TOPIC : CHEMICAL EQUILIBRIUM

EXERCISE # 1

Section (A)

2. At equilibrium all properties solution (i.e. chemical composition of eq. mixture) becomes constant.

4. At equilibrium rates of backward and forward reactions become equal.

5. Concentration of reactant & product remains const. w.r.t time.
And, rate of [AT EQUILIBRIUM] forward reaction (r_f) = rate of backward reaction.

7. Molar conc. = $\frac{\text{no. of molar (mole) } O_2}{\text{volume (in l itre)}} = \frac{869}{329} \times 2 = 1.5$ mol/litre

8. Forward reaction rate (r_f) [A] [B] = K_1 [A] [B]

Backward reaction rate (r_f) = K_b [C] [D] = K_2 [C] [D]

At equilibrium, $r_f = r_b$ $\quad \therefore K_1 [A] [B] = K_2 [C] [D]$

The concentration of reactents & products at equilibrium are related by

$$K = \frac{K_1}{K_2} = \frac{[C]\ [D]}{[A]\ [B]} \qquad \therefore \qquad K(K_c) = \frac{K_1}{K_2}$$

9. $K = \frac{r_f}{r_b} \qquad \Rightarrow \qquad 1.5 = \frac{r_f}{7.5 \times 10^{-4}} \qquad \Rightarrow \qquad r_f = 1.12 \times 10^{-3}$.

10. $K_C = \frac{[Z]^2}{[X]^2\ [Y]^2}$

11. $N_2 + O_2 \rightleftharpoons 2NO$

$$K_p = \frac{P_{NO}^2}{P_{N_2}.P_{O_2}} \qquad \text{..... (i)}$$

$2NO \rightleftharpoons N_2 + O_2$

$$K'_p = \frac{P_{N_2}.P_{O_2}}{P_{NO}^2} \qquad \text{..... (ii)}$$

From equation (i) and (ii), we have

$$K'_p = \frac{1}{K_p} = \frac{1}{100} = 0.01$$

13. $K_1 = \frac{(SO_3)}{(SO_2)(O_2)^{1/2}}$

$$K_2 = \frac{(SO_2)^4 (O_2)^2}{(SO_3)^4} = \frac{1}{(K_1)^4} \qquad \Rightarrow \qquad K_2 = \frac{1}{(K_1)^4}$$

16. Equilibrium const. is temp. dependent only.

18. Since, K_p is temperature dependent only.

20. $N_2OH_{(g)} \rightleftharpoons 2NO_{2(g)}$

$\Delta n = 2 - 1 = 1$, $K_P = K_C$ (given)

We know, $K_P = K_C (RT)^{\Delta n}$

$$1 = RT, \quad T = \frac{1}{.0821} = 12.19 \text{ K}$$

21. Relation between K_p and K_c is :

23. for $K_p = K_c$, $\Delta n = 0$

only option (3) with satisfy this condition.

24. For this reaction, $K_C = \dfrac{[X]^4 \quad [Y]^6}{[A]^4 \quad [B]^5}$

So the unit of $K_C = \left[\dfrac{\text{mole}}{\text{litre}}\right]^{(4+6)-(4+5)}$ = mole litre^{-1}

SECTION (B)

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

t=0 1 0 0

$t=t_{eq}$ $1 - x$ x x

Total moles = 1 + x

Given $\dfrac{1-x}{1+x} = 0.4$ $\Rightarrow$ $x = \dfrac{3}{7}$ $\Rightarrow$ $x_{PCl_3} = \dfrac{\frac{3}{7}}{1+\frac{3}{7}} = 0.3.$

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

3n n 0 0 t = 0

(3n—x) (n—x) x x t = teq.

(n—x) = x

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

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

t = 0 4 4 0 0

$t = t_{eq}$ 4 – 2 4 – 2 2 2

$K_C = \dfrac{2 \times 2}{2 \times 2} = 1$

7. $2P(g) + Q(g) \rightleftharpoons 3R(g) + S(g)$

t = 0 2 2 0 x/2

t = teq 2 – x 2 – x/2 3/2 x x/2

from above, at equilibrium 2 – x < 2 – x/2

$\therefore$ [P] < [Q] at equilibrium

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

Initial 1 1 0 0

At equili. (1 – x) (1 – x) x x

$\therefore$ $K_c = \dfrac{[C]\ [D]}{[A]\ [B]} = 9$ $\therefore$ $\dfrac{x.\,x}{(1-x)^2} = 9$ or $x^2 = 9 + 9x^2 - 18x$

or $8x^2 - 18x + 9 = 0$ $\therefore$ $x = \dfrac{3}{2}$ or $\dfrac{3}{4}$

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

10. $N_2 + 3H_2 \rightleftharpoons 2\,NH_3$

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

11. $K_C = \dfrac{\left(\dfrac{0.2}{2}\right)^2 \times \left(\dfrac{0.8}{2}\right)}{\left(\dfrac{1}{2}\right)} = = 0.04 \times 0.4 = 0.016$

12.

PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2	
1		0		0	Initial mole
					Conc. at equilibrium

Total mole of $PCl_3 = 0.7$

Concentration = 0.14

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

19. $K_p = \dfrac{P'PCl_3 \times P'Cl_2}{P'PCl_5} = \dfrac{\dfrac{b}{(a+b+c)}.P \times \dfrac{c}{(a+b+c)} \times P}{\dfrac{a}{(a+b+c)}P} \Rightarrow K_p = \dfrac{bc.P}{a\ \ (a+b+c)}$

20. $P_{C_2} = 2.80 - (0.80 + 0.40) = 1.60$ atm,

$k_p = \dfrac{P_{C_2}^2}{P_{A_2} \times P_{B_2}^3} = \dfrac{(1.60)^2}{0.80 \times (0.40)^3} = 50$

21. $\dfrac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}} = 4$, As $P_{SO_3} = P_{SO_2}$, $\dfrac{1}{P_{O_2}} = 4$ or $P_{O_2} = \dfrac{1}{4} = 0.25$ atm.

22. $2NO_2 \rightleftharpoons 2NO(g) + O_2(g)$

$K_p = \dfrac{(p_{NO})^2 (p_{O_2})}{(p_{NO_2})^2}$

given $P_{O2} = 0.25$; $P_{NO} = 0.5$

$100 = \dfrac{(0.5)^2 \quad (0.25)}{(p_{NO_2})^2} \Rightarrow (P_{NO2})^2 = \dfrac{(0.5)^2 \quad (0.25)}{100} \Rightarrow P_{NO2} = 0.025$

SECTION (C)

1. $Q_C = \dfrac{[C]\ \ [D]}{[A]\ \ [B]}, < K_C$ $\therefore$ Q_C with time

2. When $Q > K_C$, the reaction will proceed in backward direction to attain equilibrium.

3. $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $K_P = 4.28 \times 10^{-5}\ atm^{-2}$

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

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

4. $Q = \dfrac{[C]^3}{[A]^2[B]} = \dfrac{(3/3)^3}{(2/3)^2(1/3)} = 6.75$

$Q < K_C$

The reaction will proceed in forward direction to attain equilibrium.

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

2 2 2 2

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

$n_{eq} = 3 + 3 + 1 + 1 = 8$ $\qquad n(SO_3) + n(CO_2) = 4$ $\qquad \frac{n(SO_2)}{n(CO)} = \frac{1}{2} < 1$

Therefore, (4) option is correct.

SECTION (D)

1. $A_3(g) \rightleftharpoons 3A(g)$

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

$t = t_{eq}$ $\quad$ a – ax $\quad$ 3ax

Total moles = a – ax + 3ax = a + 2ax

2. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

t = 0 $\quad$ 4 $\quad$ 0 $\quad$ 0

t = eq $\quad$ 4 – 2 $\quad$ 2 $\quad$ 2 $\qquad$ $\alpha = 5$

Total mole $\quad$ 2 + 2 + 2 = 6

3.✍ $2CO_2 \rightleftharpoons 2CO + O_2$

t =0 $\quad$ 2 $\quad$ 0 $\quad$ 0

$t = t_{eq.}$ $\quad 2 - 2 \times \frac{40}{100} \quad 2 \times \frac{40}{100} \quad \frac{40}{100}$

Total moles at equilibrium = $n_{CO_2} + n_{O_2} + n_{CO} = 2 - 2 \times \frac{40}{100} + 2 \times \frac{40}{100} + \frac{40}{100} = 2.4$

4.✍ $2NO \rightleftharpoons N_2 + O_2$ $\qquad \alpha = 10\%$

t = 0 $\quad$ 4 – .4 $\quad$ .2 $\quad$ .2

3.6 $\quad$ 0.2 $\quad$ 0.2

$\Delta n = 0 \qquad \therefore \qquad K_P = K_C, K_C = \frac{(.2/V)^2}{(3.6/V)^2} = \frac{4}{36 \times 36}$

5. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

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

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

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

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

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

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

7.✍ $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$\begin{array}{llll} t=0 & 1 & 0 & 0 \\ t=t_{eq} & 1-\alpha & \alpha & \alpha \end{array}$$

$$K_P = \frac{\frac{(\alpha P)}{1+\alpha} \times \frac{(\alpha P)}{1+\alpha}}{\frac{1-\alpha}{1+\alpha} \times P} = \frac{\alpha^2 P}{1-\alpha^2} \qquad (\alpha << 1) \qquad \text{i.e.} \qquad \alpha \propto \frac{1}{\sqrt{P}}$$

10. $x \propto \sqrt{V}$ or $x \propto \sqrt{16}$ Thus , 4 times

11. We know that $d = \frac{D}{1+(n-1)\ \alpha}$ where n is number of mole of gases produced from one mole of a gas.

12. $\alpha = \frac{D-d}{(n-1)d} \Rightarrow n = \frac{1}{2}$

13. $d_0 = \frac{D}{1+(n-1)\alpha} \Rightarrow n = 1 + \frac{1}{2} = 1.5 \Rightarrow 35 = \frac{40}{1+0.5\alpha} \Rightarrow 1 + 0.5\alpha = \frac{40}{35}$

$0.5\alpha = 1.14 - 1$

$0.5\alpha = 0.14$

$\alpha = 0.28$

14. $\alpha = \frac{D-d}{(n-1)d} \Rightarrow \alpha = \frac{\frac{92}{2} - 40}{(2-1)\cdot 40} = 0.15$

SECTION (E)

1. Homogenous reactions are those in which reactants and products are present in same phase.

2.✍ $P_{NH_3} = P_{H_2S} = \frac{P}{2}$ Hence $K_p = P_{NH_3} \times P_{H_2S} = \frac{P}{2} \times \frac{P}{2} = \frac{P^2}{4}$

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

$$\begin{array}{cc} P & P \end{array}$$

$2P = 1.2$

$P = 0.6$

$K_p = P^2 = (0.6)^2 = 0.36\ atm^2$

4. $K_P = \frac{[P_{CO}]^2}{P_{CO_2}}$

$P_{CO} = P$

$P_{CO_2} + P_{CO} = 12$

$P + 2P = 12$

$P = 4$ atm

$P_{CO_2} = 4$ atm

$K_P = \frac{8 \times 8}{4} = 16$

6. $K_C = [CO_2] = 0.05$ 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 $CaCO_3$

SECTION (F)

1.✍ Gibbs equation $\Delta G = \Delta G^o - RT \ln K$
at equilibrium $\Delta G = 0$
$-\Delta G^o = RT \ln K$

2.✍ At equilibrium $\Delta G = 0 \Rightarrow$ Given $\Delta G^0 = 0 \Rightarrow$ Gibbs equation $\Delta G = \Delta G^o - RT \ln K$
$0 = 0 - RT\ln K \Rightarrow K = e^0 = 1$

3.✍ From equation it is given $T_2 > T_1$ $\therefore$ $\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{T_1 - T_2}{T_1 \; T_2}$ = negative value

4. For endothermic reaction, ΔH^o is positive so, if $T_2 > T_1$ then $K_2 > K_1$.
For exothermic reaction, ΔH^o is negative so, if $T_2 > T_1$ then $K_2 < K_1$.

5.✍ $T\uparrow$ $K_c \uparrow \Rightarrow$ Endothermic

SECTION (G)

1. On adding any reactant equilibrium shifts in forward direction, so amount of product increases.

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

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

6. Since inert gas addition has no effect at const. volume.

7. For given reactions Δng = +ve, ΔH = –ve, high temperature & low pressure favours forward reaction which increases number of moles.

8. According to $K_P = \frac{P_{PCl_3\,(g)} \times P_{Cl_2\,(g)}}{P_{PCl_5\,(g)}} = \frac{(n_{PCl_3\,(g)})_{eq.} \times (n_{Cl_2\,(g)})_{eq.}}{V \times (n_{PCl_5\,(g)})_{eq.}}$

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

11. (1) Backward shifting will take place. (2) Forward shifting will take place.
(3) Backward shifting will take place. (4) Forward shifting will take place.

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

13. With change of pressure, x will change in such a way that K_p remains a constant.

14.

	$N_2O_4\,(g) \rightleftharpoons$	$2NO_2$.
moles t=0,	1	0
moles at eq.	$1-\alpha$	2α

$$K_P = \frac{\left(\frac{2\alpha}{(1+\alpha)} \times P\right)^2}{\frac{1-\alpha}{1+\alpha} \times P} = \frac{4\alpha^2}{1-\alpha^2} \times P.$$

Let total pressure at eq. = P. or $K_P = \frac{4\alpha^2}{1-\alpha^2} \times P$.

When volume is halved, P is double. $\therefore$ α will change as K_P is independent of pressure change.

15. $H_2 \xrightarrow[2000^\circ C]{\text{Electricarc}} 2H \quad - 104.5 \text{ kcal}$

hydrogen molecule — atomic hydrogen

The reaction is endothermic. For endothermic reaction increase in temperature shift the equilibrium in forward direction. To proceed forward the pressure must be low because for the above reaction, increase of pressure will favoured backward reaction. So, for maximum yield the conditions are high temperature and low pressure.

SECTION (H)

1. A liquid and vapour is in equilibrium at its boiling point. The two phases have equal kinetic energy.

2. Since density of gold decreases after melting therefore it is favourable at low pressure and high temperature.

3. Solublity of gas is favourable at high pressure and this process is exothermic hence solubility will be more at low temperature.

4.✍ For any physical equilibrium on increasing pressure equilibrium shifts in the direction of higher density.

EXERCISE # 2

2. At equilibrium, $r_f = r_b \quad \therefore K_f[A]_{en} = K_b[B]_{en}$

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

3. Equilibrium const. is temp. dependent only.

5.✍ $N_2 + 3H_2 \rightleftharpoons 2NH_3$,

equilibrium constant = K

$$K = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$$

$2N_2 + 6H_2 \rightleftharpoons 4NH_3$

equilibrium constant = K'

$$K' = \frac{[NH_3]^4}{[N_2]^2\ [H_2]^6} = K^2 \qquad \text{[from equation (1)].}$$

6. $2NH_3 \rightleftharpoons N_2 + 3H_2 \qquad K_1' = \frac{1}{K_1}$

$N_2 + O_2 \rightleftharpoons 2NO \qquad K_2' = K_2$

$3 \times (H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O) \qquad K_3' = (K_3)^3$

$2NH_3 + \frac{5}{2}\ O_2 \rightleftharpoons 2NO + 3H_2O \quad K_4 = \frac{K_2 \times (K_3)^3}{K_1}$

7. Higher value of K i.e. high yield of product

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

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

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

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

$K^{II}{}_p = (K^I{}_p)^2 = \left[\frac{1}{4\times10^{-3}}\right]^2 = \left[\frac{1000}{4}\right]^2 = 6250 = 625\times10^2$ **6.25×10^4 atm.**

10. For pure solids & pure liquids, although they have their own active masses but they remain const, during a chemical change.

K_C & K_P are equilibrium const. in terms of concentration & partical pressures.

All options are correct.

12. $\log \frac{K_P}{K_C} + \log RT = 0$

$\log \left(\frac{K_P}{K_C} . \quad RT \right) = 0$

$K_P = K_C (RT)^{-1}$ $\quad \because \; K_P = K_C (RT)^{\Delta n}$ $\quad \Rightarrow \quad \Delta n = -1$. This is possible for option (2)

13. $K_p = K_c (RT)^{\Delta n}$, Δn^2 4 – 3 = 1

$.052\ K_c\ R \times 1000$

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

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

14. $K_P = K_C (RT)^{\Delta n}$ $\quad \Delta n = -1$

$\frac{K_P}{K_C} = \frac{1}{RT} = 0.0301.$

15.✍ $K_C = \frac{[B]^2}{[A]} = \frac{(0.4)^2}{0.1} = 1.6$

16.

	N_2	+	O_2	$\rightleftharpoons$	$2NO$
Initial	2 moles		4moles		
At Eq.	$2 - \frac{1}{2}$		$4 - \frac{1}{2}$		$2 \times \frac{1}{2} = 1$ mol

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

17.

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

18.

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
at t = 0	a	0	0
t = t_{eq}	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

20.

	$N_2O_5(g)$	$\rightleftharpoons$	$2NO_2(g)$	+	$1/2\ O_2(g)$
initial	600		0		0
eq.	600 (1–α)		1200α		300α

$600(1 - \alpha) + 1200\alpha + 300\alpha = 980 \quad \Rightarrow \quad \alpha = 0.4$

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

$P_{A2} = 0.80$ atm., $P_{B2} = 0.4$ atm.

Total pressure of the system = 2.8 atm. $\therefore P_{C2} = 2.8 - 0.8 - 0.4 = 1.6$

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

22. $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $K_P = 4.28 \times 10^{-5}$ atm^{-2}

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

$Q_P > K_P$, $\therefore$ Reaction will go Backward. $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $K_P = 4.28 \times 10^{-5}$ atm^{-2}

23. $Q_c = \frac{0.5 \times 0.1}{2^2} = \frac{.05}{4} = 1.25 \times 10^{-2}$

$K_c = 2 \times 10^{-2}$

$K_c > Q_c$ forward shiftment.

24.✍ $SO_2 \quad + \quad \frac{1}{2}O_2 \quad \rightleftharpoons \quad SO_3$

5 moles $\quad$ 5 moles $\quad$ 0

$5 - 5 \times \frac{60}{100} \quad 5 - \frac{1}{2} \times 5 \times \frac{60}{100} \quad 5 \times \frac{60}{100} = 2 + 3.5 + 3 = 8.5$ moles

25.✍ $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$\alpha = .2$, initially, $K_P = \frac{\alpha^2}{1-\alpha^2}$ $P = \frac{(0.2)^2}{1-(.2)^2} \times 1 = \frac{.04}{.96} = .042$

if $\alpha = .5$, thus, $\frac{(.5)^2}{1-(.5)^2} \times P = .042$, $P = .126$

26.✍ $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

initially, t = 0 $\quad$ a $\quad$ 0

a – a–α $\quad$ 2aα

$K_P = \frac{4\alpha^2}{1-\alpha^2}$ $\quad$ P = 380 torr = $\frac{380}{760}$ = .5 atm

$\frac{\alpha^2}{1-\alpha^2} = .335$, $\alpha^2 = .25$, $\alpha = .5$

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

$922 = (1 + \alpha) \times 61.33$

$1 + \alpha = \frac{92}{61.33}$

$\alpha = 0.5$

28.✍ $VD_{Minorobs} = \frac{D}{1 \times (n-1)d}$

$VD_{obs} = 62$, $VD_{TH^2} = 104.16$, n = 2

$\alpha = 68\%$

29.✍ $(VD)_{mix} = \frac{M_{mix}}{2} = \frac{M}{2 \; (1+\alpha)}$

So, as α increases $(VD)_{mix}$ decreases.

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

1	0	0
1–0.5	0.5	0.5

At equilibrium total mole = 1 – 0.5 + 0.5 + 0.5 = 1.5

$$m_{mix} = m_0 = \frac{M_{Initial}}{1+(n-1)\alpha}$$

$$m_0 = \frac{208.5}{1+(2-1)\times 0.5} = \frac{208.5}{1+0.5} = \frac{208.5}{1.5} = 139 \text{ g}$$

$$\text{Density} = \frac{\text{Weight}}{V} = \frac{Pm_0}{RT} = \frac{2\times 139}{0.0821\times 800} = 4.232 \text{ g/L}$$

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

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

P–P/2 $\qquad P = \frac{3P}{2} = 12$

So $\qquad K_P = \frac{P^2}{(P/2)} = 2P = 2 \times 8 = 16$ atm.

33. $K_p = 0.800$ atm $= P_{CO_2}$ = maximum pressure of CO_2 in the container to calculate maximum volume of container the P_{CO_2} = 0.8 atm and none of CO_2 should get converted into $CaCO_3(s)$.

so $\qquad$ V(0.800 atm) = (10 L) (0.2 atm)
so $\qquad$ V = 2.5 L

34. $K_p = P_{CO_2} = 8 \times 10^{-2}$

$$k_p = \frac{(P_{CO})^2}{P_{CO_2}}$$

$$(P_{CO}) = \sqrt{K_P \times P_{CO_2}} = \sqrt{2\times 8\times 10^{-2}} = 4 \times 10^{-1}$$

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

38. Addition of inert gas at constant volume has no effect on equilibrium concentrations.

39. $2A(s) + 3B(g) \rightleftharpoons 3C(g) + D(g) + O_2$
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.

40. Upon addition of NH_3, 1st equilibrium will shift backward leading to decrease in amount of CO_2. As a result , 2nd equilibrium will shift forward compensating for the amount of decreased CO_2.

So, n_{CaCO_3} (s) will definitely decrease.

Now, $K_{P_1} = P^2{}_{NH_3} \times P_{CO_2}$ & $K_{P_2} = P_{CO_2}$

Since no change in temperature would have taken place, $K_{P_1} = K_{P_2}$ will have same values at both equilibrium states. So, amount of NH_3 & CO_2 at the two equilibrium states will remain the same.

41. A liquid and vapour is in equilibrium at its boiling point. The two phases have equal kinetic energy.

43. T↓, then V↓, then P↑, equilibrium shift in such direction so as to decrease pressure, i.e., Backward direction.

EXERCISE # 3

PART - I

1. $BaO_2(s)\ \ BaO(s) + O_2(g)$; $\Delta H = +\ ve$

According to law mass action, the rate of forward reaction = r_1

$r_1 \propto [BaO_2]$ or $r_1 \propto k_1\,[BaO_2]$

But concentration of solid = 1

then, $r_1 = k_1$

similarly the rate of backward reaction = r_2

$r_2 \propto [BaO]\,[O_2]$ or $r_2 \propto k_2\,[BaO]\,[O_2]$

∵ conc. of [BaO] = 1

or $r_2 = k_2\,[O_2]$

At equilibrium

$r_1 = r_2$

$k_1 = k_2\,[O_2]$ or $k_1 = k_2 \cdot p_{CO_2}$

where, p_{CO_2} = partial pressure of CO_2

or $\dfrac{k_1}{k_2} = p_{CO_2}$ (equilibrium constant)

∵ $\dfrac{k_1}{k_2} = k$ or $k = p_{CO_2}$.

So, from the above it is clear that pressure of O_2 does not depend upon the concentration of reactants.

The given equation is an endothermic reaction. If the temperature of such reaction is increased, then dissociation of BaO_2 would increase; and more O_2 is produced.

2. $k_{eq} = \dfrac{r_f}{r_b}$

$100 = \dfrac{10^5}{r_b}$

$r_b = 10^3$

3. For reaction, $N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g)$

$Q\ (\text{Quotient}) = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$, $\Delta N = 2 - 4 = -2$

At equilibrium Q is equal to K_c but for the progress of reaction towards right side Q > K_c.

4. $2NH_3 + \dfrac{5}{2}\,O_2\ \ 2NO\ +\ 3H_2O$

$2NH_3 \rightleftharpoons 3H_2\ +\ N_2$; $\dfrac{1}{K_1}$ ....(1)

$N_2\ +\ O_2 \rightleftharpoons 2NO$; K_2......................(2)

$3H_2\ +\ \dfrac{3}{2}\,O_2 \rightleftharpoons 3H_2O$ $(K_3)^3$ .... (3)

so on adding eq (1), (2) and (3)

we get $2NH_3 + O_2 \longrightarrow 2NO\ + 3H_2O$

5. $3H_2\ +\ N_2 \rightleftharpoons 2NH_3$

At t=0	30	30	0
At $t=t_{eq}$	30–15	30–5	10

6. Because K_P depends only on temperature. So, if then is constant, then K_P will also be constant.

7. Consider the eq. (i)

$$NO\ (g) + \frac{1}{2}\ O_2\ (g) \rightleftharpoons NO_2\ (g)$$

$$K_1 = \frac{[N_2]^2[O_2]}{[NO_2]^2}$$

$$\frac{1}{K_1} = \frac{1}{\dfrac{[NO_2]}{[NO]\quad [O_2]^{1/2}}} = \frac{[NO]\ [O_2]^{1/2}}{[NO_2]}$$

$$\left(\frac{1}{K_1}\right)^2 = \left\{\frac{[NO]\quad [O_2]^{1/2}}{[NO_2]}\right\}^2 = \frac{[NO]^2\ [O_2]}{[NO_2]^2} = K_2$$

$$\frac{1}{K_1^2} = K_2$$

8. For the reaction, $CH_4 + 2O_2\ (g) \rightleftharpoons CO_2\ (g) + 2\ H_2O\ (\ell), \Delta_r H = -\ 170.8\ kJ\ mol^{-1}$

This equilibrium is an example of heterogeneous chyemical equilibrium. Hence, for it

$$K_c = \frac{[CO_2]}{[CH_4]\quad [O_2]} \qquad .....(i)$$

(equilibrium constant on the basis of conc.)

and $$K_p = \frac{p_{CO_2}}{p_{CH_4} \times p_{O_2^2}} \qquad .....(ii)$$

(equilibrium constant according to partial pressure)

Thus, in it concentration of CO_2 (g) and H_2O (ℓ) are not equal at equilibrium.

The equilibrium constant $(K_p) = \dfrac{[CO_2]}{[CH_4]\quad [O_2]}$ is not correct expression.

On addition $CH_4 \rightleftharpoons$ (g) or O_2 (g) at equilibrium, K_c will be decreased according to expression (i) but K_c remains constant at constant temperature for a reaction, so for maintaining the constant value of K_c, the concentration of CO_2 will increased in same order. Hence, on addition of CH_4 or O_2 equilibrium will cause to the right.

This reaction is an example of exothermic reaction.

9. $$HI\ (g) \rightleftharpoons \frac{1}{2} H_2(g) + \frac{1}{2}\ I_2\ (g)$$

$$K = \frac{[I_2]^{1/2}\ [H_2]^{1/2}}{[HI]} \qquad ....\ (i)$$

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

$$K' = \frac{[HI]^2}{[H_2]\quad [I_2]} \qquad ....\ (ii)$$

From Eqs. (i) and (ii)

$$K \times \sqrt{K'} = 1$$

$$K' = \frac{1}{K^2} = \frac{1}{(8)^2} = \frac{1}{64}$$

10. $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$ $K = \dfrac{\left[Fe^{+3}\right]\left[OH^-\right]^3}{\left[Fe(OH)_3\right]}$ ....(i)

To maintain equilibrium constant, let the concentration of Fe^{3+} is increased x times, on decreasing the concentration of OH^- by $\dfrac{1}{4}$ times $K = \dfrac{\left[xFe^{+3}\right]\left[\dfrac{1}{4}\times OH^-\right]^3}{\left[Fe(OH)_3\right]}$ ....(ii)

From Eqs (i) and (ii) $\dfrac{1}{64} \times x = 1$

$x = 64$ times

11.

		X $\rightleftharpoons$	Y + Z	
At	t=0	1	0	0
At	$t = t_{eq}$	$1-\alpha$	α	α

		A $\rightleftharpoons$	2B
At	t=0	1	0
At	$t = t_{eq}$	$1-\alpha$	2α

$$K_{P_1} = \frac{\dfrac{\alpha}{1+\alpha}P_1 \times \dfrac{\alpha}{1+\alpha}P_1}{\dfrac{1-\alpha}{1+\alpha}P_1} \text{ ....(i)} \qquad K_{P_2} = \frac{\dfrac{4\alpha^2}{(1+\alpha)^2}P_2^2}{\dfrac{1-\alpha}{1+\alpha}P_2} \text{ ....(ii)}$$

Divide equation (i) by (ii) we get :

$$\frac{K_{P_1}}{K_2} = \frac{1}{4}\frac{P_1}{P_2} \quad \Rightarrow \quad \frac{P_1}{P_2} = \frac{36}{1} \quad \therefore \quad P_1 : P_2 = 36 : 1$$

12. $2AB_2\,(g) \rightleftharpoons 2\,AB(g) + B_2\,(g)$

	$2AB_2$	AB	B_2
t = 0	1	0	0
$t = l_{eq}$	1–x	x	$\dfrac{x}{2}$

Total mole at eq = $1 + \dfrac{x}{2}$

$$P_{AB_2} = \frac{1-x}{1+\frac{x}{2}} \times p \ , \ P_{AB} = \frac{1-x}{1+\frac{x}{2}} \times p \ , \ P_{B_2} = \frac{\frac{x}{2}}{1+\frac{x}{2}} \times p$$

Use $K_p = \dfrac{P_{B_2} \times (P_{AB})^2}{\left(P_{AB_2}\right)^2}$ and neglect x as compare to 1, means 1–x 1

13. Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$; $K_a = 1.5 \times 10^{-5}$ ..... (i)

$HCN \rightleftharpoons H^+ + CN^-$; $K_{a_1} = 4.5 \times 10^{-10}$ ..... (ii)

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_2COO^-$ K = ?

On subtracting Eq. (ii) from Eq. (i), we get

$CH_3COOH + CN^- \rightleftharpoons HCN + CH_3COO^-$

$$K = \frac{K_a}{K_{a_1}} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} = \frac{10^5}{3} = 3.33 \times 10^4$$

14.

	$2A_{(g)}$	+	$B_{(g)}$	$3C_{(g)}$	+	$D_{(g)}$	
Initial moles :	1		1	0		0	
Moles of eq. :	1 – (2 × 0.25)		1 – 0.25		3 × 0.25		0.25
	= 0.5		= 0.75	= 0.75		= 0.75	

Equilibrium constant,

K = ⇒ K =

15. When $K_p > Q$, rate of forward reaction > rate of backward reaction. $\therefore$ Reaction is sontaneous.

When $\Delta G° < RT \ln Q$, $\Delta G°$ is positive, reverse reaction is feasible, thus reaction is non-spontaneous.
When $K_p = Q$, rate of forward reaction = rate of backward reaction. $\therefore$ Reaction is in equilibrium.
When $T\Delta S > \Delta H$, ΔG will be negative only when $\Delta H = +$ ve.

16. $K_p = K_c(RT)^{\Delta n}$.

17. $N_2 + O_2 \quad 2NO \qquad K_1 \qquad .... \text{(i)}$

$2NO + O_2 \quad 2NO_2 \qquad K_2 \qquad .... \text{(ii)}$

$$NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2 \qquad K = \sqrt{\frac{1}{k_1.k_2}}$$

18. $A_2 + B_2 \rightleftharpoons 2AB \qquad K_C$

$$k_C = \frac{(2.8\times10^{-3})^2}{3\times10^{-3}\times4.2\times10^{-3}} = \frac{(2.8)^2}{3\times4.2} = 0.62$$

19. According to Le-Chatalier principle.

20. $$\log\frac{K_2}{K_1} = \frac{\Delta H^0}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$T_2 > T_1$ So $K_p < K_P'$ (exothermic reaction)

(assuming $T_2 > T_1$, although it is not mentioned, which temprature is higher

If $T_1 > T_2$ then $K_p > K_P'$ then answer should be (2).

21. $$K = 1.6 \times 10^{12} = \left[\frac{\text{Product}}{\text{Reactant}}\right]$$

K have high value so products have very high conc than reactant.

22. $\Delta G° = -2.303\ RT \log K$

23. $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$, Kp = 1.6 atm

$$\text{Moles of } CO_2 = \frac{PV}{RT} = \frac{0.4\times20}{RT} = \frac{8}{RT}$$

$Kp = P_{CO2} = 1.6$

$$P_{CO2} = \frac{nRT}{V}$$

$$1.6 = \frac{\frac{8}{RT}\times RT}{V} \Rightarrow V = \frac{8}{1.6} = 5L$$

24. $2NH_3 \rightleftharpoons N_2 + 3H_2 \quad \frac{1}{K_1^2}$

$N_2 + O_2 \rightleftharpoons 2NO\ K_2$

$3H_2 + \frac{3}{2}O_2 \rightleftharpoons 3H_2O$

$$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$$

$$K = \frac{K_2K_3^3}{K_1^2}$$

25. $A_2(g) + B_2(g) \rightleftharpoons x_2(g) \qquad \Delta H_r = -X$ kJ

Δn_g = –ve & ΔH = –ve (exothermic reaction) so ideal condition for formation of product is High pressure & low temperature.

26. For the chemical reaction

Rate of reaction = $-\frac{d(N_2)}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt}$

PART - II

1. $I_2(g) \rightleftharpoons 2I(g)$, ΔH°_r (298 K) = + 150 kJ

According to Le-Chatelier's principle the condition favouring formation of I are

(i) High concentration of I_2

(ii) High temperature (reaction is endothermic so, on increasing the temperature equilibrium will shift in the direction where heat is absorbed).

(iii) Low pressure (moles of products are more than moles of reactant, so if pressure is increased equilibrium will shift in the direction where volume is less.)

3. For a reaction, $K_c = \frac{[\text{Product}]}{[\text{Reactant}]}$. Hence, if $K_c > 1$, then [Product] > [Reactant].

4. $K_c = \frac{[NH_3]^2}{[N_2]\ [H_2]^3}$

$K_c = \frac{mol^2 \times L \times L^3}{L^2 \times mol \times mol^3} = L^2\ mol^{-2}$

5.

A (g)	+	B (g)	C (g)	+	D (g)	
2		2	0		0	(initially)
(2 – 3x) = x		(2 – 3x) = x	3x		3x	(at equilibrium)

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

$$K_p = \frac{p_C . p_D}{p_A . p_B} = \frac{\left(\frac{3x}{V}\right)^2}{\left(\frac{2-3x}{V}\right)^2} = \frac{9 \times \left(\frac{1}{2}\right)^2}{4 - 12 \times \frac{1}{2} + 9 \times \left(\frac{1}{2}\right)^2} = 9$$

6. $2NO + O_2 \rightleftharpoons 2NO_2$

In this reaction,

Number of moles of gaseous reactants, $n_1 = 3$

Number of moles of gaseous products $n_p = 2$

Since, n_p is less than n_r, according to Le-Chatelier principle, increase in pressure shifts the equilibrium in forward direction, ie, more NO_2 is formed.

The reaction given above is exothermic.

7. From given equations

We have

$$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3} \Rightarrow \quad K_2 = \frac{[NO]^2}{[N_2][O_2]} \Rightarrow \quad K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$$

For the given reaction

$$K = \frac{[NO]^2\ [H_2O]^3}{[NH_3]^2\ [O_2]^{5/2}} \Rightarrow \quad \frac{K_2K_3^3}{K_1} = \frac{[NO]^2\ [H_2O]^3}{[NH_3]^2\ [O_2]^{5/2}} \Rightarrow \quad K = \frac{K_2K_3^3}{K_1}$$

8. $3Fe(s) + 4H_2O(\text{stream}) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$K_p = \frac{(p_{H_2})^4}{(p_{H_2O})^4}$ only gaseous products and reactants.

17.

2ICl	=	I_2	+	Cl_2
0.6				
0.6 – 2x		x		x

$K_C = 0.14 = \frac{x^2}{(0.6-2x)^2}$

$0.37 = \frac{x}{0.6-2x}$

0.224 – 0.748 x

= x

1.748x = 0.224

x = 0.128

18.

	A +	2B $\rightleftharpoons$	2C
initial mole	2	2	0
at equilibrium mole	2 – x	2–2x	2x
	1.5	1	1
equilibrium conc.	$\frac{1.5}{10}$	$\frac{1}{10}$	$\frac{1}{10}$

C form 1 mole at equilibrium

2x = 1

x = ½ = 0.5

$K_C = \frac{[C]^2}{[A][B]^2}$

$= \frac{\left[\frac{1}{10}\right]^2}{\left[\frac{15}{10}\right]\left[\frac{1}{10}\right]^2}$ = 6.67

19. $K_P = P_{CO_2}$.

Pressure will increase only by increasing temperature as it will change K_P value.

PART - III

1. In this reaction the ratio of number of moles of reactants to products in same i.e., 2 : 2, hence change in volume will not alter the number of moles .

2. If in the reaction the ratio of number of moles of reactants to products in same i.e., 1 : 1, then change in volume will not alter the number of moles .

3. The conversion of SO_2 to SO_3 is an exothermic reaction, hence there is no need to increase the temperature. There is also a decrease in volume or moles in product side. Thus the reaction is favoured by low temperature and high pressure. (Le-Chatelier's principle).

4. $C_{[N_2O_4]} = 4.8 \times 10^{-2}$ mol L^{-1}, $C_{[NO_2]} = 1.2 \times 10^{-2}$ mol L^{-1}

$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{1.2\times10^{-2}\times1.2\times10^{-3}}{4.8\times10^{-2}}$ = $0.3 \times 10^{-2} = 3 \times 10^{-3}$ mol L^{-1}

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

6. $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

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

7. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; $K_c = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$

$NO(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$; $K_c = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} = \frac{100}{2} = 50$

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

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

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

(i) Decrease in temperature, (ii) Addition of reactants, (iii) Increase in pressure i.e., decrease in volume.

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

	$NH_4HS(s)$	$NH_3(g)$	$H_2S(g)$
Initial presens	0	0.5	0
At equi.	0	0.5+x	x

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

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

11. Given : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

	$PCl_5(g)$	$PCl_3(g)$	$Cl_2(g)$
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 $PCl_3 \left(\frac{x}{1+x}\right) = P$.

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

$\frac{[SO_2][O_2]^{1/2}}{[SO_3]} = K_C = 4.9 \times 10^{-2}$ ....(i)

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

$\frac{[SO_3]}{[SO_2][O_2]^{1/2}} = K'_C = \frac{1}{4.9 \times 10^{-2}}$ For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$\frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_C^2 = \frac{1}{4.9 \times 4.9 \times 10^{-4}} = \frac{10000}{24.01} = 416.49$

13. c = a + b

14. $$\begin{array}{cccccc} X & \rightleftharpoons & 2Y & Z & \rightleftharpoons & P \quad + \quad Q \\ 1-\alpha & & 2\alpha & 1-\alpha & & \alpha \qquad\quad \alpha \end{array}$$

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

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

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

15. PV = nRT

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

P = 3170 Pa

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

T = 300 K

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

$$n = \frac{3170 \times 10^{-3}}{8.314 \times 300} = 1.27 \times 10^{-3}\ mol.$$

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

0.5 atm

0.5–p 2p

Total pressure = 0.5 – P + 2P = 0.8

P = 0.3

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

$K_p = 1.8$

17. $K_p = K_c\ (RT)^{\Delta n_g}$

$$\Delta n_g = -\frac{1}{2}$$

18. $\Delta G = \Delta G° + RT \ln Q = 2494.2 + 8.314 \times 300 \ln 4 =$ positive

$$\Delta G = RT\ell n\ \frac{Q}{K}$$

Since, ΔG is positive so, Q > K, so reaction shifts in reverse direction.

19. $$\begin{array}{lcccccc} & A & + & B & \rightleftharpoons & C & + & D \\ t = 0 & 1 & & 1 & & 1 & & 1 \\ t_{eq} & 1-x & & 1-x & & 1+x & & 1+x \end{array}$$

$$\Rightarrow \frac{(1+x)^2}{(1-x)^2} = 100 \qquad \Rightarrow \frac{1+x}{1-x} = 10$$

$$\Rightarrow 1 + x = 10 - 10x \qquad \Rightarrow 11x = 9$$

$$\Rightarrow x = \frac{9}{11} \qquad \Rightarrow [D] = 1 + \frac{9}{11}$$

$$\Rightarrow [D] = 1.818$$

20. (A & B)

$\ell nK = \ell nA - \frac{\Delta H}{R} \times \frac{1}{T} \quad \Rightarrow \quad \text{Slope} = -\frac{\Delta H}{R}$; ΔH = –ve

21. (2) = 3 × (–(1)) $\therefore$ $K_2 = \left(\frac{1}{K_1}\right)^3 \Rightarrow K_2 = K_1^{-3}$

22. $k_P/k_c = (RT)^{\Delta n_g}$

(1) $\Delta n_g = 0 \quad \Rightarrow \quad \frac{k_p}{k_c} = 1$

(2) $\Delta n_g = 2 - 1 = 1 \quad \Rightarrow \quad \frac{k_p}{k_c} = (RT)^1 = (24.62)^1$

(3) $\Delta n_g = 2 - 4 = -2 \quad \Rightarrow \quad \frac{k_p}{k_c} = (RT)^{-2} = (24.62)^{-2} = 1.65 \times 10^{-3}$

23. $NH_4HS \longrightarrow H_2S + NH_3$

0.1(1–0.3) 0.03 0.03

$K_C = \frac{0.03}{3} \times \frac{0.03}{3} = 10^{-4} \Rightarrow \quad K_P = K_C\,(RT)^{\Delta n} = 10^{-4} \times (0.0821 \times 600)^2 = 0.242$

24 $2NH_3 \rightleftharpoons N_2 + 3H_2$ $K'_P = \frac{1}{k_P}$

$P_{Total} = P = P_{N_2} + P_{H_2} + P_{NH_3} \simeq P_{N_2} + P_{H_2}$

$$P_{N_2} = \frac{P}{4} \quad \Rightarrow \quad P_{H_2} = \frac{3P}{4} \quad \Rightarrow \quad \frac{1}{k_P} = \frac{\left(\frac{P}{4}\right)\left(\frac{3P}{4}\right)^3}{\left(P_{NH_3}\right)^2} \Rightarrow \quad P_{NH_3} = \frac{3^{\frac{3}{2}}P^2}{16}\left(k_P\right)^{1/2}$$

25. $A + 2B \rightleftharpoons 2C + D$

initially conc. a 1.5a

at eq. a-x 1.5 a–2x 2x x

at equilibrium a–x = 1.5a –2x

0.5 a = x

a = 2x

$$k_C = \frac{(2x)^2(x)}{(a-x)(1.5a-2x)^2} = \frac{4x^2.x}{(x)(x)^2} = 4$$

26. $A(s) \rightleftharpoons B(g) + C(g)$ $k_{P_1} = x\ \text{atm}^2$

P_1 $P_1 + P_2$

$D(s) \rightleftharpoons C(g) + E(g)$ $k_{P_2} = y\ \text{atm}^2$

$P_1 + P_2$ P_2

$k_{P_1} = P_1(P_1 + P_2)$

$k_{P_2} = P_2(P_1 + P_2)$

$k_{P_1} + k_{P_2} = (P_1 + P_2)^2$

$x + y = (P_1 + P_2)^2 \quad \Rightarrow \quad P_1 + P_2 = \sqrt{x+y}$

$2(P_1 + P_2) = 2\sqrt{x+y}$

$P_{Total} = P_B + P_C + P_E = 2(P_1 + P_2) = 2\sqrt{x+y}$