


Chemical equilibrium



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.

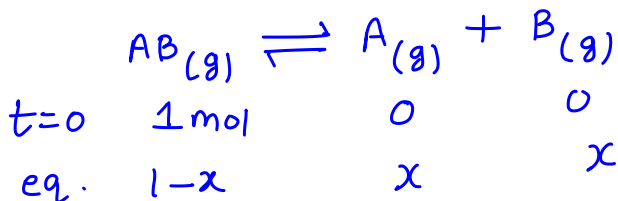
(A) 0.45

(B) 0.30

(C) 0.60

~~(D) 0.90~~

Solⁿ →



$$P_{AB} = \frac{1-x}{1+x} \times P$$

$$P_A = P_B = \frac{x}{1+x} \times P$$

$$K_p = \frac{P_A \cdot P_B}{P_{AB}} = \frac{\frac{x}{1+x} \times P \cdot \frac{x}{1+x} \times P}{\frac{1-x}{1+x} \times P}$$

$$= \frac{x^2 P}{1-x^2} = 4P$$

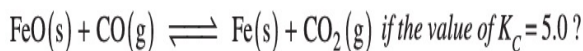
$$x^2 = 4 - 4x^2$$

$$5x^2 = 4$$

$$x = \frac{2}{\sqrt{5}} = 0.894 = 0.9 \text{ mol}$$

$$n_A = x = 0.9 \text{ mol}$$

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



☒ (A)

0.125 M

☐ (B)

0.0125 M

☐ (C)

1.25 M

☐ (D)

12.5

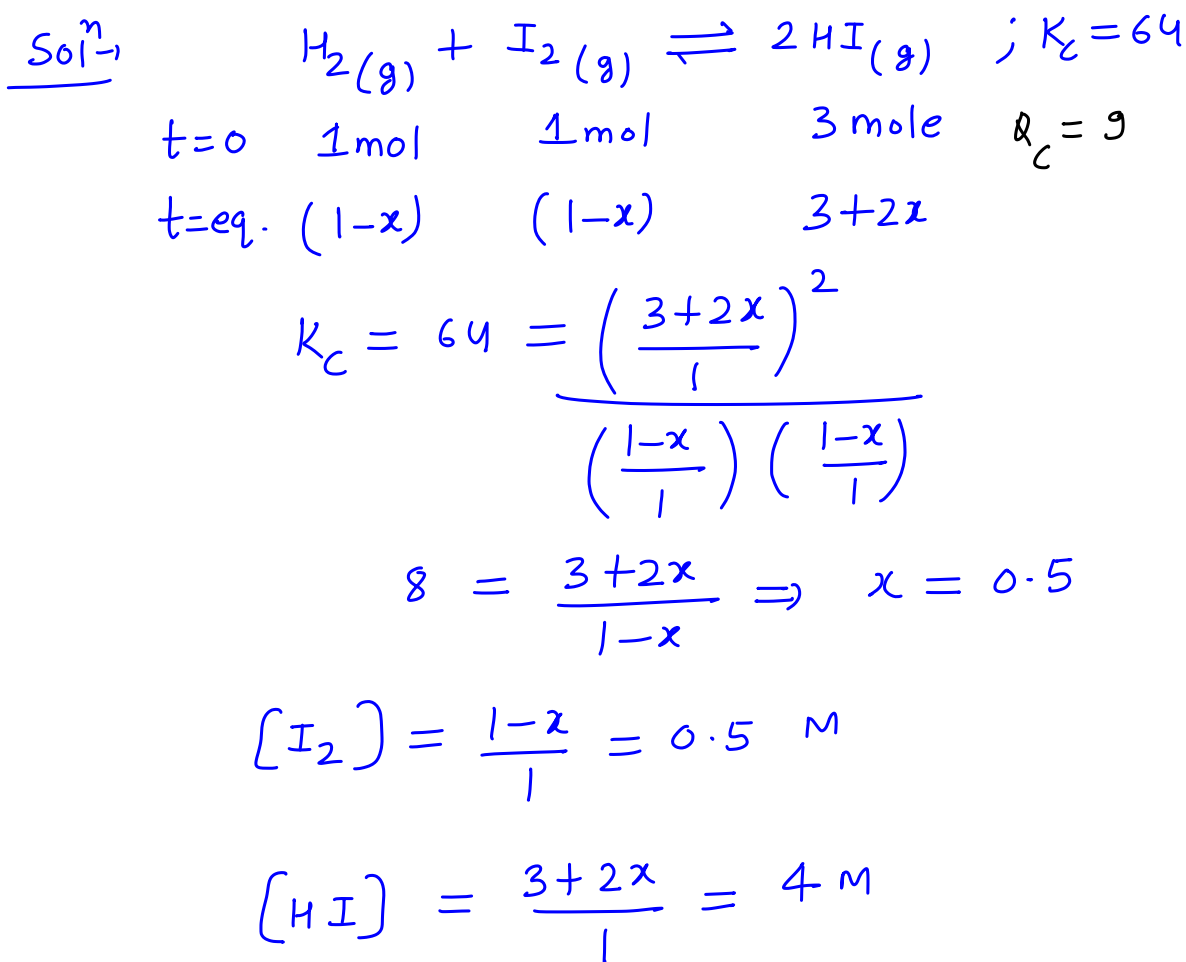
Solⁿ →

$$K_c = \frac{[\text{CO}_2]_{eq}}{[\text{CO}]_{eq}} = 5$$

$$\frac{[\text{CO}_2]_{eq}}{0.025} = 5 \Rightarrow [\text{CO}_2]_{eq} = 0.125 \text{ M}$$

Illustration - 4

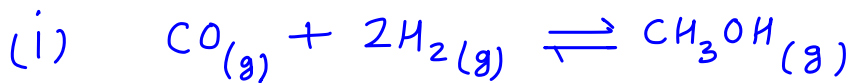
The value of K_c for the reaction : $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$ is 64 at 773 K. If one mole of H_2 , one mole of I_2 and three moles of HI are taken in a 1L flask, find the concentrations of I_2 and HI at equilibrium at 773 K.



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 ; $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$. 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_p and K_c
- (ii) The final pressure if the same amount of CO and H_2 as before are used but no catalyst so that the reaction does not take place.

Solⁿ →



$$t=0 \quad 0.25 \text{ mol} \quad a \text{ mol} \quad 0$$

$$t=eq. \quad (0.25-x) \quad (a-2x) \quad x \text{ mol} \\ = 0.15 \quad = (a-0.2) \quad = 0.1 \text{ mol}$$

$$(n_{\text{Total}})_{eq} = 0.15 + (a-0.2) + 0.1 \\ = (a+0.05)$$

$$PV = nRT$$

$$8.2 \times 1.5 = (a+0.05) \times 0.082 \times 500$$

$$a = 0.25 \text{ mol}$$

$$K_c = \frac{\left(\frac{0.1}{1.5}\right)}{\left(\frac{0.15}{1.5}\right)^1 \left(\frac{0.05}{1.5}\right)^2} = 600 \text{ M}^{-2}$$

$$K_p = K_c (RT)^{\Delta n_g} \\ = 600 (0.0821 \times 500)^{-2} \text{ atm}^{-2}$$

$$(ii) \quad n_{\text{Total}} = n_{CO} + n_{H_2} \\ = 0.25 + 0.25 = 0.5 \text{ mol}$$

$$PV = nRT$$

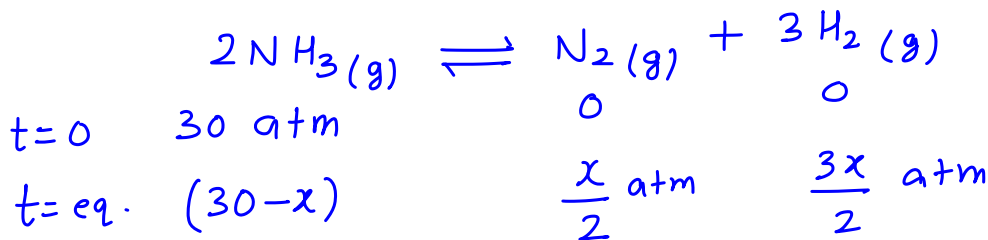
$$P \times 1.5 = 0.5 \times 0.0821 \times 500$$

$$P = 13.68 \text{ atm}$$

Example - 3 Ammonia under a pressure of 15 atm. at 27°C is heated to 327°C in 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.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{15}{300} = \frac{P_2}{600}$$

$$\Rightarrow P_2 = 30 \text{ atm}$$

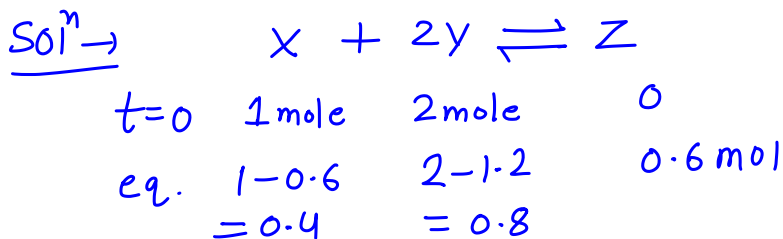


$$30 - x + \frac{x}{2} + \frac{3x}{2} = 50$$

$$x = 20$$

$$\begin{aligned} \% \text{ NH}_3 \text{ decomposed} &= \frac{20}{30} \times 100 \\ &= 66.67\% \end{aligned}$$

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?



$$K_c = 0.35 = \frac{\left(\frac{0.6}{V}\right)}{\left(\frac{0.4}{V}\right) \left(\frac{0.8}{V}\right)^2}$$

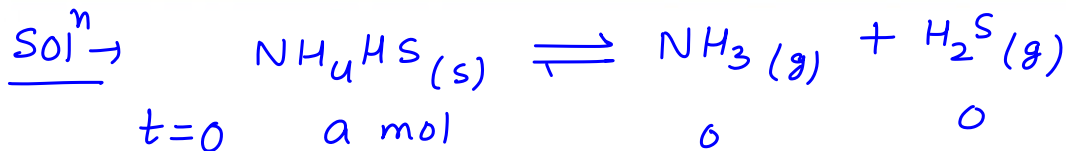
$$V = 0.39 \text{ lit.}$$

$$PV = nRT$$

$$P \times 0.39 = 1.8 \times 0.0821 \times 473$$

$$P = 179.23 \text{ atm}$$

Illustration - 2 Solid $NH_4HS(s)$ (Ammonium hydrogen **Sulphide**) 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.



eq. $a-x$ $x \text{ mol}$ $x \text{ mol}$

$$\text{Total moles at eq.} = x + x = 2x \text{ mol}$$

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{x}{2x} \times P = \frac{P}{2} \text{ atm}$$

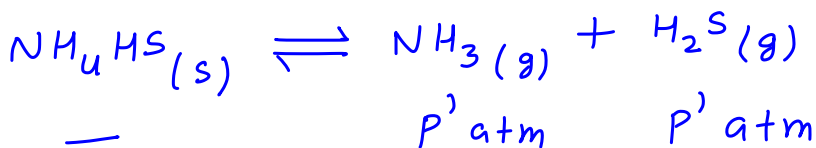
$$K_p = 0.34 = \frac{P}{2} \times \frac{P}{2}$$

$$P = 1.17 \text{ atm}$$

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{P}{2} = 0.585 \text{ atm}$$

method -2

t = eq.



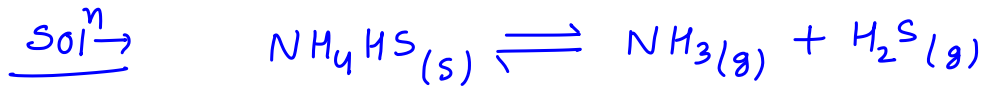
$$K_p = 0.34 = P' \cdot P'$$

$$\Rightarrow P' = 0.58 \text{ atm}$$

$$\begin{aligned} \text{Total Pressure at eq.} &= 2P' \\ &= 1.16 \text{ atm} \end{aligned}$$

81. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask when the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH_4HS decomposition at this temperature is :

(A) 0.11 atm^2 (B) 0.17 atm^2 (C) 0.18 atm^2 (D) 0.30 atm^2



$t=0$ ————— 0.5 atm 0

$eq.$ ————— $(0.5 + P)$ P

$$0.5 + P + P = 0.84$$

$$P = 0.17 \text{ atm}$$

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}}$$

$$= 0.67 \times 0.17 = 0.1139 \text{ atm}^2$$

10. $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, $K_c = 4$. This reversible reaction is studied graphically as shown in the given figure. Select the correct statements out of I, II and III.

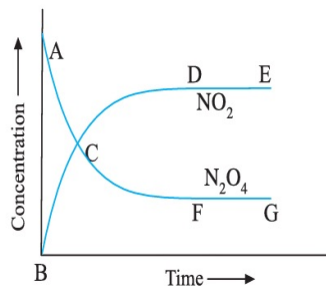
I: Reaction quotient has maximum value at point A

II: Reaction proceeds left to right at a point when $[\text{N}_2\text{O}_4] = [\text{NO}_2] = 0.1 \text{ M}$

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

(A) I, II ✓ (B) II, III

(C) II ✓ (D) I, II, III



Solⁿ → (I) at Point A : $[\text{N}_2\text{O}_4] = \text{Max}$

$$[\text{NO}_2] = 0$$

$$Q = 0 \text{ (min.)}$$

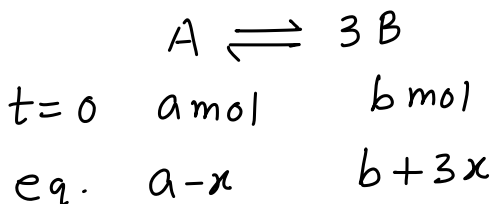
$$(II) \quad Q_c = \frac{(0.1)^2}{0.1} = 0.1, \quad K_c = 4$$

$$Q_c < K_c \Rightarrow \text{Forward direction}$$

(III) at point D or F (eq. is established)

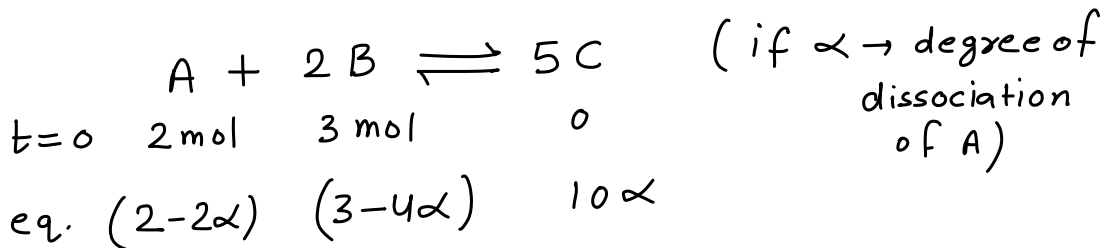
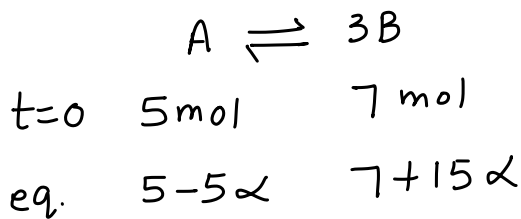
$$\Rightarrow Q = K_{eq} \Rightarrow Q_c = K_c$$

Degree of dissociation (α) \rightarrow It is the ratio of no. of dissociated moles of a reactant and no. of initial moles.

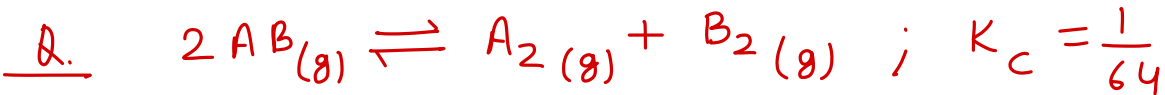


$$\boxed{\alpha = \frac{x}{a}} \Rightarrow x = a\alpha$$

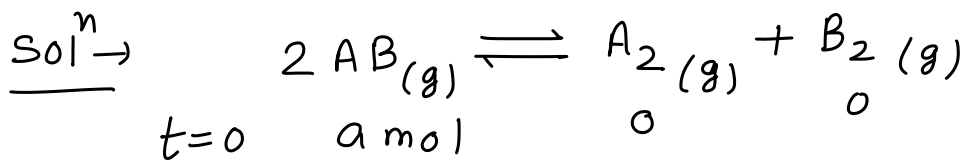
% dissociation = 100α



$$\text{Degree of dissociation of B} = \frac{4\alpha}{3}$$



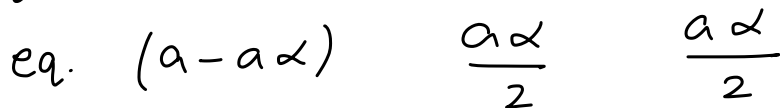
Find the % dissociation of $AB_{(g)}$?



$t=0$ $a \text{ mol}$

0

0



$$K_c = \frac{1}{64} = \frac{\left(\frac{a\alpha}{2v}\right)^1 \left(\frac{a\alpha}{2v}\right)^1}{\left(\frac{a - a\alpha}{v}\right)^2}$$

$$\frac{1}{8} = \frac{\alpha}{2(1-\alpha)}$$

$$4\alpha = 1 - \alpha$$

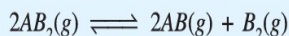
$$\Rightarrow 5\alpha = 1$$

$$\alpha = 0.2$$

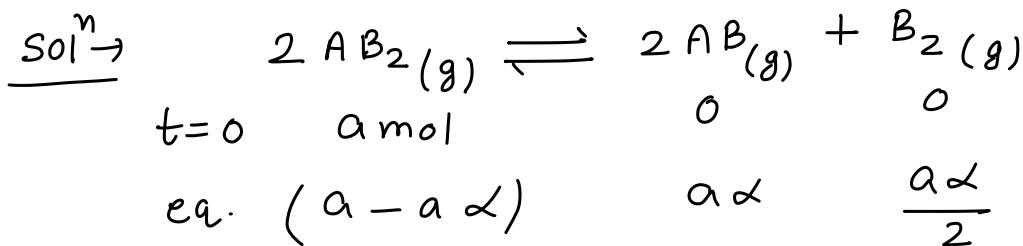
$$\begin{aligned} \% \text{ dissociation of } AB &= 0.2 \times 100 \\ &= 20\% \end{aligned}$$

Illustration - 14

At temperature T , a compound $AB_2(g)$ dissociates according to the reaction :



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 .



$$\begin{aligned} \text{Total moles at eq.} &= a - a\alpha + a\alpha + \frac{a\alpha}{2} \\ &= a \left(1 + \frac{\alpha}{2} \right) \simeq a \end{aligned}$$

$$\begin{aligned} \text{If } \alpha \ll 1 \Rightarrow \quad &1 - \alpha \simeq 1 \\ &1 + \alpha \simeq 1 \\ &1 + \frac{\alpha}{2} \simeq 1 \end{aligned}$$

$$P_{AB_2} = \frac{a(1-\alpha)}{a\left(1+\frac{\alpha}{2}\right)} \times P \simeq P$$

$$P_{AB} = \frac{a\alpha}{a\left(1+\frac{\alpha}{2}\right)} \times P \simeq \alpha P$$

$$P_{B_2} = \frac{a\alpha/2}{a\left(1+\frac{\alpha}{2}\right)} \times P \simeq \frac{\alpha P}{2}$$

$$K_p = \frac{P_{AB}^2 \cdot P_{B_2}^1}{P_{AB_2}^2} = \frac{(\alpha P)^2 \left(\frac{\alpha P}{2} \right)}{P^2}$$

$$K_p = \frac{\alpha^3 P}{2}$$

122. The degree of dissociation of I_2 molecule at 1000°C and under 1.0 atmospheric pressure is 40% by volume. If the dissociation is reduced to 20% at the same temperature, the total equilibrium pressure on the gas will be :

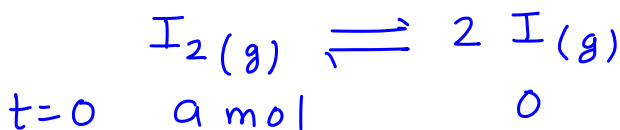
(A) 1.57 atm

(B) 2.57 atm

(C) 3.57 atm

✓ (D) 4.57 atm

Solⁿ →



t=0 a mol 0

eq. 0.6 a mol 0.8 a mol

$$K_p = \frac{P_I^2}{P_{I_2}} = \frac{\left(\frac{0.8a}{1.4a} \times 1 \right)^2}{\left(\frac{0.6a}{1.4a} \times 1 \right)^1}$$

$$K_p = 0.76$$



t=0 a mol 0

eq. (0.8a) 0.4 a

$$K_{P_2} = \frac{\left(\frac{0.4a}{3+2a} x P \right)^2}{\left(\frac{0.8a}{3+2a} x P \right)} = \frac{P}{6}$$

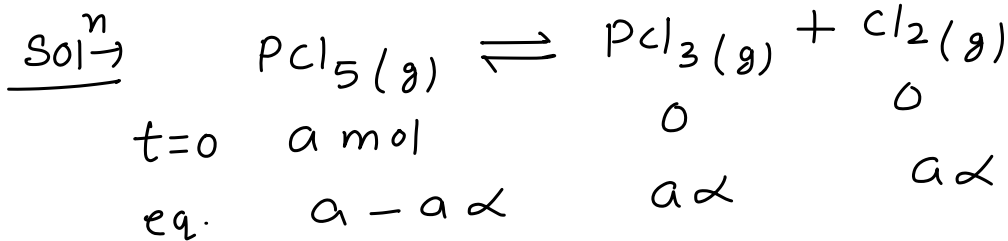
$$K_{P_1} = K_{P_2}$$

$$0.76 = \frac{P}{6} \Rightarrow P = 4.56 \text{ atm}$$



If $\alpha \ll 1$ then deduce the expression

b/w K_p, α and total pressure (P) ?

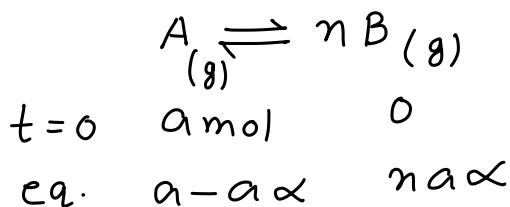


$$P_{\text{PCl}_3} = P_{\text{Cl}_2} = \frac{a\alpha}{a(1+\alpha)} \times P \simeq \alpha P$$

$$P_{\text{PCl}_5} = \frac{a(1-\alpha)}{a(1+\alpha)} \times P \simeq P$$

$$K_p = \frac{\alpha \cancel{p} \times \alpha p}{\cancel{p}} \Rightarrow K_p = \alpha^2 p$$

Degree of dissociation (α) in terms of vapour density or molar mass \rightarrow



$$\frac{(n_{\text{Total}})_{\text{eq.}}}{(n_{\text{Total}})_{t=0}} = \frac{a - a\alpha + na\alpha}{a + 0}$$

$$= 1 - \alpha + n\alpha = \frac{\left(\frac{\cancel{W}}{M_{\text{eq.}}} \right)}{\left(\frac{\cancel{W}}{M_{t=0}} \right)}$$

$$1 - \alpha + n\alpha = \frac{M_{t=0}}{M_{t=\text{eq.}}} = \frac{M_{\text{theo.}} (M_t)}{M_{\text{obs.}} (M_o)}$$

$$\frac{M_t}{M_o} = 1 - \alpha + n\alpha$$

$$\frac{M_t}{M_o} = 1 + \alpha(n-1)$$

$$\alpha(n-1) = \frac{M_t}{M_o} - 1$$

$$\Rightarrow \alpha = \frac{M_t - M_o}{M_o(n-1)}$$

where M_t = theoretical molar mass
(molar mass of initial mix.)

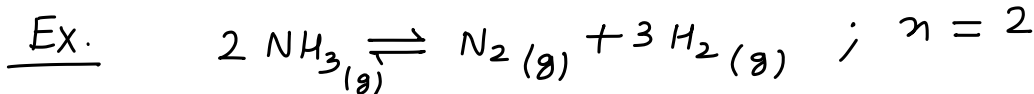
M_o = observed molar mass
(molar mass of eq. mix.)

$$V.D. = \frac{M}{2} \Rightarrow \alpha = \frac{d_t - d_o}{d_o(n-1)}$$

where d_t = theoretical V.D.

d_o = observed V.D.

n = no. of moles of gaseous products
obtained by 1 mol gaseous reactant



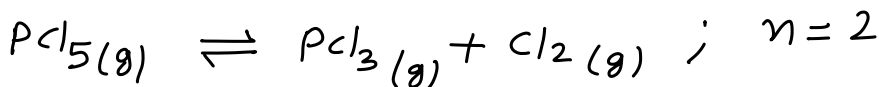
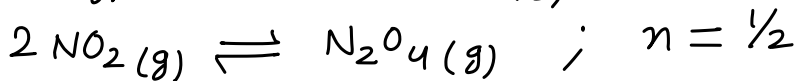
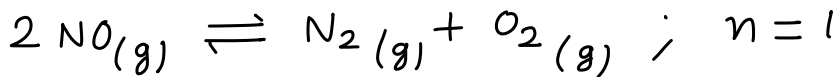
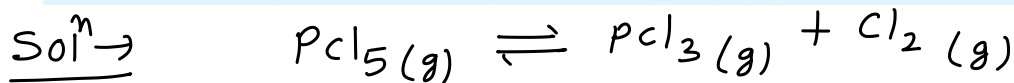


Illustration - 10 When PCl_5 is heated, it dissociates into PCl_3 and Cl_2 . The vapor density of the gas mixture at 200°C and at 250°C is 70 and 58 respectively. Find the degree of dissociation at two temperatures.



(i) $T = 200^\circ\text{C}$ $\alpha = \frac{d_t - d_0}{d_0(n-1)}$

$$\alpha = \frac{\left(\frac{208.5}{2} \right) - 70}{70(2-1)} = 0.49$$

(ii) $T_2 = 250^\circ\text{C}$

$$\alpha = \frac{\left(\frac{208.5}{2} \right) - 58}{58(2-1)} \simeq 0.8$$

109. The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.

(A)

53.5%

(B)

60%

(C)

74.5%

(D)

64.5%



Solⁿ →



$$\alpha = \frac{\left(\frac{92}{2}\right) - 30}{30(2-1)} = 0.5333$$

$$\% \text{ dissociation} = 53.33\%$$

Q.

If α is 0.4 at 400 K and 1 atm for the gaseous rxn, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ calculate density of eq. mix. at 1 atm pressure?

Solⁿ →

$$\alpha = 0.4 = \frac{M_t - M_0}{M_0(n-1)}$$

$$0.4 = \frac{(208.5) - M_0}{M_0(2-1)}$$

$$M_0 = 148.93$$

$$p = \frac{d}{M} RT$$

$$1 = \frac{d}{148.93} \times 0.0821 \times 400$$

$$d = \frac{148.93}{0.0821 \times 400}$$

$$d = 4.535 \text{ g/L}$$

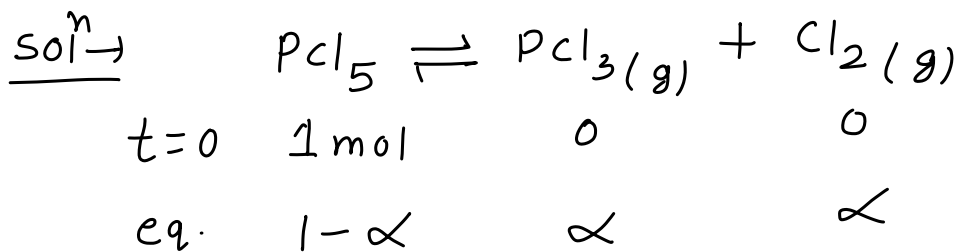
Physical significance of K_{eq} \longrightarrow

- (1) $K_{eq} < 10^{-3} \Rightarrow$ Very less conversion of reactant into Product.
- (2) $K_{eq} > 10^3 \Rightarrow$ almost 100% conversion of reactant into Product
- (3) $10^{-3} < K_{eq} < 10^3 \Rightarrow$ appreciable conc. of reactant and Product are present in eq. mix.

Q. Calculate the eq. conc. of PCl_3 and PCl_5 in a 10 lit. rigid container if 1 mole of $PCl_5(g)$ is taken to attain eq.

according to gaseous Rxⁿ $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$(i) \quad K_c = 10^{-5} \text{ at } 250 \text{ K}$$



$$K_c = 10^{-5} = \frac{\frac{\alpha}{10} \times \frac{\alpha}{10}}{\frac{1-\alpha}{10}}$$

$$\therefore K_c = 10^{-5} < 10^{-3} \Rightarrow \alpha < 1 \Rightarrow 1-\alpha \simeq 1$$

$$10^{-5} = \frac{\frac{\alpha}{10} \times \frac{\alpha}{10}}{\frac{1}{10}}$$

$$\alpha = 10^{-2}$$

$$[\text{PCl}_3]_{\text{eq}} = \frac{\alpha}{10} = 10^{-3} \text{ M}, \quad [\text{PCl}_5]_{\text{eq}} = \frac{1-\alpha}{10} \simeq 10^{-1} \text{ M}$$

$$(ii) \quad K_c = 10^{-2} \text{ at } 400 \text{ K}$$

$$K_c = 10^{-2} = \frac{\frac{\alpha}{10} \cdot \frac{\alpha}{10}}{(1-\alpha)/10}$$

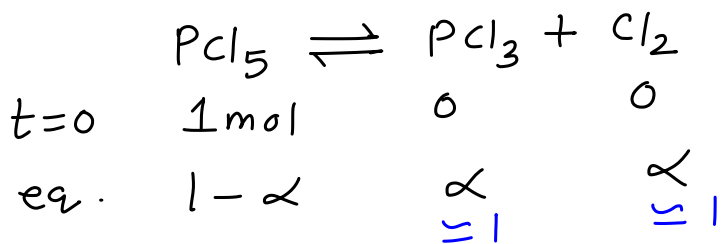
$$0.1 = \frac{\alpha^2}{1-\alpha}$$

$$\alpha^2 + 0.1\alpha - 0.1 = 0$$

$$\alpha = \frac{-0.1 + \sqrt{0.01 + 0.4}}{2} = 0.27$$

$$[PCl_3]_{eq} = \frac{\alpha}{10} = 0.027 M, [PCl_5]_{eq} = \frac{1-\alpha}{10} = 0.073 M$$

(iii) $K_c = 10^5$ at 700 K



$$K_c = 10^5 \Rightarrow \alpha \simeq 1$$

$$K_c = 10^5 = \frac{\frac{1}{10} \times \frac{1}{10}}{[PCl_5]_{eq}}$$

$$[PCl_5]_{eq} = 10^{-7} M, [PCl_3]_{eq} = \frac{1}{10} = 0.1 M$$

Homework

DTS- 1-11

Q.1,4,18,29,46,48,49,51,76,77,79,81,84,87,93,95,100,
103,105-111,118,122,126-128,130-133,135-139

JEE MAIN ARCHIVE

Q.2,3,6,14,16,17

JEE ADVANCED ARCHIVE

Q.19-22,27,28