ANALYSIS OF REVERSIBLE CHEMICAL REACTION

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 that 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 :

$$\begin{array}{c|c} 3 \operatorname{Fe}(s) + 4 \operatorname{H}_2 \operatorname{O}(g) & \qquad & \operatorname{Fe}_3 \operatorname{O}_4(s) + 4 \operatorname{H}_2(g) \\ \operatorname{N}_2(g) + 3 \operatorname{H}_2(g) & \qquad & 2 \operatorname{NH}_3(g) \\ \operatorname{N}_2(g) + \operatorname{O}_2(g) & \qquad & 2 \operatorname{NO}(g) \\ & 2 \operatorname{SO}_3(g) & \qquad & 2 \operatorname{SO}_2(g) + \operatorname{O}_2(g) \end{array}$$

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 = 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 NH₃ (ammonia) from N₂ and

H₂. The reaction between N₂(g) and H₂(g) to form NH₃(g) is a reversible reaction. Instead of " \longrightarrow ", we use double arrow for a reversible reaction " \bigcirc " i.e. N₂(g) + 3H₂(g) \bigcirc 2NH₃(g) Forward Reaction : N₂(g) + 3H₂(g) \longrightarrow 2NH₃(g) \ldots (i) Backward Reaction : 2NH₃(g) \longrightarrow N₂(g) + 3H₂(g) \ldots (ii)

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Note : Regardless of whether we start with NH₃ 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 | $\underset{\mathbf{k}_{b}}{\overset{\mathbf{k}_{f}}{\underset{\mathbf{k}_{b}}{\longrightarrow}}} pC + qD$ |
|--|--|---|
| Forward reaction. : | mA + nB | $\xrightarrow{k_{\rm f}} pC + qD$ |
| Rate of forward reaction (r_f) |) $\propto a_{\rm A}^m a_{\rm B}^n$ | a : denotes activity (active masses) |
| $\Rightarrow r_f = k_f a_A^m a_B^n$ | | $k_f =$ rate constant for forward reaction |
| Backward reaction : $pC + q$ | $q \mathbf{D} \xrightarrow{\mathbf{k}_{\mathbf{b}}} r$ | nA + nB |
| Rate of backward reaction (| $r_b \propto a_{\rm C}^{\rm P} a_{\rm D}^{\rm q}$ | |
| $\Rightarrow \qquad r_{\rm b} = k_{\rm b} \ a_{\rm C}^{\rm P} a_{\rm D}^{\rm q}$ | | $k_b =$ rate constant for backward reaction |
| | | |
| | | |

For a reversible reaction, reaction coefficient (Q) is defined as $Q = \frac{a_{\rm C}^{\rm p} a_{\rm D}^{\rm q}}{a_{\rm A}^{\rm m} a_{\rm B}^{\rm n}}$ At equilibrium:

$$r_f = r_b$$
 and Q is called equilibrium constant (K_{eq}) at this stage $K_{eq} = \frac{k_f}{k_b} = \left[\frac{a_c^p a_D^q}{a_A^m a_B^n}\right]_{at equilibrium}$

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. $a_{solid} = 1$ [for example $a_{Fe} = 1$, $a_{water} = 1$]

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

$$K_{C} = \frac{\left[C\right]^{p} \left[D\right]^{q}}{\left[A\right]^{m} \left[B\right]^{n}} \quad \text{where } \left[\right] \text{ denotes concentration}$$

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

$$K_{P} = \frac{(P_{C})^{p} (P_{D})^{q}}{(P_{A})^{m} (P_{B})^{n}} \quad P : partial pressure (= mole fraction \times total pressure)$$

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

$$K_{\chi} = \frac{\left(\chi_{C}\right)^{p} \left(\chi_{D}\right)^{q}}{\left(\chi_{A}\right)^{m} \left(\chi_{B}\right)^{n}} \quad \text{where } \chi \text{ denotes mol fraction.}$$

- (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 (<i>forward direction</i>) increasing product concentration 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 $SO_2Cl_2(g) = SO_2(g) + Cl_2(g)$; 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_{en} 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 :

 $H_2(g) + I_2(g) = 2 HI(g)$

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.

$$K_{P} = \frac{(p_{HI})^{2}}{(p_{H_{2}})(p_{I_{2}})} \qquad p_{i} = Partial pressure$$

| Moles | H ₂ | I ₂ | HI |
|----------------|----------------|----------------|------------|
| Initial | a | b | 0 |
| At equilibrium | a – x | b-x | 2 <i>x</i> |

[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} = mole fraction $\times P$

$$\Rightarrow \quad \mathbf{p}_{\mathrm{HI}} = \frac{2x}{a+b} \mathbf{P} \ ; \ \mathbf{p}_{\mathrm{H2}} = \frac{(a-x)}{a+b} \mathbf{P} \ ; \ \mathbf{p}_{\mathrm{I2}} = \frac{(b-x)}{a+b} \mathbf{P}$$

$$\Rightarrow K_{p} = \frac{(p_{HI})^{2}}{(p_{H_{2}})(p_{I_{2}})} = \frac{\left(\frac{2x}{a+b}P\right)^{2}}{\left(\frac{a-x}{a+b}P\right)\left(\frac{b-x}{a+b}P\right)} = \frac{4x^{2}}{(a-x)(b-x)}$$

Note: Try to write expression for K_c and observe.

Illustrating the concept :

 $2\mathrm{NH}_3(g) \qquad \qquad \mathrm{N}_2(g) + 3\mathrm{H}_2(g)$

Let 'a' moles of NH_3 are given initially and let x moles of NH_3 are decomposed at equilibrium and VLt be the capacity of vessel in which reaction is being studied. We will write an expression for K_c for this reaction.

$$\mathbf{K}_{c} = \frac{\left[\mathbf{N}_{2}\right] \left[\mathbf{H}_{2}\right]^{3}}{\left[\mathbf{N}\mathbf{H}_{3}\right]^{2}}$$

| Moles | NH ₃ | Nz | H ₂ |
|----------------|-----------------|-----|----------------|
| Initial | a | 0 | 0 |
| At equilibrium | a – x | x/2 | 3x/2 |

Concentrations (mol/L) at equilibrium

$$\left[\mathrm{NH}_{3}\right] = \frac{\left(\mathrm{a}-x\right)}{\mathrm{V}}, \left[\mathrm{N}_{2}\right] = \frac{x}{2\mathrm{V}}, \left[\mathrm{H}_{2}\right] = \frac{3x}{2\mathrm{V}} \Rightarrow \quad \mathrm{K}_{\mathrm{c}} = \frac{\left[\mathrm{N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}{\left[\mathrm{NH}_{3}\right]^{2}} = \frac{\left(\frac{x}{2\mathrm{V}}\right)\left(\frac{3x}{2\mathrm{V}}\right)^{3}}{\left(\frac{\mathrm{a}-x}{\mathrm{V}}\right)^{2}} = \frac{27x^{4}}{16\mathrm{V}^{2}\left(\mathrm{a}-x\right)^{2}}$$
Note: Try to write expression for K_P.

Illustrating the concept :

 $\operatorname{PCl}_{5}(g) = \operatorname{PCl}_{3}(g) + \operatorname{Cl}_{2}(g)$

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 Patm.

 $K_{p} = \frac{p_{PCl_{3}} \times p_{Cl_{2}}}{p_{PCl_{5}}}$ Find partial pressures of each component at equilibrium

| Moles | PCIs | PCl ₃ | Cl ₂ |
|----------------|-------|------------------|-----------------|
| Initial | а | 0 | 0 |
| At equilibrium | a – x | x | x |

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

$$\Rightarrow \quad \mathbf{p}_{\mathrm{PCl}_{5}} = \frac{(a-x)}{(a+x)}\mathbf{P}, \ \mathbf{p}_{\mathrm{PCl}_{3}} = \mathbf{p}_{\mathrm{Cl}_{2}} = \frac{x}{a+x}\mathbf{P}$$

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$$\Rightarrow \quad \mathbf{K}_{p} = \frac{\mathbf{p}_{\text{PCl}_{3}} \times \mathbf{p}_{\text{Cl}_{2}}}{\mathbf{p}_{\text{PCl}_{5}}} \quad \Rightarrow \quad \mathbf{K}_{p} = \frac{\left(\frac{x}{a+x}\mathbf{P}\right)\left(\frac{x}{a+x}\mathbf{P}\right)}{\left(\frac{a-x}{a+x}\mathbf{P}\right)} \quad \Rightarrow \quad \mathbf{K}_{p} = \frac{x^{2}\mathbf{P}}{\left(a^{2}-x^{2}\right)}$$

Fo

$$K_{c} = \frac{[PCl_{3}][Cl_{2}]}{[PCl_{5}]}, \text{ find molar concentrations of each component at equilibrium.}$$

$$\left[\operatorname{PCl}_{5}\right] = \frac{\mathbf{a} - x}{\mathbf{V}}; \left[\operatorname{PCl}_{3}\right] = \left[\operatorname{Cl}_{2}\right] = \frac{x}{\mathbf{V}} \implies \qquad \mathbf{K}_{\mathrm{C}} = \frac{\left(\frac{x}{\mathbf{V}}\right)}{\left(\frac{\mathbf{a} - x}{\mathbf{V}}\right)} = \frac{x^{2}}{(\mathbf{a} - x)\mathbf{V}}$$

Illustrating the concept :

$$CH_{3}COOC_{2}H_{5}(aq) + H_{2}O(\ell) = CH_{3}COOH(aq) + C_{2}H_{5}OH(aq)$$
$$K_{c} = \frac{[CH_{3}COOH][C_{2}H_{5}OH]}{[CH_{3}COOC_{2}H_{5}]}$$

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 :

>
$$3\text{Fe}(s) + 4\text{H}_2\text{O}(g) = \text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g)$$

 $K_p = \frac{(p_{\text{H}_2})^4}{(p_{\text{H}_2\text{O}})^4}$

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

$$CaCO_3(s) = CaO(s) + CO_2(g)$$

$$K_p = p_{CO_2}$$

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

>
$$\operatorname{NH}_4\operatorname{HS}(s)$$
 = $\operatorname{NH}_3(g) + \operatorname{H}_2\operatorname{S}(g)$

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

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

> If
$$K_1$$
 be the equilibrium constant for $A + B$
Equilibrium constant for reverse reaction $C + D$
Equilibrium constant for $nA + nB$
 $nC + nD$ is $(K_1)^n$, *n* can be fraction also (+ve only)

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If K₁ be equilibrium constant for P S
Q and K₂ be equilibrium constant for R S

then equilibrium constant for P + R = Q + S is K_1 . K_2

If K₁ be the equilibrium constant for A = B and K₂ be the equilibrium constant for C = D

then equilibrium constant for the reaction : A - C = B - D i.e. A + D = B + C is

$$\frac{K_1}{K_2}$$

Relation between $\rm K_p$, $\rm K_c$ and $\rm K_{\gamma}$

For the equilibrium mA + nB = pC + qD

$$K_{P} = \frac{p_{C}^{p} p_{D}^{q}}{p_{A}^{m} p_{B}^{n}} \quad \text{and} \quad K_{C} = \frac{\left[C\right]^{p} \left[D\right]^{q}}{\left[A\right]^{m} \left[B\right]^{n}} \quad \text{and} \quad K_{\chi} = \frac{\left(\chi_{C}\right)^{p} \left(\chi_{D}\right)^{q}}{\left(\chi_{A}\right)^{m} \left(\chi_{B}\right)^{n}}$$

Use ideal gas equation : $pV = nRT \implies p = \frac{n}{V} RT = CRT$ (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,
$$K_P = \frac{p_C^p p_D^q}{p_A^m p_B^n} \implies K_P = \frac{(\chi_C P_T)^p (\chi_D P_T)^q}{(\chi_A P_T)^m (\chi_B P_T)^n} = (P_T)^{\Delta n_g} K_{\chi}$$
 (where $P_T = \text{Total Pressure}$)

Note: For $\Delta n_g = 0$, $K_P = K_C = K_{\chi}$ For example ;

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

Illustration - 1 For a homogenous gaseous reaction X(g) + 2Y(g) = 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 × 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 | х | Ŷ | z |
|----------------|-----|----------------|---|
| Initial | 1 | 2 | 0 |
| At equilibrium | 1-x | 2 – 2 <i>x</i> | x |

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

Let P = equilibrium pressure

$$\Rightarrow P_{X} = \frac{1-x}{3-2x} P,$$

$$p_{Y} = \frac{2-2x}{3-2x} P, p_{Z} = \frac{x}{3-2x} P$$

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

$$\Rightarrow x = 0.6 \text{ (given)}$$

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

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

[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:

 $NH_4HS(s) = NH_3(g) + H_2S(g)$; since

 NH_4HS is a solid, hence $a_{NH_4HS} = 1$ and its undissociated 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 | NH₄HS | NH ₃ | H ₂ S |
|----------------|-------|-----------------|------------------|
| Initial | а | 0 | 0 |
| At equilibrium | a – x | x | x |

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

P = ?
$$K_p = 0.34$$

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

(for equimolar proportions, partial pressures are equal)

$$K_{P} = p_{H_{2}S} \cdot p_{NH_{3}} \qquad (a_{NH_{4}HS} = 1)$$

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

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

$$\Rightarrow$$
 $p_{NH_3} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm}$ and $p_{H_2S} = \frac{P}{2} = \frac{1.17}{2} = 0.585 \text{ atm}$

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 : $A_2(g) + B_2(g) = 2AB(g)$ 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 two moles of B_2 , how many moles of AB will be formed at 100°C ?

SOLUTION :

 $A_2(g) + B_2(g) = 2AB(g)$

As the two vessels are connected, the final volume is now 3.0 L. Let x mole 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 | 2 <i>x</i> |

$$K_{C} = \frac{\left[AB\right]^{2}}{\left[A_{2}\right]\left[B_{2}\right]} = 49$$

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 :

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

 $\Rightarrow \text{ Moles of AB(g) formed at equilibrium} = 2x = 1.56$

Illustration - 4 The value of K_c for the reaction : $H_2(g) + I_2(g) = 2HI(g)$ 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

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{3^2}{1 \times 2} = 9[V = 1L]$$

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 | l ₂ | н |
|----------------|----------------|----------------|--------|
| Initial | 1 | 1 | 3 |
| At equilibrium | 1-x | 1-x | 3 + 2x |

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$$K_{C} = \frac{[HI]^{2}}{[H_{2}][I_{2}]} = 64$$

Concentration of species at equilibrium are : H_2] = (1 - x)/1, [I_2] = (1 - x)/1, [AB] = (3 + 2x)/1

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

 $\Rightarrow \quad x = 0.05$ $[I_2] = \frac{1 - x}{1} = 1 - 0.5 = 0.5 M$ $[HI] = \frac{3 + 2x}{1} = 3 + 1.0 = 4.0 M$

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 : $I_2(g) = 2I(g)$.



 $\Rightarrow \text{ Total pressure at equilibrium} \\ = (0.07 - p) + 2p = 0.1 \text{ (given)}$

SOLUTION : Analysing in terms of pressure directly :

 $\Rightarrow p = 0.03$ atm.

$$K_{\rm P} = \frac{(p_{\rm I})^2}{p_{\rm I_2}} = \frac{(2p)^2}{(0.07 - p)} = \frac{(2 \times 0.03)^2}{0.07 - 0.03}$$

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 $2H_2S(g) = 2H_2(g) + S_2(g)$ is 1.0×10^{-7} .

SOLUTION :

 $2H_2S(g) = 2H_2(g) + S_2(g);$

Volume of vessel = V = 0.5 L

Let *x* be the degree of dissociation

| Moles | H ₂ S | H₂ | S ₂ |
|----------------|------------------|--------------|-----------------|
| Initially | 0.1 | 0 | 0 |
| At equilibrium | 0.1 - 0.1x | 0.1 <i>x</i> | 0.1 <i>x</i> /2 |

$$K_{C} = \frac{[H_{2}]^{2}[S_{2}]}{[H_{2}S]^{2}} = \frac{\left(\frac{0.1x}{V}\right)^{2} \left(\frac{0.1x}{2V}\right)}{\left(\frac{0.1-0.1x}{V}\right)^{2}} = 10^{-7}$$

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

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

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

Degree of dissociation (α)

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

 \Rightarrow 1 % dissociation of H₂S.

Section 1

LE-CHAPTELIER'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 Principal 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 :

 $N_2(g) + 3H_2(g) 2NH_3(g)$ $\Delta H = -92 \text{ kJ for Forward Reaction}$

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

Note : ΔH : Enthalpy Change is a measure of heat evolved or heat absorbed in a chemical reaction. It is negative when heat is evolved and positive when heat is absorbed during a chemical change. You will learn details of it later in the Chapter on Chemical Energetics.

Note that in the above reaction :

- (a) Forward reaction is exothermic (favours formation of NH_3) and backward reaction is endothermic (favours decomposition of NH_3)
- (b) Formation of NH_3 results in decrease in number of moles (from 4 total moles of N_2 and H_2 to 2 total moles of NH_3) is a decrease in volume to right (in forward reaction)
- (c) Both reactants and products are gases and they will be influenced by changes in *P*, *T* and changing concentrations.

Effect of Temperature

Temperature can be increased by adding heat and can be decreased by taking out heat from the system.

- Increase the temperature by supplying heat: According to Le Chatelier's principle the disturbed equilibrium state will move in that direction where heat is being absorbed (*where stress is relieved*) i.e. in endothermic direction. In case of given situation, reverse direction will be favoured (*that being endot hermic*) till whole of extra heat in consumed.So NH₃ will decompose on increasing temperature.
- Decrease the temperature by extracting heat: According to Le Chatelier's principle, the system will go in the direction where heat is evolved i.e. in exothermic direction. In given situation, forward reaction will be favoured (i.e. formation of NH₃) till the new equilibrium is again established.

Note : *The new equilibrium state has a new value of equilibrium constant K on changing the temperature.*



Effect of Pressure

- Increase in pressure would result in decrease in volume thereby increasing the concentration (mol/L). The system will shift in a direction where number of moles decreases (decreasing concentration). In given situation, there is decrease in number of moles in forward direction, so increasing pressure favours forward reaction (i.e, formation of NH₃).
- Decreasing the pressure would mean lower number of moles/L. The system will shift in a direction which will produce more moles. In given situation, there is increase is number of moles in reverse direction, so decreasing pressure favours backward reaction (i.e., decomposition of NH₃)

Effect of Concentration :

The Concentration can be changed in two ways :

(a) By removing some of a component or (b) By adding some more of a component.

According to Le Chatelier's principle :

- > The addition of any component to a side (reactants and products) of a reaction in equilibrium shifts the equilibrium in the direction away from that side or one can say that equilibrium shifts in that direction which consumes the increased concentration.
- In given situation ;

increasing amount of pure N_2 and H_2 would favour formation of NH_3 . increasing amount of NH_3 would favour decomposition of NH_3

- > The removal of any component from a side (reactants and products) of a reaction in equilibrium shifts the equilibrium in the direction towards that side, or one can say the equilibrium shifts in that direction which produces the decreased concentration.
- > In given situation :

Decreasing the amount of NH_3 from right side drives the equilibrium to forward direction i.e. favours formation of NH_3 . Decreasing amount of N_2 or H_2 from left drives the equilibrium to reverse direction i.e. favours decomposition of NH_3

Effect of Catalyst :

- Catalyst increases the rate of both forward and backward reactions simultaneously and to the same extent in a reversible reaction. By increasing both rates, *catalyst reduces the time to reach equilibrium state*.
- Catalyst does not change the relative amounts of either reactants or products, hence it has no effect on equilibrium constant

Evaluation of K_{ea} at different temperatures :

If K_1 be the equilibrium constant at T_1 (in Kelwin) and K_2 be the equilibrium constant at T_2 (in Kelwin) $(T_2 > T_1)$, the two constants are related by Van't Hoff equation as follows :

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$
 Where *R* is gas constant and ΔH° is the standard heat of reaction.

Note : The value of ΔH is negative for exothermic reaction and is positive for endothermic reaction.

Le Chatelier's principle and Physical equilibrium :

Consider the physical equilibrium of change of state :

solid _____ liquid

Effect of pressure on melting :

When a solid melts, there is a decrease in volume for some solids (ice, diamond, carborundum, magnesium nitride, quartz etc.) and there is an increase in volume for some solids (sulphur, iron, copper, silver, gold etc.).

When ice melts, there is a decrease in volume. On this kind of system where there is a decrease in volume due to melting, increasing pressure will reduce the melting point of the system. Thus, increasing the pressure will favor the melting of ice.

Similarly, when sulphur melts, there is an increase in volume. On this kind of system where there is an increase in volume due to melting, decreasing pressure will reduce the melting point of the system. Thus, decreasing the pressure will favor the melting of sulphur.

Vapour pressure of liquids :

Consider liquid _____ vapour equilibrium :

This is an endothermic reaction in forward direction. Hence rise in temperature will favour evaporation. This means, increase in temperature results in increase in vapour pressure of the system.

Effect of pressure on boiling point :

As we increase pressure on the system : Liquid _____ vapour ; vapours condense lowering the vapour pressure of system. This means boiling point rises on increasing pressure as to reach the pressure required for the liquid to start boiling, needs to be increased.

Effect of temperature on solubility :

In most cases, formation of solution (solute in solvent) is an endothermic process. In such cases, increasing temperature, increases the solubility of solutes. In cases, where dissolution of solute is followed by evolution of heat; increasing temperature lowers the solubility of solutes.

Solubility of gases in liquid : As the temperature increases, the solubility of a gas decreases. This means that more gas is present in a solution with a lower temperature as compared to a solution with higher temperature.

Effect of pressure on solubility :

When a gas dissolves in liquid, there is a decrease in volume of the gas $(X(g) \longrightarrow X(aq))$. Thus, increase of pressure will favour the dissolution of gas in liquid.



Illustration - 7 For the reaction : $CO_2(g) + H_2(g) = CO(g) + H_2O(g)$, K is 0.63 at 727°C and

1.26 *at* 927°*C*.

- (a) What is the average ΔH for the temperature range considered ? [Use $\log_{10} 2 = 0.3$]
- (b) What is the value of K at $1227^{\circ}C$?

SOLUTION :

(a) $T_1 = 1000 \text{ K}, T_2 = 1200 \text{ K},$

 $K_1 = 0.63, K_2 = 1.26$

Using the Vant' Hoff equation :

$$\log_{10} \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$
$$\Rightarrow \qquad \log_{10} \left(\frac{1.26}{0.63} \right) = \frac{\Delta H}{2.303(2)} \left(\frac{1200 - 1000}{1200 \times 1000} \right)$$

 $\Rightarrow \Delta H = 8.32 \text{ kcal/mol}$

Note : The units of R and H must be same.

(b) Let
$$K_2$$
 be the equilibrium constant at $T_2 = 1500$ K

 $T_1 = 1000 \text{ K}$ and then $K_1 = 0.63$

$$\Rightarrow \qquad \log_{10}\left(\frac{K_2}{0.63}\right) = \frac{8.32 \times 10^3}{2.303(2)} \left(\frac{1500 - 1000}{1500 \times 1000}\right)$$
$$\Rightarrow \qquad \log_{10}\frac{K_2}{0.63} \approx 0.6 = \log_{10} 4$$
$$\Rightarrow \qquad K_2 = 0.63 \times 4 = 2.52$$

Illustration- 8 What would be the effect of increasing the volume of each of the following systems at equilibrium?

(i) $2CO(g) + O_2(g) = 2CO_2(g)$ (ii) $Ni(s) + 4CO(g) = Ni(CO)_4(g)$ (iii) $N_2O_4(g) = 2NO_2(g)$

SOLUTION :

Increasing volume (at constant temperature) will result in a decrease in the concentration of all the gases. As per Le-Chatelier's Principle, the reaction should move in a direction of increase in total number of gaseous moles (thereby increasing concentration). Thus, shift is in a direction of $\Delta n_g > 0$

| (i) | $2CO(g) + O_2(g) = 2CO_2(g)$ | $[\text{Backward direction} \because (\Delta n_g)_{\text{Backward direction}} > 0]$ |
|--------------|--|---|
| (ii) | $Ni(s) + 4CO(g) \longrightarrow Ni(CO)_4(g)$ | [Backward direction $:: (\Delta n_g)_{\text{Backward direction}} > 0$] |
| (iii) | $N_2O_4(g) = 2NO_2(g)$ | [Forward direction :: $(\Delta n_g)_{\text{forward direction}} > 0$] |

Illustration- 9What happens when an inert gas is added to(i) $PCl_5(g) = PCl_3(g) + Cl_2(g)$ (ii) $2SO_2(g) + O_2(g) = 2SO_3(g)$ at equilibrium at : (a) constant volume and temperature, (b) constant pressure and temperature.

SOLUTION :

Lets discuss what happens when an inert gas is added to the following reaction at equilibrium stage

$$m A(g) + nB(g) \longrightarrow P^{C}(g) + qD(g)$$

If the reaction is at equilibrium, we have :

$$K_{eq} = Q$$
(i)

Any factor (e.g. change in conc. of Reactants/Products or both) can have impact (in terms of change in the conc. of reactants/products) On that reaction at equilibrium only if that factor changes the equations

(i) so that $K_{eq} \neq Q$

Two cases occur :

(a) Inert gas addition at constant pressure :

$$K_{eq} = Q = \frac{p_C^p p_D^q}{p_A^m p_B^n}$$
 (at equilibrium)

and partial pressure $(p) = \chi P_{Total}$

where
$$\chi = \frac{n}{n_{Total}}$$
 = Mole fraction

Thus, when an inert gas is added, χ of each of the gas decreases and since $\mathsf{P}_{_{Total}}$ is constant, partial pressure decreases leading to a new equation :

 $Q > K_{eq}$ or $Q < K_{eq}$

which will depend on whether

$$\Delta n_g = \sum (n_g)_R - \sum (n_g)_R < 0 \text{ or } > 0$$

respectively

$$\Rightarrow \qquad \text{PCl}_{5}(g) = \text{PCl}_{3}(g) + \text{Cl}_{2}(g)$$

 $\Delta n_g = 1 > 0 \implies Q < K_{eq}$

(Reaction will move in forward direction)

Degree of Dissociation and Density :

When a gas decomposes (dissociates), its volume increase in accordance with increase in the total number of moles (at constant pressure). As the total mass remains same, its density decreases in the same proportion.

- Initial mass of gas mixture = mass of gas mixture at any time = $\rho_i V_i = \rho_f V_f$ [mass = density × \Rightarrow volume]
- $= n_i M_{mix,i} = nf M_{mix,f} [mass = moles \times Mole. mass]$

where ρ_i = Initial density of the mixture; ρ_f = Final density of the mixture; V_i and V_f = Initial and final volume of the system

Mmix, $i \equiv$ Initial molecular weight of the mixture and $M_{mix, f} \equiv$ Final molecular weight of the mixture.

Similarly, $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

 $\Delta n_g = -1 < 0 \implies Q > K_{eq}$

(Reaction will move in the backward direction)

(b) Inert gas addition at constant volume :

$$K_{eq} = Q = \frac{p_C^p p_D^q}{p_A^m p_B^n}$$
 (at equilibrium)

and partial pressure $(p) = \chi P_{Total}$

where
$$\chi = \frac{n}{n_{Total}}$$
 = Mole fraction

Now, when inert gas is added at constant volume, P_{Total} \uparrow and $\chi \downarrow$ but partial pressure of each gas remains same, since :

Partial pressure (p) = $\frac{n}{n_{Total}}$. P_{Total} and using Dalton's Law and ideal gas equation :

Check :
$$\frac{P_{Total}}{n_{Total}} = \frac{RT}{V} = const.$$

 P_{Total} . $V = n_{\text{Total}} RT$

Thus, $K_{eq} = Q$ even on adding inert gas at constant volume Thus, adding inert gas at constant volume has no effect on a reaction at equilibrium.

Section 2

$$\Rightarrow \qquad \frac{n_{f}}{n_{i}} = \frac{M_{mix,i}}{M_{mix,f}} = \frac{d_{i}}{d_{f}}$$

where $d_i \equiv$ Initial vapour density of the mixture and $d_f \equiv$ Final vapour density of the mixture. Consider the dissociation of PCl_s to clearly understand the concept.

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

| Moles | PCI ₅ | PCl ₃ | Cl ₂ |
|----------------|------------------|------------------|-----------------|
| Initial | a | 0 | 0 |
| At equilibrium | $a - a\alpha$ | aα | act. |

where α = degree of disscitation of = x / a

Total moles = $a + a\alpha$

 $\Rightarrow \qquad \frac{a}{a + a\alpha} = \frac{d_{mix}}{d_0} = \frac{d_{mix}}{d_{PCl_5}} d_{mix} = \text{ density of mixture PCl}_5, \text{ PCl}_3, \text{ Cl}_2$

Using the correlation for vapour density and moles, we have : $\frac{M_{mix, i}}{M_{mix, f}} \equiv \frac{M_{PCl_5}}{M_{mix, f}} = \frac{1 + \alpha}{1}$

 $M_{mix,f}$ can be found out by experiments. Thus, α can be calculated.

Illustration - 10 When PCl_5 is heated, it dissociates inot PCl_3 and Cl_2 . The vapor density of the gas mixture at 200°C and at 250°C is 70 and 58 respectively. Find the degree of dissociation at two temperatures.

SOLUTION :

| $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$ | | | | | |
|---|------------------|------------------|-----------------|--|--|
| Moles | PCI ₅ | PCl ₃ | Cl ₂ | | |
| Initial Moles | a | 0 | 0 | | |

Total moles = $a + a\alpha$ Using the result

a – aα

aα

aα

$$= \left\lfloor \frac{d_0}{d_{\text{mix}}} = \frac{a + a\alpha}{a} \right\rfloor$$

At equilibrium

$$d_0 = \text{density of PCl}_5$$

At
$$T = 200^{\circ}C$$
 (v.d. \equiv vapour density)

$$\Rightarrow \frac{d_0}{d_{\text{mix}}} = \frac{v.d._{\text{PCl}_5}}{v.d._{\text{mix}}} = \frac{M_0/2}{70} = \frac{a + a\alpha}{a}$$
$$= \frac{208.5/2}{70} = 1 + \alpha \quad \Rightarrow \quad \alpha = 0.49$$

At
$$T = 250^{\circ}C$$

$$\frac{d_0}{d_{\text{mix}}} = \frac{v.d._{\text{PC15}}}{v.d._{\text{mix}}} = \frac{M_0/2}{58} = \frac{a + a\alpha}{a}$$

$$=\frac{208.5/2}{58}=1+\alpha \quad \Rightarrow \quad \alpha = 0.80$$

Section 2

Illustration - 11 K_p for the reaction $PCl_5(g) = PCl_3(g) + Cl_2(g)$ at 250°C is 0.82. Calculate the degree of dissociation at given temperature under a total pressure of 5 atm. What will be the degree of dissociation if the equilibrium pressure is 10 atm. at same temperature.

SOLUTION :

Let 1 mole of PCl₅ be taken initially. If 'x' moles of PCl₅ dissociate at equilibrium, its degree of dissociation = x

| Moles | PCI ₅ | PCl ₃ | Cl ₂ |
|----------------|------------------|------------------|-----------------|
| Initially | 1 | 0 | 0 |
| At equilibrium | 1 - x | x | x |

Total moles = 1 - x + x + x = 1 + x

$$P = 5$$
 atm and $K_p = 0.82$

$$p_{PCl_5} = \left(\frac{1-x}{1+x}\right)P$$
; $p_{PCl_3} = \frac{x}{1+x}P$

and $p_{Cl_2} = \frac{x}{1+r}P$

Now,
$$K_p = \frac{(P_{PCl_5})(p_{Cl_2})}{(p_{PCl_5})}$$

$$\Rightarrow K_{p} = \frac{x^{2}}{1 - x^{2}}P = 0.82$$

or $\frac{x^{2}(5)}{1 - x^{2}} = 0.82 \Rightarrow x^{2} = \sqrt{\frac{0.82}{5.82}}$
 $x = 0.375 \text{ (or } 37.5\%)$

Now the new pressure P = 10 atm.

Let y be the new degree of dissociation. As the temperature is same (250° C), the value of K_p will remain same.

Proceeding in the same manner,

$$K_{p} = \frac{y^{2}P}{1-y^{2}} \implies 0.82 = \frac{y^{2}}{1-y^{2}} \times 10$$

 $\Rightarrow y = \sqrt{\frac{0.82}{10.82}} \text{ or } y = 0.275 \text{ (or } 27.5\%)$

Note:

- By increasing pressure, degree of dissociation has decreased, i.e., the system shifts to reverse direction. Compare the result by applying Le Chatelier's principle.
- Read the following example very carefully, In the following example, the volume is suddenly doubled, so first the initial concentration of all species at equilibrium will be halved and a new equilibrium will be re-established.

Illustration - 12 At a given temperature and a total pressure of 1.0 atm for the homogenous gaseous reaction $N_2O_4(g) = 2NO_2(g)$, the partial pressure of NO_2 is 0.5 atm.

- (a) Find the value of K_p .
- (b) If the volume of the vessel is decreased to half of its original volume, at constant temperature, what are the partial pressures of the components of the equilibrium mixture ?

SOLUTION :

For equilibrium system, $N_2O_4(g) = 2NO_2(g)$, the total pressure is 1.0 atm.

$$\Rightarrow$$
 The total pressure = $P_{N_2O_4} + P_{NO_2} = 1.0$

$$\Rightarrow$$
 P_{N2O4} = 0.5 atm and P_{NO2} = 0.5 atm

(i)
$$K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{0.5^2}{0.5} = 0.5 \text{ atm}$$

(ii) As volume is decreased to half its original volume, equilibrium is disturbed and the new initial conditions for the re-establishment of new equilibrium are :

$$P_{N_2O_4} = 1.0$$
 atm and $P_{NO_2} = 1.0$ atm

[: P is doubled as V is halved at constant T]

According to Le Chatelier principle, when volume is decreased, the system moves in that direction where there is decrease in number of moles. Hence, the system (here) will move in reverse direction, as there is a decrease in mole ($\Delta n_g = 2$ -1=1) i.e, the NO₂ will be converted to N₂O₄.

Let the decrease in pressure of NO_2 be x atm.

| Pressure | N ₂ O ₄ | NO2 |
|----------------|-------------------------------|-------|
| Initial | 1.0 | 1.0 |
| At equilibrium | 1 + x/2 | 1 - x |

$$\Rightarrow K_{\rm P} = \frac{(1-x)^2}{(1+x/2)} = 0.5$$

$$\Rightarrow 4x^2 - 9x + 2 = 0$$

$$\Rightarrow x = 2$$
 or 0.25

$$(x \neq 2, \text{ as initial pressure} = 1.0)$$

$$\Rightarrow x = 0.25$$

$$P_{N_2O_4} = 1 + \frac{x}{2} = 1.125 \text{ atm}$$

and
$$P_{NO_2} = 1 - x = 0.75$$
 atm

Illustration - 13 1 mole of N_2 and 3 moles of PCl_5 are placed in a 82.1L container heated to 127° C. The equilibrium pressure is 2.0 atm. Assuming ideal behaviour, Calculate the degree of dissociation of PCl_5 and value of K_n for its dissociation.

SOLUTION :

Dissociation of PCl_5 is written as :

$$PCl_5(g) = PCl_3 + Cl_2(g)$$

Let *x* be the no. of moles of PCl_5 decomposed at equilibrium.

| Moles | PCI ₅ | PCl ₃ | Cl ₂ |
|----------------|------------------|------------------|-----------------|
| Initial | 3 | 0 | 0 |
| At equilibrium | 3-x | x | x |

Now total gaseous moles in the container $= n_T$

 $\Rightarrow n_{T} = \text{moles of } (\text{PCl}_{5} + \text{PCl}_{3} + \text{Cl}_{2}) + \text{moles of } N_{2}$

 \Rightarrow n_T = 3 - x + x + x + 1 = 4 + x

The mixture behaves ideally, hence $PV = n_T$ RT

Let us calculate no. of moles by using gas equation

$$\Rightarrow n_{\rm T} = \frac{\rm PV}{\rm RT} = \frac{2 \times 82.1}{0.082 \times 400} \Rightarrow n_{\rm T} = 5$$

Now, equating the two values of n_T , we have :

$$4 + x = 5 \implies \qquad x = 1.$$

 \Rightarrow Degree of dissociation = 1/3 = 0.333

$$K_{\rm P} = \frac{P_{\rm PCl_3} \times P_{\rm Cl_2}}{P_{\rm PCl_5}}$$

Now $P_{PCl_5} = \frac{3-x}{4+x}P$ P = equilibrium pressure

$$= \frac{2}{5} \times 2.0 = 0.8 \text{ atm}$$

$$P_{Cl_2} = P_{PCl_3} = \frac{x}{4+x} P = \frac{1}{5} \times 2.0 = 0.4 \text{ atm}$$

$$\Rightarrow K_p = \frac{0.4 \times 0.4}{0.8} = 0.20 \text{ atm}$$

2

Note:

The inert gases like N₂ or noble gases (He, Ne etc) though do not take part in the reaction, but still they affect the degree of dissociation and equilibrium concentrations for the reactions in which $\Delta n_g \neq 0$. They add to the total pressure of the equilibrium mixture (p α n)..

Illustration - 14 At temperature T, a compound $AB_2(g)$ dissociates according to the reaction : $2AB_2(g) = 2AB(g) + B_2(g)$

with a degree of dissociation α which is small compared to the unity. Deduce the expression for α in terms of the equilibrium constant K_p and the total pressure P.

SOLUTION :

| $2AB_2(g)$ | === 2AB(g | $\mathbf{g}) + \mathbf{B}_2(\mathbf{g})$ |) | ; $\mathbf{p}_{\mathbf{B}_2} = \frac{\mathbf{a}\alpha / 2}{\mathbf{a} + \mathbf{a}\alpha / 2} \mathbf{.P}$ |
|-----------------------------|----------------------------------|--|--|---|
| Moles | AB2 | AB | B ₂ | $A = a = (1 - a) + \frac{a\alpha}{2} \approx a$ |
| Initial | а | 0 | 0 | As $a \ll 1$ $a + 2$ |
| At equilibrium | $a - a\alpha$ | aa. | <i>a</i> α/2 | $a - a\alpha \approx a$ |
| \Rightarrow Total mol | $es = n_T = a$ | $+\frac{a\alpha}{2}$ | | $\Rightarrow p_{AB} \approx \alpha P; p_{AB_2} \approx P; p_{B_2} = \frac{\alpha}{2} P$ |
| $K_p = \frac{(p_A)}{(p_A)}$ | $(p_{B_2})^2(p_{B_2})^2$ | L | | $\Rightarrow K_{p} = \frac{(\alpha P)^{2} \cdot \left(\frac{\alpha}{2}P\right)}{(P)^{2}} = \frac{\alpha^{3}}{2}P$ |
| $p_{AB} = \frac{1}{a+a}$ | $\frac{a\alpha}{-a\alpha/2}$.P; | $p_{B_2} = \frac{a}{a + a}$ | $\frac{1-\alpha\alpha}{1-\alpha\alpha/2}$ P; | $\implies \alpha = \sqrt[3]{\frac{2K_p}{P}}$ |

Illustration - 15

The equilibrium constant K_p of the reaction: $2SO_2(g) + O_2(g) = 2SO_3(g)$ is 900 at 800 K. A mixture containing SO₃ and O₂ having initial partial pressures of 1 and 2 atm. respectively heated at constant volume is allowed to equilibrate. Calculate the pratial pressures of each gas at 800 K.

SOLUTION :

Now: $2SO_2(g) + O_2 = 2SO_3(g) K_p = 900$

 \Rightarrow 2SO₃(g) \implies 2SO₂(g)

 $+O_2(g)K_p = 1/900$

and initial pressure of $SO_3 = 1$ and $O_2 = 2$ atm.

Let x be the decrease in pratial pressure of SO_3 at equilibrium.

| Partial pressure | SO3 | SO2 | 02 |
|------------------|-------|-----|---------|
| Initial | 1 | 0 | 2 |
| At equilibrium | 1 - x | x | 2 + x/2 |

$$\Rightarrow K_p = \frac{\left(P_{SO_2}\right)^2 \times PO_2}{\left(P_{SO_3}\right)}$$
$$\Rightarrow K_P = \frac{x^2 \times \left(2 + \frac{x}{2}\right)}{\left(1 - x\right)^2} = \frac{1}{900}$$

$$\Rightarrow \frac{x^2(4+x)}{2(1-x)^2} = \frac{1}{900}$$

Assume that x is very small (as $K_p \ll 1$ and O_2 is already present at the time of dissociation).

$$\Rightarrow \quad \stackrel{(4+x) \sim 4 \text{ and } (1-x) \sim 1}{x^2(4) - 1} \Rightarrow x = 1 \quad = 0.0$$

$$\Rightarrow \frac{x(4)}{2(1)^2} = \frac{1}{900} \Rightarrow x = \frac{1}{30\sqrt{2}} = 0.023$$

$$\Rightarrow P_{SO_2} = x = 0.023 atm$$

and
$$P_{SO_2} = 1 - x = 0.977$$
 atm

and
$$P_{O_2} = 2 + \frac{x}{2} = 2.0115 \ atm$$

Note: Check the correctness of your approximation. $(4+x) = (4+0.023) \sim 4$ and $(1-x) = (1-0.023) \sim 1$

SUBJECTIVE SOLVED EXAMPLES

Example - 1 H_2 and I_2 are mixed at 400°C in a 1.0 L container and when equilibrium is established, the following concentrations are present : [HI] = 0.8 M, $[H_2] = 0.08 M$ and $[I_2] = 0.08 M$. If now an additional 0.4 mol of HI are added, what are the new equilibrium concentrations, when the new equilibrium $H_2(g) + I_2(g) = 2HI(g)$ is re-established?

SOLUTION :

First determine the equilibrium constant

$$K_c$$
 for $H_2(g) + I_2(g) = 2HI(g)$

$$K_{c} = \frac{[HI]^{2}}{[H_{2}][I_{2}]} = \frac{(0.8)^{2}}{0.08 \times 0.08} = 100$$

When 0.4 mol of HI are added, equilibrium is disturbed.

At that instant, [HI] = 0.8 + 0.4 = 1.2 M

$$\Rightarrow Q > K_c$$
 since $Q = \frac{(1.2)^2}{0.08 \times 0.08} = 225$

 \Rightarrow Backward reaction dominates and the equilibrium shifts to the left.

Let 2x = concentration of HI consumed (while going left) then concentration of each of H₂ and I₂ formed = x

$$\Rightarrow [HI] = 1.2 - 2x, [H_2] = 0.08 + x,$$
$$[I_2] = 0.08 + x \text{ and } K_c = 100$$

$$\Rightarrow \quad \mathbf{K}_{c} = \frac{\left(1.2 - 2x\right)^{2}}{\left(0.08 + x\right)\left(0.08 + x\right)} = 100$$

 \Rightarrow Take square root on both side to get :

$$x = 0.033$$

Finally, the equilibrium concentrations are : $[HI] = 1.2 - 2x = 1.2 - 0.033 \times 2 = 1.13 \text{ M}$ $[H_2] = 0.08 + x = 0.08 + 0.033 = 0.11 \text{ M}$ $[I_2] = 0.08 + x = 0.08 + 0.033 = 0.11 \text{ M}$

Example - 2 0.25 mol of CO taken in a 1.5 L flask is maintained at 500 K along with a catalyst so that the following reaction can take place ; $CO(g) + H_2g = CH_3OH(g)$. Hydrogen is introduced until the total pressure of the system is 8.2 atm. at equilibrium and 0.1 mol of methanol is formed. Calculate :

(i) K_n and K_c

(ii) The final pressure if the amount of CO and H_2 as before are used but no catalyst so that the reaction does not take place.

SOLUTION:

First balance the equation as :

$$CO(g) + 2H_2(g) = CH_3OH(g)$$

$$K_C = \frac{\left[CH_3OH\right]}{\left[CO\right]\left[H_2\right]^2}$$

Let y moles of H_2 were present initially

| Moles | со | H2 | СН ₃ ОН |
|----------------|-----------------|------|--------------------|
| Initially | 0.25 | у | 0 |
| At equilibrium | 0.25 <i>- x</i> | y-2x | x |

x = 0.10 (given)

- $\Rightarrow \text{ moles of CO} = 0.25 0.10 = 0.15,$ moles of H₂ = y - 0.2 and moles of CH₃OH = 0.10
- \Rightarrow Total moles = $n_T = 0.15 + (y 0.2) + 0.10 = 0.05 + y$

Equilibrium pressure (P) = 8.2 atm

Volume of vessel (V) = 1.5 L, T = 500 K

Using the Gas equation, PV = nRT, we have :

$$n_T = \frac{PV}{RT} = \frac{8.2 \times 1.5}{0.0821 \times 500} = 0.3$$

 $\Rightarrow 0.30 = 0.05 + y \quad y = 0.25 \text{ moles}$

 \Rightarrow moles of H₂ at equilibrium = y - 0.2

$$= 0.25 - 0.2 = 0.05$$

Now find K_c as follows :

$$K_{c} = \frac{\left[CH_{3}OH\right]}{\left[CO\right]\left[H_{2}\right]^{2}} = \frac{\frac{0.10}{1.5}}{\frac{0.15}{1.5}\left(\frac{0.05}{1.5}\right)^{2}} = 600$$

Now find K_{p} using the relation :

$$K_p = K_c (RT)^{\Delta n_g}$$
$$\Delta n_g = 1 - 3 = -2$$

$$\Rightarrow K_p = 600 (0.0821 \times 500)^{-2} = 0.356$$

(ii) When no reaction takes place, then the total pressure is simply due to H_2 and CO present initially.

$$n_T = n_{(CO)} + n_{H_2} = 0.25 + 0.25 = 0.5$$

$$\Rightarrow P = \frac{nRT}{V} = \frac{0.5 \times 0.0821 \times 500}{1.5} = 13.68 \text{ atm}$$

**

Example-3 Ammonia under a pressure of 15 atm. at 27°C is heated to 327°C is a closed vessel in the presence of catalyst. Under these conditions, NH_3 partially decomposes to H_2 and N_2 . The vessel is such that the volume remains effectively constant, whereas the pressure increases to 50 atm. Calculate the % age of NH_3 actually decomposed.

SOLUTION :

Ammonia decomposes to N₂ and H₂ as follows :

$$2NH_{3}(g) = 3H_{2}(g) + N_{2}(g)$$
$$NH_{3} \longrightarrow NH_{3}$$

at 27°C at 327°C

(15 atm.) (P = ?) V remains constant

First, let us find initial pressure of NH₃ at 327°C.

$$\Rightarrow P \propto T$$
 (V is constant)

$$\Rightarrow \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow P_2 = \frac{P_1 T_1}{T_1} = \frac{15 \times 600}{300} = 30 \text{ atm}$$

| Partial pressure | NH ₃ | H ₂ | N ₂ |
|------------------|-----------------|----------------|----------------|
| Initial | 30 | 0 | 0 |
| At equilibrium | 30 <i>- x</i> | 3 <i>x</i> /2 | <i>x</i> /2 |

Now final equilibrium pressure = 50 atm

$$\Rightarrow 50=30-x+\frac{3}{2}x+\frac{x}{2} \Rightarrow x=20 \text{ atm}$$

$$\Rightarrow$$
 % NH₃ decomposed = $\frac{20}{30} \times 100 = 66.7$ %

Alternative method :

$$2NH_3(g) = 3H_2(g) + N_2(g)$$

| Moles | NH ₃ | H ₂ | N ₂ |
|----------------|-----------------|----------------|----------------|
| Initial | a | 0 | 0 |
| At equilibrium | a – aα | 3aα/2 | aα/2 |

Total mole = $a + a \alpha$ \Rightarrow

$$\frac{\text{initial moles}}{\text{final moles}} = \frac{\text{initial presseur}}{\text{final pressure}}$$
$$\frac{a}{a + a\alpha} = \frac{30}{50} \implies \alpha = \frac{20}{30}$$
% dissociation = $\frac{20}{30} \times 100 = 66.7\%$

Example - 4 Solid Ammonium carbamate dissociates as : $NH_2COONH_4(s) = 2NH_3(g) + CO_2(g)$. In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium ammonia is added such that the partial pressure of NH₃ at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure. Also find the partial pressure of ammonia gas added.

 \Rightarrow

SOLUTION:

 $NH_2COONH_4(s) = 2NH_3(g) +$ $CO_{2}(g)$ Let P = original equilibrium pressure,

From the mole ratio of NH₃ and CO₂ at equilibrium, we have ;

$$P_{NH_3} = \frac{2}{3}P \text{ and } P_{CO_2} = \frac{P}{3}$$
$$\Rightarrow \quad K_P + \left(P_{NH_3}\right)^2 \cdot P_{CO_2}$$
$$= \left(\frac{2}{3}P\right)^2 \left(\frac{P}{3}\right) = \frac{4}{27}P^3$$

Now NH₃ is added such that , $P_{NH_3} = P$ Find the pressure of CO_2 .

$$\Rightarrow \quad \frac{4}{27} P^3 = P^2_{P_{CO_2}} \Rightarrow \quad P_{CO_2} = \frac{4}{27} P$$

Total new pressure = $P_{new} = P_{NH_3} + P_{CO_2}$

$$\Rightarrow P_{New} = P + \frac{4}{27}P = \frac{31}{27}P$$

$$\Rightarrow \qquad \text{Ratio} = \frac{P_{New}}{P_{original}} = \frac{\frac{31}{27}P}{P} = \frac{31}{27}$$

Let x be the partial pressure of NH_3 added at original equilibrium.

$$NH_2COOHNH_4(s) \longrightarrow NH_3(g) + CO_2(g)$$

At eq : $\frac{2}{3}P = \frac{1}{3}P$

At eq:

When NH3 is added : $\frac{2}{3}P + x = \frac{1}{3}P$

At new eq:
$$\frac{2}{3}P + x - 2y = \frac{1}{3}P - y$$

$$\Rightarrow \qquad \frac{2}{3}p + x - 2y = P_{NH_3}$$
$$= P \text{ and } \frac{1}{3}P - y = P_{CO_2} = \frac{4}{27}P$$

$$\Rightarrow$$
 Solve to get : $x = \frac{19}{27} P$

Solved Examples

Example - 5 Two solids X and Y dissociates into gaseous products at a certain temperature as follows :

X(s) = A(g) + C(g), and Y(s) = B(g) + C(g). At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 80 mm. Calculate.

- (a) the value of K_{p} for two reactions.
- (b) the ratio of moles of A and B in the vapour state over a mixture of X and Y.
- (c) the total pressure of gases over a mixture of X and Y.

SOLUTION :

**

(a) X(s) = A(g) + C(g)

At equilibrium, A and C are in equal proportions, so their pressures will be same.

 $p_A = p_C$

Also $p_A + p_C = 40 \implies p_A = p_C = 20 \text{ mm}$

$$\Rightarrow$$
 K_P = p_A.p_C = 20² = 400 mm²

Similarly for Y(s) = B(g) + C(g),

$$P_{B} = P_{C} = 40 \, \text{mm} (P_{B} + P_{B} = 80)$$

- \Rightarrow K_P = P_B.P_C = 40² = 1600 mm²
- (b) Now for a mixture of X and Y, we will have consider both the equilibrium simultaneously.

$$X(s) \longrightarrow A(g) + C(g)$$

and $Y(s) \longrightarrow B(g) + C(g)$

Let
$$p_A = a \text{ mm}, p_B = b \text{ mm}$$

Not that the pressure of C due to dissociation of X will also be *a* mm and similarly the ressure of C due to dissociation of Y will also be *b* mm. $\Rightarrow p_B = (a + b) \text{ mm}$ $K_p (\text{for } X) = p_A \cdot p_C = a(a + b) = 400 \dots (i)$ $K_p (\text{for } Y) = p_B \cdot p_C = b(a + b) = 1600 \dots (ii)$

Form (i) and (ii), we get :

$$\frac{a}{b} = \frac{1}{4}$$

as volume and temperature are constant, the mole ratio will be same as the pressure ratio.

(c) The total pressure $= P_T = p_A + p_B + p_C$

$$=a+b+(a+b)=2(a+b)$$

Adding (i) and (ii),

$$a + b = \sqrt{K_{PX} + K_{PY}} = \sqrt{2000} = 20\sqrt{5} \text{ mm}$$

 \Rightarrow Total pressure = 2 (a + b) = 89.44 mm

**

Example - 6 Consider the equilibrium : $P(g) + 2Q(g) \longrightarrow R(g)$. When the reaction between P and Q is carried out at a certain temperature, the equilibrium concentrations of P and Q are 3 M and 4 M respectively. When the volume of the vessel is doubled and equilibrium is allowed to re-established, the concentration of Q is found to be 3 M. Find the :

- (a) Value of K_c
- (b) Concentration of R at two equilibrium stages.

SOLUTION :

$$P(g) + 2Q(g) \longrightarrow R(g)$$

at equilibrium, [P] = 3 M, [Q] = 4 M and let [R] = x M,

$$K_{C} = \frac{[R]}{[P][Q]^{2}} = \frac{x}{3 \times 4^{2}} = \frac{x}{48}$$
 ...(i)

Now the volume is doubled, hence the concentrations are halved and a new equilibrium will re-established with same value of K_c . Calculate Q and determine the direction of equilibrium.

$$Q = \frac{[R]}{[P][Q]^2} = \frac{x/2}{(3/2)(4/2)^2} = \frac{x}{12}$$

 $\Rightarrow Q > K_c \text{ Hence the system will} \\ \text{predominately move in backward direction} \\ \text{so as to achieve new equilibrium state. Let} \\ \text{y M be the decrease in concentration of R.} \end{cases}$

| Concentrations | Р — | Q | R |
|--------------------|---------|--------|-----------------|
| Initially | 1.5 | 2 | x/2 |
| At new equilibrium | 1.5 + y | 2 + 2y | <i>x</i> /2 – y |

Given : [Q] = 3 M at new equilibrium

- \Rightarrow 2+2y=3 \Rightarrow y=0.5 M
- \Rightarrow At new equilibrium, [P] = 1.5 + 0.5 = 2 M;

$$[Q] = 3 M (given); [R] = x/2 - 0.5 M$$

$$\Rightarrow Q = \frac{[R]}{[P][Q]^2} = \frac{(x/2 - 0.5)}{(2)(3)^2}$$

Equating this value of K_{C} with (i)

$$\Rightarrow \frac{(x/2-0.5)}{(2)(3)^2} = \frac{x}{48} \Rightarrow x = 4M$$

Hence [R] = 4 M and

at new equilibrium [R] = x/2 - 0.5 = 1.5 M

and
$$K_{C} = \frac{x}{48} = \frac{1}{12}$$

**

Example - 7 The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.6 M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic condition, when 0.1 mol each of H, and I, are heated at 440 K in a closed vessel of capacity 2.0 L.

SOLUTION :

First find the value of K_c for dissociation of HI from its degree of dissociation.

$$2 \operatorname{HI}(g) = H_2(g) + I_2(g)$$

(degree of dissociation is 0.8)

| Concentrations | н | H ₂ | I ₂ |
|--------------------|--------|----------------|----------------|
| Initially | a | 0 | 0 |
| At new equilibrium | a – aα | aα/2 | aα/2 |

$$K_{C} = \frac{[H_{2}][I_{2}]}{[HI]^{2}} = \frac{(a\alpha/2)(a\alpha/2)}{(a-a\alpha)^{2}} = \frac{\alpha^{2}}{4(1-\alpha)^{2}}$$

Here
$$\alpha = 0.8 \Rightarrow K_{C} = \frac{0.8^{2}}{4(1-0.8)^{2}} = 4$$

Now we have to start with 0.1 mol each of H_2 and I_2 and the following equilibrium will be established.

| Moles | H2 | l ₂ | н |
|--------------------|---------|----------------|------------|
| Initially | 0.1 | 0.1 | 0 |
| At new equilibrium | 0.1 - x | 0.1 - x | 2 <i>x</i> |

$$\Rightarrow K_{C} = \frac{[HI]^{2}}{[H_{2}][I_{2}]} = \frac{(2x/V)^{2}}{\underbrace{(0.1-x)}_{V} - \underbrace{(0.1-x)}_{V}} = \frac{1}{4}$$

 $\Rightarrow x = 0.02$

Now find the moles of I_2 left un-reacted at equilibrium.

$$n(I_2)=0.1-0.02=0.08$$

 I_2 reacts with sodium thiosulphate (Na₂S₂O₃) as follows :

Applying the mole concept, we have,

2 moles of $Na_2S_2O_3 \equiv 1$ mole of I_2

 \Rightarrow 0.08 mole of I₂ = 2×0.08

$$= 0.16$$
 moles of Na₂S₂O₃

$$\Rightarrow$$
 Moles = MV₁

 $(M = molarity, V_{L} = volume in litres)$

$$\Rightarrow 0.16 = 1.6 V_{I}$$

$$\Rightarrow$$
 V_L = 0.1 L = 100 mL

**

Example - 8 At 25°C and 1 atm, N_2O_4 dissociates by the reaction $N_2O_4(g) = 2NO_2(g)$ If it is 35% dissociated at given condition, find the volume of above mixture will diffuse if 20 ml of pure O_2 diffuses in 10 minutes at same temperature and pressure.

SOLUTION :

For equilibrium system,

 $N_2O_4(g) = 2NO_2(g),$

| Moles | N ₂ O ₄ | NO 2 | |
|----------------|-------------------------------|--------------|--|
| Initial | а | | |
| At equilibrium | $a - a\alpha$ | 2 <i>a</i> α | |

 \Rightarrow Total moles at equilibrium = a + a α

$$p_{N_2O_4} = \frac{a - a\alpha}{a + a\alpha} P \text{ and } p_{NO_2} = \frac{2a\alpha}{a + a\alpha} P$$

Here P = 1.0 atm and

$$K_{p} = \frac{p_{NO_{2}}^{2}}{p_{N_{2}O_{4}}} = \frac{4a^{2}p}{1-\alpha^{2}} [\alpha = 0.35]$$

$$\Rightarrow K_{p} = \frac{4 \times (0.35)^{2}}{1 - (0.35)^{2}} \times 1 = 0.56 \text{ atm}$$

Using
$$\frac{a+a\alpha}{a} = \frac{M_{\text{mix},i}}{M_{\text{mix},f}} = \frac{M_{\text{N}_2\text{O}_4}}{M_{\text{mix},f}}$$

$$\Rightarrow 1+0.35 = \frac{92}{M_{\text{mix},\text{f}}}$$

$$M_{\rm mix,f} = \frac{92}{1.35} = 68.15$$

Let V(ml) volume of mixture diffused in.

From Graham's law of diffusion.

$$\frac{r_{O_2}}{r_{mix,f}} = \sqrt{\frac{M_{mix,f}}{M_{O_2}}}$$
$$\frac{20/10}{V/10} = \sqrt{\frac{68.15}{32}} \Rightarrow V = 13.70 \,\text{ml}$$

Evonal

Example - 9

value of K_c .

For the reaction $MH_3(g) = \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g);$

Show that the degree of dissociation of NH_3 is given as $\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{P}{K_p}\right]^{-1/2}$ where P is the equilibrium pressure and α is the degree of dissociation. If K_p of the above reaction is 82.1 atm at 727°C, determine the

SOLUTION :

Let α be the degree of dissociation of $NH_3(g)$.

$$NH_{3}(g) = \frac{1}{2}N_{2}(g) + \frac{3}{2}H_{2}(g)$$

Initial moles 1 0 0
At equilibrium $1-\alpha \quad \alpha/2 \quad 3\alpha/2$
Total number of moles at equilibrium $=1+\alpha$
Now,

$$p_{\rm NH_3} = \frac{1-\alpha}{1+\alpha} P, p_{\rm N_2} = \frac{\alpha/2}{1+\alpha}$$

and
$$p_{\rm H_2} = \frac{3\alpha/2}{1+\alpha} P$$
$$K_p = \frac{\left(p_{\rm N_2}\right)^{1/2} \left(p_{\rm H_2}\right)^{3/2}}{p_{\rm NH_3}}$$

$$\Rightarrow \frac{\left[\frac{\alpha}{2(1+\alpha)}P\right]^{1/2}\left[\frac{3\alpha}{2(1+\alpha)}P\right]}{\frac{1-\alpha}{1+\alpha}\times P}$$

$$= \left[\frac{3\sqrt{3}P}{4}\right] \left[\frac{\alpha^2}{1-\alpha^2}\right]$$
$$\Rightarrow \quad \frac{1-\alpha^2}{\alpha^2} = \frac{3\sqrt{3}}{4} \frac{P}{K_p}$$
$$\Rightarrow \quad \frac{1}{\alpha^2} = \left[1 + \frac{3\sqrt{3}}{4} \frac{P}{K_p}\right]$$
or
$$\alpha = \left[1 + \frac{3\sqrt{3}}{4} \frac{P}{K_p}\right]^{-1/2}$$

 Δn_g , change in number of the moles of the given reaction = +1

$$K_P = K_C (RT)^{\Delta n_g} \Longrightarrow K_C = K_P (RT)^{-\Delta n_g}$$
$$\Longrightarrow K_C = 82.1 \times [0.0821 \times 1000]^{-1} = 1.0 \text{ mol/ L}$$

| THINGS TO REMEMBER | | | | |
|--------------------|-------------|--|--|--|
| 1. | To p Use | redict the net direction of a system, calculate Q and compare it with its K_{eq} . : Q < K_{eq} (Forward reaction) ; Q > K_{eq} (Backward reaction) Q = K_{eq} (No net reaction i.e. system is at equilibrium) | | |
| 2. | 2. | Le Chatelier's Principle : (↑ : increases ; ↓ decreases) | | |
| | (i) | T^{\uparrow} Reaction is shifted in a direction where energy is getting absorbed $\overrightarrow{HT^{\circ}}$ Forward Reaction $\overrightarrow{HT^{\circ}}$ Backward Reaction | | |
| | | $T\downarrow \Rightarrow$ Reaction is shifted in a direction where energy is getting absorbed $H\downarrow^20$ Forward Reaction $H\downarrow^20$ Forward Reaction $H\downarrow^20$ Backward Reaction | | |
| | (ii) | P [↑] : Reaction is shifted in a direction where $\Delta n_g < 0$ | | |
| | | $P\downarrow$: Reaction is shifted in a direction where $\Delta n_g > 0$ | | |
| | (iii) | Inert gas addition : | | |
| | | Constant V : No effect | | |
| | (iv) | Constant P: Reaction is shifted in a direction where $\Delta n_g > 0$ V^{\uparrow} : Reaction is shifted in a direction where $\Delta n_g > 0$ | | |
| | (1V) | $V \downarrow$: Reaction is shifted in a direction where $\Delta n_g < 0$ | | |
| | (v) | Melting (with increase in volume e.g. $S(s) = S(l)$ | | |
| | | $P\downarrow \Rightarrow$ More melting; $T\uparrow \Rightarrow$ More melting | | |
| | | $P^{\uparrow} \Rightarrow$ Less melting $T^{\downarrow} \Rightarrow$ Less melting | | |
| | | Melting (with decrease in volume) e.g. Ice water | | |
| | | $P\downarrow \Rightarrow$ Less melting ; T↑ \Rightarrow More melting | | |
| | | $P^{\uparrow} \Rightarrow$ More melting; $T^{\downarrow} \Rightarrow$ Less melting | | |
| | | (Note that Melting is endothermic process) | | |
| | 3. | Degree of dissociation and Density : | | |
| | | $\frac{n_i}{n_f} = \frac{M_{mix,f}}{M_{mix,i}} = \frac{d_f}{d_i}$ | | |
| | | $= \left(\frac{1}{1+\alpha} \text{ for a sample reaction } : \mathcal{X}(g) \longrightarrow \mathcal{Y}(g) + \mathcal{Z}(g)\right)$ | | |

4. Whenever an approximation is applied, always check for approximations assumed before finalizing the answer.

Things to Remember