HINTS & SOLUTIONS

EXERCISE - 1

Single Choice

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. $A + B \rightleftharpoons C + D$

	A	B	C	D	
	3n	n	0	0	t = 0
	(3n–x)	(n–x)	x	x	t = teq.

$(n-x) = x$

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

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

	A	B	C	D
Initial	1	1	0	0
At equili.	(1 – x)	(1 – x)	x	x

$\therefore \quad K_c = \dfrac{[C][D]}{[A][B]} = 9$

$\therefore \quad \dfrac{x\,.x}{(1-x)^2} = 9$ or $x^2 = 9 + 9x^2 - 18x$ or

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

$\therefore \quad x = \dfrac{3}{2}$ or $\dfrac{3}{4}$

Hence, among the given options, the option (3) i.e., 0.75 is correct.

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

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

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

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

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

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

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

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

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

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

$P_{A_2} = 0.80$ atm., $\qquad P_{B_2} = 0.4$ 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. $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 2HCl(g) + O_2(g)$

$K_p = 0.03 \quad T = 427°C = 700\,K$

$K_p = K_C(RT)^1$

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

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

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

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

so, $\Delta n_g = -1.$

19. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad K_p = 4\times10^{-3}$

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

$K'_p = \left(\frac{1}{4\times10^{-3}}\right)$

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

$K''_p = (K'_p)^2 = \left[\frac{1}{4\times10^{-3}}\right]^2 = \left[\frac{1000}{4}\right]^2 = 6250 = 625\times10^2$

6.25×104 atm.

20. **(i)** $2\,NO + O_2 \rightleftharpoons 2\,NO_2$

(ii) $NO_2 + SO_2 \rightleftharpoons SO_3 + NO$

(iii) $2\,SO_3 \rightleftharpoons 2\,SO_2 + O_2$

Now, -2 **(ii)** = **(i)** + **(iii)**

so, $K_{C_3} \times K_{C_1} = 1/K^2_{C_2}$

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

$= 11$

23. $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O\,(\bullet).$

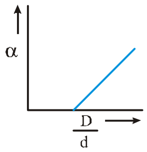
a	a	0	0
a 0.33a	a − 0.33a	0.33a	0.33a

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

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

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

The point at which $\alpha = 0$.



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

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

t=0	a	0	0
$t = t_{eq.}$	$a(1-\alpha)$	$a\alpha$	$a\left(\frac{\alpha}{2}\right)$

Total mole at eq. $= a\left(1 + \frac{\alpha}{2}\right)$

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

$P_{SO_2} = \left(\frac{\alpha}{1+(\alpha/2)}\right)P_0 = \left(\frac{2\alpha}{2+\alpha}\right)\times P_0$

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

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

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 × 100 gm of $CaCO_3$ = 32.5 gm of $CaCO_3$

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

P–P/2 $\qquad P = \frac{3P}{2} = 12$

so, $K_p = \frac{P^2}{(P/2)} = 2P = 2\times8 = 16$ atm.

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

at point — A

$Q = \frac{[\text{Product}]}{[\text{Reactant}]} = 0$

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

$2 \quad 2 \qquad 2 \quad 2$

$2+x \quad 2+x \qquad 2-x \quad 2-x \qquad x = 1$

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

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

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 ΔH is obtained.

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

ΔH = Positive.

41. $CuSO_4 . 5H_2O(s) \rightleftharpoons CuSO_4 . 3H_2O(s) + 2H_2O(g)$

$K_p = 2.25 \times 10^{-4}$

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

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

$= 50\%$

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

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

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

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

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

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

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 $\quad$ 2mole $\quad$ 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 $\quad$ 2mole $\quad$ 3mole

$t = 0 \quad 1 \quad (2+a) \quad 3$

$(1-x) \quad (2+a)-x \quad (3+2x)$

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

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

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

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

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

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

$7.11 = 1.5 + a.$

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

52. $AB \rightleftharpoons A^+ + B^- \qquad AB + B^- \rightleftharpoons AB_2^-$

$a-x-y \quad y \quad (y-x) \qquad (a-x-y) \quad y-x \qquad x$

$$K_1 = \frac{y(y-x)}{(a-x-y)} \qquad K_2 = \frac{x}{(a-x-y)(y-x)}$$

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

53. $N_2 + O_2 \rightleftharpoons 2NO$

Initial: N_2 2 moles; O_2 4moles

At Eq.: N_2 $2-\frac{1}{2}$; O_2 $4-\frac{1}{2}$; NO $2\times\frac{1}{2}=1$ mol

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

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

Moles at eqm: $2-x$; $4-x$; $2x$

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

$$[AB(g)]=\frac{2\times1.33}{4}=0.66 \text{ M}$$

55. $X_2 + Y_2 \rightleftharpoons 2XY$

$\frac{1}{3}-x$ $\quad \frac{2}{3}-x \quad 2x \quad 2x=0.6 \Rightarrow x=0.3$

$[x_2]=\frac{1}{3}-0.3 \qquad [y_2]=\frac{2}{3}-0.3$

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

60. $2O_3(g) \rightleftharpoons 3O_2(g) \quad K_p=4\times10^{14} \qquad p_{O_2} >> p_{O_3}$

$$K_p=\frac{p_{O_2}^3}{p_{O_3}^2} \qquad p_{O_2}+P_{O_3}=8 \Rightarrow P_{O_2}\simeq 8 \text{ atm.}$$

$$4\times10^{14}=\frac{8^3}{p_{O_3}^2} \qquad p_{O_3}^2=11.3\times10^{-7}$$

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

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

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

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

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

$$P_{NO_2}=0.025$$

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

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

$1-\alpha \simeq 1$ and $1+\alpha \simeq 1 \Rightarrow 27\times10^{-8}\,P_o^2=\frac{27}{16}\,P_o^2\times\alpha^4$

$\alpha=2\times10^{-2}$

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

$1-\alpha \qquad \alpha \qquad \frac{\alpha}{2}$

$$M_{mix}=\frac{0.9\times0.082\times1000}{1.23}=60$$

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

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

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

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

$1-\alpha \qquad \frac{\alpha}{2} \qquad 2x \qquad 1-\alpha \simeq 1$

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

70. $N_2+3H_2 \rightleftharpoons 2NH_3,\ K_P=4.28\times10^{-5}\ \text{atm}^{-2}$

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

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

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

Equilibrium temperature is 300°C that is 573 K.

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

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{15}{300} = \frac{P_2}{573}$$

$P_2 = 28.65$ atm at 300°C.

$$\begin{array}{llll} & NH_3(g) \rightleftharpoons & \frac{1}{2}N_2(g) + & \frac{3}{2}H_2(g). \\ t=0 & 28.65\text{ atm} & 0 & 0 \\ t = t_{eq.} & [28.65-x] & \frac{x}{2}\text{ atm} & \frac{3}{2}x \end{array}$$

But according to question.

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

$x = 11.46.$

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

76. $$\begin{array}{llll} & Br_2(\bullet) + Cl_2(g) \rightleftharpoons & 2BrCl(g) \\ t=0 & 1 & 0 \\ & (1-x) & 2x \end{array}$$

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

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

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

Moles of $Br_2(\bullet)$ 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 = $\frac{5}{6}$ moles.

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

77. $H_2O(\bullet) \rightleftharpoons H_2O(g)$

$K_p = (P_{H_2O})$

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

$$\log\frac{K_2}{0.0118} = \frac{597.4 \times 10^3}{2.303 \times 8.314}\left[\frac{1}{1300} - \frac{1}{1200}\right]$$

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

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

84. $$\begin{array}{llll} (1)\ A(s) \rightleftharpoons & D(g) & +\ C(g) & K_p = (20)^2 \\ & 20\text{ atm} & 20\text{ atm} & \end{array}$$

$$\begin{array}{llll} (2)\ B(s) \rightleftharpoons & E(g) & +\ F(g) & K_p = (30)^2 \\ & 30\text{ atm} & 30\text{ atm} & \end{array}$$

(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. $$\begin{array}{lll} A(s) \rightleftharpoons & X & +\ Y \\ & \alpha & \alpha+\beta \end{array}$$

$$\begin{array}{lll} B(s) \rightleftharpoons & Y & +\ Z \\ & \beta+\alpha & \beta \end{array}$$

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

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

$P_{total} = (\alpha+\beta) + \alpha + \beta = 2(\alpha+\beta)$

$\Rightarrow 2(\alpha+\beta) = 50 \Rightarrow \alpha+\beta = 25$

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

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

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

$$\begin{array}{llll} X(s) \rightleftharpoons & A(g) & + & 2B(g) \\ & x & & (2x+2y)\ ; \end{array}$$

$$\begin{array}{llll} Y(s) \rightleftharpoons & C(g) & + & 2B(g) \\ & y & & (2y+2x)\ ; \end{array}$$

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

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

$\Rightarrow \quad x = 0.1$ atm;

$\therefore \quad y = 0.05$ atm

Total pressure of gases $= P_A + P_B + P_C$

$= 3(x+y)$

$= 0.45$ 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. $K = \dfrac{r_f}{r_b} \quad \Rightarrow \quad 1.5 = \dfrac{r_f}{7.5\times10^{-4}} \quad \Rightarrow \quad r_f = 1.12\times10^{-3}$.

90. $K_P = \dfrac{P_{CO(g)}.P_{H_2(g)}}{P_{H_2O(g)}} = \dfrac{(P_{H_2(g)})^2}{P_{H_2O(g)}}$ (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. 4×10^4, Since Equilibrium const. is temp. dependent only.

EXERCISE - 2

Part # I : Multiple Choice

6. **(A)** $\Rightarrow [CH_4] = \dfrac{16}{16\times10} = 0.1$ M

(B) $\Rightarrow [H_2O] = \dfrac{18}{18\times10} = 0.1$ M

(C) $\Rightarrow [Cl_2] = \dfrac{35.5}{71\times10} = 0.05$ M

(D) $\Rightarrow [CO_2] = \dfrac{44}{44\times10} = 0.1$ M

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

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

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

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

(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

$$\begin{array}{llll} \Rightarrow\ AB_2(g) + & B_2C(g) \longrightarrow & AB_3(g) + & BC(g) \\ a & b & 0 & 0 \\ a-x & b-x-y & x & x-y \end{array}$$

$$\begin{array}{llll} BC(g)\ + & B_2C(g) \longrightarrow & B_3C_2(g) & \\ x-y & b-x-y & y & \text{As } y > x \end{array}$$

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.
$$\begin{array}{lllll} & 2NO \rightleftharpoons & N_2 & + \ O_2 & \alpha = 10\% \\ t=0 & 4-.4 & .2 & .2 & \\ & 3.6 & 0.2 & 0.2 & \end{array}$$

$\Delta n = 0$,

$$\therefore K_P = K_C, \quad K_C = \frac{(.2/V)^2}{(3.6/V)^2} = \frac{4}{36\times36}$$

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

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

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

23. At equilibrium $\Delta G = 0$

Given $\Delta G^0 = 0$

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

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

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↓, then V↓, then P↑, 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.

$$\begin{array}{llll} & PCl_5 \rightleftharpoons & PCl_3 + & Cl_2 \\ \text{at } t=0 & a & 0 & 0 \\ t=tq & a-x & x & x \end{array}$$

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

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

28.

$$\begin{array}{llll} & H_2(g) + & I_2(g) \rightleftharpoons & 2HI(g) \\ t=0 & 4.5 & 4.5 & 0 \\ t=\text{teq.} & 4.5-x & 4.5-x & 2x \\ \text{put} & x=1.5 & & \\ & 4.5-1.5 & 4.5-1.5 & 2\times1.5=3 \\ & \downarrow & \downarrow & \downarrow \\ & 3 & 3 & 3 \end{array}$$

$$K_C = \frac{(3)^2}{3\times3} = 1$$

29.

$$\begin{array}{llll} & H_2(g) + & I_2(g) \rightleftharpoons & 2HI(g) \\ t=0 & 1.5 & 1.5 & 0 \\ t=\text{tev} & 1.5-x & 1.5-x & 2x \end{array}$$

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

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

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

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

32.

$$\begin{array}{llll} & N_2 + & 3H_2 \rightleftharpoons & 2NH_3 \\ t=0 & 1\text{ mole} & 2\text{ mole} & 0 \\ t=eq & 1-x & 2-3x & 2x=0.8 \end{array}$$

$x = 0.4$

mole of $N_2 = 0.6$

mole of $H_2 = 0.8$

34.

$$\begin{array}{lllll} & Co + & H_2O \rightleftharpoons & CO_2 + & H_2 \\ t=0 & 1 & 1 & 1 & 0 \\ t=teq & 1-x & 1-x & 1+x & x \end{array}$$

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

37.

$A + D \rightleftharpoons AD\ ;\ K_1$

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

$AD_2 + D \rightleftharpoons AD_3\ ;\ K_3$

$A + 3D \rightleftharpoons AD_3\ ;\ K$

As we know that $K = K_1.K_2.K_3$

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

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

39.

$$\begin{array}{lllll} & 2A_8 \rightleftharpoons & 2A_3 + & 3A_2 + & A_4 \\ t=0 & 2 & 0 & 0 & 0 \\ t=t_{eq} & 2-2\alpha & 2\alpha & 3\alpha & \alpha \end{array}$$

$n_T = 2 + 4\alpha$

given mole fraction of A_2 is $= 0.36$.

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

$\alpha = 0.46$

$$\text{Mole fraction of } A_8 = \frac{2-2\alpha}{2+4\alpha} = \frac{2-2\times0.46}{2+4\times0.46} = 0.28$$

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

$K_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ Concentration in gram mole/litre, therefore

$[SO_3] = \dfrac{48}{80 \times 1}$ (Where 80 is molecular weight of SO_3)

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

$[O_2] = \dfrac{9.6}{32 \times 1}$ (Where 32 is molecular weight of O_2)

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

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

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

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

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

46.

	A	+ 2B	⇌ 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. $N_2 + O_2 \rightleftharpoons 2NO$ $2x = 1.0$ mole/litre

N_2	O_2	$2NO$
a	b	0
(a − x)	(b−x)	2x

$x = 1.0/2$ 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 1.24×10^{-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. $Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$ $K = \dfrac{10^3}{7.142}$

	Fe^{3+}	SCN^-	$[Fe(SCN)]^{2+}$
Initial conc.	$\frac{10^{-3}}{56}$	b	0
Final conc.	$\frac{10^{-3}}{56} - 6 \times 10^{-6}$	$b - 6 \times 10^{-6}$	6×10^{-6}

on solving b = 0.0036 M.

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

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

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. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

PCl_5	PCl_3	Cl_2	
1	0	0	Initial mole
$\frac{1-0.7}{5}$	$\frac{0.7}{5}$	$\frac{0.7}{5}$	Conc. at equilibrium

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 α will change on changing pressure and $P_{H_2} > P_{N_2}$.

58. $K_p = K_C (RT)^{\Delta n_g} = K_C (RT)$

so, $T = \frac{K_P}{K_C} \frac{1}{R} = \frac{1}{0.0821} = 12.18\text{ K}$

59. $K_p = 0.667\text{ atm} = \frac{2}{3}\text{ atm} = \frac{4\alpha^2}{1-\alpha^2} \cdot P = \frac{4\alpha^2}{1-\alpha^2} \cdot \frac{1}{2}$

so, $\frac{4\alpha^2}{1-\alpha^2} = \frac{4}{3}$ $\Rightarrow$ $3\alpha^2 = 1 - \alpha^2$

so, $\alpha^2 = \frac{1}{4}$ $\Rightarrow$ $\alpha = \frac{1}{2}$

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)** Δn_g is +ve so as P is increased, backward shifting will take place. Total pressure even after shifting will remain same.

(B) Δn_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. $\text{Slope} = \frac{-\Delta H^\circ}{2.3R} = -\frac{230}{2.3 \times 2} = -50$

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

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)

$$\underset{3p-x-y}{2A_2(g)} \rightleftharpoons \underset{x/2}{A_4(g)}$$

$$\underset{3p-y-x}{A_2} + \underset{P-2y}{2C} \rightleftharpoons \underset{y-z}{A_2C_2}$$

$$\underset{y-z}{A_2C_2} \rightleftharpoons \underset{2z}{2AC}$$

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

$\Rightarrow$ $P_{A_2} = \frac{9}{2}$ atm.

$\Rightarrow$ $3p - x - y = \frac{9}{2}$ ... **(i)**

$\frac{x}{2} = \frac{1}{2}$ ... **(ii)**

$\Rightarrow$ $x = 1$ atm

also given $2Z = \frac{1}{2}$ .... **(iii)**

$Z = \frac{1}{4}$ atm

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

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

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

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

$y = 1$ atm.

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

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

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

Comprehension # 5 :

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

$$\Delta H^\circ = \frac{3}{2}(-241.8) + (-1575) - (-2021)$$

For 1 kg $CaSO_4.2H_2O = \frac{\Delta H^\circ}{172} \times 100 = 484$ kJ

2. $\Delta S^\circ = \frac{3}{2}(188.6) + 130.5 - 194$

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

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

EXERCISE - 4

Subjective Type

2. $n = \frac{5.6}{22.4} = 0.25$

Active mass $= \frac{0.25}{5.6} = 0.044$ 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

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

$$\therefore \quad K = \frac{K_1}{K_2}$$

6.

$$\begin{array}{lccccc} & SO_2\,(g) & + & \frac{1}{2}O_2\,(g) & \rightleftharpoons & SO_3\,(g) \\ \text{No. of mole} & 2 & & 1 & & 4 \\ \text{conc.} & \frac{2}{4} & & \frac{1}{4} & & \frac{4}{4}. \end{array}$$

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

$$= \frac{1}{(1/2)\times(1/2)} = \mathbf{4\ Ans.}$$

7. (a)

$$\begin{array}{lccccc} & 2SO_2 & + & O_2 & \rightleftharpoons & 2SO_3 \qquad K_C = 100 \text{ mole}^{-1} \text{ lit.} \\ \text{Initial mole} & a & & b & & 0 \\ & a-2x & & b-x & & 2x \\ & \frac{a}{2} & & b-\frac{a}{4} & & \frac{a}{2} \quad \text{(According to data given)} \end{array}$$

But according to question.

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

$= a - 2x = 2x.$

$a = 4x.$

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

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

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

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

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

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

So No. of mole of $O_2 = \frac{1}{10} = \mathbf{0.1}.$

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

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

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

8.

$$\begin{array}{lccccccc} & A & + & B & \rightleftharpoons & C & + & D \\ t = 0 & 2a & & a & & 0 & & 0 \\ t = t_{eq} & 2a - x & & a - x & & x & & x \end{array}$$

$$a - x = x \Rightarrow x = \frac{a}{2}$$

$$\Rightarrow K_C = \frac{\frac{a}{2} \times \frac{a}{2}}{\left(2a - \frac{a}{2}\right) \times \frac{a}{2}} = \frac{1}{3} \quad \Rightarrow \frac{1}{K_C} = 3$$

Ans. 3

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

$$\begin{array}{lll} 1 & 2 & 0 \\ \frac{1-x}{3} & \frac{2-x}{3} & \frac{2x}{3} \end{array}$$

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

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

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

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

$$\begin{array}{lll} 1\text{mol} & 3\text{ mol} & 0 \\ (1-x) & (3-3x) & 2x \end{array}$$

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

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

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

$$\Rightarrow \quad x = \frac{3 \pm \sqrt{9-4}}{2} \quad \Rightarrow \quad x = \frac{3 \pm \sqrt{5}}{2}$$

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

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

$\Rightarrow$ x = 0.38 (since x cannot be greater than 1)

$\therefore \quad [NH_3] = 0.38 \text{ x } 2 = 0.76$

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

$$\begin{array}{lllll} t=0 & n & n & n & \\ \text{teq.} & (n-y) & (n+y) & (n+y/2) & n_T = (3n+y/2) \end{array}$$

$$\text{so, } K_p = \frac{(P_{H_2(g)})^2_{eq.}.(P_{O_2(g)})_{eq.}}{(P_{H_2O(g)})^2_{eq.}} = \frac{(n+y)^2\;(n+y/2)\,P}{(n-y)^2\;(3n+y/2)}$$

14. (i) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

$$\begin{array}{lll} 0.15 & a & \\ 0.15-x & a-2x & x \end{array} \quad \Rightarrow \quad x = 0.08$$

$0.15 - x + a - 2x + x = 0.5$

$PV = nRT$

$a - 2x = 0.35$

$$n = \frac{8.2 \times 2.5}{0.082 \times 500} = 0.5$$

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

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

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

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

$$\begin{array}{llll} \text{At } t=0 & a & b & 0 \\ t = t_{eq} & (a-x) & (b-3x) & 2x \end{array}$$

$(\Delta n < 0)$ (P, T, V given)

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

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

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

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

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

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

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

$$K_P = \frac{\frac{4x^2.P^2}{(a+b-2x)^2}}{P^4.\frac{(a-x)(b-3x)^3}{(a+b-2x)^4}} = \frac{(a+b-2x)^2.4x^2}{P^2(a-x)(b-3x)^3}$$

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

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

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

$$\frac{1}{2}\text{ eq. (2)} - \frac{1}{2}\text{ eq. (1)}$$

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

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

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

$$K = \left(\frac{K_2}{K_1}\right)^{1/2} = \left(\frac{1.4\times10^{-12}}{2.1\times10^{-13}}\right)^{1/2} = \left(\frac{14}{2.1}\right)^{1/2}$$

= **2.58. Ans.**

19. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5(\bullet) + H_2O(\bullet)$

Initial 1 1 0 1

At eq. $1-x$ $1-x$ x $1+x$

$1-0.543$ $1-0.543$ 0.543 $1+0.543$

$$\left(54.3\%\text{ of 1 mole} = \frac{1 \text{ x } 54.3}{100} = 0.543\text{ mole}\right)$$

Hence given $x = 0.543$ mole

Applying law of mass action :

$$K_C = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{0.543\times1.543}{0.457\times0.457} = 4.0$$

21. $N_2O_4 \rightleftharpoons 2NO_2$

1 0

1–.25 .50

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

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

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

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

At pressure 0.1 atm,

$N_2O_4 \rightleftharpoons 2NO_2$

1 0

(1–α) 2a

$$P_{N_2O_4} = \left(\frac{1-\alpha}{1+\alpha}\right)\times0.1 \quad ; \quad P_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right)\times0.1$$

$$K_P = \frac{\left(\frac{2\alpha}{1+\alpha}\times0.1\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)\times0.1} \quad ; \quad K_P = \frac{4\alpha^2\times0.1}{(1+\alpha)(1-\alpha)}$$

$$0.266 = \frac{0.1\times4\alpha^2}{1-\alpha^2}$$

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

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

t=0 a 0 0

$a(1-\alpha)$ $(a\alpha)$ $\frac{(a\alpha)}{2}$

$$\text{Total mole} = a\left[1-\alpha+\alpha+\frac{\alpha}{2}\right] \qquad \frac{a[2+\alpha]}{2}$$

$$P_{AB_2} = \frac{a(1-\alpha)\times2}{a(2+\alpha)}\times P \quad ; \quad P_{AB} = \frac{a\alpha\times2}{a(2+\alpha)}\times P$$

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

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

$\alpha << 1.$

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

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

time t = 0 1atm 0

At. eq. (1–x) 4x

Pressure of eq. $1-0.29$ $4\times0.29.$

$$K_p = \frac{(P_{S_2})^4}{P_{S_8}} = \frac{(4\times0.29)^4}{0.71}.$$

$K_p = 2.55$ **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

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

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

So Total pressure in the container will be

$P_T = P + 2P + 3P = 6P = 3$ atm **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)**]

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

Θ T↑ K↓ ⇒ 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

$\boldsymbol{\Delta G^0 = 3.8}$ **KCal**

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

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

$(p_{H_2O})^4 = K_P$ $p_{H_2O} = (K_P)^{1/4} = 2 \times 10^{-3}$ atm

$H_2O(\bullet) \rightleftharpoons H_2O(g)$ $p_{H_2O} = \frac{7.6}{760} = 1.0 \times 10^{-2}$

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

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

$\therefore$ n_{H_2O} absorbed = 3.56×10^{-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.
$$\begin{array}{llll} A(s) \rightleftharpoons & B(g) + & C(g) & K_{p1} = 300 \\ — & P_1 & (P_1+P_2) & K_{p1} = P_1(P_1+P_2) \\ D(s) \rightleftharpoons & E(g) + & C(g) & K_{p2} = 600 \\ & P_2 & P_1+P_2 & K_{p2} = P_2(P_1+P_2) \end{array}$$

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

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

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

$K_{p1} = P_1(P_1+P_2)$

$K_{p1} = P_1\,(P_1+2P_1)$

$300 = P_1\,(3P_1)$

$P_1^{\,2} = 100 \qquad (P_1 = 10)$

$P_2 = 20$ atm

Now Total pressure

$P_B + P_E + P_C$

$(P_1+P_2) + (P_1+P_2) = (10+20) + (30) = \mathbf{60\ atm.}$

39.
$$\begin{array}{lll} N_2(g) \;+ & 3H_2(g) & \rightleftharpoons 2NH_3\,(g) \\ 9P - x - y & 13P - 3x - 2Y & 2x \\ N_2(g) \;+ & 2H_2(g) & \rightleftharpoons N_2H_4(g) \\ 9P - x - y & 13p - 3x - 2Y & Y \end{array}$$

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

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

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

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

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

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

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

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

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

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

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

41.
$$\begin{array}{llll} A(g) \rightleftharpoons & B(g) \;+ & C(g) & K_c = 4 \\ 1 & 2 & 2 & \\ 0.5 & 1 & 1 & Q_c = 2 < Kc \\ 0.5 - x & 1 + x & 1 + x & 4 = \dfrac{(1+x)^2}{0.5 - x} \end{array}$$

$x = 0.162 \; [A] = 0.338$

$[B] = [C] = 1.162$

42.
$$\begin{array}{llll} & 2HI\,(g) \rightleftharpoons & H_2\,(g) + & I_2\,(g) \\ t = 0 & a & 0 & 0 \\ t & (a - 2x) & x & x \end{array}$$

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

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

$$\text{so,} \quad x = \frac{0.5}{\sqrt{54.8}} = \frac{0.5}{7.40} = 0.0675\text{ M}$$

45.
$$\begin{array}{llll} & PCl_5 \rightleftharpoons & PCl_3 + & Cl_2 \\ \text{Initial moles} & 0.1 & 0 & 0 \\ \text{At. Eq.} & 0.1 - x & x & x \end{array}$$

Total number of moles at equilibrium

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

But total number of moles,

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

$0.1 + x = 0.18$

$x = 0.08$

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

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

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

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

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

47. **(a)**

A	$+$	$2B \rightleftharpoons$	$2C$
a		$2a$	
$a - x$		$2a - 2x$	$2x$

Total moles at equilibrium $3a - x$

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

$$2x = 1.2a - 0.4x$$

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

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

Now	A	$+$	$2B \rightleftharpoons 2C$	
	$\frac{a}{2}$		a	a

$$\text{Total moles} = \frac{5a}{2}$$

$$P_A = \frac{\frac{a}{2}}{\frac{5a}{2}} \times 8 = \frac{8}{5}\ \text{atm}$$

$$P_B = \frac{a}{5a/2} \times 8 = \frac{16}{5}\ \text{atm}$$

$$P_C = \frac{a}{5a/2} \times 8 = \frac{16}{5}\ \text{atm}$$

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

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

(b)

	A	$+$	$2B$	$\rightleftharpoons$	$2C$
Mole fraction	0.16		0.32		0.52
Partial pressure	0.16 P		0.32 P		0.52 P

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

$$P = \frac{0.52 \times 0.52 \times 8}{0.16 \times 0.32 \times 0.32 \times 5} = \mathbf{26.4\ atm}$$

49.

	$PCl_5\,(g)$	$\rightleftharpoons$	$PCl_3\,(g)$	$+$	$Cl_2\,(g).$
Initial	3		0		1
	$(3-x)$		x		$1+x$
	2		1		2

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

Now from Ideal gas equation

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

$$P = 0.082 \times 20 = 1.64\ \text{atm.}$$

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

$$PV = nRT.$$

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

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

$$5 = 4 + x.$$

$$x = 1.$$

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

$$P_{PCl_5} = \frac{2}{5} \times 2.05\,; \qquad P_{PCl_3} = \frac{1}{5} \times 2.05$$

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

$$K_P = \frac{\left(\frac{1}{5} \times 2.05\right)\left(\frac{2}{5} \times 2.05\right)}{\left(\frac{2}{5} \times 2.05\right)} = \mathbf{[0.41]}$$

50.

	$PCl_5\,(g) \rightleftharpoons$	$PCl_3\,(g) +$	$Cl_2\,(g)$	
$t = 0$	$\frac{8.34}{208.5}$	0	0	
teq.	$\left(\frac{8.34}{208.5} - x\right)$	x	x	$n_T = \left(\frac{8.34}{208.5} + x\right)$

Given, $(1\ \text{atm})\,(2.05\ \text{L}) = \left(\frac{8.34}{208.5} + x\ \text{mole}\right)(0.082\ \text{L atm mole}^{-1}\,\text{K}^{-1})\,(500\ \text{K})$

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

$$x = 0.05 - 0.04 = 0.01$$

$$\text{so,}\quad \alpha = \frac{0.01}{0.04} = 0.25 = 25\%$$

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

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 $= -RT \ln Kp$

$K_p (300\text{ K}) = 8.935 \times 10^4$

$K_p (1200\text{ K}) = 0.7753$

$Q = 1$

at 300 K : $Q < K$, Hence forward direction.

at 1200 K : $Q > K$, Hence backward direction.

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

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

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

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

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

(ii) Since ΔG is +ve and thus reaction will not proceed in forward direction.

Also for reverse reaction :

$$2NO_2 \rightleftharpoons N_2O_4$$

Mole at t=0 5 5

Mole at eq. $(5-2x)$ $(5+x)$

$\therefore$ $\Delta G = -2.303\ RT \log K_C$.

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

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

$\therefore$ $x = 1.25$.

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

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

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

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

$1-\alpha$ 2α $M_{mix} = 51.0696$

0.2 $0.8 \times 2 = 1.6$

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

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

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

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} ; $[NO_2] = (1–x)$ mol L^{-1} ;

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

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

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

$1 + x = 4 - 4x$ or $5x = 3$

or $x = \dfrac{3}{5} = 0.6$ 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. $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$

P P

For backward reaction

$Q_p \geq K_p$

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

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

$P^3 \leq 8$ atm^3

$P \leq 2$ atm

$P_{Total} = 2P = 4$ 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 $\Rightarrow$ $P_{H_2S} = P_{A'} = P/2 = 25$ mm

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

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

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

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

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

P_1 $P_1 + P_2$

$$\begin{array}{llll} B(s) & \rightleftharpoons B'(g) & + & H_2S(g) \\ & P_2 & & P_2+P_1 \end{array}$$

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

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

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

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

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

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

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

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

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

✈ $P`_{N_2O_4} = 1.7$ 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

$$\begin{array}{lllll} \text{For II equilibrium} & NO\ + & NO_2 & \rightleftharpoons & N_2O_3 \\ \text{Initial pressures} & P & 2P & & 0 \\ \text{Pressures at equi.} & (P-x) & (2P-x-3.4) & & x \end{array}$$

✈ 3.4 atm of NO_2 are uesed for I equilibrium to have $P`_{N_2O_4}$ =1.7 atm

$$\begin{array}{lllll} \text{At equilibrium} & (P-x) & 0.5 & & x \end{array}$$

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

Total pressure at equilibrium (Given 5.05 atm)

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

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

$\therefore$ $5.05 = P+2.20$

$\therefore$ $P = 5.05-2.20$

$\therefore$ $P = 2.85$ atm

✈ $2P-x-3.4 = 0.5$

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

$\therefore$ $x = 5.70-3.90$

$\therefore$ $x =$ **1.80 atm**

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

Now K_p for $NO+NO_2 \rightleftharpoons N_2O_3$

$$K_p = \frac{P`_{N_2O_3}}{P`_{NO}\times P`_{NO_2}} = \frac{1.80}{1.05\times 0.5} = \mathbf{3.43\ atm^{-1}}$$

62.

$$\begin{array}{llllllll} & CO_2(g) & + & H_2(g) & \rightleftharpoons & CO(g) & + & H_2O(g) \\ t=0 & 0.45 & & 0.45 & & & & \\ t=t_{eq.} & 0.45-x & & 0.45-x & & x & & x \\ & K_c=0.11 & & & & & & \end{array}$$

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

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

(b)

$$\begin{array}{lllllll} CO_2(g) & + & H_2(g) & \rightleftharpoons & CO(g) & + & H_2O(g) \\ 0.34 & & 0.34 & & 0.11 & & 0.11 \\ 0.68 & & 0.68 & & 0.11 & & 0.11 \\ 0.68-x & & 0.68-x & & 0.11+x & & 0.11+x \\ K_c=0.11 & & ; & & Q_c<K_c & & \end{array}$$

$$0.11 = \left(\frac{0.11+x}{0.68-x}\right)^2 \qquad \frac{0.11+x}{0.68-x} = 0.33 = \frac{1}{3}$$

$0.33+3x = 0.68-x$

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

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

63 . Let initial equilibrium concentration of C = x M

$$\begin{array}{lllll} & A & \rightleftharpoons & 2B & + & C \\ t=t_{eq} & 3 & & 4 & & x \end{array}$$

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

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

$$\begin{array}{llllll} & A & \rightleftharpoons & 2B & + & C \\ \text{after doubling volume} & \frac{3}{2} & & 2 & & \frac{x}{2} \end{array}$$

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

Conc. at new equilibrium $(1.5-a)$ $\quad 2+2a$ $\quad \left(\frac{x}{2}+a\right)$ Hence forward shift.

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

so $a = 0.5$

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

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

so $27x+27 = 32x$

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

= **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. $CO(g) + CI_2(g) \rightleftharpoons COCI_2(g)$

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

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

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

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

$$NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g);$$

$$K_c = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4\times10^{-4}}} = \frac{1}{2\times10^{-2}}$$

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

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. $CI_2(g) + 3F_2(g) \rightleftharpoons 2CIF_3(g);\ \Delta H = -329$ 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 $= 0.5 + 2x = 0.84$ $\qquad \therefore\ x = 0.17$ atm

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

7.

Given :	$PCI_5(g) \rightleftharpoons$	$PCI_3(g) +$	$CI_2(g)$
$t = 0$	1	0	0
t_{eq}	1–x	x	x

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

Thus partial pressure of $PCI_3 = \left(\dfrac{x}{1+x}\right)P.$

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

$$\frac{[SO_2][O_2]^{1/2}}{[SO_3]} = K_C = 4.9\times10^{-2} \qquad \text{...........(i)}$$

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

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

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

$$\frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_C{}^2 = \frac{1}{4.9\times4.9\times10^{-4}} = \frac{10000}{24.01}$$

$= 416.49$

9. $c = a + b$

10.

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

$$K_{p_1} = \frac{\left(\dfrac{2\alpha}{1+\alpha}P_{T_1}\right)^2}{\left(\dfrac{1-\alpha}{1+\alpha}P_{T_1}\right)} \qquad K_{p_2} = \frac{\left(\dfrac{\alpha}{1+\alpha}P_{T_2}\right)\left(\dfrac{\alpha}{1+\alpha}P_{T_2}\right)}{\left(\dfrac{1-\alpha}{1+\alpha}P_{T_2}\right)}$$

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

$$\frac{1}{9} = \frac{4P_{T_1}}{P_{T_2}}; \qquad \frac{P_{T_1}}{P_{T_2}} = \frac{1}{36}$$

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

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

$$n = \frac{3170\times10^{-3}}{8.314\times300} = 1.27\times10^{-3}\ \text{mol.}$$

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

0.5 atm

$0.5-p \qquad\qquad 2p$

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. ΔG^o at $300K = 2494.2$ J

2A ‡ˆˆ† B + C

$\Delta G^o = -RT\ \ell n K$

$-2494.2 = -8.314 \times 300\ \ell n K$

$K = 10$

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

$Q > K_C \Rightarrow$ reverse direction.

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

$1 \quad 1 \qquad\qquad 1 \quad 1$

$Q_c = 1 < K_{eq}$

$\therefore$ fore ward shift

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

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

$1 + x = 10 - 10x$

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

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

17. $CO_2(g) + 2H_2O(\ell) \rightarrow CH_4(g) + 2O_2(g)\ ;\ \Delta_rH^o = 890.3$

$\Delta_fH^o \ -393.5 \ -285.8 \qquad ? \qquad 0$

$$\Delta_rH^o = \sum(\Delta_fH^o)_{products} - \sum(\Delta_fH^o)_{Reactants}$$

$$890.3 = \left[1\times(\Delta_fH^o)_{CH_4} + 2\times 0\right] - \left[1\times(393.5) + 2(285.8)\right]$$

$(\Delta_fH^o)_{CH_4} = 890.3 - 965.1 = -74.8$ 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. $\Delta G^o = \Delta H^o - T\Delta S^o = -54.07 \times 1000 - 298 \times 10$

$= -54070 - 2980 = -57050$

$\Delta G^o = -2.303\ RT \log_{10} K$

$-57050 = -2.303 \times 298 \times 8.314 \log_{10} K$

$= -5705 \log_{10} K$

$\log_{10} K = 10$

3. At equilibrium ΔG (Gibbs energy) $= 0$ but ΔG^o (standard Gibbs energy) $\neq 0$

As ΔG (Gibbs energy) is more negative reaction will be more spontaneous.

MOCK TEST

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

Initial

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

$K_p = (2P)^2 (P)$ ...(i)

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

$NH_2COONH_4(s)$ ƒ $2NH_3(g) + CO_2(g)$

Final $\qquad 3P \qquad P'$

$$Kp = (3P)^2 (P') \text{ ...}\textbf{(ii)}$$

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

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

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

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

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

$\qquad\qquad x \qquad\quad x_2$

$$K_p = P_{Hg(g)} \text{ x } (PO_2) \frac{1}{2}$$

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

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

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

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

4.

	Fe^{3+}	+	SCN^-	$\rightleftharpoons$	$[Fe(SCN)]^{2+}$
Initial conc.	$\frac{10^{-3}}{56}$		b		0
Final conc.	$\frac{10^{-3}}{56} - 6 \times 10^{-6}$		$b - 6 \times 10^{-6}$		6×10^{-6}

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

on solving $b = 0.0036$ M

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

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

6.

	$Br_2(\ell)$ +	$Cl_2(g)$ $\rightleftharpoons$	$2BrCl(g)$
$t = 0$		1	0
		$(1 - x)$	$2x$

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

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

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

Moles of $Br_2(\ell)$ required for maintaing 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 = $\frac{5}{6}$ moles.

8.

	$PCl_5(g)$ $\rightleftharpoons$	$PCl_3(g)$	+ $Cl_2(g)$
$t = 0$	5	0	0
$t = t_{eq}$	$5 - 5 \times 0.2$	5×0.2	5×0.2
	4 mole	1 mole	1 mole

Total moles at equilibrium = 4 + 1 + 1 + 1 (N_2)
= 7 moles

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

10. Given $K_C < 2$ therefore in case of B and C $K_C = \frac{2 \times 4}{6} = \frac{4}{3}$ 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	$a(1 - \alpha)$	$2a\alpha$

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

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

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

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

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

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 logK and $\frac{1}{T}$ is positive, $\Delta H_{\text{reaction}}$ would be negative, i.e., the forward reaction would be exothermic.

23.

	A	+	B	f	2C
at t = 0	2 a		a		0
$t = t_{eq}$	2a – x		a – x		2x

$\Rightarrow$ 2a – = 2x $\quad\Rightarrow$ $x = \frac{2}{3}a$

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

24.

	A(g)	+	B(g)	f	C(g)	+	D(g)
at t = 0	1		1		1		1
$t = t_{eq}$	1 + x		1 + x		1 – x		1 – x

$$Q_C = \frac{(1/2)(1/2)}{(1/2)(1/2)} = 1 > K_C$$

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

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

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

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

25. **Case – I**

	C_2H_5OH +	CH_3COOH f	$CH_3COOC_2H_5$ +	H_2O
Mole before reacton	1	1	0	0
Mole at equilibrium	1 – x	1 – x	x	x

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

∴ Mole at equilibrium	$\left(1-\frac{2}{3}\right)$	$\left(1-\frac{2}{3}\right)$	$\frac{2}{3}$	$\frac{2}{3}$

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

Note : Volume terms are eliminated

Case - II

	C_2H_5OH +	CH_3COOH f	$CH_3COOC_2H_5$ +	H_2O
Mole before reaction	1	1	0	0
Mole at equilibrium	(2 – x)	(2 – x)	x	x

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

or $\quad x = 1.33.$

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↑, reaction will go in the backward direction.

(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	p_1 –	p_2

$$k_p = \frac{P_2^2}{P_1} = 10 \quad \text{or} \quad P_1 = 0.1\,P_2^2 \qquad ...(1)$$

but $p_1 + p_2 = 5.6$ atm

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

using $p = CRT$

$$C_1\,(\text{for } CO_2) = \frac{1.6}{0.082\times1000} = 0.0195\text{ M}$$

$$C_2\,(\text{for } CO) = \frac{4.0}{0.082\times1000} = 0.0488\text{ M.}$$

31.

	$H_2(g)$ +	$Br_2(g) \rightleftharpoons$	$2HBr(g)$
Initial pressure	0	0	10.0 bar
At equilibrium	p/2	p/2	(10.0-p)

$$k_p = \frac{p^2{}_{HBr}}{P_{H_2}\times P_{Br_2}}$$

$$1.6\times10^5 = \frac{(10-p)^2}{(p/2)(p/2)}$$

Taking square root of bith sides

$$4\times10^2 = \frac{10-p}{p/2}$$

$$200\ \ p = 10 - p$$

$$p = \frac{10}{201}\text{bar}$$

$$p_{H_2} = p/2 = \frac{1}{2}\left(\frac{10}{201}\right)\text{bar} = 2.5\times10^{-2}\text{ bar}$$

$$p_{Br_2} = p/2 = 2.5\times10^{-2}\text{ bar}$$

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

32. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

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

Let y moles of Cl_2 are introduced then at new equilibrium

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

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

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

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

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

$$P_{PCl_2} = \frac{8\times3}{12} = 2$$

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

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

$\therefore$ **Ans. is 667 – 666**

33. $2NH_3 \rightleftharpoons N_2 + 3H_2$

$2NH_3$	N_2	$3H_2$
a	0	0
a - 2x	x	3x

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

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

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

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

$\therefore$ % of NH_3 decomposed $= \frac{2x}{a}\times100 =$ **50%**

34. Q $\quad LiCl\,.\,3NH_3(s) \rightleftharpoons LiCl.\,NH_3(s) + 2NH_3(g)$

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

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

	$LiCl.\,3NH_3(s)$ +	$2NH_3(g) \rightleftharpoons$	$LICl.\,3NH_3(g)$
Initial mole	0.1	a	0
Final mole at eq.	0	(a – 0.2)	0.1

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

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

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

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

$\therefore$ $P'_{NH_3}=3\,atm$

Q $PV=nRT$

$3\times5=n\times0.0821\times313$

$\therefore$ $n=0.5837$

i.e., $(a-0.2)=0.5837$

$\therefore$ 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

$$\begin{array}{llll} N_2(g) & + \quad 3H_2(g) & f & 2\,NH_3(g) \\ 9P-y-x & \quad 13P-3x-2y & & 2x \\ N_2(g) & + \quad 2H_2(g) & f & N_2H_4(g) \\ 9P-y-x & \quad 13P-3x-2y & & y \end{array}$$

Total pressure = $P_{N_2}+P_{H_2}+P_{NH_3}+P_{N_2H_4}=3.5\,atm$ ...(1)

$=(9P-x-y)+(13\,P-3x-2y)+2x+y=3.5$ atm ...(1)

$P_{NH_3}=2x=0.5$ atm ...(2)

$P_{H_2}=(13P-3x-2y)=1$ atm ...(3)

from (1) $\Rightarrow(9P-x-y)+1\text{ atm}+0.5+y=3.5$

$\Rightarrow(9P-x)=2$ atm

so $9P=2.25$

$P=0.25$ atm

from (3) equation $2y=1.5$

$y=0.75$ 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, $K_{p_1}=\frac{P^2_{NH_3}}{P^3_{H_2}.P_{N_2}}=\frac{0.5\times0.5}{1\times1\times1\times1.25}=0.2\text{ atm}^{-2}$

$K_{p_2}=\frac{P_{N_2H_4}}{P_{N_2}.P^2_{H_2}}=\frac{0.75}{1\times1\times1.25}=0.6\text{ atm}^{-2}$