

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.

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

$$8. \text{ Forward reaction rate } (r_f) [A] [B] = K_1 [A] [B]$$

$$\text{Backward reaction rate } (r_b) = K_2 [C] [D] = K_2 [C] [D]$$

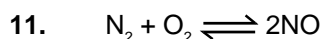
$$\text{At equilibrium, } r_f = r_b \quad \therefore K_1 [A] [B] = K_2 [C] [D]$$

The concentration of reactants & products at equilibrium are related by

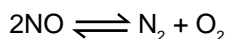
$$K = \frac{K_1}{K_2} = \frac{[C] [D]}{[A] [B]} \quad \therefore K(K_c) = \frac{K_1}{K_2}$$

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

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



$$K_p = \frac{P_{NO}^2}{P_{N_2} \cdot P_{O_2}} \quad \dots (i)$$



$$K'_p = \frac{P_{N_2} \cdot P_{O_2}}{P_{NO}^2} \quad \dots (ii)$$

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

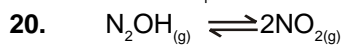
$$K'_p = \frac{1}{K_p} = \frac{1}{100} = 0.01$$

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

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

16. Equilibrium const. is temp. dependent only.

18. Since,  $K_p$  is temperature dependent only.



$$\Delta n = 2 - 1 = 1, \quad K_p = K_c \text{ (given)}$$

$$\text{We know, } K_p = K_c (RT)^{\Delta n}$$

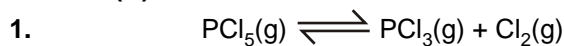
$$1 = RT, \quad T = \frac{1}{.0821} = 12.19 \text{ K}$$

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,  $K_c = \frac{[X]^4 [Y]^6}{[A]^4 [B]^5}$

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

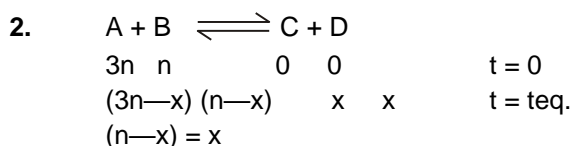
### SECTION (B)



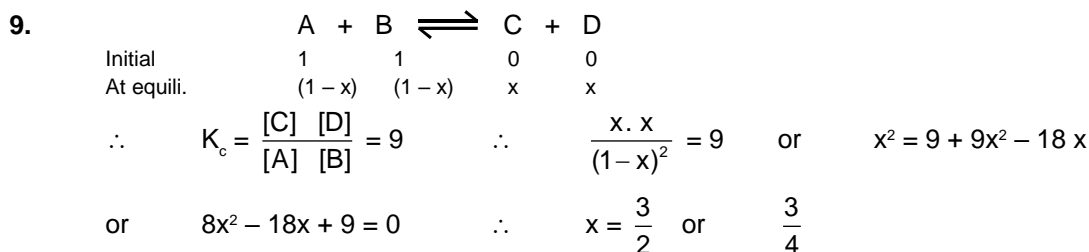
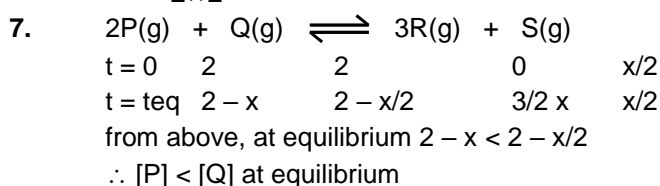
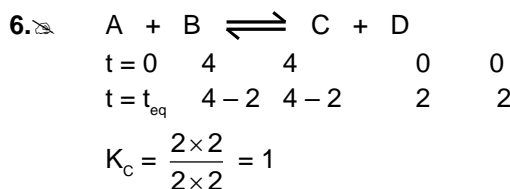
t=0	1	0	0
t=t <sub>eq</sub>	1-x	x	x

Total moles = 1 + x

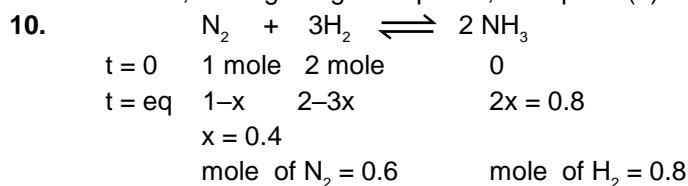
Given  $\frac{1-x}{1+x} = 0.4 \Rightarrow x = \frac{3}{7} \Rightarrow x_{\text{PCl}_3} = \frac{\frac{3}{7}}{1+\frac{3}{7}} = 0.3.$



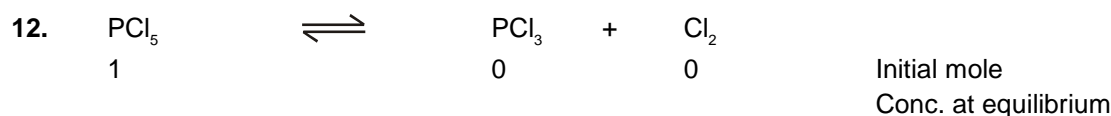
$n = 2x \quad x = \frac{n}{2}$



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



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



Total mole of  $\text{PCl}_3 = 0.7$

Concentration = 0.14

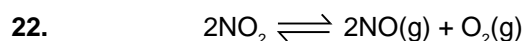
$$K_c = \frac{x^2}{(1-x)V} = \frac{0.7 \times 0.7}{0.3 \times 5} = \frac{49}{150}$$

$$19. \quad K_p = \frac{P' \text{PCl}_3 \times P' \text{Cl}_2}{P' \text{PCl}_5} = \frac{\frac{b}{(a+b+c)} \cdot P \times \frac{c}{(a+b+c)} \times P}{\frac{a}{(a+b+c)} \cdot P} \Rightarrow K_p = \frac{bc \cdot P}{a(a+b+c)}$$

$$20. \quad P_{\text{C}_2} = 2.80 - (0.80 + 0.40) = 1.60 \text{ atm,}$$

$$K_p = \frac{P_{\text{C}_2}^2}{P_{\text{A}_2} \times P_{\text{B}_2}^3} = \frac{(1.60)^2}{0.80 \times (0.40)^3} = 50$$

$$21. \quad \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = 4, \text{ As } P_{\text{SO}_3} = P_{\text{SO}_2}, \frac{1}{P_{\text{O}_2}} = 4 \quad \text{or} \quad P_{\text{O}_2} = \frac{1}{4} = 0.25 \text{ atm.}$$



$$K_p = \frac{(p_{\text{NO}})^2 (p_{\text{O}_2})}{(p_{\text{NO}_2})^2}$$

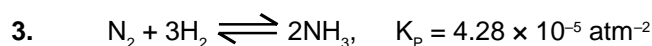
given  $P_{\text{O}_2} = 0.25$ ;  $P_{\text{NO}} = 0.5$

$$100 = \frac{(0.5)^2 (0.25)}{(p_{\text{NO}_2})^2} \Rightarrow (P_{\text{NO}_2})^2 = \frac{(0.5)^2 (0.25)}{100} \Rightarrow P_{\text{NO}_2} = 0.025$$

### SECTION (C)

1.  $Q_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}, < K_c \quad \therefore Q_c \text{ with time}$

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



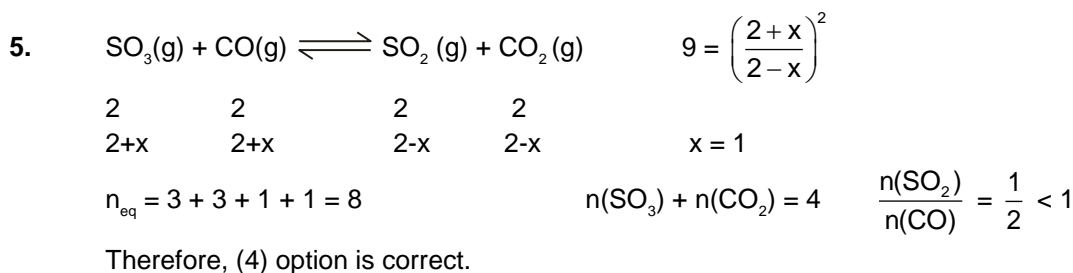
$$\text{Reaction Quotient, } Q_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} (P_{\text{H}_2})^3} = \frac{3^2}{1 \times (2)^3} = \frac{9}{8}$$

$Q_p > K_p, \quad \therefore \text{Reaction will go Backward.}$

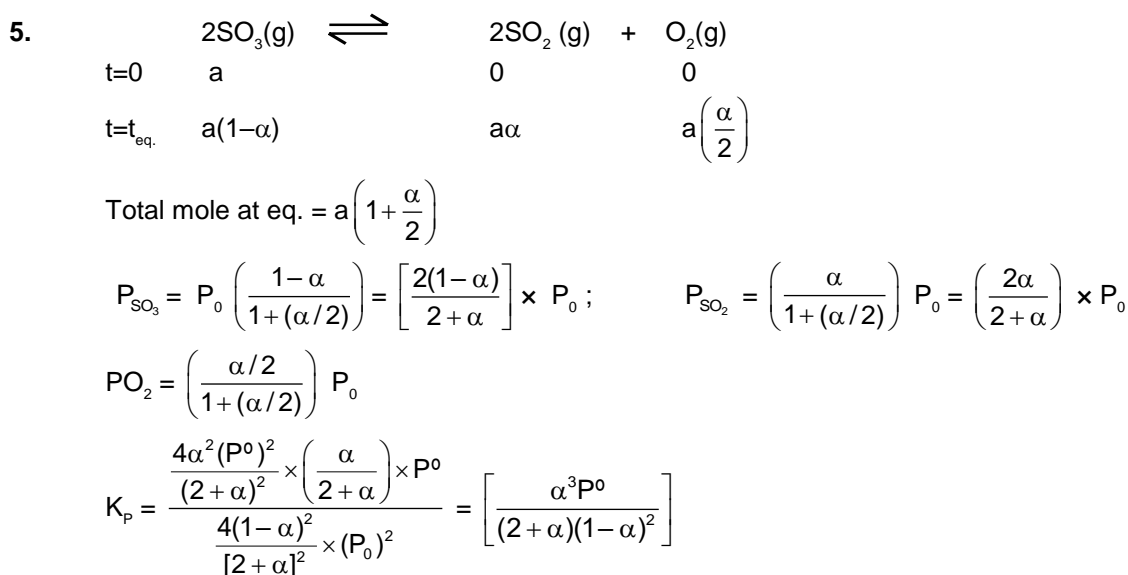
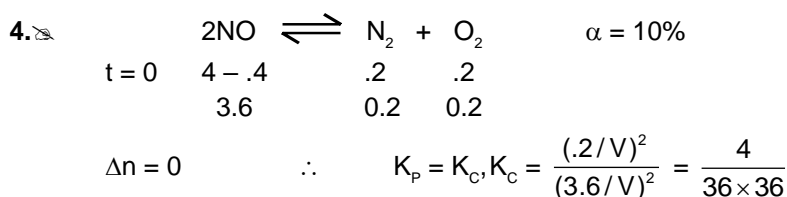
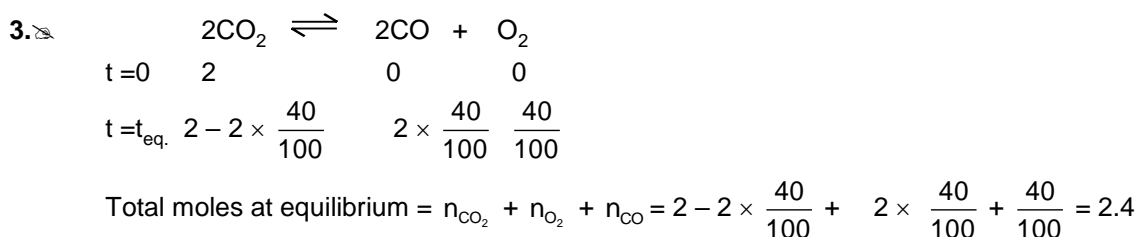
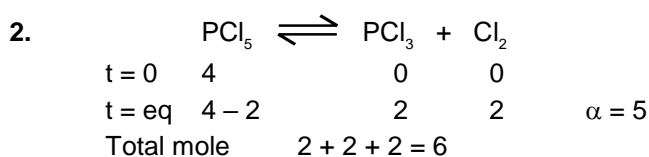
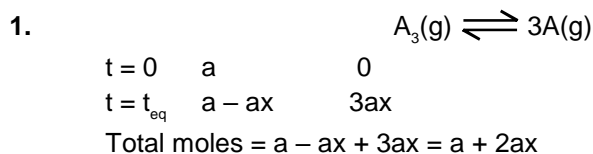
4.  $Q = \frac{[\text{C}]^3}{[\text{A}]^2 [\text{B}]} = \frac{(3/3)^3}{(2/3)^2 (1/3)} = 6.75$

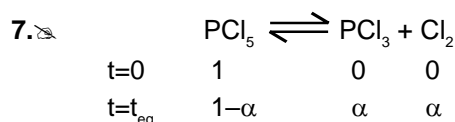
$Q < K_c$

The reaction will proceed in forward direction to attain equilibrium.



SECTION (D)





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

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

$$0.5\alpha = 1.14 - 1$$

$$0.5\alpha = 0.14$$

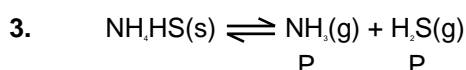
$$\alpha = 0.28$$

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.  $P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{P}{2}$  Hence  $K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = \frac{P}{2} \times \frac{P}{2} = \frac{P^2}{4}$



$$2P = 1.2$$

$$P = 0.6$$

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

4.  $K_p = \frac{[P_{\text{CO}}]^2}{P_{\text{CO}_2}}$

$$P_{\text{CO}} = P$$

$$P_{\text{CO}_2} + P_{\text{CO}} = 12$$

$$P + 2P = 12$$

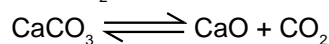
$$P = 4 \text{ atm}$$

$$P_{\text{CO}_2} = 4 \text{ atm}$$

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

6.  $K_c = [\text{CO}_2] = 0.05 \text{ mole/litre}$

$$\text{so moles of CO}_2 = 6.50 \times 0.05 \text{ moles} = 0.3250 \text{ moles}$$



$$1 \text{ mole of CO}_2 = 1 \text{ mole of CaCO}_3$$

$$0.3250 \text{ moles of CO}_2 = 0.3250 \text{ moles of CaCO}_3 = 0.3250 \times 100 \text{ gm of CaCO}_3 = 32.5 \text{ gm of CaCO}_3$$

#### SECTION (F)

1.  $\Delta G = \Delta G^\circ - RT \ln K$   
at equilibrium  $\Delta G = 0$   
 $-\Delta G^\circ = RT \ln K$
2. At equilibrium  $\Delta G = 0 \Rightarrow$  Given  $\Delta G^\circ = 0 \Rightarrow$  Gibbs equation  $\Delta G = \Delta G^\circ - RT \ln K$   
 $0 = 0 - RT \ln K \Rightarrow K = e^0 = 1$
3. From equation it is given  $T_2 > T_1 \therefore \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] = \frac{T_1 - T_2}{T_1 T_2} = \text{negative value}$
4. For endothermic reaction,  $\Delta H^\circ$  is positive so, if  $T_2 > T_1$  then  $K_2 > K_1$ .  
For exothermic reaction,  $\Delta H^\circ$  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  $\Delta n_g = +ve$ ,  $\Delta H = -ve$ , high temperature & low pressure favours forward reaction which increases number of moles.
8. According to  $K_p = \frac{P_{\text{PCl}_3(g)} \times P_{\text{Cl}_2(g)}}{P_{\text{PCl}_5(g)}} = \frac{(n_{\text{PCl}_3(g)})_{\text{eq.}} \times (n_{\text{Cl}_2(g)})_{\text{eq.}}}{V \times (n_{\text{PCl}_5(g)})_{\text{eq.}}}$   
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.

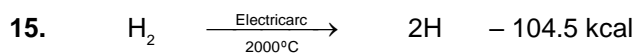


moles t=0, 1 0  
moles at eq.  $1-\alpha$   $2\alpha$

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

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.  $\therefore \alpha$  will change as  $K_p$  is independent of pressure change.



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. Solubility 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.

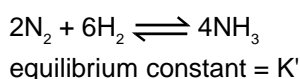
### EXERCISE # 2

2. At equilibrium,  $r_f = r_b \therefore K_f[A]_{\text{eq}} = K_b[B]_{\text{eq}}$   
 $[B]_{\text{eq}} = K_f K_b^{-1} [A]_{\text{eq}}$

3. Equilibrium const. is temp. dependent only.

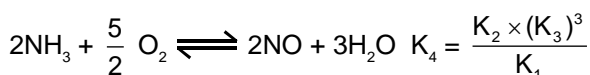
5.  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ ,  
equilibrium constant = K

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3}$$



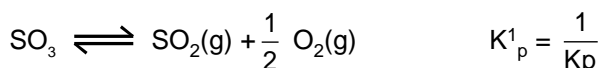
$$K' = \frac{[\text{NH}_3]^4}{[\text{N}_2]^2 [\text{H}_2]^6} = K^2 \quad [\text{from equation (1)}].$$

6.  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2 \quad K'_1 = \frac{1}{K_1}$   
 $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \quad K'_2 = K_2$   
 $3 \times (\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}) \quad K'_3 = (K_3)^3$

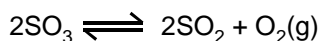


7. Higher value of K i.e. high yield of product

9.  $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) \quad K_p = 4 \times 10^{-3}$



$$K_p^1 = \left( \frac{1}{4 \times 10^{-3}} \right)$$



$$K_p^{\text{II}} = (K_p^1)^2 = \left[ \frac{1}{4 \times 10^{-3}} \right]^2 = \left[ \frac{1000}{4} \right]^2 = 6250 = 625 \times 10^2 \quad 6.25 \times 10^4 \text{ atm.}$$

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 & partial pressures.  
 All options are correct.

12.  $\log \frac{K_p}{K_c} + \log RT = 0$

$$\log \left( \frac{K_p}{K_c} \cdot RT \right) = 0$$

$$K_p = K_c (RT)^{-1} \quad \therefore K_p = K_c (RT)^{\Delta n} \quad \Rightarrow \Delta n = -1. \text{ This is possible for option (2)}$$

13.  $K_p = K_c (RT)^{\Delta n}$ ,  $\Delta n^2 4 - 3 = 1$   
 $.052 K_c R \times 1000$   
 $K_c = 5 \times 10^{-5} \times R^{-1}$   
 $K_c = \frac{5 \times 10^{-5}}{R}$

14.  $K_p = K_c (RT)^{\Delta n} \quad \Delta n = -1$   
 $\frac{K_p}{K_c} = \frac{1}{RT} = 0.0301.$

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

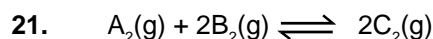
16. 
$$\begin{array}{ccccccc} & N_2 & + & O_2 & \rightleftharpoons & 2NO & \\ \text{Initial} & 2 \text{ moles} & & 4 \text{ moles} & & & \\ \text{At Eq.} & 2 - \frac{1}{2} & & 4 - \frac{1}{2} & & 2 \times \frac{1}{2} = 1 \text{ mol} & \end{array}$$
  
 Molar concentration of NO at equilibrium =  $\frac{1}{2.5} = 0.4$

17. 
$$\begin{array}{ccccccc} N_2 & + & O_2 & \rightleftharpoons & 2NO & & 2x = 1.0 \text{ mole/litre} \\ a & & b & & 0 & & x = 1.0/2 \text{ mole/litre} = 0.50 \text{ mole/litre} \\ (a-x) & & (b-x) & & 2x & & \\ \text{If } a-x = 0.25, b-x = 0.05 & & & & & & \\ [N_2] = a - x + x = 0.25 + 0.50 = 0.75 \text{ mole/litre} & & & & & & \end{array}$$

18. 
$$\begin{array}{ccccccc} PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2 & & \\ \text{at } t = 0 & & a & & 0 & & 0 \\ t = t_{eq} & & a - x & & x & & \\ P_{PCl_3} = X_{PCl_3} \times P_T = .25 \times 2 = .5 \text{ atm} & & & & & & \\ P_{PCl_3} = P_{Cl_2} = .5 \text{ atm} & & & & & & \end{array}$$

20. 
$$\begin{array}{ccccccc} N_2O_5(g) & \rightleftharpoons & 2NO_2(g) & + & 1/2 O_2(g) & & \\ \text{initial} & 600 & 0 & & 0 & & \\ \text{eq.} & 600(1-\alpha) & 1200\alpha & & 300\alpha & & \\ 600(1-\alpha) + 1200\alpha + 300\alpha = 980 & & & & \Rightarrow & \alpha = 0.4 & \end{array}$$





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

$$\text{Total pressure of the system} = 2.8 \text{ atm.} \therefore P_{C_2} = 2.8 - 0.8 - 0.4 = 1.6$$

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



$$\text{Reaction Quotient, } Q_p = \frac{P_{NH_3}^2}{P_{N_2} (P_{H_2})^3} = \frac{a}{1 \times (2)^3} = \frac{9}{8}$$

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

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.



5 moles

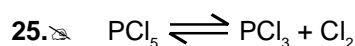
5 moles

0

$$5 - 5 \times \frac{60}{100}$$

$$5 - \frac{1}{2} \times 5 \times \frac{60}{100}$$

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



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

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



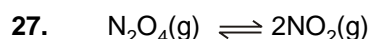
initially,

t = 0    a    0

a - a - α    2aα

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

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



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

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

$$\alpha = 0.5$$

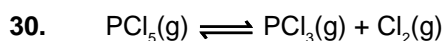
28.  $VD_{\text{Minorobs}} = \frac{D}{1 \times (n - 1)d}$

$$VD_{\text{obs}} = 62, \quad VD_{\text{THF}} = 104.16, \quad n = 2$$

$$\alpha = 68\%$$

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

So, as  $\alpha$  increases  $(VD)_{\text{mix}}$  decreases.



$$\begin{array}{ccc} 1 & 0 & 0 \\ 1-0.5 & 0.5 & 0.5 \end{array}$$

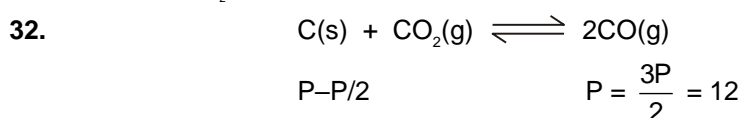
At equilibrium total mole =  $1 - 0.5 + 0.5 + 0.5 = 1.5$

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

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

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

31.  $K_p = \frac{(p_{\text{CO}})^2}{p_{\text{CO}_2}} = \frac{(2)^2}{4} = 1.$



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

33.  $K_p = 0.800 \text{ atm} = P_{\text{CO}_2}$  = maximum pressure of  $\text{CO}_2$  in the container to calculate maximum volume of container the  $P_{\text{CO}_2} = 0.8 \text{ atm}$  and none of  $\text{CO}_2$  should get converted into  $\text{CaCO}_3(\text{s})$ .

so  $V(0.800 \text{ atm}) = (10 \text{ L}) (0.2 \text{ atm})$

so  $V = 2.5 \text{ L}$

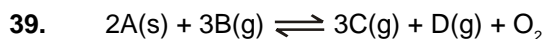
34.  $K_p = P_{\text{CO}_2} = 8 \times 10^{-2}$

$$K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}}$$

$$(P_{\text{CO}}) = \sqrt{K_p \times P_{\text{CO}_2}} = \sqrt{2 \times 8 \times 10^{-2}} = 4 \times 10^{-1}$$

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.



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  $\text{NH}_3$ , 1<sup>st</sup> equilibrium will shift backward leading to decrease in amount of  $\text{CO}_2$ . As a result, 2<sup>nd</sup> equilibrium will shift forward compensating for the amount of decreased  $\text{CO}_2$ .

So,  $n_{\text{CaCO}_3}(\text{s})$  will definitely decrease.

Now,  $K_{P_1} = P_{\text{NH}_3}^2 \times P_{\text{CO}_2}$  &  $K_{P_2} = P_{\text{CO}_2}$

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  $\text{NH}_3$  &  $\text{CO}_2$  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.  $T \downarrow$ , then  $V \downarrow$ , then  $P \uparrow$ , equilibrium shift in such direction so as to decrease pressure, i.e., Backward direction.

### EXERCISE # 3

#### PART - I

- $\text{BaO}_2(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{O}_2(\text{g})$  ;  $\Delta H = + \text{ve}$   
 According to law mass action, the rate of forward reaction =  $r_1$   
 $r_1 \propto [\text{BaO}_2]$  or  $r_1 \propto k_1 [\text{BaO}_2]$   
 But concentration of solid = 1  
 then,  $r_1 = k_1$   
 similarly the rate of backward reaction =  $r_2$   
 $r_2 \propto [\text{BaO}] [\text{O}_2]$  or  $r_2 \propto k_2 [\text{BaO}] [\text{O}_2]$   
 $\therefore$  conc. of  $[\text{BaO}] = 1$   
 or  $r_2 = k_2 [\text{O}_2]$   
 At equilibrium  
 $r_1 = r_2$   
 $k_1 = k_2 [\text{O}_2]$  or  $k_1 = k_2 \cdot p_{\text{CO}_2}$   
 where,  $p_{\text{CO}_2}$  = partial pressure of  $\text{CO}_2$   
 or  $\frac{k_1}{k_2} = p_{\text{CO}_2}$  (equilibrium constant)  
 $\therefore \frac{k_1}{k_2} = k$  or  $k = p_{\text{CO}_2}$

So, from the above it is clear that pressure of  $\text{O}_2$  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  $\text{BaO}_2$  would increase; and more  $\text{O}_2$  is produced.

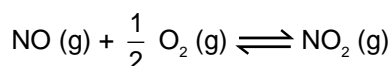
- $k_{\text{eq}} = \frac{r_f}{r_b}$   
 $100 = \frac{10^5}{r_b}$   
 $r_b = 10^3$
- For reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3(\text{g})$   
 $Q (\text{Quotient}) = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$  ,  $\Delta N = 2 - 4 = -2$

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

- $2\text{NH}_3 + \frac{5}{2} \text{O}_2 \rightleftharpoons 2\text{NO} + 3\text{H}_2\text{O}$   
 $2\text{NH}_3 \rightleftharpoons 3\text{H}_2 + \text{N}_2$  ;  $\frac{1}{K_1}$  .....(1)  
 $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$  ;  $K_2$ .....(2)  
 $3\text{H}_2 + \frac{3}{2} \text{O}_2 \rightleftharpoons 3\text{H}_2\text{O}$   $(K_3)^3$  ..... (3)  
 so on adding eq (1), (2) and (3)  
 we get  $2\text{NH}_3 + \text{O}_2 \longrightarrow 2\text{NO} + 3\text{H}_2\text{O}$
- $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$

At t=0	30	30	0
At t=t <sub>eq</sub>	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)



$$K_1 = \frac{[\text{N}_2] [\text{O}_2]}{[\text{NO}_2]^2}$$

$$\frac{1}{K_1} = \frac{1}{\frac{[\text{NO}_2]}{[\text{NO}] [\text{O}_2]^{1/2}}} = \frac{[\text{NO}] [\text{O}_2]^{1/2}}{[\text{NO}_2]}$$

$$\left( \frac{1}{K_1} \right)^2 = \left\{ \frac{[\text{NO}] [\text{O}_2]^{1/2}}{[\text{NO}_2]} \right\}^2 = \frac{[\text{NO}]^2 [\text{O}_2]}{[\text{NO}_2]^2} = K_2$$

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

8. For the reaction,  $\text{CH}_4 + 2\text{O}_2 \text{ (g)} \rightleftharpoons \text{CO}_2 \text{ (g)} + 2 \text{H}_2\text{O (l)}$ ,  $\Delta_r H = -170.8 \text{ kJ mol}^{-1}$

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

$$K_c = \frac{[\text{CO}_2]}{[\text{CH}_4] [\text{O}_2]} \quad \dots\dots(i)$$

(equilibrium constant on the basis of conc.)

$$\text{and } K_p = \frac{p_{\text{CO}_2}}{p_{\text{CH}_4} \times p_{\text{O}_2^2}} \quad \dots\dots(ii)$$

(equilibrium constant according to partial pressure)

Thus, in it concentration of  $\text{CO}_2 \text{ (g)}$  and  $\text{H}_2\text{O (l)}$  are not equal at equilibrium.

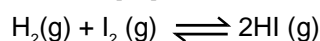
The equilibrium constant ( $K_p$ ) =  $\frac{[\text{CO}_2]}{[\text{CH}_4] [\text{O}_2]}$  is not correct expression.

On addition  $\text{CH}_4 \rightleftharpoons \text{(g)}$  or  $\text{O}_2 \text{ (g)}$  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  $\text{CO}_2$  will increased in same order. Hence, on addition of  $\text{CH}_4$  or  $\text{O}_2$  equilibrium will cause to the right.

This reaction is an example of exothermic reaction.

9.  $\text{HI (g)} \rightleftharpoons \frac{1}{2} \text{H}_2 \text{ (g)} + \frac{1}{2} \text{I}_2 \text{ (g)}$

$$K = \frac{[\text{I}_2]^{1/2} [\text{H}_2]^{1/2}}{[\text{HI}]} \quad \dots\dots (i)$$

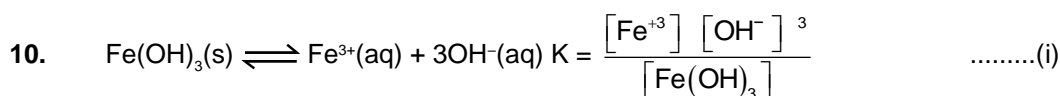


$$K' = \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]} \quad \dots\dots (ii)$$

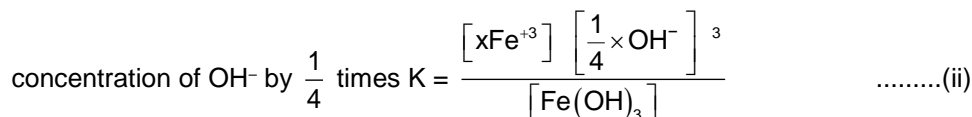
From Eqs. (i) and (ii)

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

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

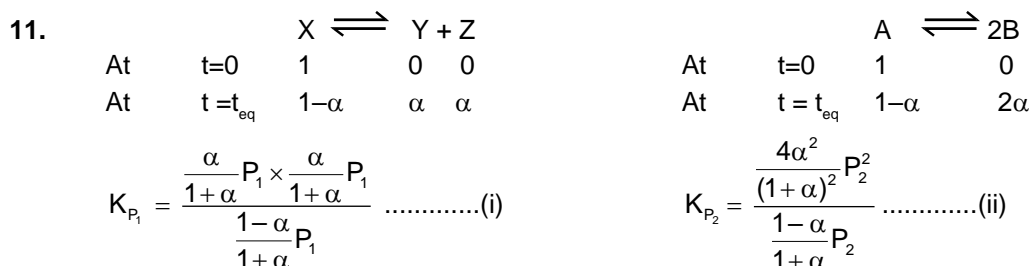


To maintain equilibrium constant, let the concentration of  $\text{Fe}^{3+}$  is increased x times, on decreasing the



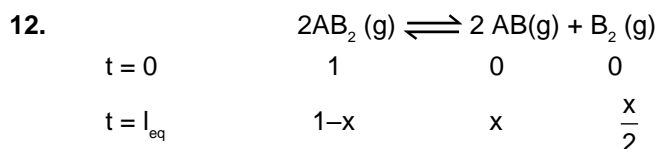
From Eqs (i) and (ii)  $\frac{1}{64} \times x = 1$

$x = 64$  times



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

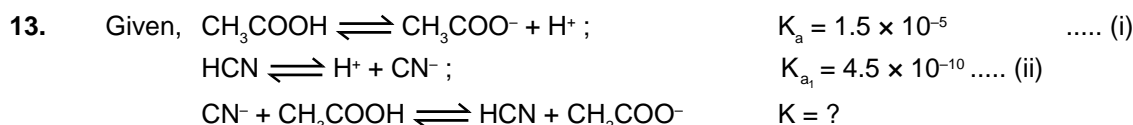
$$\frac{K_{P_1}}{K_{P_2}} = \frac{1}{4} \frac{P_1}{P_2} \Rightarrow \frac{P_1}{P_2} = \frac{36}{1} \therefore P_1 : P_2 = 36 : 1$$



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

$$P_{\text{AB}_2} = \frac{1-x}{1+\frac{x}{2}} \times p, P_{\text{AB}} = \frac{1-x}{1+\frac{x}{2}} \times p, P_{\text{B}_2} = \frac{\frac{x}{2}}{1+\frac{x}{2}} \times p$$

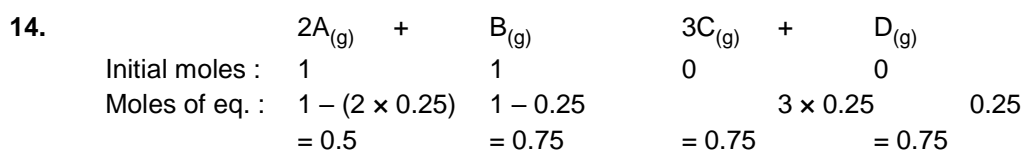
Use  $K_p = \frac{P_{\text{B}_2} \times (P_{\text{AB}})^2}{(P_{\text{AB}_2})^2}$  and neglect x as compare to 1, means  $1-x \approx 1$



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

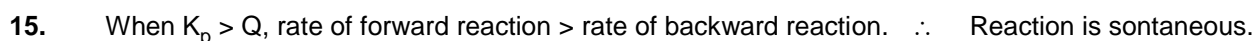
$$\text{CH}_3\text{COOH} + \text{CN}^{-} \rightleftharpoons \text{HCN} + \text{CH}_3\text{COO}^{-}$$

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



Equilibrium constant,

$K = \Rightarrow K =$



When  $\Delta G^\circ < RT \ln Q$ ,  $\Delta G^\circ$  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  $T\Delta S > \Delta H$ ,  $\Delta G$  will be negative only when  $\Delta H = +ve$ .

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



$$NO_2 \rightleftharpoons \frac{1}{2} N_2 + O_2 \quad K = \sqrt{\frac{1}{K_1 K_2}}$$

18.  $A_2 + B_2 \rightleftharpoons 2AB$   $K_c$   
 $K_c = \frac{(2.8 \times 10^{-3})^2}{3 \times 10^{-3} \times 4.2 \times 10^{-3}} = \frac{(2.8)^2}{3 \times 4.2} = 0.62$

19. According to Le-Chatelier principle.

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

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

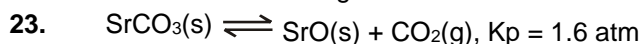
(assuming  $T_2 > T_1$ , although it is not mentioned, which temperature is higher)

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

22.  $\Delta G^\circ = -2.303 RT \log K$

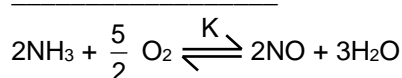
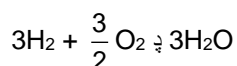
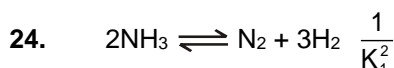


$$\text{Moles of } CO_2 = \frac{PV}{RT} = \frac{0.4 \times 20}{RT} = \frac{8}{RT}$$

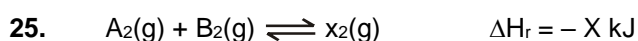
$$K_p = P_{CO_2} = 1.6$$

$$P_{CO_2} = \frac{nRT}{V}$$

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



$$K = \frac{K_2 K_3^3}{K_1^2}$$



$\Delta n_g = -ve$  &  $\Delta H = -ve$  (exothermic reaction) so ideal condition for formation of product is High pressure & low temperature.

26. For the chemical reaction

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

### PART - II

1.  $I_2(g) \rightleftharpoons 2I(g)$ ,  $\Delta H^\circ_r (298 K) = +150 \text{ kJ}$

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  $[\text{Product}] > [\text{Reactant}]$ .

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

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

5. 

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

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

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

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

In this reaction,

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

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, i.e., more  $NO_2$  is formed.

The reaction given above is exothermic.

7. From given equations

We have

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

For the given reaction

$$K = \frac{[NO]^2 [H_2O]^3}{[NH_3]^2 [O_2]^{5/2}} \Rightarrow \frac{K_2 K_3^3}{K_1} = \frac{[NO]^2 [H_2O]^3}{[NH_3]^2 [O_2]^{5/2}} \Rightarrow K = \frac{K_2 K_3^3}{K_1}$$

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

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

17.

2ICI	=	I <sub>2</sub>	+	Cl <sub>2</sub>
0.6				
0.6 - 2x		x		x

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

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

$$0.224 - 0.748x = x$$

$$1.748x = 0.224$$

$$x = 0.128$$

18.

	A +	2B	$\rightleftharpoons$	2C	
initial mole	2	2		0	C form 1 mole at equilibrium
at equilibrium mole	2 - x	2 - 2x		2x	2x = 1
	1.5	1		1	x = 1/2 = 0.5
equilibrium conc.	1.5/10	1/10		1/10	

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

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

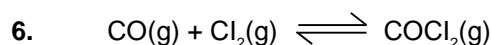
19.  $K_P = P_{CO_2}$  .  
Pressure will increase only by increasing temperature as it will change  $K_P$  value.

### PART - III

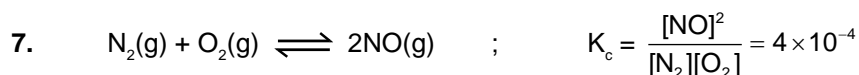
- In this reaction the ratio of number of moles of reactants to products is same i.e., 2 : 2, hence change in volume will not alter the number of moles .
- If in the reaction the ratio of number of moles of reactants to products is same i.e., 1 : 1, then change in volume will not alter the number of moles .
- The conversion of SO<sub>2</sub> to SO<sub>3</sub> 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).
- $C_{[N_2O_4]} = 4.8 \times 10^{-2} \text{ mol L}^{-1}$ ,  $C_{[NO_2]} = 1.2 \times 10^{-2} \text{ mol L}^{-1}$   

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{1.2 \times 10^{-2} \times 1.2 \times 10^{-2}}{4.8 \times 10^{-2}} = 0.3 \times 10^{-2} = 3 \times 10^{-3} \text{ mol L}^{-1}$$
- $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(g)$        $K_c = \frac{[P_4O_{10}(s)]}{[P_4(s)][O_2(g)]^5}$

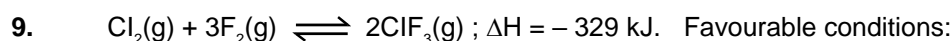
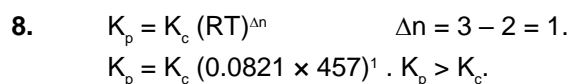




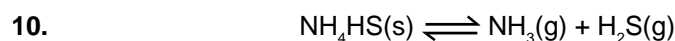
$$\Delta n = 1 - 2 = -1; K_p = K_c(RT)^{\Delta n} \therefore \frac{K_p}{K_c} = (RT)^{-1} = \frac{1}{RT}$$



$$\text{NO(g)} \rightleftharpoons \frac{1}{2} \text{N}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} ; K_c = \frac{[\text{N}_2]^{1/2}[\text{O}_2]^{1/2}}{[\text{NO}]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} = \frac{100}{2} = 50$$



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



Initial presens      0                      0.5              0

At equi.                0                      0.5+x            x

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

$$K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}} = 0.11 \text{ atm}^2.$$

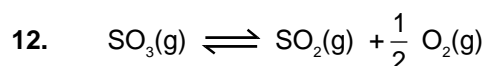


t = 0                      1                      0                      0

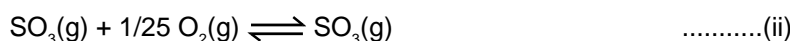
t<sub>eq</sub>                      1-x                      x                      x

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

Thus partial pressure of  $\text{PCl}_3 \left( \frac{x}{1+x} \right) = P$ .

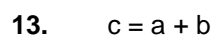


$$\frac{[\text{SO}_2][\text{O}_2]^{1/2}}{[\text{SO}_3]} = K_c = 4.9 \times 10^{-2} \quad \text{.....(i)}$$



$$\frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = K'_c = \frac{1}{4.9 \times 10^{-2}} \text{ For } 2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}$$

$$\frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = K_c^2 = \frac{1}{4.9 \times 4.9 \times 10^{-4}} = \frac{10000}{24.01} = 416.49$$



14.  $X \rightleftharpoons 2Y \quad Z \rightleftharpoons P + Q$

$1 - \alpha \quad 2\alpha \quad 1 - \alpha \quad \alpha \quad \alpha$

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

$$K_{p_2} = \frac{\left(\frac{\alpha}{1+\alpha} P_{T_2}\right) \left(\frac{\alpha}{1+\alpha} P_{T_2}\right)}{\left(\frac{1-\alpha}{1+\alpha} P_{T_2}\right)}$$

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

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

15.  $PV = nRT$   
 $V = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$   
 $P = 3170 \text{ Pa}$   
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $T = 300 \text{ K}$   
 $3170 \times 10^{-3} = n \times 8.314 \times 300$   
 $n = \frac{3170 \times 10^{-3}}{8.314 \times 300} = 1.27 \times 10^{-3} \text{ mol.}$

16.  $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO}(\text{g})$

$0.5 \text{ atm}$   
 $0.5 - p \quad 2p$   
 Total pressure =  $0.5 - p + 2p = 0.8$   
 $p = 0.3$

$$K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(2p)^2}{(0.5 - p)} = \frac{(0.6)^2}{(0.5 - 0.3)}$$

$$K_p = 1.8$$

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

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

18.  $\Delta G = \Delta G^\circ + RT \ln Q = 2494.2 + 8.314 \times 300 \ln 4 = \text{positive}$

$$\Delta G = RT \ln \frac{Q}{K}$$

Since,  $\Delta G$  is positive so,  $Q > K$ , so reaction shifts in reverse direction.

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

$t = 0 \quad 1 \quad 1 \quad 1 \quad 1$   
 $t_{\text{eq}} \quad 1-x \quad 1-x \quad 1+x \quad 1+x$

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

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

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

$$\Rightarrow [D] = 1.818$$

20. (A & B)

$$\ell n K = \ell n A - \frac{\Delta H}{R} \times \frac{1}{T} \Rightarrow \text{Slope} = -\frac{\Delta H}{R}; \Delta H = -ve$$

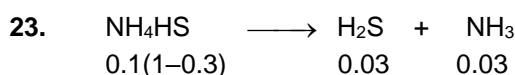
21.  $(2) = 3 \times (-1) \therefore K_2 = \left(\frac{1}{K_1}\right)^3 \Rightarrow K_2 = K_1^{-3}$

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

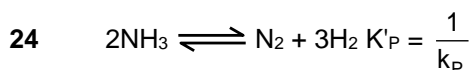
(1)  $\Delta n_g = 0 \Rightarrow \frac{k_p}{k_c} = 1$

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

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



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



$$P_{\text{Total}} = P = P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3} \approx P_{\text{N}_2} + P_{\text{H}_2}$$

$$P_{\text{N}_2} = \frac{P}{4} \Rightarrow P_{\text{H}_2} = \frac{3P}{4} \Rightarrow \frac{1}{k_P} = \frac{\left(\frac{P}{4}\right)\left(\frac{3P}{4}\right)^3}{(P_{\text{NH}_3})^2} \Rightarrow P_{\text{NH}_3} = \frac{3^{\frac{3}{2}} P^2}{16} (k_P)^{1/2}$$



initially conc. a 1.5a

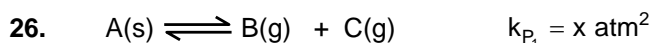
at eq. a-x 1.5a-2x 2x x

at equilibrium a-x = 1.5a-2x

$$0.5a = x$$

$$a = 2x$$

$$K_C = \frac{(2x)^2(x)}{(a-x)(1.5a-2x)^2} = \frac{4x^2 \cdot x}{(x)(x)^2} = 4$$



$$P_1 \quad P_1 + P_2$$



$$P_1 + P_2 \quad P_2$$

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

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

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

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

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

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