CHEMICAL EQUILIBRIUM

Topic-2
Relationship between Kc and Kp, Le-Chatelier's   principle, its application and numericals.

LONG ANSWER QUESTIONS

1. Derive relationship between Kc and Kp?
Ans:

RELATION BETWEEN K_P AND K_C

For a general equation,
$$aA + bB \rightleftharpoons cC + dD$$
Where, a , b, c and d are coefficients of the reacting substance

$$K_p = (P_C)^c (O_D)^d / (P_A)^a (P_B)^b$$

From gas equation
$$PV = nRT \qquad => \quad P = n/V\ RT$$
So, $P_A = [A]RT'\ P_B = [B]RT$
             $P_C = [C]RT; P_D = [D]RT$
Hence, $K_p = ([C]RT)^c.([D]RT)^d / ([A]RT)^a / ([B]RT)^b$
             or, $K_p = [C]^d[D]^d / [A]^a[B]^b \times (RT)^{[(c+d) - (a+b)]}$
             Where $\Delta n_g = \{(c + d) - (a + b)\}$ = change in the numbers of gaseous moles.

Hence, $K_p = K_c.(RT)^{\Delta n}{}_g$

         When $\Delta n = 0; K_p = K_c$

         $\Delta n > 0; K_p > K_c$

         $\Delta n < 0; \qquad K_p < K_c$

 Note: Similarly we can find equilibrium constant (K_x) in terms of mole fraction and can find out its relation with K_p and K_c.

2. At 27°C K_p value for reaction is 0.1 atm, calculate its K_c value. ?

Solution: $K_P = K_c(RT)^{Dn}$
$\Delta n = 1$
$K_c = K_P / RT = 0.1 / 0.82 \times 300 = 4 \times 10^{-3}$

Solid NH_4I dissociates according to the reaction at 400 K

$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$; $K_p = 16$ atm. In presence of catalyst HI dissociates in H_2 and I_2 as $2HI \rightleftharpoons H_2 + I_2$. If partial pressure of H_2 at this temp is 1 atm in the container when both the equilibrium exist simultaneously, calculate K_p value of second equilibrium (for the dissociation of HI).

Solution: $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$ $K_{P1} = 16$
$2HI \rightleftharpoons H_2 + I_2$
P - x   x/2 . x/2 $K_{P2} = ?$
Here x/2 = 1 atm
x = 2 atm
P(P -2) = 16
P = 5.1

3. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on addition of graphite. What is the value of Kp if the total pressure at equilibrium is 0.8 atm?
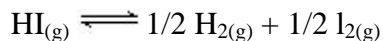
Solution: $CO_2(g)$ + $C(s)$ $\longrightarrow$ $2CO(g)$
0.5
2n

or, 0.5-n   0.5+n = 0.8

n = 0.3

$K_p = (2 \times 0.3)^2 / (0.5 – 0.3) = 1.8$ atm

4. Given that the equilibrium constant for the reaction, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is 50 at 700K. Calculate the equilibrium constant for the reaction?

$$HI_{(g)} \rightleftharpoons 1/2\ H_{2(g)} + 1/2\ I_{2(g)}$$

Solution: We have $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

$$K_c = [HI]^2 / [H_2][I_2] = 50$$

The new equilibria is

$$HI_{(g)} \rightleftharpoons [H_2]^{1/2}[I_2]^{1/2} / [HI] = 1/\sqrt{K_c}$$

$$= 1/\sqrt{50} = \sqrt{2}/10 = 0.141$$

5. One mole of N_2 is mixed with 3 moles of H_2 in a 4 litre container. If 25% of N_2 is converted into NH_3 by the following reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}.$$ **Calculate K_c and K_p of the reaction. (Temperature = 227°C and R = 0.08231).**

Solution: We have $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Percentage N_2 reacted, 25%

x = 0.25

Now, (a – x) = 1 – 0.25 = 0.75

b – 3x = 3 – 0.75 = 2.25

$$\therefore \frac{(a-x)}{V} = \frac{0.75}{4} = 0.1875$$

$$\left(\frac{b-3x}{V}\right) = \frac{2.25}{4} = 0.5625$$

$$\left(\frac{2x}{V}\right) = \frac{0.50}{4} = 0.125$$

$$\therefore K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.125)^2}{(0.1875)(0.5625)^3}$$

$= 1.48 \times 10^{-5} \, L^2 \, mol^{-2}$

Now, $K_p = Kc \cdot (RT)^{\Delta n} = 1.48 \times 10^{-5} \times [0.0821] \times (227 + 273)^{-2}$

$1.48 \times 10^{-5} / \{0.082 \times (500)\}^2$

$= 8.78 \times 10^{-9}$

6. **Explain Lechatelier principle with suitable examples**?

Ans:

Lechattelier's principle and its application to industrial processes;

The effect of change of pressure, concentration and temperature on equilibrium was studied by Henry Lewis Lechatterlier in 1885 and F. Brawn. So this is called Lechattelier- Brawn Principle or simply Lechattelier's principle.
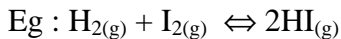
If a system at equilibrium is subjected to a stress, the system shifts the equilibrium in such a way to reduce or nullify the stress.

Effect of concentration: Increase in concentration of reactants or decrease in concentration of products favours the shift of equilibrium towards products side and rate of forward reaction is increased.
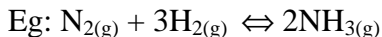
Increase in the concentration of the products or decrease in the concentration of reactants favours the shift of equilibrium towards the reactant side and rate of backward reaction is increased.

- **Effect of pressure :**
  Pressure has no effect on equilibrium if Δv or $\Delta n=0$, ($n_p = n_r$).
  Eg : $H_{2(g)} + I_{2(g)} \Leftrightarrow 2HI_{(g)}$
  Pressure has effect on equilibrium if $\Delta v \neq 0$ or $\Delta n \neq 0$, ($n_p \neq n_r$). When pressure increases, equilibrium shifts in a direction of decrease of volume or towards less mole number and vice vessa.
 Eg: $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$
  When pressure increases, equilibrium shifts towards right and forward reaction rate increases.
  Pressure does not show any marked effect on equilibrium reactions taking place in the solution phase or in the solid phase.
  Effect of temperature: increase of temperature of the equilibrium system favours endothermic reactions, and decrease of temperature of the equilibrium system favours exothermic reactions.

- **Effect of Catalyst:** Catalyst has no net effect on equilibrium. It helps the system to attain equilibrium at a faster rate by increasing the rate of forward as well as backward reaction to the same extent.
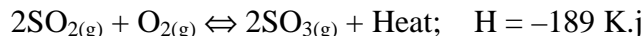 Eg:**(1)** Synthesis of ammonia by Haber's process:
  $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)} + heat$ H = – 92.0 K.J
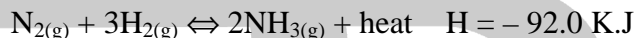
  Favourable conditions for high yield of NH_3**:**
  High pressure: 200atm, Catalyst: Fe as catalyst
  Low temperature: 773 K, Promoter: small amount of molybdenum or Al_2O_3 and K_2O.
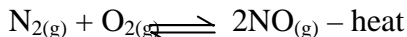   **(2)** Manufacture of H_2SO_4 by the contact process.
  $2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)} + Heat;$ H = –189 K.j

Favourable conditions for higher yield of SO_3.
- I) High pressure   : 1.5 – 1.7 atm.
- ii) Low temperature: 673 k
- iii)Catalyst   : V_2O_5 or platinised asbestos
- $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ – heat
- i) High temperature   ii) No effect of pressure
  Melting of ice:
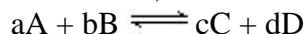 $H_2O_{(s)} + heat \rightleftharpoons H_2O$
  I) high temperature   ii) high pressure
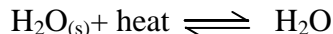
7. Explain the affect of temperature and Concentration on equilibrium?

Ans:

Effect of Concentration

Let us have a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

at a given temperature, the equilibrium constant,

$$Kc = [C]^c[D]^d / [A]^a[B]^b$$

again if α, β, γ and δ are the number of mole of A, B, C and D are at equilibrium

then, $K_c = [\gamma]^c[\delta]^d / [\alpha]^a[\beta]^b$

If any of product will be added, to keep the K_c constant, concentration of reactants will increase i.e. the reaction will move in reverse direction. Similarly if any change or disturbance in reactant side will be done, change in product's concentration will take place to minimise the effect.

Temperature Effect

The effect of change in temperature on equilibrium cannot be immediately seen because on changing temperature the equilibrium constant itself changes. So first we must find out as to how the equilibrium constant changes with temperature.

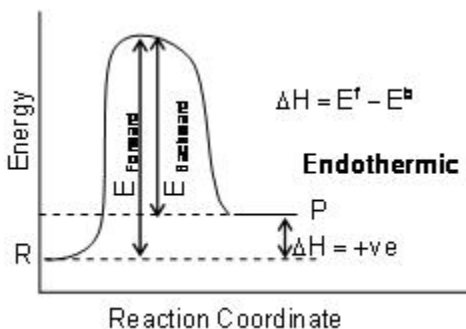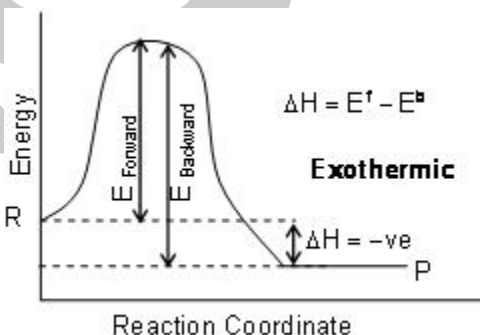For the forward reaction, according to the Arrhenius equation,

$$K_r = A_f\, e^{-e\alpha/RT}$$

And for the reverse reaction,

$$K_p = \frac{\left[p_{(NOBr)}\right]^2}{\left[p_{(NO)}\right]^2 \left[p_{(Br_2)}\right]} = \frac{\left(7.68\times10^{-2}\right)^2}{\left(5.26\times10^{-2}\right)^2 \left(1.59\times10^{-2}\right)} = 134\,atm^{-1}$$

It can be seen that

$$\frac{K_{T_2}}{K_{T_1}} = e^{\frac{(E_a - E_d)}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \quad \text{or} \quad \ln\frac{K_{T_2}}{K_{T_1}} = \frac{(E_{ar} - E_{af})}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

For any reaction, $\Delta H = E_{af} - E_{ar}$

R = Reactant, P = Product

$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{-\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{or} \qquad \ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

From the equation,

$\log K_2/K_1 = \Delta H^o / 2.303R (1/T_1 – 1/T_2)$ it is clear that

(a) If ΔH^o is +ve (endothermic), an increase in temperature ($T_2 > T_1$) will make $K_2 > K_1$, i.e., the reaction goes more towards the forward direction and vice-versa.

(b) If ΔH^o is -ve (exothermic), an increase in temperature ($T_2 > T_1$), will make $K_2 < K_1$ i.e., the reaction goes in the reverse direction.

    (i)   Increase in temperature will shift the reaction towards left in case of exothermic reactions and right in endothermic reactions.

    (ii) Increase of pressure (decrease in volume) will shift the reaction to the side having fewer moles of the gas; while decreases of pressure (increase in volume) will shift the reaction to the side having more moles of the gas.

    (iii) If no gases are involved in the reaction higher pressure favours the reaction to shift towards higher density solid or liquid.

NUMERICALS

1. **At 444°C, 15g mole of hydrogen is mixed with 5.2g mole of I_2 vapour. When equilibrium was established, 10g mole of HI was formed. Calculate the equilibrium constant for the reaction?**
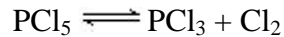
  Sol. $H2(g) + I2(g) \rightleftharpoons 2HI$
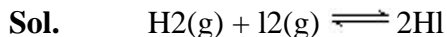
           a   b   0

        a – x   b – x   2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\frac{(a-x)}{V} \times \frac{(b-x)}{V}}$$

    So,
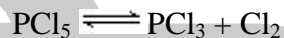
$= 4x^2 / (a–x) (b–x) = 4 \times 5^2 / 10 \times 0.2 = 50$

2. The degree of dissociation is 0.4 at 400K and 1 atm for the gaseous reaction

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

   Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400K and 1 atm pressure.

   (Atomic mass of P = 31 and Cl = 35.5)

Sol. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

   at t = 0   1   0   0

   at eqm.   1 – 0.4   0.4   0.4

   Total no. of moles after dissociation = 0.6 + 0.4 + 0.4

   Now, V = nRT / P = $1.4 \times 0.082 \times 400 / 1$ = 45.92 litres

   So, density = Molecular weight / Volume = 208.5 / 45.92 = 4.54 / litre

3. **When 3.06g of solid NH₄HS is introduced into a 2 litre evacuated flask at 27°C, 30% of the solid decomposed into gaseous ammonia and hydrogen sulphide?**

   (i) Calculate K_c for reaction at 27°C.

   (ii) What would happen to the equilibrium when more solid NH₄HS is introduced into the flask?

Sol. Moles of NH_4HS introduced into flask = 3.06 / 51 = 0.08

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S\ (g)$$
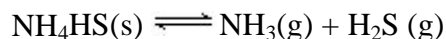
0.06 (1 – x)   0.06x   0.06x
as x = 30%, so, x = 0.3

So, 0.06×0.7 0.06´0.3 0 0.6×0.3

So, Kc = $[NH_3][H_2S]$
$0.018 \times 0.018 = 3.24 \times 10^{-2}$
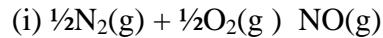Addition of $NH_4HS_{(s)}$ does not change position of equilibrium.

4. **Determine K_c for the reaction ½N₂(g) + ½O₂(g) + ½Br₂(g) —> NOBr(g) from the following information (at 298°K)?**

   $K_c = 2.4 \times 10^{30}$ for 2NO(g) —> N₂(g) + O₂(g) ;

   $K'_c = 1.4$ for NO(g) + ½Br₂(g) —> NOBr(g)

Sol. N₂(g) + O₂(g) —> 2NO (g)

   $K_c^{/} = 1/K_c = 1/2.4 \times 10^{30}$

(i) ½N$_2$(g) + ½O$_2$(g) NO(g)

$$K_c^{//} = \sqrt{K_c'} = \sqrt{\frac{1}{2.4} \times 10^{-30}} = 0.6455 \times 10^{-15}$$

(ii) NO(g) + ½Br$_2$(g) NOBr(g) = 1.4.
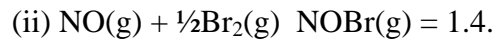
(i) + (ii) gives the net reaction:

½N$_2$(g) + ½O$_2$(g) + ½Br$_2$(g) ⇌ NOBr(g)
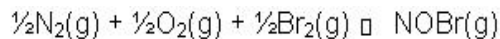
$$K = \frac{[NO]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}} \times \frac{[NOBr]}{[NO][Br_2]^{\frac{1}{2}}} = \frac{[NOBr]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}[Br_2]^{\frac{1}{2}}}$$

$$= K_c^{'} \times K_c^{''} = 0.6455 \times 10^{-15} \times 1.4 = \mathbf{9.037 \times 10^{-16}}$$

5. **The heat of reaction at constant volume for an endothermic reaction in equilibrium is 1200 cal more than at constant pressure at 300K. Calculate the ratio of equilibrium constant K$_p$ and K$_c$.**

Sol.   Given that ΔE – ΔH = 1200 cal

Also we have

nRT = –1200
or Δn = –1200 / 2 × 300 = –2 (R = 2calK^{-1} mol^{-1})
Now, K$_p$ = K$_c$ (RT)^{Δn}
K$_p$ = K$_c$ (0.0281 × 300) = 1.648 × 10^{-3}

6. The value of Kp, if the value of Kc is 2×10^{-3} for H_2 (g) $+I_2$ (g) $\leftrightarrow$ 2HI (g) at 27^0c?

Sol: $Kp = Kc [RT]^{\Delta n}$

$H_2 + I_2 \leftrightarrow 2HI$

(g)   (g)   (g)
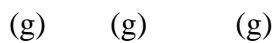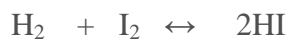
$\Delta n = $ [(no. of moles of gaseous products) – (no .of moles of gaseous reactants)]

$= [2 – (1+1)]$

$= 2 - 2$

$\Delta n = 0$

If $\Delta n = 0$ then, $Kp = Kc$

Given $Kc = 2 \times 10^{-3}$

$\therefore Kp = 2 \times 10^{-3}$