## HINTS & SOLUTIONS

**4.** Molar conc. $= \dfrac{\text{no. of moles of } O_2}{\text{volume (in litre)}} = \dfrac{96}{32} \times \dfrac{1}{2} = 1.5\,M$
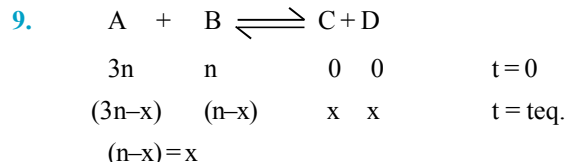
**5.** At equilibrium rates of backward and forward reactions become equal.

**6.** $K_C = \dfrac{\left[\dfrac{C}{V}\right]^2}{\left[\dfrac{B}{V}\right]\left[\dfrac{A}{V}\right]^3} \Rightarrow 9 = \dfrac{\left[\dfrac{2}{V}\right]^2}{\left[\dfrac{2}{V}\right]\left[\dfrac{2}{V}\right]^3} \Rightarrow V = 6\,L$
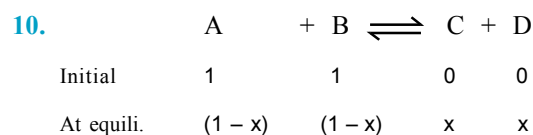
**8.** $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$  $\qquad K_c = \dfrac{K_1}{K_2} = \dfrac{b+x}{a-x}$

$a - x \quad b + x \qquad x = \dfrac{K_1 a - K_2 b}{K_1 + K_2}$

Therefore, **(A)** option is correct.

**9.**  $\quad A \; + \; B \; \rightleftharpoons \; C + D$

$\quad 3n \qquad n \qquad\quad 0 \quad 0 \qquad\qquad t = 0$

$\quad (3n–x) \quad (n–x) \qquad x \quad x \qquad t = t_{eq.}$

$\quad (n–x) = x$

$\quad n = 2x \qquad x = \dfrac{n}{2}$

**10.** $\qquad\qquad A \quad + B \rightleftharpoons C + D$

Initial $\qquad 1 \qquad\quad 1 \qquad 0 \quad 0$

At equili. $\quad (1 – x) \quad (1 – x) \quad x \quad x$
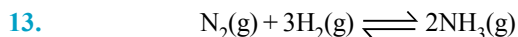
$\therefore \quad K_c = \dfrac{[C][D]}{[A][B]} = 9$

$\therefore \quad \dfrac{x \cdot x}{(1-x)^2} = 9 \ \text{ or } \ x^2 = 9 + 9x^2 - 18x \qquad\text{or}$

$8x^2 - 18x + 9 = 0$

$\therefore \quad x = \dfrac{3}{2} \qquad \text{ or } \quad \dfrac{3}{4}$
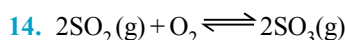
Hence, among the given options, the option (3) i.e., 0.75 is correct.

**13.** $\qquad\qquad N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At equilibrium $\quad \dfrac{P}{3} \qquad P, \qquad\qquad \dfrac{P}{3} + P + P_{NH_3} = 2P$

$P_{NH_3} = \dfrac{2P}{3} \qquad K_p = \dfrac{\dfrac{2P}{3} \times \dfrac{2P}{3}}{\dfrac{P}{3} \times P^3} = \dfrac{1}{P^2} \cdot \dfrac{4}{3}$

$\Rightarrow K_p = \dfrac{4}{3P^2}$

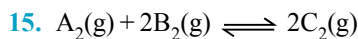**14.** $2SO_2(g) + O_2 \rightleftharpoons 2SO_3(g)$

$K_p = 4.0 \text{ atm}^{-2}$

$K_p = \dfrac{(SO_3)^3}{(SO_2)^2(O_2)}$

Given that at equilibrium the amount of $SO_2$ and $SO_3$ is the same so

$\dfrac{(SO_3)^2}{(SO_2)^2(O_2)} = 4 \ \Rightarrow \ [O_2] = \dfrac{1}{4} = 0.25 \text{ atm.}$

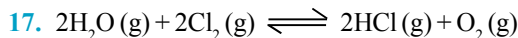**15.** $A_2(g) + 2B_2(g) \rightleftharpoons 2C_2(g)$

$P_{A_2} = 0.80 \text{ atm.}, \qquad P_{B_2} = 0.4 \text{ atm.}$

Total pressure of the system $= 2.8$ atm.

$\therefore P_{C_2} = 2.8 - 0.8 - 0.4 = 1.6$

$K_p = \dfrac{P_{C_2}^2}{P_{A_2} \times P_{B_2}^3} = \dfrac{(1.6)^2}{0.8 \times (0.4)^2} = 20$

**17.** $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 2HCl(g) + O_2(g)$

$K_p = 0.03 \; T = 427^\circ C = 700 \text{ K}$

$K_p = K_C(RT)^1$

$K_C = \dfrac{K_P}{RT} = \left[\dfrac{0.03}{0.082 \times 700}\right]$

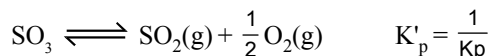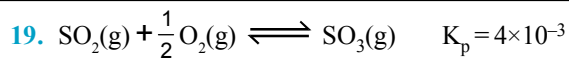$K_C = 5.23 \times 10^{-4}$

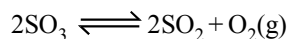**18.** Using $\quad K_p = K_C (RT)^{\Delta n_g}$

so, $\log \dfrac{K_P}{K_C} = \Delta n_g \log RT$

so, $\Delta n_g = -1$.

**255**

**19.** $SO_2(g) + \dfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ $\qquad K_p = 4 \times 10^{-3}$

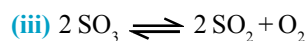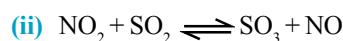$SO_3 \rightleftharpoons SO_2(g) + \dfrac{1}{2}O_2(g)$ $\qquad K'_p = \dfrac{1}{K_p}$

$$K'_p = \left(\dfrac{1}{4 \times 10^{-3}}\right)$$
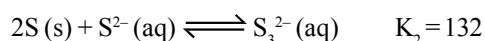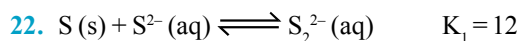
$2SO_3 \rightleftharpoons 2SO_2 + O_2(g)$

$$K''_p = (K'_p)^2 = \left[\dfrac{1}{4 \times 10^{-3}}\right]^2 = \left[\dfrac{1000}{4}\right]^2 = 6250 = 625 \times 10^2$$
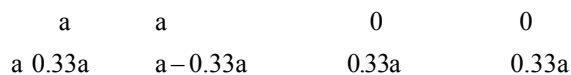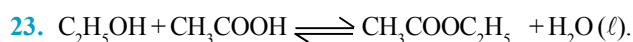
**6.25 × 10⁴ atm.**

**20.** **(i)** $2NO + O_2 \rightleftharpoons 2NO_2$
**(ii)** $NO_2 + SO_2 \rightleftharpoons SO_3 + NO$
**(iii)** $2SO_3 \rightleftharpoons 2SO_2 + O_2$

Now, $\quad -2\,\textbf{(ii)} = \textbf{(i)} + \textbf{(iii)}$

so, $\quad K_{C_3} \times K_{C_1} = 1/K^2_{C_2}$
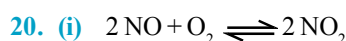
**22.** $S(s) + S^{2-}(aq) \rightleftharpoons S_2^{2-}(aq)$ $\qquad K_1 = 12$
$2S(s) + S^{2-}(aq) \rightleftharpoons S_3^{2-}(aq)$ $\qquad K_2 = 132$

Now, $S_2^{2-}(aq) + S(s) \rightleftharpoons S_3^{2-}(aq)$ $\qquad K_{eq} = \dfrac{K_2}{K_1} = \dfrac{132}{12}$

$$= 11$$

**23.** $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O(\ell).$
$\quad$ a $\qquad$ a $\qquad\qquad$ 0 $\qquad\quad$ 0
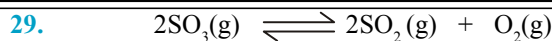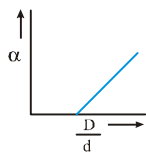a 0.33a $\quad$ a − 0.33a $\qquad$ 0.33a $\qquad$ 0.33a

$$K_C = \dfrac{(0.33a) \times (0.33a)}{(0.67a) \times (0.67a)} = K_C = 1/4.$$

**26.** $\alpha = \left[\dfrac{D-d}{d}\right]$ ; $\alpha = \left[\dfrac{D}{d} - 1\right]$. ; $\left(\dfrac{D}{d}\right) = \alpha + 1.$

$\alpha = \dfrac{D-d}{(n-1)d}$ ; $\alpha = \dfrac{D-d}{d}$ ; $\alpha = \left(\dfrac{D}{d}\right) - 1.$

The point at which $\alpha = 0$.

$\left[\dfrac{D}{d} - 1\right] = 0$ ; So, $\left(\dfrac{D}{d}\right) = 1.$



**29.** $\qquad 2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

t=0 $\qquad$ a $\qquad\qquad$ 0 $\qquad\quad$ 0

$t=t_{eq.} \quad a(1-\alpha) \qquad a\alpha \qquad a\left(\dfrac{\alpha}{2}\right)$
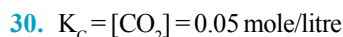
Total mole at eq. $= a\left(1 + \dfrac{\alpha}{2}\right)$

$P_{SO_3} = \left(\dfrac{1-\alpha}{1+(\alpha/2)}\right)P_0 = \left[\dfrac{2(1-\alpha)}{2+\alpha}\right] \times P_0$ ;
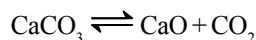
$P_{SO_2} = \left(\dfrac{\alpha}{1+(\alpha/2)}\right)P_0 = \left(\dfrac{2\alpha}{2+\alpha}\right) \times P_0$

$PO_2 = \left(\dfrac{\alpha/2}{1+(\alpha/2)}\right)P_0$

$$K_P = \dfrac{\dfrac{4\alpha^2(P^o)^2}{(2+\alpha)^2} \times \left(\dfrac{\alpha}{2+\alpha}\right) \times P^o}{\dfrac{4(1-\alpha)^2}{[2+\alpha]^2} \times (P_0)^2} = \left[\dfrac{\alpha^3 P^o}{(2+\alpha)(1-\alpha)^2}\right]$$

**30.** $K_C = [CO_2] = 0.05$ mole/litre

so moles of $CO_2 = 6.50 \times 0.05$ moles = 0.3250 moles

$CaCO_3 \rightleftharpoons CaO + CO_2$

1 mole of $CO_2$ = 1 mole of $CaCO_3$

0.3250 moles of $CO_2$ = 0.3250 moles of $CaCO_3$
= $0.3250 \times 100$ gm of $CaCO_3 = 32.5$ gm of $CaCO_3$

**31.** $\qquad C(s) + CO_2(g) \rightleftharpoons 2CO(g)$
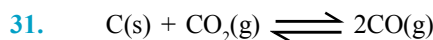
$\quad P - P/2 \qquad\qquad\qquad P = \dfrac{3P}{2} = 12$

so, $K_P = \dfrac{P^2}{(P/2)} = 2P = 2 \times 8 = 16$ atm.

**33.** **(I)** $N_2O_4 \rightleftharpoons 2NO_2 \qquad\qquad K_c = 4$
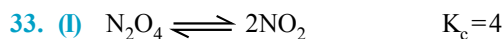
at point — A

$Q = \dfrac{[Product]}{[Reactant]} = 0$

So, Q have minimum value at point A.

**(II)** at point $[N_2O_4] = [NO_2] = 0.1$ M

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.1 \times 0.1}{0.1} = 0.1$$

$Q < K_c$

So, reaction proceeds left to right

**(III)** $K_c = Q$      at point [D & F].

**34.** $SO_3(g) + CO(g) \rightleftharpoons SO_2(g) + CO_2(g)$   $9 = \left(\dfrac{2+x}{2-x}\right)^2$

$$\begin{array}{cccc} 2 & 2 & 2 & 2 \\ 2+x & 2+x & 2-x & 2-x \qquad x=1 \end{array}$$

$n_{eq} = 3 + 3 + 1 + 1 = 8$      $n(SO_3) + n(CO_2) = 4$

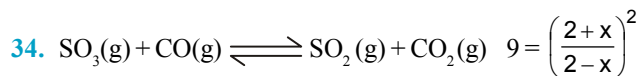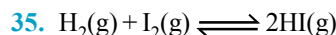$$\frac{n(SO_2)}{n(CO)} = \frac{1}{2} < 1$$

Therefore, **(D)** option is correct.

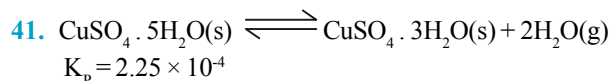**35.** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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

$$\log \frac{50}{66.9} = \frac{\Delta H}{2.303R}\left[\frac{1}{623} - \frac{1}{721}\right]$$

After calculation negative value of $\Delta H$ is obtained.

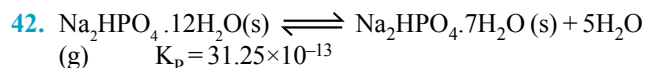**37.** $\log K_2 / \log K_1 = \dfrac{-\Delta H}{2.303}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$

$\Delta H =$ Positive.

**41.** $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$
$K_P = 2.25 \times 10^{-4}$

$K_P = p^2{}_{H_2O} = 2.25 \times 10^{-4}$      $p_{H_2O} = 1.5 \times 10^{-2}$

Vapour pressure $= \dfrac{22.8}{760} = 3 \times 10^{-2}$   R.H. $= \dfrac{P_{H_2O}}{V.P.} \times 100$

                                   $= 50\%$

Therefore, **(B)** option is correct.

**42.** $Na_2HPO_4 \cdot 12H_2O(s) \rightleftharpoons Na_2HPO_4 \cdot 7H_2O(s) + 5H_2O$
(g)      $K_P = 31.25 \times 10^{-13}$

$K_P = (P_{H_2O})^5$

$(P_{H_2O})^5 = 31.25 \times 10^{-13}$

$(P_{H_2O}) = (3125)^{1/5} \times (10^{-15})^{1/5}$

$(P_{H_2O}) = 5 \times 10^{-3}$

**44.** High temperature will favour backward reaction as reaction is exothermic. While on increasing pressure reaction will shift in direction higher density.

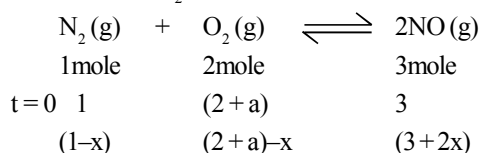**45.** For constant volume, reaction quotient (Q) will remain constant.

For constant pressure, reaction quotient (Q) will remain constant when $\Delta n_g = 0$.

**47.** On adding inert gas at constant pressure effect on equilibrium will be similar to as if volume of container has been increased.

**49.**      $N_2(g)$  +  $O_2(g)$  $\rightleftharpoons$  $2NO(g)$
       1mole      2mole      3mole
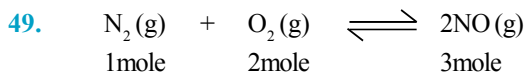
$$K_C = \frac{(3)^2}{1 \times 2} = \left(\frac{9}{2}\right).$$

Let a mole of $O_2$ is added, Then,

     $N_2(g)$  +  $O_2(g)$  $\rightleftharpoons$  $2NO(g)$
       1mole      2mole      3mole
$t = 0$   1          $(2+a)$          3
       $(1-x)$      $(2+a)-x$    $(3+2x)$

$$[NO] = \left[\frac{3+2x}{100}\right] = 0.04 \quad ; \quad (3+2x) = 4.$$

$2x = 1,$          $x = 0.5.$

$$K_C = \frac{(3+2x)^2}{(1-x)(2+a-x)} = \frac{9}{2}.$$

$$K_C = \frac{(4)^2}{0.5[(1.5)-a]} = \frac{9}{2}.$$

$$= \frac{16}{0.5(1.5+a)} = \frac{9}{2}.$$

$$= \frac{35}{4.5} = [1.5 + a]$$

$7.11 = 1.5 + a.$

$$a = \frac{101}{18} = 5.61$$

**52.** $AB \rightleftharpoons A^+ + B^-$     $AB + B^- \rightleftharpoons AB_2^-$
    $a-x-y$    y   (y-x)   (a-x-y)   y-x        x
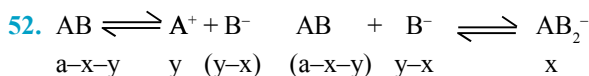
$$K_1 = \frac{y(y-x)}{(a-x-y)} \qquad K_2 = \frac{x}{(a-x-y)(y-x)}$$

$$\frac{K_1}{K_2} = \frac{\left[\dfrac{y(y-x)}{(a-x-y)}\right]}{\dfrac{x}{(a-x-y)(y-x)}} \qquad \Rightarrow \quad \frac{K_1}{K_2} = \frac{y}{x}(y-x)^2$$

**53.** $\quad\quad\quad N_2 \quad + \quad O_2 \quad \rightleftharpoons \quad 2NO$

Initial $\quad$ 2 moles $\quad$ 4moles

At Eq. $\quad 2 - \dfrac{1}{2} \quad\quad 4 - \dfrac{1}{2} \quad\quad\quad 2 \times \dfrac{1}{2} = 1$ mol

Molar concentration of NO at equilibrium $= \dfrac{1}{2.5} = 0.4$

**54.** $\quad\quad\quad A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

Moles at eqm $\quad 2 - x \quad\quad 4 - x \quad\quad 2x$

$$K_C = \frac{4x^2}{(2-x)(4-x)} \quad\quad \Rightarrow \quad x = \frac{32}{24} = 1.33 \text{ mole}$$

$$[AB(g)] = \frac{2 \times 1.33}{4} = 0.66 \text{ M}$$

**55.** $X_2 \quad + \quad Y_2 \quad \rightleftharpoons \quad 2XY$

$\dfrac{1}{3} - x \quad\quad \dfrac{2}{3} - x \quad\quad\quad 2x \quad\quad 2x = 0.6 \Rightarrow \quad x = 0.3$
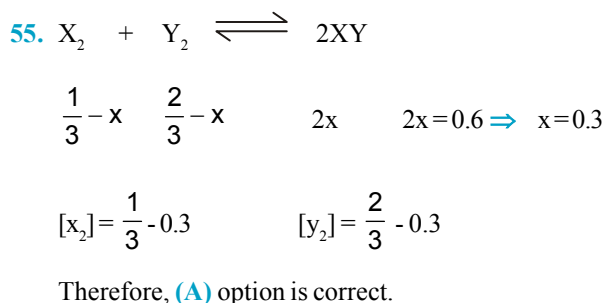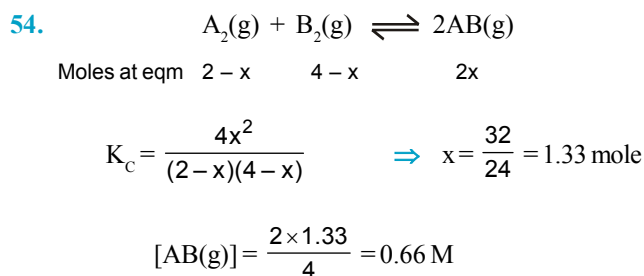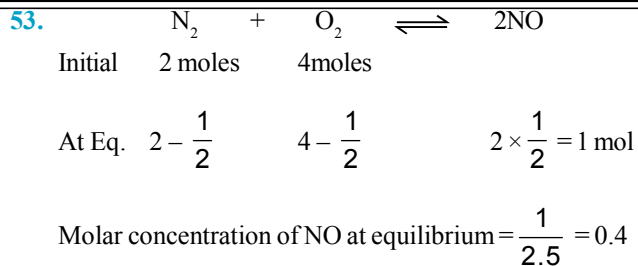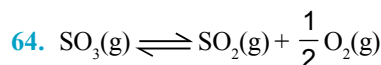
$[x_2] = \dfrac{1}{3} - 0.3 \quad\quad\quad [y_2] = \dfrac{2}{3} - 0.3$

Therefore, **(A)** option is correct.

**60.** $2O_3(g) \rightleftharpoons 3O_2(g) \quad K_p = 4 \times 10^{14} \quad\quad p_{O_2} \gg p_{O_3}$

$K_p = \dfrac{p_{O_2}^3}{p_{O_3}^2} \quad\quad\quad\quad p_{O_2} + P_{O_3} = 8 \Rightarrow P_{O_2} \simeq 8$ atm.

$4 \times 10^{14} = \dfrac{8^3}{p_{O_3}^2} \quad\quad\quad p_{O_3}^2 = 11.3 \times 10^{-7}$

Therefore, **(B)** option is correct.

**62.** $2NO_2 \rightleftharpoons 2NO(g) + O_2(g) \quad ; \quad K_p = \dfrac{(p_{NO})^2 (p_{O_2})}{(p_{NO_2})^2}$

given, $\quad P_{O_2} = 0.25 \quad\quad ; \quad P_{NO} = 0.5$

$100 = \dfrac{(0.5)^2 (0.25)}{(p_{NO_2})^2}$

$(P_{NO_2})^2 = \dfrac{(0.5)^2 (0.25)}{100}$

$P_{NO_2} = 0.025$

**63.** $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \quad K_p = \dfrac{\dfrac{\alpha\ Po}{2(1+\alpha)}\left\{\dfrac{3\alpha\ Po}{2(1+\alpha)}\right\}^3}{\left\{\dfrac{1-\alpha}{1+\alpha}Po\right\}^2}$

$\quad\quad 1 - \alpha \quad\quad\quad \dfrac{\alpha}{2} \quad\quad \dfrac{3\alpha}{2}$

$1 - \alpha \simeq 1$ and $1 + \alpha \simeq 1 \quad \Rightarrow 27 \times 10^{-8} P_o^2 = \dfrac{27}{16} P_o^2 \times \alpha^4$
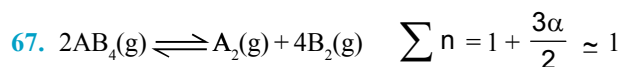
$\alpha = 2 \times 10^{-2}$

**64.** $SO_3(g) \rightleftharpoons SO_2(g) + \dfrac{1}{2} O_2(g)$

$\quad\quad 1 - \alpha \quad\quad\quad \alpha \quad\quad \dfrac{\alpha}{2}$

$M_{mix} = \dfrac{0.9 \times 0.082 \times 1000}{1.23} = 60$

$M_{mix} = \dfrac{\alpha.M_{SO_2} + \dfrac{\alpha}{2}.M_{O_2} + (1-\alpha)M_{SO_3}}{1 + \dfrac{\alpha}{2}}$

$1 + \dfrac{\alpha}{2} = \dfrac{80}{60} \quad \dfrac{\alpha}{2} = \dfrac{20}{60}$

$\alpha = \dfrac{2}{3}$

**67.** $2AB_4(g) \rightleftharpoons A_2(g) + 4B_2(g) \quad \sum n = 1 + \dfrac{3\alpha}{2} \simeq 1$

$\quad 1 - \alpha \quad\quad\quad \dfrac{\alpha}{2} \quad\quad 2x \quad\quad 1 - \alpha \simeq 1$

$K_p = \dfrac{\left(\dfrac{\alpha}{2}P\right)\left(\dfrac{2\alpha}{1} \times P\right)^4}{(P)^2} = 8P^3\alpha^5$

**70.** $N_2 + 3H_2 \rightleftharpoons 2NH_3, \quad K_p = 4.28 \times 10^{-5} \text{ atm}^{-2}$

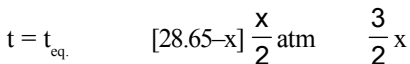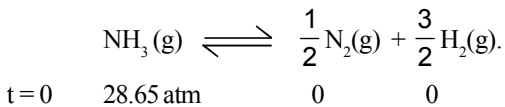Reaction Quotient, $Q_P = \dfrac{P_{NH_3}^2}{P_{N_2} (PH_2)^3} = \dfrac{3^2}{1 \times (2)^3} = \dfrac{9}{8}$

$Q_P > K_P, \quad\quad \therefore$ Reaction will go Backward.

**72.** $P_1 = 15$ atm ; $T_1 = 300$ K.

Equilibrium temperature is 300ºC that is 573 K.

So first of all we have to calculate pressure of $NH_3$ at 573 K.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{15}{300} = \frac{P_2}{573}$$
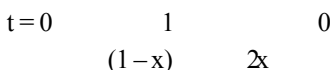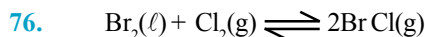
$P_2 = \mathbf{28.65\ atm}$ at 300ºC.

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

$t = 0$ \qquad 28.65 atm \qquad 0 \qquad 0

$t = t_{eq.}$ \qquad $[28.65\text{–}x] \dfrac{x}{2}$ atm \qquad $\dfrac{3}{2} x$

But according to question.

$$P_{total} = 28.65 - x + \frac{x}{2} + \frac{3}{2} x \quad \text{or} \quad 28.65 + x = 40.11.$$

$x = 11.46.$

Degree of dissociation of $NH_3 = \dfrac{11.46}{28.65} = 0.4.$

**76.** \qquad $Br_2(\ell) + Cl_2(g) \rightleftharpoons 2Br\,Cl(g)$

$t = 0$ \qquad\qquad 1 \qquad\qquad 0

\qquad\qquad $(1-x)$ \qquad 2x

$$k_p = \frac{(P_{BrCl})^2}{P_{Cl_2}} = 1 \text{ so, } P_{Cl_2} = (P_{BrCl})^2 = 0.01 \text{ atm}$$

then at equilibrium, \quad $\dfrac{n_{BrCl}}{n_{Cl_2}} = \dfrac{0.1}{0.01} = 10 = \dfrac{2x}{1-x}$
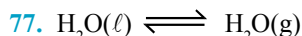
So, $10 - 10x = 2x$ or \quad $x = \dfrac{10}{12} = \dfrac{5}{6}$ moles

Moles of $Br_2(\ell)$ required for maintaining vapour pressure of 0.1 atm

$$= 2 \times \frac{5}{6} \text{ moles} = \frac{10}{6} \text{ moles} = \text{moles of BrCl(g)}.$$

Moles required for taking part in reaction $=$ moles of $Cl_2$

used up $= \dfrac{5}{6}$ moles.

Hence total moles required $= \dfrac{5}{6} + \dfrac{10}{6} = \dfrac{15}{6}$ moles.

**77.** $H_2O(\ell) \rightleftharpoons H_2O(g)$

$K_p = (P_{H_2O})$

When neon is added at constant pressure, we have to increase volume of the container. So more water will evaporate to mantain equilibrium.

**80.** $K = A\,e^{-\Delta H/RT}$

$$\log K = \log A - \frac{\Delta H}{2.303RT}.$$

$$\log K = \log A - \frac{\Delta H}{2.303R} \times \frac{1}{T}.$$

$$\log K = \left[ -\frac{\Delta H}{2.303R} \right] \times \frac{1}{T} + \log A.$$
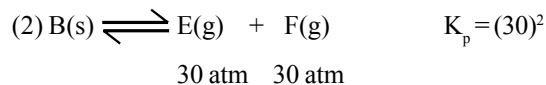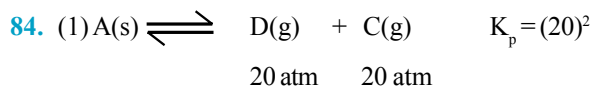
$$\frac{-\Delta H}{2.303R} = 1.$$

$\Delta H = -2.303\ R = -4.606$ cal.

**81.** $\log \dfrac{K_2}{K_1} = \dfrac{\Delta H^\circ}{2.303R} \left[ \dfrac{1}{T_1} - \dfrac{1}{T_2} \right]$
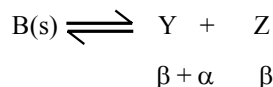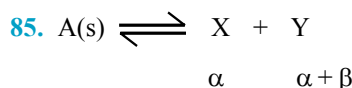
$$\log \frac{K_2}{0.0118} = \frac{597.4 \times 10^3}{2.303 \times 8.314} \left[ \frac{1}{1300} - \frac{1}{1200} \right]$$

$\log K_2 = -2 + \log (0.0118) = -3.928 \Rightarrow K_2 = 1.18 \times 10^{-4}$

Therefore, **(A)** option is correct.

**84.** (1) $A(s) \rightleftharpoons \quad D(g) + C(g) \qquad K_p = (20)^2$

\qquad\qquad\qquad 20 atm \quad 20 atm

(2) $B(s) \rightleftharpoons E(g) + F(g) \qquad K_p = (30)^2$

\qquad\qquad 30 atm \quad 30 atm

(3) container Kp is same so on doubling the volume partial pressure does not change but moles of C, D, E, F will change to maintain their partial pressure. So total pressure $= 40 + 60 = 100$ atm.

**85.** $A(s) \rightleftharpoons \quad X + Y$

\qquad\qquad\qquad $\alpha$ \quad $\alpha + \beta$

$B(s) \rightleftharpoons Y + Z$

\qquad\qquad $\beta + \alpha$ \quad $\beta$

$\Rightarrow K_{P_1} = \alpha\,(\alpha + \beta)$

\quad $K_{P_2} = \beta\,(\alpha + \beta)$

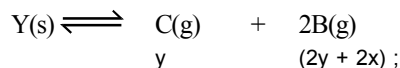$P_{total} = (\alpha + \beta) + \alpha + \beta = 2\,(\alpha + \beta)$
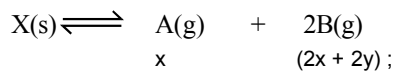
$\Rightarrow 2\,(\alpha + \beta) = 50 \Rightarrow \alpha + \beta = 25$

$\Rightarrow 250 = 25\,\alpha \quad \Rightarrow \alpha = 10, \beta = 15$

$\Rightarrow K_{P_2} = \beta\,(\alpha + \beta) = 15 \times 25 = 375$

**87.** Let x is partial pressure of A and y is partial pressure of C when both equilibrium simultaneously established in a vessel

$$X(s) \rightleftharpoons \quad A(g) \quad + \quad 2B(g)$$
$$\qquad\qquad\quad x \qquad\qquad (2x + 2y) \ ;$$

$$Y(s) \rightleftharpoons \quad C(g) \quad + \quad 2B(g)$$
$$\qquad\qquad\quad y \qquad\qquad (2y + 2x) \ ;$$

$$\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y} \quad \Rightarrow \quad x = 2y$$

$$K_{P_1} = x(2x + 2y)^2$$

$\Rightarrow \quad x = 0.1$ atm;

$\therefore \quad y = 0.05$ atm

Total pressure of gases $= P_A + P_B + P_C$
$$= 3(x + y)$$
$$= 0.45 \text{ atm.}$$

**88.** At equilibrium, $\quad r_f = r_b$

$\therefore K_f[A]_{en} = K_b[B]_{en}$

$[B]_{eq} = K_f K_b^{-1} [A]_{eq}$

**89.** $K = \dfrac{r_f}{r_b} \quad \Rightarrow \quad 1.5 = \dfrac{r_f}{7.5 \times 10^{-4}} \quad \Rightarrow \quad r_f = 1.12 \times 10^{-3}.$

**90.** $K_P = \dfrac{P_{CO(g)} \cdot P_{H_2(g)}}{P_{H_2O(g)}} = \dfrac{(P_{H_2(g)})^2}{P_{H_2O(g)}} \quad$ (as $P_{CO(g)} = P_{H_2(g)}$)

**91.** Because reaction is exothermic.

**92.** Concentration of reactant & product remains const. w.r.t time.

And, rate of [AT EQUILIBRIUM] forward reaction ($r_f$) = rate of backward reaction ($r_b$).

**93.** Equilibrium const. is temp. dependent only.

**94.** $K_p = K_c (RT)^{\Delta n}, \Delta n = 4 - 3 = 1$

$0.05 = K_c R \times 1000$

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

**95.** Since, $K_p$ is temperature dependent only.

**96.** $4 \times 10^4$, Since Equilibrium const. is temp. dependent only.

**EXERCISE - 2**

**Part # I : Multiple Choice**

**6.** **(A)** $\Rightarrow [CH_4] = \dfrac{16}{16 \times 10} = 0.1$ M

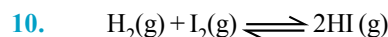**(B)** $\Rightarrow [H_2O] = \dfrac{18}{18 \times 10} = 0.1$ M

**(C)** $\Rightarrow [Cl_2] = \dfrac{35.5}{71 \times 10} = 0.05$ M

**(D)** $\Rightarrow [CO_2] = \dfrac{44}{44 \times 10} = 0.1$ M

**7.** According to $K_P = \dfrac{P_{PCl_3(g)} \times P_{Cl_2(g)}}{P_{PCl_5(g)}}$

$$= \dfrac{(n_{PCl_3(g)})_{eq.} \times (n_{Cl_2(g)})_{eq.}}{V \times (n_{PCl_5(g)})_{eq.}}$$

and on adding inert gas at constant pressure effect on equilibrium will be similar to as if volume of container has been increased.

**10.** $\qquad H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

**(A)** For changing pressure volume has to be changed, though number of moles of HI(g) do not get changed but its concentration will get changed.
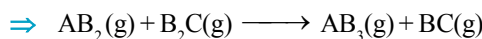
**(B)** Temperature change will change $K_P$ and hence concentration.

**(C)** Volume change will change concentration, not the number of moles.
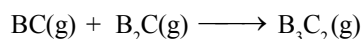
**(D)** Same equilibrium will be attained from either direction.

**(E)** Catalyst does not change equilibrium concentrations.

**12.** Let reactions is started with a mole of $AB_2$ and b mole of $B_2C$

$\Rightarrow \quad AB_2(g) + B_2C(g) \longrightarrow AB_3(g) + BC(g)$
$$\qquad a \qquad\quad b \qquad\qquad 0 \qquad\quad 0$$
$$\quad a - x \quad b - x - y \qquad x \qquad x - y$$

$$BC(g) + B_2C(g) \longrightarrow B_3C_2(g)$$
$$\quad x - y \quad\quad b - x - y \qquad\quad y \qquad \text{As } y > x$$

Clearly $[AB_3]_{eq} > [B_3C_2]_{eq}$ and $[AB_3]_{eq} > [BC]_{eq}$

**17.** Adding inert gas at constant volume does not affect state of equilibrium

**19.** $N_2 + 3H_2 \rightleftharpoons 2NH_3$ as the reaction is exothermic so more $NH_3$ will be obtained at lower temperature.
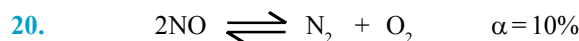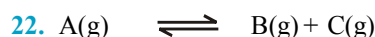
**20.** $\qquad\quad 2NO \rightleftharpoons \quad N_2 \quad + \quad O_2 \qquad \alpha = 10\%$
$$t = 0 \quad 4 - .4 \qquad .2 \qquad .2$$
$$\qquad\quad 3.6 \qquad\quad 0.2 \qquad 0.2$$

$\Delta n = 0,$

$\therefore K_P = K_C, \quad K_C = \dfrac{(.2/V)^2}{(3.6/V)^2} = \dfrac{4}{36 \times 36}$

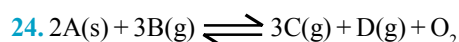**21.** $\alpha = \dfrac{D-d}{d} = \dfrac{46-30}{30} = 0.533 = 53.3\%$

**22.** $A(g) \rightleftharpoons B(g) + C(g)$

$M_{Ob} = \dfrac{M_{th}}{M+(n-1)\,\alpha}$    $80 = \dfrac{100}{1+\alpha}$    $\alpha = \dfrac{1}{4} = 0.25$

**23.** At equilibrium $\Delta G = 0$

Given $\Delta G^0 = 0$

Gibbs equation $\Delta G = \Delta G^\circ - RT \ln K$

$0 = 0 - RT\ln K$        $\Rightarrow K = e^0 = 1$

**24.** $2A(s) + 3B(g) \rightleftharpoons 3C(g) + D(g) + O_2$

If pressure on system is reduced to half its original value then equilibrium will shift in forward direction to increase no.of moles of gas to compensate reduction of pressure.

$\therefore$ Amounts of C & D will increase.

**25.** $T\downarrow$, then $V\downarrow$, then $P\uparrow$, equilibrium shift in such direction so as to dec. pressure, i.e., Backward direction.

**26.** $aA + bB \rightleftharpoons cC + dD$
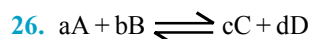
At high temp. & low pressure equilibrium is shifting in backward direction. It means $(a+b) > (c+d)$ & heat will reaction in the formation of producers is $\Delta H < 0$.
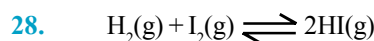
**27.** $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
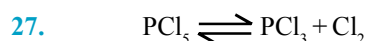
at $t = 0$        a        0        0

$t = tq$        a $-$ x        x        x

$P_{PCl_3} = X_{PCl_3} \times P_T = .25 \times 2 = .5$ atm

$P_{PCl_3} = P_{Cl_2} = .5$ atm

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

$t = 0$        4.5        4.5        0

$t = teq.$    4.5 $-$ x    4.5 $-$ x    2x

put        x $= 1.5$

4.5 $-$ 1.5    4.5 $-$ 1.5    2 $\times$ 1.5 = 3

$\downarrow$        $\downarrow$        $\downarrow$

3        3        3

$K_C = \dfrac{(3)^2}{3\times 3} = 1$

**29.** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
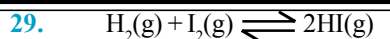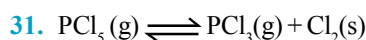
$t = 0$        1.5        1.5        0

$t = tev$    1.5 $-$ x    1.5 $-$ x    2x

We know, 1.5 $-$ x = 1.25, or x = .25

$K_c = \dfrac{(.5)^2}{(1.25)^2} = .16$

**30.** Since inert gas addition has no effect at const. volume.

**31.** $PCl_5 (g) \rightleftharpoons PCl_3(g) + Cl_2(s)$

at eq, mole of $PCl_3$ = mole of $Cl_2$

So $K = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{\left[\dfrac{0.2}{10}\right]\left[\dfrac{0.2}{10}\right]}{\dfrac{0.1}{[10]}} = 0.04$

**32.** $N_2 \quad + \quad 3H_2 \rightleftharpoons 2\,NH_3$
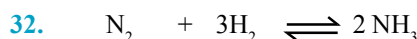
$t = 0$        1 mole    2 mole        0

$t = eq$        1$-$x        2$-$3x        2x = 0.8

        x = 0.4

        mole of $N_2 = 0.6$

        mole of $H_2 = 0.8$

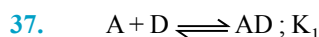**34.** $Co + H_2O \rightleftharpoons CO_2 + H_2$

$t = 0$        1        1        1        0

$t = teq$    1 $-$ x    1 $-$ x    1 + x    x

at equilibrium, only $CO_2$ has $(1 + x)$ moles.

**37.** $A + D \rightleftharpoons AD\,;\, K_1$

$AD + D \rightleftharpoons AD_2\,;\, K_2$

$\underline{AD_2 + D \rightleftharpoons AD_3\,;\, K_3}$

$A + 3D \rightleftharpoons AD_3\,;\, K$
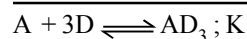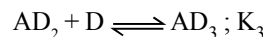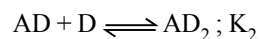
As we know that $K = K_1.K_2.K_3$

Or, $\log K = \log K_1 + \log K_2 + \log K_3$

**38.** $K_p = \dfrac{(p_{CO})^2}{p_{CO_2}} = \dfrac{(2)^2}{4} = 1.$

**39.** $2A_8 \rightleftharpoons 2\,A_3 + 3\,A_2 + A_4$
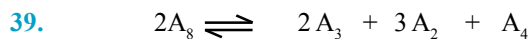
$t = 0$        2        0        0        0

$t = t_{eq}$    2$-$2$\alpha$    2$\alpha$    3$\alpha$    $\alpha$

$n_T = 2 + 4\alpha$

given mole fraction of $A_2$ is $= 0.36$.

$0.36 = \dfrac{3\alpha}{2+4\alpha}$

$\alpha = 0.46$

Mole fraction of $A_8 = \dfrac{2-2\alpha}{2+4\alpha} = \dfrac{2-2\times 0.46}{2+4\times 0.46} = 0.28$

**44.** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Concentration in gram mole/litre, therefore

$$[SO_3] = \frac{48}{80 \times 1}$$

(Where 80 is molecular weight of $SO_3$)
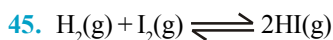
$$[SO_2] = \frac{128}{64 \times 1}$$

(Where 64 is molecular weight of $SO_2$)

$$[O_2] = \frac{9.6}{32 \times 1}$$

(Where 32 is molecular weight of $O_2$)

Thus, $K_C = \dfrac{\left(\dfrac{48}{80}\right)^2}{\left(\dfrac{12.8}{64}\right)^2\left(\dfrac{9.6}{32}\right)} = 0.30$

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

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

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

or $\dfrac{[HI]^2}{[I_2]^2} = K_C$  or  $\dfrac{[HI]}{[I_2]} = \sqrt{K_C} = \sqrt{49} = 7$

**46.**

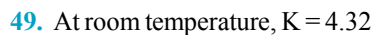|  | A | + | 2B | $\rightleftharpoons$ | 2C | + | D |
|---|---|---|---|---|---|---|---|
| Initial mole | 1.1 |  | 2.2 |  | 0 |  | 0 |
| At Eq. | 1.1−x |  | 2.2−2x |  | 2x |  | x |
|  | 1.1−0.1 |  | 2.2−0.2 |  | 0.2 |  | 0.1 |
|  | 1 |  | 2 |  | 0.2 |  | 0.1 |
| Active mass | $\frac{1}{1}$ |  | $\frac{2}{1}$ |  | 0.2 |  | 0.1 |

$$K_C = \frac{[C]^2[D]}{[A][B]^2} = \frac{\frac{2}{10} \times \frac{2}{10} \times \frac{1}{10}}{1 \times 2 \times 2} = \frac{1}{1000} = 0.001$$

**47.**

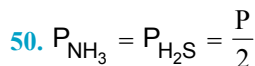|  | $N_2$ | + | $O_2$ | $\rightleftharpoons$ | 2NO | |
|---|---|---|---|---|---|---|
|  | a |  | b |  | 0 |  |
|  | (a−x) |  | (b–x) |  | 2x |  |

$2x = 1.0$ mole/litre

$x = 1.0/2$ mole/litre $= 0.50$ mole/litre
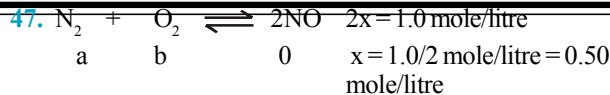
If $a - x = 0.25$, $b - x = 0.05$

$[N_2] = a = a - x + x = 0.25 + 0.50 = 0.75$ mole/litre

**49.** At room temperature, $K = 4.32$
and at 425°C, equilibrium constant become $1.24 \times 10^{-4}$ i.e. it is decreases with increase in temperature. So, it is exothermic reaction.
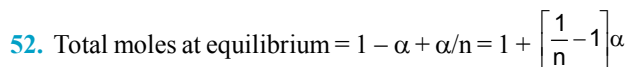
**50.** $P_{NH_3} = P_{H_2S} = \dfrac{P}{2}$

Hence $K_p = P_{NH_3} \times P_{H_2S} = \dfrac{P}{2} \times \dfrac{P}{2} = \dfrac{P^2}{4}$

**51.**

$$Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+} \qquad K = \frac{10^3}{7.142}$$
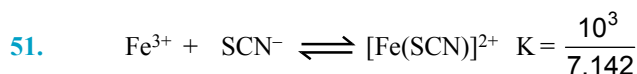
Initial conc. $\dfrac{10^{-3}}{56}$  b   0

Final conc. $\dfrac{10^{-3}}{56} - 6 \times 10^{-6}$   $b - 6 \times 10^{-6}$   $6 \times 10^{-6}$

on solving $b = 0.0036$ M.

**52.** Total moles at equilibrium $= 1 - \alpha + \alpha/n = 1 + \left[\dfrac{1}{n} - 1\right]\alpha$

So using $\dfrac{d_i}{d_f} = 1 + \left[\dfrac{1}{n} - 1\right]\alpha$ .

**53.** $\dfrac{K_A}{K_B} = \dfrac{[PQ]}{[P][Q]}$ ..... (i)  ;  $\dfrac{K_C}{K_D} = \dfrac{[R]}{[PQ]}$ ..... (ii)
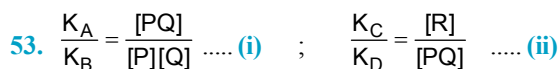
On multiply equation **(i)** and **(ii)** we get

$$\frac{K_A \cdot K_C}{K_B \cdot K_D} = \frac{[R]}{[P][Q]}$$

**55.** Catalyst can't disturb the state of the equilibrium.

**56.**
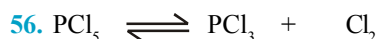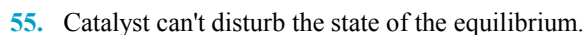
|  | $PCl_5$ | $\rightleftharpoons$ | $PCl_3$ | + | $Cl_2$ |  |
|---|---|---|---|---|---|---|
| Initial mole | 1 |  | 0 |  | 0 |  |
| Conc. at equilibrium | $\frac{1-0.7}{5}$ |  | $\frac{0.7}{5}$ |  | $\frac{0.7}{5}$ |  |

Total mole of $PCl_3 = 0.7$

Concentration $= 0.14$

$$K_C = \frac{x^2}{(1-x)V} = \frac{0.7 \times 0.7}{0.3 \times 5} = \frac{49}{150}$$

**57.** $K_p$ depends only on temperature so $\alpha$ will change on changing pressure and $P_{H_2} > P_{N_2}$.

**58.** $\qquad K_P = K_C (RT)^{\Delta n_g} = K_C (RT)$

so, $\qquad T = \dfrac{K_P}{K_C} \dfrac{1}{R} = \dfrac{1}{0.0821} = 12.18 \, K$

**59.** $K_p = 0.667 \, atm = \dfrac{2}{3} \, atm = \dfrac{4\alpha^2}{1-\alpha^2} \cdot P = \dfrac{4\alpha^2}{1-\alpha^2} \cdot \dfrac{1}{2}$

so, $\dfrac{4\alpha^2}{1-\alpha^2} = \dfrac{4}{3} \qquad \Rightarrow \quad 3\alpha^2 = 1 - \alpha^2$

so, $\alpha^2 = \dfrac{1}{4} \qquad\qquad \Rightarrow \quad \alpha = \dfrac{1}{2}$

---
### Part # II : Assertion & Reason
---

**2.** By definitions.

**5.** Value of equilibrium constant is not dependent on concentration of any species.

### EXERCISE - 3
---
### Part # I : Matrix Match Type
---

**1. (A)** $\Delta n_g$ is +ve so as P is increased, backward shifting will take place. Total pressure even after shifting will remain same.

**(B)** $\Delta n_g$ is –ve so as V is increased, backward shifting will take place. But $P_{final} < P_{initial}$.

**(C)** No change but $P_{final} < P_{initial}$ as volume has increased.

**(D)** Forward shifting will take place and $P_{final} < P_{initial}$.

---
### Part # II : Comprehension
---

**Comprehension # 1 :**

**1.** Slope $= \dfrac{-\Delta H^\circ}{2.3R} = -\dfrac{230}{2.3 \times 2} = -50$

**3.** Using equation, $\log \dfrac{K_2}{K_1} = \dfrac{\Delta H^\circ}{2.30 \, R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

**Comprehension # 2 :**

**3.** Number of moles will remain unchanged but due to decreased volume pressure will get increased and also the concentrations.

**Comprehension # 3 :**

**Sol. (1 to 3)**

$2A_2(g) \rightleftharpoons A_4(g)$
$3p - x - y \qquad x/2$

$A_2 + 2C \rightleftharpoons A_2C_2$
$3p - y - x \quad P - 2y \qquad y - z$

$A_2C_2 \rightleftharpoons 2AC$
$y - z \qquad\quad 2z$

$\dfrac{P_{A_4}}{P_{A_2}^2} = K_{P_1} \qquad \Rightarrow \quad \left(P_{A_2}\right)^2 = \dfrac{P_{A_4}}{K_{P_1}} = \dfrac{\frac{1}{2}}{2/81} = \dfrac{81}{4}$

$\Rightarrow \quad P_{A_2} = \dfrac{9}{2} \, atm.$

$\Rightarrow \quad 3p - x - y = \dfrac{9}{2} \qquad\qquad \text{... (i)}$

$\dfrac{x}{2} = \dfrac{1}{2} \qquad\qquad\qquad \text{... (ii)}$

$\Rightarrow \quad x = 1 \, atm$

also given $2Z = \dfrac{1}{2} \qquad\qquad \text{.... (iii)}$

$Z = \dfrac{1}{4} \, atm$

$P_{total} = 3p - x - y + x/2 + p - 2y + y - z + 2z = 4p - x/2 - 2y + z$

$= 4 \times p - \dfrac{1}{2} - 2 \times \dfrac{1}{2} + \dfrac{1}{4} = \dfrac{27}{4} \, atm. \Rightarrow \quad P = 2$ atm.

**Sol.1** $3P - x - y = \dfrac{9}{2}$

$6 - \dfrac{1}{2} - y = \dfrac{9}{2}$

$y = 1 \, atm.$

$P_{A_2C_2} = y - z = 1 - \dfrac{1}{4} = \dfrac{3}{4} \, atm.$

**Sol.2** $\dfrac{n_{A_2}}{n_{AC}} = \dfrac{P_{A_2}}{P_{AC}} = \dfrac{3P - x - y}{2z} = \dfrac{\frac{9}{2}}{1/2} = 9$

**Sol.3** $K_p = \dfrac{P_{A_2C_2}}{P_{AC}^2} = \dfrac{3/4}{\left(\dfrac{1}{2}\right)^2} = 3$

**Comprehension # 5 :**

**1.** $CaSO_4.2H_2O(s) \rightarrow CaSO_4.\dfrac{1}{2}H_2O(s) + \dfrac{3}{2}H_2O(g)$

$\Delta H° = \dfrac{3}{2}(-241.8) + (-1575) - (-2021)$

For 1 kg $CaSO_4.2H_2O = \dfrac{\Delta H°}{172} \times 100 = 484$ kJ

**2.** $\Delta S° = \dfrac{3}{2}(188.6) + 130.5 - 194$

$\Delta G° = \Delta H° - (298)\Delta S° = -8.314 \times 298 \ln (P_{H_2O})^{3/2}$

$\Rightarrow P_{H_2O} = 8.1 \times 10^{-3}$ bar

### EXERCISE - 4
#### Subjective Type

**2.** $n = \dfrac{5.6}{22.4} = 0.25$

Active mass $= \dfrac{0.25}{5.6} = 0.044$ M.

**5.** Forward reaction rate $(r_f) = K_1[A][B]$
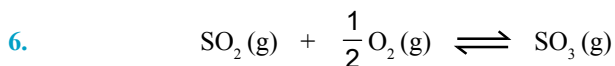
Backward reaction rate $(r_f) = K_2[C][D]$

At equilibrium, $r_f = r_b$

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

The concentration of reactents & products at equilibrium are related by

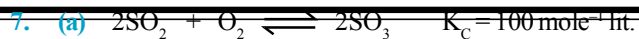$K = \dfrac{K_1}{K_2} = \dfrac{[C][D]}{[A][B]}$

$\therefore K = \dfrac{K_1}{K_2}$

**6.** $SO_2(g) + \dfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

No. of mole  2        1        4

conc.  $\dfrac{2}{4}$       $\dfrac{1}{4}$       $\dfrac{4}{4}$.

$K_C = \dfrac{[SO_3]}{[SO_2][O_2]^{1/2}} = \dfrac{1}{(1/2)(1/4)^{1/2}}$

$= \dfrac{1}{(1/2)\times(1/2)} = $ **4 Ans.**

**7. (a)**  $2SO_2 + O_2 \rightleftharpoons 2SO_3$     $K_C = 100$ mole$^{-1}$ lit.

Initial mole     $a$        $b$        $0$

$a-2x$        $b-x$        $2x$

$\dfrac{a}{2}$        $b - \dfrac{a}{4}$        $\dfrac{a}{2}$   (According to data given)

But according to question.

No. of mole of $SO_2 = $ No. of mole of $SO_3$.

$= a - 2x = 2x.$

$a = 4x.$

$x = \dfrac{a}{4}.$

Now, $K_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

But No. of mole of $SO_3$ and $SO_2$ are equal at eq. so.

$K_C = \dfrac{1}{[O_2]}$

$[O_2] = \dfrac{1}{K_C}$   ;   $[O_2] = \dfrac{1}{100}.$

But $[O_2] = \dfrac{\text{mole of } O_2 \text{ at eq.}}{10} = \dfrac{1}{100}.$

So No. of mole of $O_2 = \dfrac{1}{10} = $ **0.1.**

**(b)** $K_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = \dfrac{\left(\dfrac{2n_{SO_2}}{V}\right)^2}{\left(\dfrac{n_{SO_2}}{V}\right)^2 \times \left(\dfrac{n_{O_2}}{V}\right)}$

$K_C = \dfrac{4}{\left(\dfrac{n_{O_2}}{V}\right)}$ ;

$n_{O_2} = \dfrac{4 \times V}{K_C} = \dfrac{4 \times 10}{100} = 0.4.$

**8.**    $A + B \rightleftharpoons C + D$

t = 0     $2a$        $a$        $0$        $0$

t = $t_{eq}$     $2a - x$        $a - x$        $x$        $x$
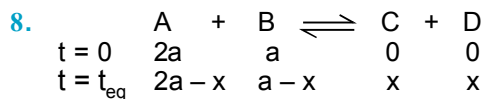
$a - x = x \Rightarrow x = \dfrac{a}{2}$

$\Rightarrow K_C = \dfrac{\dfrac{a}{2} \times \dfrac{a}{2}}{\left(2a - \dfrac{a}{2}\right) \times \dfrac{a}{2}} = \dfrac{1}{3} \Rightarrow \dfrac{1}{K_C} = 3$
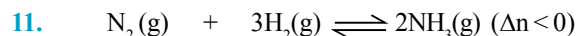
**Ans. 3**

**9.** $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$    $K_C = 50$

$$1 \qquad 2 \qquad 0$$

$$\frac{1-x}{3} \qquad \frac{2-x}{3} \qquad \frac{2x}{3}$$

$$50 = \frac{\dfrac{2x}{3}\cdot\dfrac{2x}{3}}{\dfrac{1-x}{3}\cdot\dfrac{2-x}{3}} = \frac{4x^2}{(1-x)(2-x)} = \frac{4x^2}{2-3x+x^2}$$

$$\Rightarrow \quad 100 - 150x + 50x^2 = 4x^2$$

$$\therefore \text{ no. of mol of } AB = \frac{2x}{3} = 1.868.$$

**11.**    $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   $(\Delta n < 0)$

$$1\,mol \qquad 3\,mol \qquad 0$$
$$(1-x) \qquad (3-3x) \qquad 2x$$

$P_{eq} = 1\,atm, \ T = 400\,K$

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

$$\frac{x^2}{(1-x)^4} = 1 \Rightarrow x = (1-x)^2 \Rightarrow x^2 - 3x + 1 = 0$$
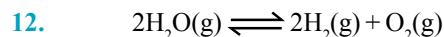
$$\Rightarrow \quad x = \frac{3 \pm \sqrt{9-4}}{2} \quad \Rightarrow \quad x = \frac{3 \pm \sqrt{5}}{2}$$

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

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

$$\Rightarrow \quad x = 0.38 \text{ (since x cannot be greater than 1)}$$
$$\therefore \quad [NH_3] = 0.38 \times 2 = 0.76$$

**12.**    $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

$$t = 0 \quad n \qquad\qquad n \qquad n$$
$$teq. \quad (n-y) \qquad (n+y) \quad (n+y/2) \quad n_T = (3n+y/2)$$

$$\text{so, } K_p = \frac{(P_{H_2(g)})^2_{eq.}\cdot(P_{O_2(g)})_{eq.}}{(P_{H_2O(g)})^2_{eq.}} = \frac{(n+y)^2\,(n+y/2)\,P}{(n-y)^2\,(3n+y/2)}$$
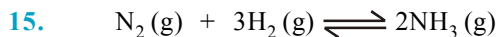
**14. (i)**    $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

$$0.15 \qquad a$$
$$0.15-x \qquad a-2x \qquad x \qquad \Rightarrow \quad x = 0.08$$
$$0.15-x+a-2x+x = 0.5 \qquad\qquad PV = nRT$$

$$a - 2x = 0.35 \qquad\qquad n = \frac{8.2 \times 2.5}{0.082 \times 500} = 0.5$$

$$K_c = \frac{\dfrac{0.08}{2.5}}{\dfrac{0.07}{2.5} \times \left(\dfrac{0.35}{2.5}\right)^2} = \frac{20000}{343} = 58.3$$

$$K_p = 58.3 \times (RT)^{-2} = \frac{58.3}{(0.082 \times 500)^2} = \frac{58.3}{41 \times 41} = 0.035$$

**(ii)** Total pressure will remain 8.2 atm as catalyst reduces only time taken to achieve equilibrium, does not affect equilibrium condition / concentrations.

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

$$\text{At } t = 0 \quad a \qquad\quad b \qquad\qquad 0$$
$$t = t_{eq} \quad (a-x) \quad (b-3x) \qquad 2x$$
$$(\Delta n < 0) \ (P, T, V \text{ given})$$

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

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

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

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

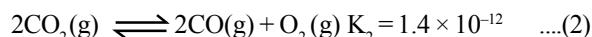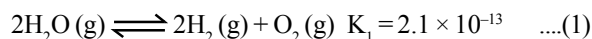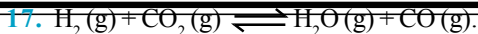$$[P_{NH_3}] = \frac{(2x)\cdot P}{a+b-2x}$$

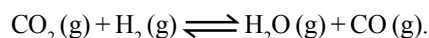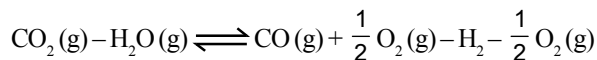$$\therefore \quad K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3}$$

$$= \frac{\left(\dfrac{2x}{a+b-2x}\cdot P\right)^2}{\left[\left(\dfrac{a-x}{a+b-2x}\right)\cdot P\right]\left[\dfrac{(b-3x)P}{a+b-2x}\right]^3}$$

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

**17.** $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$.

$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \quad K_1 = 2.1 \times 10^{-13} \quad ....(1)$

$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g) \quad K_2 = 1.4 \times 10^{-12} \quad ....(2)$

$\dfrac{1}{2}$ eq. (2) $-$ $\dfrac{1}{2}$ eq. (1)

$CO_2(g) - H_2O(g) \rightleftharpoons CO(g) + \dfrac{1}{2}O_2(g) - H_2 - \dfrac{1}{2}O_2(g)$

$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$.

$\dfrac{1}{2}$ [eq. (2) $-$ eq. (1)]

$K = \left(\dfrac{K_2}{K_1}\right)^{1/2} = \left(\dfrac{1.4 \times 10^{-12}}{2.1 \times 10^{-13}}\right)^{1/2} = \left(\dfrac{14}{2.1}\right)^{1/2}$

$= \mathbf{2.58. \, Ans.}$
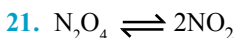
**19.** $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$
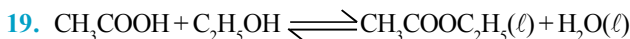
| | | | |
|---|---|---|---|
| Initial | 1 | 1 | 0 | 1 |
| At eq. | $1-x$ | $1-x$ | $x$ | $1+x$ |
| | $1-0.543$ | $1-0.543$ | $0.543$ | $1+0.543$ |

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

Hence given $x = 0.543$ mole

Applying law of mass action :

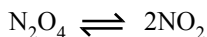$K_C = \dfrac{[ester][water]}{[acid][alcohol]} = \dfrac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$

**21.** $N_2O_4 \rightleftharpoons 2NO_2$

$\quad\quad 1 \quad\quad\quad 0$

$\quad\quad 1{-}.25 \quad\quad .50$

$\quad\quad .75 \quad\quad\quad .50 \quad\quad n_{total} = 1.25$

$P_{N_2O_4} = \left(\dfrac{.75}{1.25}\right); \quad P_{NO_2} = \left(\dfrac{.50}{1.25}\right)$

$K_P = \dfrac{(P_{NO_2})^2}{(P_{N_2O_4})} = \dfrac{(.50/1.25)^2}{(.75/1.25)} = \dfrac{.50 \times .50}{1.25 \times .75}$

$= \dfrac{4}{15} = 0.266$.

At pressure 0.1 atm,

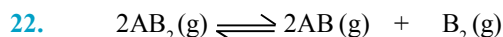$\quad N_2O_4 \rightleftharpoons 2NO_2$

$\quad\quad 1 \quad\quad\quad 0$

$\quad (1-\alpha) \quad\quad 2a$

$P_{N_2O_4} = \left(\dfrac{1-\alpha}{1+\alpha}\right) \times 0.1 \quad ; \quad P_{NO_2} = \left(\dfrac{2\alpha}{1+\alpha}\right) \times 0.1$

$K_P = \dfrac{\left(\dfrac{2\alpha}{1+\alpha} \times 0.1\right)^2}{\left(\dfrac{1-\alpha}{1+\alpha}\right) \times 0.1} \quad ; \quad K_P = \dfrac{4\alpha^2 \times 0.1}{(1+\alpha)(1-\alpha)}$

$0.266 = \dfrac{0.1 \times 4\alpha^2}{1-\alpha^2}$

$0.665 = (1+0.665)\alpha^2. \quad \Rightarrow \quad \alpha = 63.25\%.$

**22.** $\quad\quad 2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

$t=0 \quad\quad a \quad\quad\quad\quad 0 \quad\quad\quad 0$

$\quad\quad a(1-\alpha) \quad\quad (a\alpha) \quad\quad \dfrac{(a\alpha)}{2}$

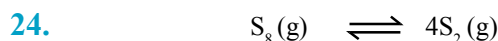Total mole $= a[1 - \alpha + \alpha + \dfrac{\alpha}{2}] \quad\quad \dfrac{a[2+\alpha]}{2}$

$P_{AB_2} = \dfrac{a(1-\alpha) \times 2}{a(2+\alpha)} \times P \quad ; \quad P_{AB} = \dfrac{a\alpha \times 2}{a(2+\alpha)} \times P$

$P_{B_2} = \dfrac{\left(\dfrac{a\alpha}{2}\right)}{\dfrac{a(2+\alpha)}{2}} = \left[\dfrac{\alpha}{2+\alpha}\right] \times P$.

$K_P = \dfrac{\left(\dfrac{2\alpha}{2+\alpha} \times P\right)^2 \left(\dfrac{\alpha}{2+\alpha} \times P\right)}{\left(\dfrac{2(1-\alpha)}{2+P} \times P\right)^2}$

$\alpha << 1.$

$K_P = \dfrac{\alpha^3 P}{2} \quad ; \quad \alpha = \left(\dfrac{2K_P}{P}\right)^{1/3} \quad i.e. \; x = \left(\dfrac{2K_P}{P}\right)^{1/3}$

**24.** $\quad\quad\quad\quad S_8(g) \rightleftharpoons 4S_2(g)$

time $t = 0 \quad\quad 1 atm \quad\quad\quad 0$

At. eq. $\quad\quad (1-x) \quad\quad\quad 4x$

Pressure of eq. $\quad 1-0.29 \quad\quad\quad 4 \times 0.29.$

$K_P = \dfrac{(P_{S_2})^4}{P_{S_8}} = \dfrac{(4 \times 0.29)^4}{0.71}$.

$\mathbf{K_P = 2.55 \, atm3.}$

**26.**
$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

t = 0    –    1    2    3

carbon solid will start forming when there will be equilibrium in the container

$$K_p = \frac{P_{co}.P_{H_2}}{P_{H_2O}} = 3 \text{ atm} = \frac{(2P)(3P)}{P} = 6P = 3 \text{ atm}$$

So   $P = \dfrac{1}{2}$ atm

So   Total pressure in the container will be

$$P_T = P + 2P + 3P = 6P = 3 \text{ atm} \qquad \textbf{Ans. 3}$$

**28.** $SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$

0.04    0.04      0.3    0.3

0.04-x   0.04-x    0.3+x   0.3+x

$$Q_c = \frac{(0.3)^2}{(0.04)^2} = 56.25$$

Here, $Q_c < K_c$ hence reaction will proceed in forward direction to reach at state of equilibrium

$$K_c = \frac{(0.3+x)^2}{(0.04-x)^2} = 81$$

x = 0.006
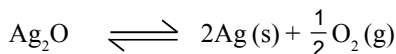
**30.** Equation **(iii)** = – [2 × **(i)** + **(ii)**]

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

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

**31.** T = 445°C = 445 + 273 = 718K

P = 207atm

n = 1 mole

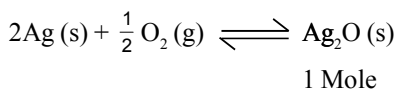$$Ag_2O \rightleftharpoons 2Ag(s) + \frac{1}{2}O_2(g)$$

$$K_p = \sqrt{P_{O_2}} = (207)^{1/2} = 14.39$$

$\Delta G^0 = \Delta G^0 + 2.303 \, RT \log K_{eq}.$

But at eq. $\Delta G = 0$,

$\Delta G^0 = -2.303 \, RT \log K_{eq}.$

But for formation,

$$2Ag(s) + \frac{1}{2}O_2(g) \rightleftharpoons Ag_2O(s)$$

1 Mole

$$K_p = \frac{1}{(Po_2)^{1/2}} = \frac{1}{(207)^{1/2}}$$

$$\Delta G^0 = -2.303 \times 8.312 \times 718 \log \frac{1}{(207)^{1/2}}$$

$$\Delta G^0 = \frac{2.303 \times 8.312 \times 718}{2} \times \log 207$$

$\Delta G^0 = 6872.17 \log 207$

$\Delta G^0 = 15915.75 \, J$

$\Delta G^0 = 3789.46 \, Cal$

$\Delta G^0 = 3.789 \, KCal$

$\textbf{\Delta G}^0 = \textbf{3.8 KCal}$

**33.** $SrCI_2 . 6H_2O(s) \rightleftharpoons SrCI_2 . 2H_2O(s) + 4H_2O(g)$

$K_p = 16 \times 10^{-12}$

$$(P_{H_2O})^4 = K_P \qquad P_{H_2O} = (K_p)^{1/4} = 2 \times 10^{-3} \text{ atm}$$

$$H_2O(\ell) \rightleftharpoons H_2O(g) \qquad P_{H_2O} = \frac{7.6}{760} = 1.0 \times 10^{-2}$$

$$n_{H_2O} = \frac{PV}{RT} = \frac{10^{-2} \times 1}{0.082 \times 274} = 4.45 \times 10^{-4}$$

$$n_{H_2O} = \frac{2 \times 10^{-3}}{0.082 \times 274} = 8.9 \times 10^{-5}$$

$\therefore n_{H_2O}$ absorbed = $3.56 \times 10^{-4}$

$\therefore$ wt absorbed = 6.4 mg.

**36. (a)** $K_p = \dfrac{p_{CO} \times p_{H_2}^3}{p_{CH_4} \times p_{H_2O}}$

**(b) (i)** The value of $K_p$ remains unchanged on increasing the pressure. When pressure is increased then according to Le-Chatelier's principle the equilibrium shifts in the direction where there is less number of moles of gases i.e., backward direction in case of the given reaction.

**(ii)** In case of endothermic reactions the value of $K_p$ increases with increases in temperature. With increases in temperature, the equilibrium shift in the endothermic direction i.e., forward direction in case of the given reaction.

**(iii)** $K_p$ will remain undisturbed. Equilibrium composition will remain unchanged. However, in the presence of catalyst, the equilibrium would be attained quickly.

**37.. (i)** In this case $n_p$ is equal to $n_r$

This reaction will not be affected by increase of pressure.

**(ii)** $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

In this reaction, moles of gases on product side ($n_p = 2$) is more than that on reactant side ($n_r = 1$). This reaction **will be affected** by increase in pressure. Increase in pressure shifts the equilibrium in that direction where there is less no. of moles gases. In this reaction, increase in pressure will cause the reaction to go into the the **left direction**.
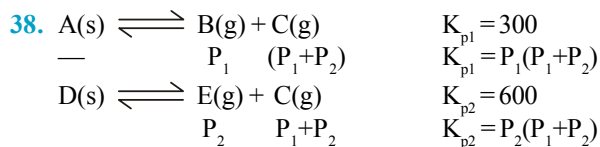
**(iii)** $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
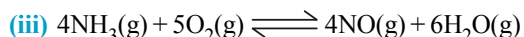
The reaction **would be affected** by increase in pressure because $n_p$ is different from $n_r$.

Increase in pressure shifts the equilibrium in **left direction** because $n_r$ is less than $n_p$.

**(iv)** $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$
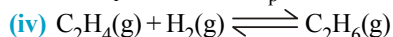
The reaction **would be affected** by increase in pressure. Increase in pressure will shift the equilibrium **towards right** because $n_p$ is less than $n_r$.

**38.**

$$A(s) \rightleftharpoons B(g) + C(g) \qquad K_{p1} = 300$$
$$\underline{\quad} \qquad P_1 \quad (P_1 + P_2) \qquad K_{p1} = P_1(P_1 + P_2)$$
$$D(s) \rightleftharpoons E(g) + C(g) \qquad K_{p2} = 600$$
$$P_2 \quad P_1 + P_2 \qquad K_{p2} = P_2(P_1 + P_2)$$

$$\left(\frac{Kp_1}{Kp_2}\right) = \frac{P_1(P_{1+}P_2)}{P_2(P_1+P_2)}$$

$$\frac{300}{600} = \left(\frac{P_1}{P_2}\right)$$

$$\frac{P_1}{P_2} = \frac{1}{2} \quad P_2 = 2P_1$$

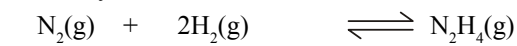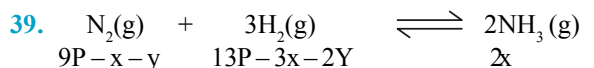$$K_{p1} = P_1(P_1 + P_2)$$
$$K_{p1} = P_1(P_1 + 2P_1)$$
$$300 = P_1(3P_1)$$
$$P_1^2 = 100 \qquad (P_1 = 10)$$
$$P_2 = 20 \text{ atm}$$

Now Total pressure

$$P_B + P_E + P_C$$
$$(P_1 + P_2) + (P_1 + P_2) = (10+20) + (30) = \textbf{60 atm.}$$

**39.**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$9P - x - y \quad 13P - 3x - 2Y \qquad 2x$$

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$$
$$9P - x - y \quad 13p - 3x - 2Y \qquad Y$$

given $9P - x - y + 13P - 3x - 2y + 2x + y = 7P_o$

$\Rightarrow \qquad 22P - 2x - 2y = 7P_o$ .........(1)

then $\qquad 2x = P_o$ .........(2)

and $\qquad 13P - 3x - 2y = 2P_o$ .........(3)

$$\begin{array}{r} 22P - 2y = 5P_o \\ \underline{-13P - 2y = \frac{7}{2}P_o} \\ 9P = \frac{9}{2}P_o \end{array} \qquad P = \frac{P_o}{2}$$

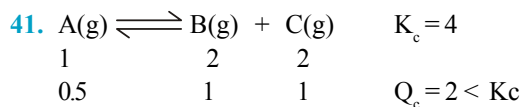$$9P - x - y = \frac{9P_o}{2} - \frac{P_o}{2} - \frac{3P_o}{2} = \frac{5P_o}{2}$$

$$2y = \frac{13 - 7}{2}P_o = 3P_o$$

$$13P - 3x - 2y = \frac{13P_o}{2} - \frac{3P_o}{2} - \frac{6P_o}{2} = 2P_o \quad y = \frac{3}{2}P_o$$

$$K_1 = \frac{(2x)^2}{(9p - x - y)(13p - 3x - 2y)^3}$$

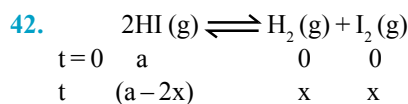$$= \frac{P_o^2}{\frac{5}{2}P_o \cdot (2P_o)^3} = \frac{1}{20P_o^2}$$

$$K_2 = \frac{\frac{3}{2}P_o}{\left(\frac{5}{2}P_o\right)(2P_o)^2} = \frac{3}{20P_o^2}$$

**41.**

$$A(g) \rightleftharpoons B(g) + C(g) \qquad K_c = 4$$
$$1 \qquad\qquad 2 \qquad 2$$
$$0.5 \qquad\quad 1 \qquad 1 \qquad Q_c = 2 < Kc$$

$$0.5 - x \qquad 1 + x \quad 1 + x \qquad 4 = \frac{(1+x)^2}{0.5 - x}$$

$$x = 0.162 \; [A] = 0.338$$
$$[B] = [C] = 1.162$$

**42.**

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
$$t = 0 \quad a \qquad\qquad 0 \qquad 0$$
$$t \qquad (a - 2x) \qquad x \qquad x$$

Given: $\dfrac{x^2}{(a - 2x)^2} = \dfrac{1}{54.8}$

so, $\dfrac{a - 2x}{x} = \sqrt{54.8}$ and $(a - 2x) = 0.5$ M

so, $x = \dfrac{0.5}{\sqrt{54.8}} = \dfrac{0.5}{7.40} = 0.0675$ M

**45.**

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial moles $\quad 0.1 \qquad\quad 0 \qquad 0$

At. Eq. $\qquad\quad 0.1 - x \qquad x \qquad x$
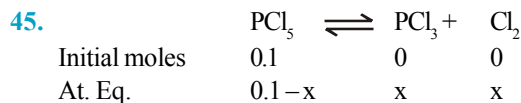
Total number of moles at equilibrium

$= (0.1 - x) + x + x = 0.1 + x$

But total number of moles,

$$n = \frac{PV}{RT} = \frac{1\,bar \times 8L}{0.083 \text{ L bar mol}^{-1}\text{K}^{-1} \times 540K} = 0.18$$
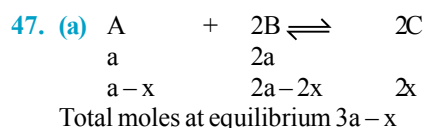
$0.1 + x = 0.18$

$x = 0.08$

$[PCl_5] = \dfrac{0.1 - 0.08}{8} M = 2.5 \times 10^{-3} M$

$[PCl_3] = \dfrac{0.08}{8} M = 0.01 M$

$[Cl_2] = \dfrac{0.08}{8} M = 0.01 M$

$K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{0.01 \times 0.01}{2.5 \times 10^{-3}} = 4 \times 10^{-2}$

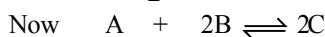$K_p = K_c (RT)^{\Delta n} = 4 \times 10^{-2} \times (0.083 \times 540) = 1.79\ bar$

**47. (a)**

$\begin{array}{cccc} A & + & 2B \rightleftharpoons & 2C \\ a & & 2a & \\ a-x & & 2a-2x & 2x \end{array}$

Total moles at equilibrium $3a - x$

Mole fraction of $C = \dfrac{2x}{3a - x} = 0.4$

$2x = 1.2a - 0.4x$

$x = \dfrac{1.2a}{2.4}$

$x = \dfrac{a}{2}$

Now $\quad A \quad + \quad 2B \rightleftharpoons 2C$

$\quad\quad \dfrac{a}{2} \quad\quad a \quad\quad a$

Total moles $= \dfrac{5a}{2}$
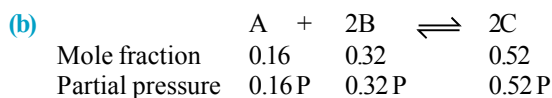
$P_A = \dfrac{\frac{a}{2}}{\frac{5a}{2}} \times 8 = \dfrac{8}{5}\ atm$

$P_B = \dfrac{a}{5a/2} \times 8 = \dfrac{16}{5}\ atm$
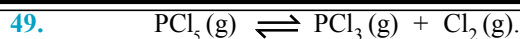
$P_C = \dfrac{a}{5a/2} \times 8 = \dfrac{16}{5}\ atm$

$K_p = \dfrac{(P_C)^2}{(P_B)^2 \cdot P_A} = \dfrac{5}{8}$

**$K_p = 0.625\ atm^{-1}$**

**(b)**

| | A + | 2B ⇌ | 2C |
|---|---|---|---|
| Mole fraction | 0.16 | 0.32 | 0.52 |
| Partial pressure | 0.16 P | 0.32 P | 0.52 P |

$K_p = \dfrac{(0.52P)^2}{0.16P \times (0.32P)^2} = \dfrac{5}{8}$

$P = \dfrac{0.52 \times 0.52 \times 8}{0.16 \times 0.32 \times 0.32 \times 5} = \textbf{26.4 atm}$

**49.**

$\begin{array}{cccc} & PCl_5\,(g) & \rightleftharpoons\ PCl_3\,(g) & +\ Cl_2\,(g). \\ \text{Initial} & 3 & 0 & 1 \\ & (3-x) & x & 1+x \\ & 2 & 1 & 2 \end{array}$

Initial total moles $= (3+1) = 4$.

Now from Ideal gas equation

$PV = nRT = P \times 100 = 4 \times 0.082 \times 500$

$P = 0.082 \times 20 = 1.64\ atm$.

At equilibrium Total mole $= 3 - x + x + 1 + x = (4 + x)$

$PV = nRT.$

$2.05 \times 100 = (4+x) \times 0.082 \times 500.$
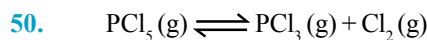
$2.05 = (4+x) \times 0.41.$

$5 = 4 + x.$

$x = 1.$

$\alpha = \dfrac{\text{No. of mole dissociated}}{\text{Initially total mole taken}} = \dfrac{1}{3} = 0.33.$

$P_{PCl_5} = \dfrac{2}{5} \times 2.05 ; \quad P_{PCl_3} = \dfrac{1}{5} \times 2.05$

$P_{Cl_2} = \dfrac{2}{5} \times 2.05$

$K_p = \dfrac{\left(\frac{1}{5} \times 2.05\right)\left(\frac{2}{5} \times 2.05\right)}{\left(\frac{2}{5} \times 2.05\right)} = \textbf{[0.41]}$

**50.**

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

$t = 0 \ \dfrac{8.34}{208.5} \quad\quad 0 \quad\quad 0$

teq. $\left(\dfrac{8.34}{208.5} - x\right) \quad x \quad x \quad n_T = \left(\dfrac{8.34}{208.5} + x\right)$

Given, $(1\ atm)(2.05\ L) = \left(\dfrac{8.34}{208.5} + x\ mole\right)(0.082\ L$

$atm\ mole^{-1}\ K^{-1})(500\ K)$

so, $\dfrac{8.34}{208.5} + x = \dfrac{2.05}{0.082 \times 500} = 0.05\ mole$

$x = 0.05 - 0.04 = 0.01$

so, $\alpha = \dfrac{0.01}{0.04} = 0.25 = 25\%$

$K_p = \dfrac{\alpha^2}{1 - \alpha^2} \cdot P = \left(\dfrac{1/16}{1 - (1/16)}\right) = \dfrac{1}{15}\ atm.$

**52.** $\Delta G^o = \Delta H^o - T\Delta S^o$ ; $K = e^{-\Delta G^o/RT}$

At 300 K, $\Delta G^o = [(-41.16)-(300 \times -0.0424)] \times 1000$
$= -28440$ J/mol $= -RT \ln Kp$

At 1200 K, $\Delta G^o = [(-32.93)-(1200 \times -0.0296)] \times 1000$
$= +2590$ J/mol $= -RT \ln Kp$

$K_p(300\,K) = 8.935 \times 10^4$

$K_p(1200\,K) = 0.7753$

$Q = 1$

at 300 K : $\quad Q < K \quad$ , Hence forward direction.
at 1200 K : $\quad Q > K \quad$ , Hence backward direction.

**53. (i)** $\qquad N_2O_4 \rightleftharpoons 2NO_2 \quad ; \quad G^o_{N_2O_4} = 100$ kJ mol$^{-1}$

conc. at t = 0 $\quad$ 5 $\qquad$ 5 $\qquad G^o_{N_2O_4} = 50$ kJ mol$^{-1}$

$\Delta G^o$ for reaction $= 2 \times G^o_{N_2O_4} - G^o_{N_2O_4} = 2 \times 50 - 100 = 0$

Now, $\quad \Delta G = \Delta G^o + 2.303\,RT \log Q$

$\Delta G = 0 + 2.303 \times 8.314 \times 10^{-3} \times 298 \log \dfrac{5^2}{5} = \mathbf{+3.99\ kJ.}$

**(ii)** Since $\Delta G$ is +ve and thus reaction will not proceed in forward direction.

Also for reverse reaction :

$\qquad 2NO_2 \rightleftharpoons N_2O_4$
Mole at t=0 $\quad$ 5 $\qquad$ 5
Mole at eq. $\quad (5-2x) \qquad (5+x)$
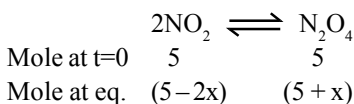
$\therefore \qquad \Delta G = -2.303\,RT \log K_C$ .

$\therefore \qquad \Delta G^o = 0 \qquad \therefore \quad K_C = 1.$

or $\qquad 1 = \dfrac{5+x}{(5-2x)^2}$

$\therefore \qquad x = 1.25.$

Thus, $\quad [NO_2]_{at\ eq.} = 5 - 2.5 = \mathbf{2.5}$

$\qquad [N_2O_4]_{at\ eq.} = 5 + 1.25 = \mathbf{6.25.}$

**56.** $N_2O_4 \rightleftharpoons 2NO_2(g) \qquad d_{mix} = \dfrac{PM_{mix}}{RT}$

$M_{mix} = \dfrac{1.8 \times 0.082 \times 346}{1} = 51.0696$

$\begin{array}{lll} 1-\alpha & 2\alpha & M_{mix} = 51.0696 \\ 0.2 & 0.8 \times 2 = 1.6 & \end{array}$

$M_{mix} = \dfrac{92}{1+\alpha} \qquad 1+\alpha = \dfrac{92}{51} \qquad \alpha = 0.8$

$K_p = \dfrac{\left(\dfrac{1.6}{1.8} \times 1\right)^2}{\left(\dfrac{0.2}{1.8} \times 1\right)} = 7.11 \qquad K_p = K_c RT \qquad K_c = \dfrac{K_p}{RT}$

$K_c = \dfrac{7.11}{0.082 \times 346} = 0.25$

**58.** $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) = NO(g)$

Suppose x moles of $SO_2$ react with x moles of $NO_2$ to form x moles of $SO_3$ and x moles of No to attain equilibrium. The equilibrium concentration, therefore woud be

$[SO_2] = (1-x)$ mol L$^{-1}$; $\qquad [NO_2] = (1-x)$ mol L$^{-1}$;

$[SO_3] = (1+x)$ mole L$^{-1}$; $\qquad [NO] = (1+x)$ miole L$^-$

$K_c = \dfrac{[SO_3][NO]}{[SO_2][NO_2]} = \dfrac{(1+x)(1+x)}{(1-x)(1-x)} = 16$

$\dfrac{(1+x)^2}{(1-x)^2} = 16 \qquad$ or $\qquad \dfrac{(1+x)}{(1-x)} = 4$

$1+x = 4 - 4x \qquad$ or $\quad 5x = 3$

or $\quad x = \dfrac{3}{5} = 0.6$ mole

$[NO_2] = (1-x) = (1-0.6) = 0.4$ mol L$^{-1}$

$[NO] = (1+x) = (1+0.6) = 1.6$ mol L$^{-1}$

**59.** $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$
$\qquad\qquad\quad P \qquad\qquad\qquad P$

For backward reaction

$Q_p \geq K_p$

$\dfrac{P}{P^4} \geq K_p$

$\therefore \quad \dfrac{1}{P^3} \geq 0.125$ atm$^{-3}$

$P^3 \leq 8$ atm$^3$

$P \leq 2$ atm

$P_{Total} = 2\,P = 4$ atm.

**60.** $A(s) \rightleftharpoons A'(g) + H_2S(g)$

$B(s) \rightleftharpoons B'(g) + H_2S(g)$

$A(s) \rightleftharpoons A'(g) + H_2S(g)$

$P = 50$ mm $\quad \Rightarrow \quad P_{H_2S} = P_{A'} = P/2 = 25$ mm

$B(s) \rightleftharpoons B'(g) + H_2S(g)$

$P = 68$ mm $\quad \Rightarrow \quad P_{H_2S} = P_{B'} = P/2 = 34$ mm

**(i)** $K_{p_1} = (25)^2 = 625$ mm$^2$ ; $\qquad K_{p_2} = (34)^2 = 1156$ mm$^2$

**(ii)** Ratio of moles is same as that of partial pressure so,

$\begin{array}{ccc} A(s) & \rightleftharpoons \quad A'(g) & + \quad H_2S(g) \\ & P_1 & P_1 + P_2 \end{array}$

$B(s) \rightleftharpoons B'(g) + H_2S(g)$

$\quad\quad\quad P_2 \quad\quad\quad P_2+P_1$
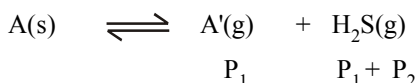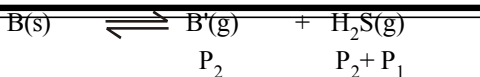
$K_{P_1} = P_{A'} \times P_{H_2S} = P_1(P_1+P_2)$ ......... **(i)**

$K_{P_2} = P_{B'} \times P_{H_2S} = P_2(P_1+P_2)$ ......... **(ii)**

$\dfrac{K_{P_1}}{K_{P_2}} = \dfrac{P_1}{P_2} = \dfrac{625}{1156}$

**(iii)** total pressure $= P_1 + P_2 + (P_1+P_2) = 2(P_1+P_2)$

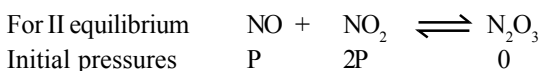**(i) + (ii)** $= (P_1+P_2)^2$

$\sqrt{K_{p_1} + K_{p_2}} = P_1 + P_2$

$P_T = 2 \times (\sqrt{K_{p_1} + K_{p_2}}) = 84.4$ mm.

**61.** For I equilibrium $2NO_2 \rightleftharpoons N_2O_4$

$$K_p = \dfrac{P`_{N_2O_4}}{(P`_{N_2O_4})^2} = 6.8 \quad\quad .... (1)$$

$\because \quad P`_{N_2O_4} = 1.7$ atm $\therefore$ By Eq. (1); $P`_{NO_2} = 0.5$ atm

The equilibria are maintained using NO and $NO_2$ in the ratio 1 : 2

For II equilibrium $\quad NO + NO_2 \rightleftharpoons N_2O_3$

Initial pressures $\quad\quad P \quad\quad 2P \quad\quad\quad 0$

Pressures at equi. $\quad (P-x) \quad (2P-x-3.4) \quad x$

$\because \quad$ 3.4 atm of $NO_2$ are uesed for I equilibrium to have

$P`_{N_2O_4} = 1.7$ atm

At equilibrium $\quad\quad (P-x) \quad\quad 0.5 \quad\quad\quad x$

($\because P`_{NO_2}$ is same for both the equilibria since both reactions are at equilibrium at a time.)

Total pressure at equilibrium (Given 5.05 atm)

$= P`_{NO} + P`_{NO_2} + P`_{N_2O_3} + P`_{N_2O_4}$

$= P - x + 0.5 + x + 1.7$

$\therefore \quad\quad\quad 5.05 = P + 2.20$

$\therefore \quad\quad\quad P = 5.05 - 2.20$

$\therefore \quad\quad\quad P = 2.85$ atm

$\because \quad\quad\quad 2P - x - 3.4 = 0.5$

$\quad\quad\quad 2 \times 2.85 - x - 3.4 = 0.5$

$\therefore \quad\quad\quad x = 5.70 - 3.90$

$\therefore \quad\quad\quad x = \textbf{1.80 atm}$

$\therefore \quad\quad\quad P`_{NO} = 2.85 - 1.80 = \textbf{1.05 atm}$

Now $K_p$ for $\quad NO + NO_2 \rightleftharpoons N_2O_3$

$$K_p = \dfrac{P`_{N_2O_3}}{P`_{NO} \times P`_{NO_2}} = \dfrac{1.80}{1.05 \times 0.5} = \textbf{3.43 atm}^{-1}$$
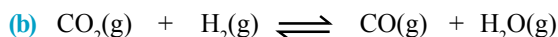
**62.** $\quad CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
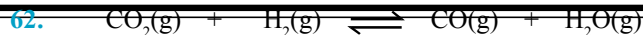
$t = 0 \quad\quad 0.45 \quad\quad 0.45$

$t = t_{eq.} \quad 0.45 - x \quad 0.45 - x \quad\quad x \quad\quad\quad x$

$\quad\quad K_c = 0.11$

$0.11 = \left(\dfrac{x/v}{0.45-x}\right)^2 \quad\quad \dfrac{x}{0.45-x} = 0.33 \quad x = 0.11$

**(a)** $n_{CO} = n_{H_2O} = 0.11 \quad\quad n_{CO_2} = n_{H_2} = 0.34$

**(b)** $\quad CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

$\quad\quad 0.34 \quad\quad 0.34 \quad\quad 0.11 \quad\quad 0.11$

$\quad\quad 0.68 \quad\quad 0.68 \quad\quad 0.11 \quad\quad 0.11$

$\quad 0.68-x \quad 0.68-x \quad 0.11+x \quad 0.11+x$

$\quad K_c = 0.11 \quad ; \quad Q_c < K_c$
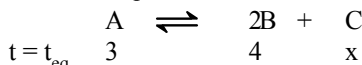
$0.11 = \left(\dfrac{0.11+x}{0.68-x}\right)^2 \quad \dfrac{0.11+x}{0.68-x} = 0.33 = \dfrac{1}{3}$

$0.33 + 3x = 0.68 - x$

$4x = 0.35 \ x = 0.0875 \ n_{CO} = n_{H_2O} = 0.1975$

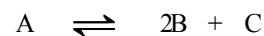$n_{CO_2} = n_{H_2} = 0.5925$

**63 .** Let initial equilibrium concentration of $C = x$ M

$\quad\quad\quad A \rightleftharpoons 2B + C$

$t = t_{eq} \quad 3 \quad\quad 4 \quad\quad x$

$$K_C = \dfrac{x \times 4^2}{3} = \dfrac{16x}{3} \quad\quad ..........(i)$$

Now on doubling the volume concentrations will become half of initial so

$\quad\quad\quad A \rightleftharpoons 2B + C$

after doubling volume $\quad \dfrac{3}{2} \quad\quad 2 \quad\quad \dfrac{x}{2}$

$Q_C = \dfrac{x.4 \times 2}{2 \times 3} = \dfrac{4x}{3} < K_C$

Conc. at new equilibrium $(1.5 - a) \quad\quad 2 + 2a$

$\left(\dfrac{x}{2} + a\right)$ Hence forward shift.

Now given that $(2 + 2a) = 3$

so $\quad a = 0.5$

so $\quad [A] = 1M \quad\quad [B] = 3 \quad\quad [C] = \dfrac{1}{2}(x+1)$

so $\quad K_C = \dfrac{(1+x) \times 9}{2 \times 1} = \dfrac{16x}{3}$

so $\quad 27x + 27 = 32x$

so $\quad x = \dfrac{27}{5} = 5.4$ and $K_C = \dfrac{16}{3} \times \dfrac{27}{5} \times \dfrac{144}{5}$

$= \textbf{28.8. Ans.}$

## EXERCISE - 5

### Part # I : AIEEE/JEE-MAIN

**1.** $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(g)$ $\quad K_c = \dfrac{[P_4O_{10}(s)]}{[P_4(s)][O_2(g)]^5}$

**2.** $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

$\Delta n = 1 - 2 = -1;\ K_p = K_c(RT)^{\Delta n}$

$\therefore \dfrac{K_p}{K_c} = (RT)^{-1} = \dfrac{1}{RT}$

**3.** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$;

$K_c = \dfrac{[NO]^2}{[N_2][O_2]} = 4\times10^{-4}$

$NO(g) \rightleftharpoons \dfrac{1}{2} N_2(g) + \dfrac{1}{2} O_2(g)$;
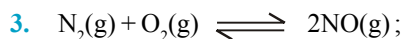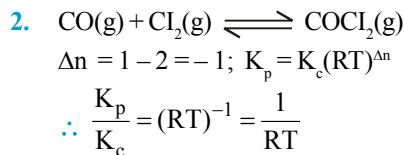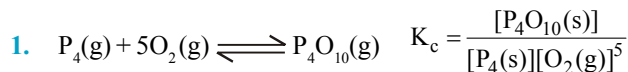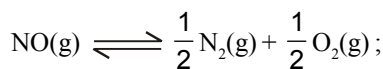
$K_c = \dfrac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} = \dfrac{1}{\sqrt{K_c}} = \dfrac{1}{\sqrt{4\times10^{-4}}} = \dfrac{1}{2\times10^{-2}}$

$= \dfrac{100}{2} = 50$

**4.** $K_p = K_c(RT)^{\Delta n}$ $\qquad \Delta n = 3 - 2 = 1.$

$K_p = K_c(0.0821 \times 457)^1.\ K_p > K_c.$

**5.** $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$; $\Delta H = -329$ kJ.
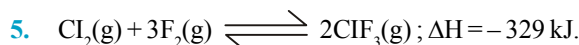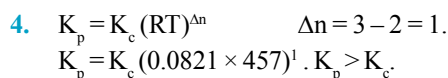
Favourable conditions:

**(i)** Decrease in temperature,

**(ii)** Addition of reactants,

**(iii)** Increase in pressure i.e., decrease in volume.

**6.**
$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

| | | |
|---|---|---|
| Initial presens | 0 | 0.5 | 0 |
| At equi. | 0 | 0.5+x | x |

Total pressure $= 0.5 + 2x = 0.84$ $\quad \therefore\ x = 0.17$ atm

$K_p = P_{NH_3} \times P_{H_2S} = 0.11$ atm$^2$.

**7.** Given : $\quad PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
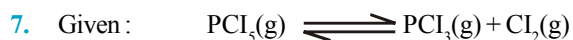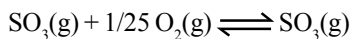
| | | | |
|---|---|---|---|
| t = 0 | 1 | 0 | 0 |
| $t_{eq}$ | 1–x | x | x |

Total number of moles $= 1 - x + x + x = 1 + x$

Thus partial pressure of $PCl_3 = \left(\dfrac{x}{1+x}\right) P.$

**8.** $SO_3(g) \rightleftharpoons SO_2(g) + \dfrac{1}{2} O_2(g)$
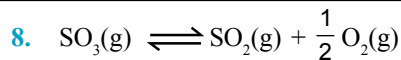
$\dfrac{[SO_2][O_2]^{1/2}}{[SO_3]} = K_C = 4.9 \times 10^{-2}$ ..........(i)

$SO_3(g) + 1/25\ O_2(g) \rightleftharpoons SO_3(g)$

$\dfrac{[SO_3]}{[SO_2][O_2]^{1/2}} = K'_C = \dfrac{1}{4.9\times10^{-2}}$ ..........(ii)

For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
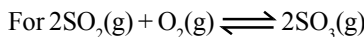
$\dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = K_C^2 = \dfrac{1}{4.9\times4.9\times10^{-4}} = \dfrac{10000}{24.01}$

$= 416.49$

**9.** $c = a + b$

**10.**

| X | $\rightleftharpoons$ | 2Y | | Z | $\rightleftharpoons$ | P | + | Q |
|---|---|---|---|---|---|---|---|---|
| $1-\alpha$ | | $2\alpha$ | | $1-\alpha$ | | $\alpha$ | | $\alpha$ |

$K_{P_1} = \dfrac{\left(\dfrac{2\alpha}{1+\alpha} P_{T_1}\right)^2}{\left(\dfrac{1-\alpha}{1+\alpha} P_{T_1}\right)}$ $\qquad K_{P_2} = \dfrac{\left(\dfrac{\alpha}{1+\alpha} P_{T_2}\right)\left(\dfrac{\alpha}{1+\alpha} P_{T_2}\right)}{\left(\dfrac{1-\alpha}{1+\alpha} P_{T_2}\right)}$

$\dfrac{K_{P_1}}{K_{P_2}} = \dfrac{\left(\dfrac{2\alpha}{1+\alpha} P_{T_1}\right)^2}{\left(\dfrac{1-\alpha}{1+\alpha} P_{T_2}\right)} \times \dfrac{\left(\dfrac{1-\alpha}{1+\alpha} P_{T_2}\right)}{\left(\dfrac{\alpha}{1+\alpha} P_{T_2}\right)\left(\dfrac{\alpha}{1+\alpha} P_{T_2}\right)}$

$\dfrac{1}{9} = \dfrac{4P_{T_1}}{P_{T_2}}$ ; $\qquad \dfrac{P_{T_1}}{P_{T_2}} = \dfrac{1}{36}$
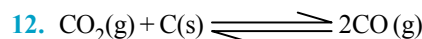
**11.** $PV = nRT$

$V = 1\ dm^3 = 10^{-3}\ m^3$

$P = 3170\ Pa$

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

$T = 300\ K$

$3170 \times 10^{-3} = n \times 8.314 \times 300$

$n = \dfrac{3170\times10^{-3}}{8.314\times300} = 1.27 \times 10^{-3}$ mol.

**12.** $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

0.5 atm

|  0.5–p  |  2p  |
|---|---|

Total pressure $= 0.5 - P + 2P = 0.8$

$P = 0.3$

$$K_p = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(2P)^2}{(0.5-P)} = \frac{(0.6)^2}{(0.5-0.3)}$$

$K_p = 1.8$

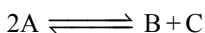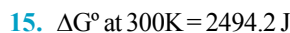**13.** $N_2 + O_2 \longrightarrow 2NO \qquad K = 4 \times 10^{-4}$

$NO \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2 \quad K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$

**14.** For reaction :

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$$
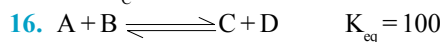
$$\Delta N_g = -\frac{1}{2} = x$$

**15.** $\Delta G°$ at $300K = 2494.2$ J

$$2A \rightleftharpoons B + C$$
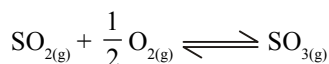
$\Delta G° = -RT \ln K$

$-2494.2 = -8.314 \times 300 \ln K$

$K = 10$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times \dfrac{1}{2}}{\left(\dfrac{1}{2}\right)^2} = 4.$$

$Q > K_C \Rightarrow$ reverse direction.

**16.** $A + B \rightleftharpoons C + D \qquad K_{eq} = 100$

|  1  |  1  |  1  |  1  |
|---|---|---|---|

$Q_c = 1 < K_{eq}$

$\therefore$   fore ward shift

$t_{eq}$ n – x|(1 – x)| (1 + x) | (1 + x)

$$\frac{(1+x)(1+x)}{(1-x)(1-x)} = 100 \Rightarrow \frac{1+x}{1-x} = 10$$
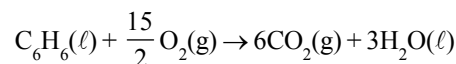
$1 + x = 10 - 10x$

$$x = \frac{9}{11}$$

$\therefore [D] = 1 + x = 1 + \dfrac{9}{11} = 1.818$ **Ans.**

**17.** $CO_2(g) + 2H_2O(\ell) \rightarrow CH_4(g) + 2O_2(g) ; \Delta_r H° = 890.3$

$\Delta_r H° \quad -393.5 -285.8 \quad ? \qquad 0$
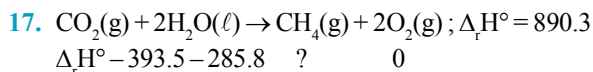
$$\Delta_r H° = \sum (\Delta_f H°)_{products} - \sum (\Delta_f H°)_{Reactants}$$

$$890.3 = \left[1 \times (\Delta_f H°)_{CH_4} + 2 \times 0\right] - \left[1 \times (393.5) + 2(285.8)\right]$$

$$(\Delta_f H°)_{CH_4} = 890.3 - 965.1 = -74.8 \text{ kJ/mol}$$

$$C_6H_6(\ell) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell)$$

**Part # II : IIT-JEE ADVANCED**

**1.** When nitrogen is added at equilibrium condition, the equilibrium will shift according to Le-chatelier principle at equilibrium $\Delta G = 0$ and catalyst changes the rate of forward and backward reactions by equal extent. $K_P$ of reaction is a function of temperature only.

**2.** $\Delta G° = \Delta H° - T\Delta S° = -54.07 \times 1000 - 298 \times 10$
$= -54070 - 2980 = -57050$

$\Delta G° = -2.303 \text{ RT} \log_{10} K$
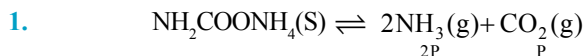
$-57050 = -2.303 \times 298 \times 8.314 \log_{10} K$

$= -5705 \log_{10} K$

$\log_{10} K = 10$

**3.** At equilibrium $\Delta G$ (Gibbs energy) $= 0$ but $\Delta G°$ (standard Gibbs energy) $\neq 0$

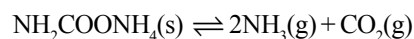As $\Delta G$ (Gibbs energy) is more negative reaction will be more spontaneous.

**MOCK TEST**

**1.** $\qquad NH_2COONH_4(S) \rightleftharpoons \underset{2P}{2NH_3(g)} + \underset{P}{CO_2(g)}$

Initial

$$K_p = (P_{NH_2})^2 (P_{CO_2})$$

$$K_p = (2P)^2 (P) \text{ ...}(i)$$

$$P_T(\text{initial}) = 3P$$

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

Final $\qquad\qquad\qquad 3P \qquad\quad P'$
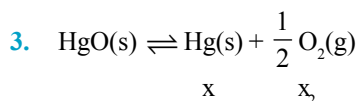
**273**

$Kp = (3P)^2 (P') \ldots$ **(ii)**

From eq. **(i)** and **(ii)**

$(2P)^2 (P) = (3P)2 (P')$

$P' = \dfrac{4P}{9}$

$\dfrac{P_T(New)}{P_T(Old)} = \dfrac{3P + P'}{3P} = \dfrac{3P + \dfrac{4P}{9}}{3P} = \dfrac{31}{27}$

2. Formation of ammonia is an exothermix process therefore it is facourable at lower temperature. But at lower temperature rate of the reaction becomes slow.

3. $HgO(s) \rightleftharpoons Hg(s) + \dfrac{1}{2} O_2(g)$

       x        $x_2$

$K_p = P_{Hg(g)} \times (PO_2) \dfrac{1}{2}$

Total moles at equilibrium $= \dfrac{3x}{2}$

$P_{Hg} = \dfrac{x}{3x/2} = \dfrac{2}{3}P$

$PO_2 = \dfrac{x/2}{3x/2}P = \dfrac{1}{3}P$

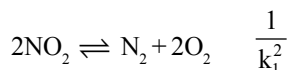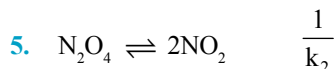$K_P = \dfrac{2}{3}P\left(\dfrac{1}{3}P\right)^{1/2} = \dfrac{2}{3^{3/2}}P^{3/2}$

4.            $Fe^{3+}$   +   $SCN^-$   $\rightleftharpoons$   $[Fe(SCN)]^{2+}$

Initial conc.    $\dfrac{10^{-3}}{56}$        b          0

Final conc.    $\dfrac{10^{-3}}{56} - 6 \times 10^{-6}$    $b - 6 \times 10^{-6}$      $6 \times 10^{-6}$

$K = \dfrac{10^3}{7.142}$

on solving b $= 0.0036$ M

5. $N_2O_4 \rightleftharpoons 2NO_2$        $\dfrac{1}{k_2}$

  $2NO_2 \rightleftharpoons N_2 + 2O_2$        $\dfrac{1}{k_1^2}$

6. $Br_2(\ell)$   +   $Cl_2(g) \rightleftharpoons 2BrCl(g)$

    t = 0        1        0

            $(1 - x)$      2x

$k_p = \dfrac{(P_{BrCl})^2}{P_{Cl_2}} = 1$ so, $P_{Cl_2} = (P_{BrCl})^2 = 0.01$ atm

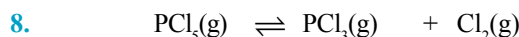then at equilibrium,    $\dfrac{n_{BrCl}}{n_{Cl_2}} = \dfrac{0.1}{0.01} = 10 = \dfrac{2x}{1-x}$

So, $10 - 10x = 2x$    or    $x = \dfrac{10}{12} = \dfrac{5}{6}$ moles

Moles of $Br_2(\ell)$ required for maintaing vapour pressure of 0.1 atm

$= 2 \times \dfrac{5}{6}$ moles $= \dfrac{10}{6}$ moles = moles of $BrCl(g)$.

Moles required for taking part in reaction = moles of $Cl_2$

used up $= \dfrac{5}{6}$ moles.

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

  t = 0      5          0          0

  t = $t_{eq}$    $5 - 5 \times 0.2$   $5 \times 0.2$    $5 \times 0.2$

           4 mole     1 mole     1 mole

Total moles at equilibrium $= 4 + 1 + 1 + 1\,(N_2)$

              = 7 moles

$k_p = \dfrac{\left(\dfrac{1}{7} \times 1\,atm\right)\left(\dfrac{1}{7} \times 1\,atm\right)}{\left(\dfrac{4}{7} \times 1\,atm\right)} = \dfrac{1}{28}$ atm.

10. Given $K_C < 2$ therefore in case of B and C $K_C = \dfrac{2 \times 4}{6} = \dfrac{4}{3}$

and concentrated of $PCl_3$ and $Cl_2$ together will decrease or increase as reaction can go in the forward or backward direction.

11.          $N_2O_4$   $\rightleftharpoons$   $2NO_2$

  t = 0      a          0

  t        $a(1 - \alpha)$    $2a\alpha$

vapour density $= \dfrac{46}{1 + \alpha} = 30.67$

so $1 + \alpha = 1.5 = 0.5 = 50\%$

Total pressure $= \dfrac{1.5 \times 1.5 \times 0.082 \times 300}{8.2} = 6.75$ atm

so $k_p = \dfrac{4\alpha^2}{1 - \alpha^2}P = 9$ atm

and for density of mixture $= \dfrac{138}{8.2}$ gm/L $= 16.83$ gm / L.

13. **(A)** As reactionis endothermic therefore it will go in the

forward direction hence moles of CaO will increase.

**(C)** With the increase or decrease of volume particle pressure of the gases will remain same.

**(D)** Due to the addition of inest gas at constant pressure reaction will proceed in the direct in which more number of gaseous moles are formed.
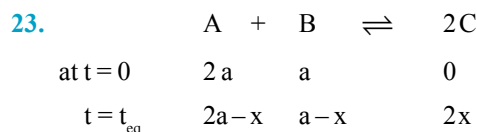
15. As concentration of reaction (gaseous) are increased at equilibrium reaction will go in the forward direction.

Also above reaction is endothermic therefore increase in temperature will favour it.

19. Solubility of gas is favourable at high pressure and this process is exothermic hence solubility will be more at low temperature.
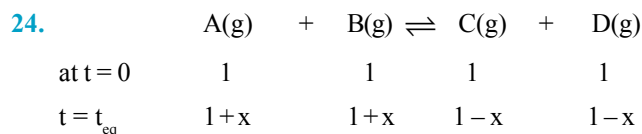
20. Since density of gold decreases after melting therefore it is favourable at low pressure and high temperature.

22. Since the slpe of the straight line graph between $\log K$ and $\dfrac{1}{T}$ is positive, $\Delta H_{reaction}$ would be negative, i.e., the forward reaction would be exothermic.

23.
$$A \;+\; B \;\rightleftharpoons\; 2C$$

at t = 0    2 a    a    0

t = t$_{eq}$    2a – x    a – x    2x

$$\Rightarrow \; 2a - = 2x \qquad \Rightarrow \; x = \frac{2}{3}a$$

$$\Rightarrow \; K_C = \frac{(2x)^2}{(29-x)(a-x)} = \frac{4.\left(\frac{2}{3}\right)^2}{\left(2-\frac{2}{3}\right)\left(1-\frac{2}{3}\right)} = \frac{4\times 4}{4\times 1} = 4$$

24.
$$A(g) \;+\; B(g) \rightleftharpoons C(g) \;+\; D(g)$$

at t = 0    1    1    1    1

t = t$_{eq}$    1 + x    1 + x    1 – x    1 – x
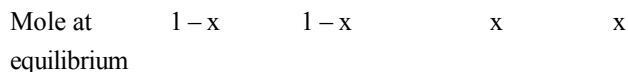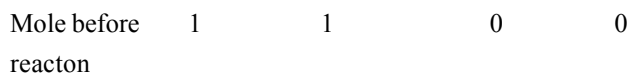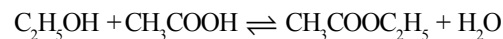
$$Q_C = \frac{(1/2)(1/2)}{(1/2)(1/2)} = 1 > K_C$$

$$\Rightarrow \; \frac{(1-x)(1-x)}{(1+x)(1+4)} = \frac{1}{4} \qquad \Rightarrow \; \frac{1-x}{1+x} = \frac{1}{2}$$

$$2 - 2x = 1 + x$$

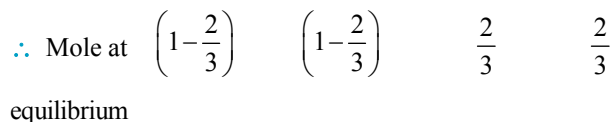$$\Rightarrow \quad x = \frac{1}{3}$$

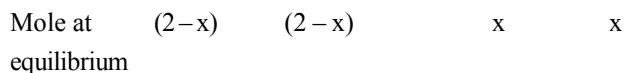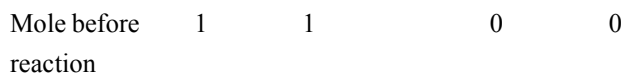$$\therefore \quad [C] = \frac{1-x}{2} = \frac{1}{3}M$$

25. **Case – I**
$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Mole before reacton    1    1    0    0

Mole at equilibrium    1 – x    1 – x    x    x

$$\therefore \quad x = \frac{2}{3}$$

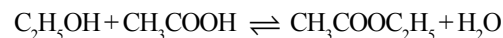$\therefore$ Mole at equilibrium    $\left(1-\dfrac{2}{3}\right)$    $\left(1-\dfrac{2}{3}\right)$    $\dfrac{2}{3}$    $\dfrac{2}{3}$

$$\therefore \qquad K_C = \frac{\dfrac{2}{3}\times\dfrac{2}{3}}{\dfrac{1}{3}\times\dfrac{1}{3}} = 4$$

**Note** : Volume terms are eliminated

**Case - II**
$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Mole before reaction    1    1    0    0

Mole at equilibrium    (2 – x)    (2 – x)    x    x

$$KC = 4 = \frac{x^2}{(2-x)^2} \qquad \text{or} \quad \therefore \quad \frac{x}{(2-x)} = 2$$

or    x = 1.33.

26. (A – p, t) ; (B – q, r) ; (C – q, s)

**(A)** $\Delta ng = 0$ so independent of pressure
Exothermic so high temperature

**(B)** $\Delta ng = (-)$ ve High pressure
Exothermic so Low Temperature

**(C)** $\Delta ng = (+)$ve so low pressure
Exothermic so Low Temperature

28. **(A)** As $\Delta n > 0$ therefore if $P \uparrow$, reaction will go in the backward direction.

**275**

**(B)** As $\Delta n < 0$ therefore if $V \uparrow, P \downarrow$ reaction will go in the direction in which more number of gaseous moles are formed i.e. backward direction.

**(C)** As $\Delta n = 0$ hence no effect.

**(D)** If concentrated of product is decreased reaction will go in the forward direction.

**30.** 195488.

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

partial pressure at equilibrium $\quad p_1 \quad\quad - \quad\quad p_2$
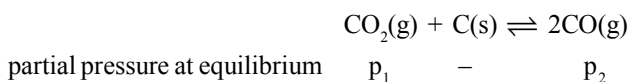
$$k_p = \frac{P_2^2}{P_1} = 10 \quad \text{or} \quad P_1 = 0.1\, P_2^2 \quad \ldots(1)$$

but $p_1 + p_2 = 5.6$ atm

solving $p_1 = 1.6$ atm and $p_2 = 4$ atm

using $p = CRT$

$$C_1 \text{(for } CO_2) = \frac{1.6}{0.082 \times 1000} = 0.0195\text{ M}$$

$$C_2 \text{(for } CO) = \frac{4.0}{0.082 \times 1000} = 0.0488\text{ M}.$$

**31.**
$$H_2(g) \quad + \quad Br_2(g) \quad \rightleftharpoons \quad 2HBr(g)$$

Initial pressure $\quad 0 \quad\quad\quad 0 \quad\quad\quad 10.0$ bar

At equilibrium $\quad p/2 \quad\quad p/2 \quad\quad (10.0\text{-}p)$
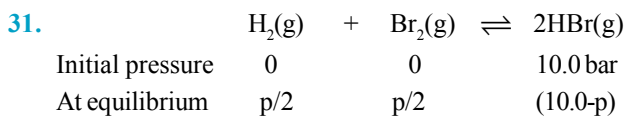
$$k_p = \frac{p^2_{HBr}}{P_{H_2} \times P_{Br_2}}$$

$$1.6 \times 10^5 = \frac{(10-p)^2}{(p/2)(p/2)}$$

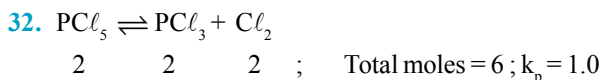Taking square root of bith sides

$$4 \times 10^2 = \frac{10-p}{p/2}$$

$$200\, p = 10 - p$$
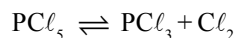
$$p = \frac{10}{201}\text{ bar}$$

$$p_{H_2} = p/2 = \frac{1}{2}\left(\frac{10}{201}\right)\text{bar} = 2.5 \times 10^{-2}\text{ bar}$$

$$p_{Br_2} = p/2 = 2.5 \times 10^{-2}\text{ bar}$$

$$p_{HBr} = 10 - p \approx 10\text{ bar}$$

**32.** $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$\quad 2 \quad\quad 2 \quad\quad 2 \quad ; \quad$ Total moles $= 6$ ; $k_p = 1.0$

Let y moles of $Cl_2$ are introduced then at new equilibrium

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$\therefore \quad 2+x \quad\quad 2-x \quad 2+y-x \quad ; \quad$ Total moles $= 12$

Total moles of $PCl_5 + PCl_3 = 4$ and moles of $Cl_2 = 8$

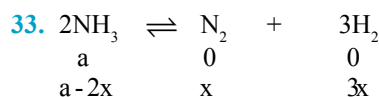$$\therefore \quad P_{PCl_5} = \frac{(2+x)3}{12} = \frac{2+x}{4}$$

$$P_{PCl_3} = \frac{(2-x)3}{12} = \frac{2-x}{4}$$

$$P_{PCl_2} = \frac{8 \times 3}{12} = 2$$

$$\therefore \quad k_p = 1 = \frac{\dfrac{(2+x)}{4}\left(\dfrac{2}{1}\right)}{\left(\dfrac{2+x}{4}\right)}$$

$\therefore \quad x = \dfrac{2}{3}$ and hence from equation (1) $y = \dfrac{20}{3} = 6.67$ moles

$\therefore \quad$ **Ans. is 667 – 666**

**33.**
$$2NH_3 \quad \rightleftharpoons \quad N_2 \quad + \quad 3H_2$$
$$a \quad\quad\quad 0 \quad\quad\quad 0$$
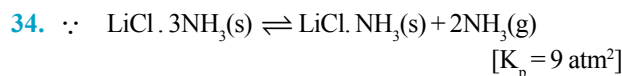$$a - 2x \quad\quad x \quad\quad\quad 3x$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \Rightarrow \quad P_2 = 20\text{ atm.}$$

Now $\quad \dfrac{a+2x}{a} = \dfrac{30}{20}$

$$2a + 4x = 3a$$

$$\Rightarrow \quad x = \frac{1}{4}a .$$

$\therefore \quad$ % of $NH_3$ decomposed $= \dfrac{2x}{a} \times 100 =$ **50%**

**34.** $\because \quad LiCl . 3NH_3(s) \rightleftharpoons LiCl. NH_3(s) + 2NH_3(g)$

$$[K_p = 9\text{ atm}^2]$$

$\therefore \quad LiCl. 3NH_3(s) + \quad 2NH_3(g) \rightleftharpoons LiCl. 3NH_3(g)$

Initial mole $\quad 0.1 \quad\quad\quad a \quad\quad\quad 0$

Final mole at eq. $\quad 0 \quad\quad (a-0.2) \quad\quad 0.1$

$$\left[k_{p_1} = \frac{1}{9}(atm)^{-2}\right]$$

Let initial mole of $NH_3$ should be a to bring in completed of reaction.

At eq. $\quad K_{p_1} = \dfrac{1}{(P'_{NH_3})^2}$

or $\qquad \dfrac{1}{9} = \dfrac{1}{(P'_{NH_3})^2}$

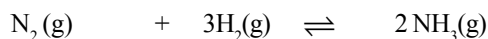$\therefore \qquad P'_{NH_3} = 3\,atm$

$\because \qquad PV = nRT$

$\qquad 3 \times 5 = n \times 0.0821 \times 313$

$\therefore \qquad n = 0.5837$

i.e., $\quad (a - 0.2) = 0.5837$

$\therefore \quad$ Initial mole of $NH_3 = a = 0.5837 + 0.2 = 0.7837$ mole.

**35.** Let the initial partial pressures of $N_2$ and $H_2$ be 9P and 13 P respectively

$$N_2\,(g) \qquad + \quad 3H_2(g) \quad \rightleftharpoons \quad 2\,NH_3(g)$$
$$9P - y - x \qquad\quad 13P - 3x - 2y \qquad 2x$$
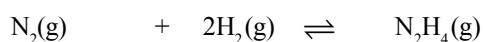
$$N_2(g) \qquad + \quad 2H_2\,(g) \quad \rightleftharpoons \quad N_2H_4(g)$$
$$9P - y - x \qquad\quad 13P - 3x - 2y \qquad y$$

Total pressure $= P_{N_2} + P_{H_2} + P_{NH_3} + P_{N_2H_4} = 3.5\,atm \qquad ...(1)$

$= (9P - x - y) + (13\,P - 3x - 2y) + 2x + y = 3.5$ atm   ...(1)

$P_{NH_3} = 2x = 0.5$ atm $\qquad\qquad ...(2)$

$P_{H_2} = (13P - 3x - 2y) = 1$ atm   ...(3)

from $(1) \Rightarrow (9P - x - y) + 1$ atm $+ 0.5 + y = 3.5$

$\qquad\qquad \Rightarrow (9P - x) = 2$ atm

so $\qquad 9P = 2.25$

$P = 0.25$ atm

from (3) equation $2y = 1.5$

$\qquad\qquad\qquad y = 0.75$ atm

so $P_{N_2} = 9P - x - y = 1.25$ atm

$P_{H_2} = 1\,atm$

$P_{NH_3} = 0.5\,atm$

$P_{N_2H_4} = 0.75\,atm$

So, $K_{p_1} = \dfrac{P_{NH_3}^2}{P_{H_2}^3 . P_{N_2}} = \dfrac{0.5 \times 0.5}{1 \times 1 \times 1 \times 1.25} = 0.2\ atm^{-2}$

$K_{p_2} = \dfrac{P_{N_2H_4}}{P_{N_2} . P_{H_2}^2} = \dfrac{0.75}{1 \times 1 \times 1.25} = 0.6\ atm^{-2}$