the total pressure at equilibrium and partial pressure of each component.*

SOLUTION :

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$; since NH_4HS is a solid, hence $a_{NH_4HS} = 1$ and its un-dissociated amount will not effect the total pressure (due to gaseous NH_3 and H_2S only). Let 'x' be its moles decomposed at equilibrium and P be the equilibrium pressure.

Moles	NH_4HS	NH_3	H_2S
Initial	a	0	0
At equilibrium	$a - x$	x	x

Total moles at equilibrium = moles of $(NH_3 + H_2S) = 2x$

(only gaseous moles)

$P = ?\qquad K_P = 0.34$

$$p_{H_2S} = \frac{x}{2x}P = \frac{P}{2} \text{ and } p_{NH_3} = \frac{x}{2x}P = \frac{P}{2}$$

(for equimolar proportions, partial pressures are equal)

$$K_P = p_{H_2S} \cdot p_{NH_3} \qquad (a_{NH_4HS} = 1)$$

$$\Rightarrow \quad 0.34 = \frac{P}{2} \times \frac{P}{2}$$

$$\Rightarrow \quad \frac{P^2}{4} = 0.34 \Rightarrow P = \sqrt{4 \times 0.34} = 1.17 \text{ atm}$$

$$\Rightarrow \quad p_{NH_3} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm}$$

$$\text{and} \quad p_{H_2S} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm}$$

Note : In heterogeneous reactions, or even in homogenous gaseous reactions, sometimes it is better to analyse the species directly in terms of partial pressures, rather first taking moles and then calculating their partial pressures.

Illustration - 3 *The value of K_c for the reaction : $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100°C is 49. If 1.0 L flask containing one mole of A_2 is connected with a 2.0 L flask containing one mole of B_2, how many moles of AB will be formed at 100°C ?*

SOLUTION :

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

As the two vessels are connected, the final volume is now 3.0 L. Let x mol each of A_2 and B_2 react to form $2x$ moles of AB_2 (*from stoichiometry of reaction*)

Moles	A_2	B_2	AB
Initial	1	1	0
At equilibrium	$1 - x$	$1 - x$	$2x$

$$K_C = \frac{[AB]^2}{[A_2]\,[B_2]} = 49$$

Concentration of species at equilibrium are :

$[A_2] = (1 - x)/3, [B_2] = (1 - x)/3, [AB] = 2x/3$

$$K_C = \frac{\left(\frac{2x}{3}\right)^2}{\left(\frac{1-x}{3}\right)\left(\frac{1-x}{3}\right)} = \frac{4x^2}{(1-x)^2} = 49$$

Taking square root on both sides :

$$\Rightarrow \quad \frac{2x}{1-x} = 7 \quad \Rightarrow \quad x = 0.78$$

$\Rightarrow$ Moles of AB(g) formed at equilibrium $= 2x$

$= 1.56$

Illustration - 4 *The value of K_c for the reaction : $H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$ is 64 at 773 K. If one mole of H_2, one mole of I_2 and three moles of HI are taken in a 1L flask, find the concentrations of I_2 and HI at equilibrium at 773 K.*

SOLUTION : For the reaction $Q = \dfrac{[HI]^2}{[H_2][I_2]} = \dfrac{3^2}{1 \times 1} = 9$ [V = 1 L]

> ***Note :*** When $\Delta n_g = 0$, not only $K_P = K_C$, but volume terms always cancels in the expression of K.

$\Rightarrow$ $Q < K_{eq}$ (= 64). Hence the reaction proceeds to forward direction to achieve equilibrium.

Let x mole of H_2 and I_2 combine to produce $2x$ mole of HI.

Moles	H_2	I_2	HI
Initial	1	1	3
At equilibrium	$1 - x$	$1 - x$	$3 + 2x$

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = 64$$

Concentration of species at equilibrium are :

$[H_2] = (1 - x)/1$, $[I_2] = (1 - x)/1$, $[AB] = (3 + 2x)/1$

$$K_C = \frac{\left(\frac{3+2x}{1}\right)^2}{\left(\frac{1-x}{1}\right)\left(\frac{1-x}{1}\right)} = \frac{(3+2x)^2}{(1-x)^2} = 64$$

$\Rightarrow$ $x = 0.5$

$$[I_2] = \frac{1-x}{1} = 1 - 0.5 = 0.5\,M$$

$$[HI] = \frac{3+2x}{1} = 3 + 1.0 = 4.0\,M$$

Illustration - 5 *At 1000 K, the pressure of iodine gas is found to be 0.1 atm due to partial dissociation of $I_2(g)$ into $I(g)$. Had there been no dissociation, the pressure would have been 0.07 atm. Calculate the value of K_P for the reaction : $I_2(g) \rightleftharpoons 2I(g)$.*

SOLUTION : Analysing in terms of pressure directly :

Partial pressure	I_2	I
Initial	0.07	0
At equilibrium	$0.07 - p$	$2p$

$\Rightarrow$ Total pressure at equilibrium

$= (0.07 - p) + 2p = 0.1$ (given)

$\Rightarrow$ $p = 0.03$ atm.

$$K_P = \frac{(p_I)^2}{p_{I_2}} = \frac{(2p)^2}{(0.07 - p)} = \frac{(2 \times 0.03)^2}{0.07 - 0.03}$$

Substituting value of p

$\Rightarrow$ $K_P = 0.09$ atm units.

Illustration - 6 *Calculate the % age dissociation of $H_2S(g)$ if 0.1 mole of H_2S is kept in a 0.5 L vessel at 1000 K. The value of K_C for the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ is 1.0×10^{-7}.*

SOLUTION :

$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$;

Volume of vessel = $V = 0.5$ L

Let x be the degree of dissociation

Moles	H_2S	H_2	S_2
Initially	0.1	0	0
At equilibrium	$0.1 - 0.1x$	$0.1x$	$0.1x/2$

$$K_C = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{0.1x}{V}\right)^2\left(\frac{0.1x}{2V}\right)}{\left(\frac{0.1 - 0.1x}{V}\right)^2} = 10^{-7}$$

Assuming $0.1 - 0.1x \approx 0.1$, we get :

$\Rightarrow$ $\dfrac{x^3}{2V} = 10^{-6}$ $\Rightarrow$ $x = 0.01$

[Check : $0.1 - 0.1x \approx 0.1$]

Degree of dissociation (α)

$$= \frac{\text{Amount dissociated}}{\text{Initial amount}} = \frac{0.1\,x}{0.1} = x$$

$\Rightarrow$ 1 % dissociation of H_2S.

IN-CHAPTER EXERCISE - A

1. For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $K_p = 3.4$. At an instant, the partial pressures of SO_2, O_2 and SO_3 were found to be 0.40 atm, 0.20 atm and 0.60 atm respectively. Comment on the status of equilibrium process.

2. For $I_2(g) \rightleftharpoons 2I(g)$; $K_p = 1.80 \times 10^{-10}$. The partial pressures of $I_2 = 1.0$ atm. and $I = 0.5 \times 10^{-6}$ atm. after 50 minutes. Comment on the status of equilibrium process.

3. Write an expression for K_p and K_c for the following heterogeneous & homogenous equilibrium.

(i) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ **(ii)** $H_2O(\ell) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$

(iii) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ **(iv)** $2HgO(s) \rightleftharpoons 2Hg(\ell) + O_2(g)$

4. Find K_p for $SO_2(g) + CO_2(g) \rightleftharpoons SO_3(g) + CO(g)$

K_p for $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$ is 1.80 atm. units and

K_p for $CO_2(g) \rightleftharpoons CO(g) + 1/2O_2(g)$ is 5×10^{-10} atm. units.

5. 3 mole of $SO_3(g)$ are taken in a 8.0 L container at 800°C. At equilibrium, 0.60 mol of $O_2(g)$ are formed. Find the value of K_c for $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

6. For $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$, $K_p = 8 \times 10^{-8}$ atm. units at a certain temperature. Find the degree of dissociation of $COCl_2$ at given temperature if the equilibrium pressure is 2.0 atm.

7. $N_2O_4(g)$ is dissociated to an extent of 20% at equilibrium pressure of 1.0 atm and 57°C. Find the %age dissociation of N_2O_4 at 0.2 atm and 57°C.

Choose the correct alternative. Only one choice is correct. However, question marked '*' may have more than one correct option.

8. The equilibrium :

$$P_4(g) + 6Cl_2(g) \rightleftharpoons 4PCl_3(g)$$

is attained by mixing equal moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium :

(A) $[Cl_2] > [PCl_3]$ **(B)** $[Cl_2] > [P_4]$ **(C)** $[P_4] > [Cl_2]$ **(D)** $[PCl_3] > [P_4]$

9. In the following equilibriums :

I : $A + 2B \rightleftharpoons C$; $K_{eq} = K_1$

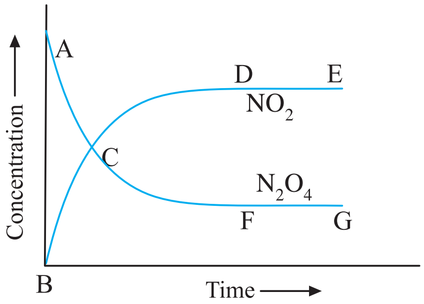
II : $C + D \rightleftharpoons 3A$; $K_{eq} = K_2$

III : $6B + D \rightleftharpoons 2C$; $K_{eq} = K_3$

hence :

(A) $3K_1 \times K_2 = K_3$ **(B)** $K_1^3 \times K_2^2 = K_3$

(C) $3K_1 \times K_2^2 = K_3$ **(D)** $K_1^3 \times K_2 = K_3$



10. $N_2O_4 \rightleftharpoons 2NO_2, K_c = 4$. *This reversible reaction is studied graphically as shown in the given figure. Select the correct statements out of I, II and III.*

I : *Reaction quotient has maximum value at point A*

II : *Reaction proceeds left to right at a point when* $[N_2O_4] = [NO_2] = 0.1$ M

III : $K_c = Q$ *when point D or F is reached* :

(A) *I, II* (B) *II, III*

(C) *II* (D) *I, II, III*

11. *One mole of* N_2O_4 *(g) at 300 K is kept in a closed container under one atmosphere. It is heated to* 600 *K when* 20% *of* N_2O_4*(g) is converted to* NO_2*(g)*

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

Hence resultant pressure is :

(A) 1.2 *atm* (B) 2.4 *atm* (C) 2.0 *atm* (D) 1.0 *atm*

12. *In each of the following, total pressure set-up at equilibrium is assumed to be equal and is one atm with equilibrium constants* K_p *given* :

I : $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g), K_1$ II : $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g), K_2$

III : $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g), K_3$

In the increasing order :

(A) $K_1 = K_2 = K_3$ (B) $K_1 < K_2 < K_3$ (C) $K_3 < K_2 < K_1$ (D) *None of these*

13. *What concentration of* CO_2 *be in equilibrium with* 0.025 *M CO at* 120°*C for the reaction* :

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g) \text{ if the value of } K_C = 5.0\ ?$$

(A) 0.125 *M* (B) 0.0125 *M* (C) 1.25 *M* (D) 12.5

14. *Which of the following relative value of* k_f *(rate constant of forward reaction) and* k_b *(rate constant of backward reaction) results in an equilibrium mixture that contain large amount of reactants and small amounts of products ?*

(A) $k_f > k_b$ (B) $k_f = k_b$ (C) $k_f < k_b$ (D) *None of these*

15. *If a chemical reaction is at equilibrium, it means that* :

(A) *The reactants are completely transformed into the products*

(B) *Product formation is minimum*

(C) *Equal amounts of reactants and products are present*

(D) *The rates of the forward and the backward reactions are equal*

***16.** *The equilibrium of the reaction* $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ *will be shifted when* :

(A) $Q < K_p$ (B) $Q > K_p$ (C) $Q = K_p$ (D) *can not be shifted*

***17.** *What are the characteristics of a chemical equilibrium ?*

(A) *Permanency of equilibrium* (B) *Approachability from either side*

(C) *Incompleteness of reaction* (D) *Changes with temperature*

18. *For the equilibrium* $AB(g) \rightleftharpoons A(g)+B(g)$ *at a given temperature, the pressure at which one-third of AB is dissociated is numerically equal to*

(A) 8 *times* K_p **(B)** 16 *times* K_p **(C)** 4 *times* K_p **(D)** 9 *times* K_p

19. *In a revesible reaction, if the concentration of reactants are doubled, the equilibrium constant K will :*

(A) *change to* 1/4 *K* **(B)** *change to* 1/2 *K*

(C) *change to* 2 *K* **(D)** *remain the same*

20. *For the equilibrium* $AB(g) \rightleftharpoons A(g)+B(g)$, K_p *is equal to four times the total pressure. Calculate the number of moles of A formed if one mol of AB is taken initially.*

(A) 0.45 **(B)** 0.30 **(C)** 0.60 **(D)** 0.90

***21.** *When two reactants, A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction*

(A) *is zero* **(B)** *increase with time*

(C) *rate of change of Q decreases with time* **(D)** *rate of change of Q increases with time*

22. *At equilibrium,* $X+Y \rightleftharpoons 3Z$, *1 mole of X,* 2 *mole of Y and* 4 *moles of Z are contained in a* 3.0 *L vessel. Comment on the status of equilibrium system, if at a particular time instant, the value of reaction coefficient Q is found to be* 15 :

(A) *at equilibrium* **(B)** *in forward direction*

(C) *in backward direction* **(D)** *None of these*

LE-CHATELIER'S PRINCIPLE Section - 2

How an equilibrium state relieves the external stress ?

How a state in equilibrium (*a stable state*) adjusts to the ***external stress*** (*change in Temperature, pressure or concentration of reactants/products*) is generalised in Le Chatelier's principle.

Le Chatelier's Principle states that :

> *If a stress is applied to a system in equilibrium, the equilibrium condition is upset; A net reaction occurs in that direction which tends to relieve the external stress and finally a new equilibrium is attained.*

To understand its application to a system, let us consider following example:

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

$\Delta H = -92$ kJ for *Forward Reaction*

$\Delta H = +92$ kJ for *Backward Reaction*