7.Equilibrium(Part-I)

Some Important Points and Terms of the Chapter

1. **Equilibrium** represents the state of a process in which the properties like temperature, pressure etc do not show any change with the passage of time
2. **Chemical equilibrium:** When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is *dynamic* in nature as it consists of a *forward* reaction in which the reactants give product(s) and *reverse* reaction in which product(s) gives the original reactants. Equilibrium is possible only in a closed system at a given temperature. A mixture of reactants and products in the equilibrium state is called an equilibrium mixture.
3. In a **Homogeneous system**, all the reactants and products are in the same phase. For example, in the gaseous reaction, $N_2 (g) + 3H_2(g) \rightarrow 2NH_3(g)$, reactants and products are in the homogeneous phase.
4. Equilibrium in a system having more than one phase is called **heterogeneous equilibrium.** The equilibrium between water vapor and liquid water in a closed container is an example of heterogeneous equilibrium. $H_2O(l) \rightarrow H_2O(g)$

5. **Henry Law**:-It states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent
6. **Law of Chemical Equilibrium:** It may be stated as, at a given temperature the ratio of product of equilibrium concentration of the products to that of the reactants with each concentration terms raised to power equal to the respective stoichiometric coefficient in the balanced chemical reaction has a constant value. This constant value is known as Equilibrium constant. For a general reaction of the type $aA + bB \Leftrightarrow cC + dD$

$K_c = [C]^c[D]^d/[A]^a[B]^b$ This expression is known as Law Of Chemical Equilibrium

7. **Relationship between Kp and Kc**: $K_p = K_c(RT)^{\Delta n}$
8. **Units of Equilibrium Constant**: The value of equilibrium constant Kc can be calculated by substituting the concentration terms in mol/L and for Kp partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For the reactions (i)$H_2(g) + I_2(g) \rightarrow 2HI$, Kc and Kp have no unit.(ii)$N_2O_4(g) \rightarrow 2NO_2(g)$, Kc has unit mol/L and Kp has unit bar
9. **Characteristics Of Equilibrium Constant**
    - Equilibrium constant is applicable only when concentrations of the reactants and products have attained their equilibrium state.
    - The value of equilibrium constant is independent of initial concentrations of the reactants and products.
    - Equilibrium constant is temperature dependent having one unique value for aparticular reaction represented by a balanced equation at a given temperature.
    - The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
    - The equilibrium constant *K* for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.
10. **Applications of equilibrium constant** :
    - Predict the extent of a reaction on the basis of its magnitude.

- Predict the direction of the reaction, and
- Calculate equilibrium concentrations.

11. **Le Chatelier's Principle:** It states that if a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction that tends to undo the effect of the change imposed.

- **Effect of change of concentration:** When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration change. For eg:- $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$

If H_2 is added to the reaction mixture at equilibrium, the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction whereas H_2 is consumed i.e more of H_2 and I_2 react to form HI and finally the equilibrium shifts in forward direction.

- **Effect of change of pressure**: When the pressure is increased the equilibrium shifts in the direction in which the number of moles of the gas decreases.

Consider the reaction, $CO (g) + 3H_2 (g) \Leftrightarrow CH_4 (g) + H_2O (g)$ Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4 (g) + H_2O$). so by Le Chatelier's principle. The increase in pressure will shift the equilibrium in the forward direction, a direction in which the number of moles of the gas or pressure decreases.

- **Effect of change of Temperature:** When a change in temperature occurs, the value of equilibrium constant changes. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction. The equilibrium constant for an exothermic reaction (-ve ΔH) decreases as the temperature increases. The equilibrium constant for an endothermic reaction (+ve ΔH) increases as the temperature increases. When the Temperature is increased the equilibrium shifts in the direction in of endothermic reaction.

Consider a reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ $\Delta H = -92.38$Kj/mol

According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left (backward direction i.e direction of endothermic reaction) and decreases the equilibrium concentration of ammonia.

- **Effect of Inert Gas Addition**: If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.
- **Effect of a Catalyst:** A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Summary of Le Chatelier's Principle

Type of Effect or Change	**Direction of Equilibrium**
Addition of more reactants	Forward direction
Addition of more products	Backward direction
Increase in temperature	Towards endothermic reaction
Decrease in temperature	Towards exothermic reaction
Addition of Catalyst	No effect
Increase in Pressure	where the no. of gaseous moles are less
Decrease in Pressure	where the no. of gaseous moles are more

Addition of Inert gas at const.Volume	No effect
Addition of Inert gas at const.pressure	where the no. of gaseous moles are more

Unit-7

EQUILIBRIUM(Part-I)

1.Question based on law of chemical equilibrium, Equilibrium constant, Applications of Equilibrium Constants, Relation Between Kp & Kc.

1. What do mean by law of chemical equilibrium? Explain with an example.

2. Write the expression for the equilibrium constant, *Kc* for each of the following reactions:

   (i) $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$

   (ii) $2Cu(NO_3)_2\ (s) \rightleftharpoons 2CuO\ (s) + 4NO_2\ (g) + O_2\ (g)$

   (iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH\ (aq) + C_2H_5OH\ (aq)$

   (iv) $Fe^{3+}\ (aq) + 3OH^-\ (aq) \rightleftharpoons Fe(OH)_3\ (s)$

   (v) $I_2\ (s) + 5F_2 \rightleftharpoons 2IF_5$

3. Find out the value of *Kc* for each of the following equilibria from the value of *Kp*:

   (i) $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g);\ K_p = 1.8 \times 10^{-2}$ at 500 K

   (ii) $CaCO_3\ (s) \rightleftharpoons CaO(s) + CO_2(g);\ K_p = 167$ at 1073 K

4. Write the balanced chemical equation corresponding to this equilibrium constant expression for a gas reaction. \

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

5. What is *K*c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2]$= 0.60M, $[O_2]$ = 0.82M and $[SO_3]$ = 1.90M $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$
6. The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}$M. $[H_2] = 3.0 \times 10^{-2}$ M and $[NH_3] = 1.2 \times 10^{-2}$M. Calculate equilibrium constant.
7. At equilibrium, the concentrations of$N_2 = 3.0 \times 10^{-3}$M, $O_2 = 4.2 \times 10^{-3}$M and NO= 2.8×10^{-3}M in a sealed vessel at800K. What will be *K*c for the reaction:$N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$
8. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_3, 1.59M Cl_2 and 1.41 M PCl_5.Calculate *Kc* for the reaction,$PCl_5 \Leftrightarrow PCl_3 + Cl_2$
9. For the equilibrium,$2NOCl(g) \Leftrightarrow 2NO(g) + Cl_2(g)$ the value of the equilibrium constant, *Kc* is 3.75×10^{-6} at 1069 K. Calculate the *Kp* for the reaction at this temperature?

2.Question based on Calculating Equilibrium Concentrations, Le Chatelierís principleEffect of Pressure Change, Concentration Change, Temperature Change, Inert Gas Addition & Catalyst

10. The value of *Kc* = 4.24 at 800K for the reaction, CO (g) + H_2O (g) ⇔ CO_2 (g) + H_2 (g) Calculate equilibrium concentrations of CO_2, H_2, CO and H_2O at 800 K, if only CO and H_2O are present initially at concentrations of 0.10M each.The value of *Kp* for the reaction,CO_2 (g) + C (s) ⇔ 2CO (g) is 3.0 at 1000 K. If initially $p\ CO_2$= 0.48 bar and $p\ CO$ = 0 bar and puregraphite is present, calculate theequilibrium partial pressures of CO and CO_2.
11. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl5 was found to be0.5 × 10^{-1} mol L^{-1}. If value of *K*c is 8.3 × 10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?PCl_5 (g) ⇔ PCl_3 (g) + Cl_2(g)
12. What do you mean by Lechatelier's principle? Explain with an example?
13. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

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

    (b) $CaO\ (s) + CO_2\ (g) \rightleftharpoons CaCO_3\ (s)$

    (c) $3Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$
14. Which of the following reactions will get affected by increasing the pressure?Also, mention whether change will cause the reaction to go into

forward or backward direction.

(i) $COCl_2 (g) \rightleftharpoons CO (g) + Cl_2 (g)$

(ii) $CH_4 (g) + 2S_2 (g) \rightleftharpoons CS_2 (g) + 2H_2S (g)$

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

(iv) $2H_2 (g) + CO (g) \rightleftharpoons CH_3OH (g)$

(v) $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

(vi) $4 NH_3 (g) + 5O_2 (g) \rightleftharpoons 4NO (g) + 6H_2O(g)$

15. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$CH_4[g] + H_2O [g] \rightleftharpoons CO [g] + 3H_2[g]$

a) Write as expression for K_p for the above reaction.

b) How will the values of K_p and the composition of equilibrium mixture be affected by

i) Increasing the pressure
ii) Increasing the temperature
iii) Using a catalyst

16. Describe the effect of: - a) Addition of H_2 b) Addition of CH_3OH c) Removal of CO d) Removal of CH_3OH On the equilibrium of the reaction: $2 H_2[g] + CO[g] \rightleftharpoons CH_3OH [g]$

17. At 473 K, equilibrium constant *Kc* for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as, $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$ $\Delta_r H^0 = 124.0$ kJ mol^{-1}

a) write an expression for *Kc* for the reaction.

b) what is the value of *Kc* for the reverse reaction at the same temperature. c) what would be the effect on *K*c if (i) more PCl_5 is added (ii) pressure is increased(iii) the temperature is increased ?

3.Question based on Relationship Between Equilibrium Constant K, And Gibbs Energy G

18. The value of ΔG^0 for the phosphorylation of glucose in glycolysis is 13.8 kJ / mol. Find the value of K_c at 298 K
19. Hydrolysis of sucrose gives, Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose
    Equilibrium constant K_c for the reaction is $2 \text{ X } 10^{13}$ at 300K. Calculate ΔG^0 at 300K.
20. Calculate a) ΔG^0 and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298K NO (g) + ½ O_2 (g) $\rightleftharpoons$ NO_2 (g) where $\Delta_f G^0$ (NO_2) = 52.0 kJ/mol $\Delta_f G^0$ (NO) = 87.0 kJ/mol $\Delta_f G0$ (O2) = 0 kJ/mol.

Question 7.1:

A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

a) What is the initial effect of the change on vapour pressure?

b) How do rates of evaporation and condensation change initially?

c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

- **Answer**

(a) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume.

(b) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially.

(c) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system.

Question 7.2:

What is K_c for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2] = 0.60$ M, $[O_2] = 0.82$ M and $[SO_3] = 1.90$ M?

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

- **Answer**

The equilibrium constant (K_c) for the give reaction is:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$
$$= \frac{(1.90)^2 \text{ M}^2}{(0.60)^2(0.821)\text{M}^3}$$
$$= 12.239 \text{ M}^{-1} \text{(approximately)}$$

Hence, K_c for the equilibrium is 12.239 M^{-1}.

Question 7.3:

At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms

$$I_2 \ (g) \longleftrightarrow 2I \ (g)$$

Calculate K_p for the equilibrium.

- **Answer**

Partial pressure of I atoms,

$$p_I = \frac{40}{100} \times p_{\text{total}}$$

$$= \frac{40}{100} \times 10^5$$
$$= 4 \times 10^4 \text{ Pa}$$

Partial pressure of I_2 molecules,

$$p_{I_2} = \frac{60}{100} \times p_{\text{total}}$$

$$= \frac{60}{100} \times 10^5$$
$$= 6 \times 10^4 \text{ Pa}$$

Now, for the given reaction,

$$K_p = \frac{(pI)^2}{p_{I_2}}$$
$$= \frac{(4 \times 10^4)^2 \text{ Pa}^2}{6 \times 10^4 \text{ Pa}}$$
$$= 2.67 \times 10^4 \text{ Pa}$$

Question 7.4:

Write the expression for the equilibrium constant, K_c for each of the following reactions:

(i) $2\,\text{NOCl(g)} \longleftrightarrow 2\,\text{NO(g)} + \text{Cl}_2\text{(g)}$

(ii) $2\,\text{Cu(NO}_3)_2\text{(s)} \longleftrightarrow 2\text{CuO(s)} + 4\,\text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$

(iii) $\text{CH}_3\text{COOC}_2\text{H}_5\text{(aq)} + \text{H}_2\text{O(l)} \longleftrightarrow \text{CH}_3\text{COOH(aq)} + \text{C}_2\text{H}_5\text{OH(aq)}$

(iv) $\text{Fe}^{3+}\text{(aq)} + 3\text{OH}^-\text{(aq)} \longleftrightarrow \text{Fe(OH)}_3\text{(s)}$

(v) $\text{I}_2\text{(s)} + 5\text{F}_2 \longleftrightarrow 2\,\text{IF}_5$

- **Answer**

(i) $$K_c = \frac{\left[NO_{(g)}\right]^2\left[Cl_{2(g)}\right]}{\left[NOCl_{(g)}\right]^2}$$

(ii) $$K_c = \frac{\left[CuO_{(s)}\right]^2\left[NO_{2(g)}\right]^4\left[O_{2(g)}\right]}{\left[Cu\left(NO_3\right)_{2(s)}\right]^2}$$

$$= \left[NO_{2(g)}\right]^4\left[O_{2(g)}\right]$$

(iii) $$K_c = \frac{\left[CH_3COOH_{(aq)}\right]\left[C_2H_5OH_{(aq)}\right]}{\left[CH_3COOC_2H_{5(aq)}\right]\left[H_2O_{(l)}\right]} = \frac{\left[CH_3COOH_{(aq)}\right]\left[C_2H_5OH_{(aq)}\right]}{\left[CH_3COOC_2H_{5(aq)}\right]}$$

(iv) $$K_c = \frac{\left[Fe(OH)_{3(s)}\right]}{\left[Fe^{3+}{}_{(aq)}\right]\left[OH^-_{(aq)}\right]^3}$$

$$= \frac{1}{\left[Fe^{3+}{}_{(aq)}\right]\left[OH^-_{(aq)}\right]^3}$$

(v) $$K_c = \frac{[IF_5]^2}{\left[I_{2(s)}\right][F_2]^5}$$

$$= \frac{[IF_5]^2}{[F_2]^5}$$

Question 7.5:

Find out the value of K_c for each of the following equilibria from the value of K_p:

(i) $2NOCl(g) \longleftrightarrow 2NO(g) + Cl_2(g);\quad K_p = 1.8 \times 10^{-2}$ at 500 K

(ii) $CaCO_3(s) \longleftrightarrow CaO(s) + CO_2(g);\quad K_p = 167$ at 1073 K

- **Answer**

The relation between K_p and K_c is given as:

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

(a) Here,

$\Delta n = 3 - 2 = 1$

$R = 0.0831\ barLmol^{-1}K^{-1}$

$T = 500\ \text{K}$

$K_p = 1.8 \times 10^{-2}$

Now,

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

$$\Rightarrow 1.8\times10^{-2} = K_c\left(0.0831\times500\right)^1$$

$$\Rightarrow K_c = \frac{1.8\times10^{-2}}{0.0831\times500}$$
$$= 4.33\times10^{-4}\left(\text{approximately}\right)$$

(b) Here,

$\Delta n = 2 - 1 = 1$

$R = 0.0831\ \text{barLmol}^{-1}\text{K}^{-1}$

$T = 1073\ \text{K}$

$K_p = 167$

Now,

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

$$\Rightarrow 167 = K_c\left(0.0831\times1073\right)^{\Delta n}$$

$$\Rightarrow K_c = \frac{167}{0.0831\times1073}$$
$$= 1.87\left(\text{approximately}\right)$$

Question 7.6:

For the following equilibrium, $K_C = 6.3\times10^{14}\ \text{at}\ 1000\ \text{K}$

$\text{NO(g)} + \text{O}_3\text{(g)} \longleftrightarrow \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction?

- **Answer**

It is given that K_C for the forward reaction is 6.3×10^{14}.

Then, K_C for the reverse reaction will be,

$$K'_C = \frac{1}{K_C}$$

$$= \frac{1}{6.3 \times 10^{14}}$$

$$= 1.59 \times 10^{-15}$$

Question 7.7:

Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?

- **Answer**

For a pure substance (both solids and liquids),

$$[\text{Pure substance}] = \frac{\text{Number of moles}}{\text{Volume}}$$

$$= \frac{\text{Mass/molecular mass}}{\text{Volume}}$$

$$= \frac{\text{Mass}}{\text{Volume} \times \text{Molecular mass}}$$

$$= \frac{\text{Density}}{\text{Molecular mass}}$$

Now, the molecular mass and density (at a particular temperature) of a pure substance is always fixed and is accounted for in the equilibrium constant. Therefore, the values of pure substances are not mentioned in the equilibrium constant expression.

Question 7.8:

Reaction between N_2 and O_2 takes place as follows:

$$2N_2(g) \quad + \quad O_2(g) \quad \longleftrightarrow \quad 2N_2O(g)$$

If a mixture of 0.482 mol of N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

- **Answer**

Let the concentration of N_2O at equilibrium be *x*.

The given reaction is:

	$2N_{2(g)}$	+	$O_{2(g)}$	$\longleftrightarrow$	$2N_2O_{(g)}$
Initial conc.	0.482 mol		0.933 mol		0
At equilibrium	$(0.482 - x)$ mol		$(1.933 - x)$ mol		x mol

Therefore, at equilibrium, in the 10 L vessel:

$$[N_2] = \frac{0.482 - x}{10},\ [O_2] = \frac{0.933 - x/2}{10},\ [N_2O] = \frac{x}{10}$$

The value of equilibrium constant i.e., $K_C = 2.0 \times 10^{-37}$ is very small. Therefore, the amount of N_2 and O_2 reacted is also very small. Thus, x can be neglected from the expressions of molar concentrations of N_2 and O_2.

Then,

$$[N_2] = \frac{0.482}{10} = 0.0482\,\text{mol}\,L^{-1} \text{ and } [O_2] = \frac{0.933}{10} = 0.0933\,\text{mol}\,L^{-1}$$

Now,

$$K_C = \frac{\left[N_2O_{(g)}\right]^2}{\left[N_{2(g)}\right]^2\left[O_{2(g)}\right]}$$

$$\Rightarrow 2.0 \times 10^{-37} = \frac{\left(\frac{x}{10}\right)^2}{(0.0482)^2(0.0933)}$$

$$\Rightarrow \frac{x^2}{100} = 2.0 \times 10^{-37} \times (0.0482)^2 \times (0.0933)$$

$$\Rightarrow x^2 = 43.35 \times 10^{-40}$$

$$\Rightarrow x = 6.6 \times 10^{-20}$$

$$[N_2O] = \frac{x}{10} = \frac{6.6 \times 10^{-20}}{10}$$

$$= 6.6 \times 10^{-21}$$

Question 7.9:

Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$$2NO(g) + Br_2(g) \longleftrightarrow 2NOBr(g)$$

When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2.

- **Answer**

The given reaction is:

$$\underset{2\text{mol}}{2NO_{(g)}} + \underset{1\text{mol}}{Br_{2(g)}} \longleftrightarrow \underset{2\text{mol}}{2NOBr_{(g)}}$$

Now, 2 mol of NOBr are formed from 2 mol of NO. Therefore, 0.0518 mol of NOBr are formed from 0.0518 mol of NO.

Again, 2 mol of NOBr are formed from 1 mol of Br.

Therefore, 0.0518 mol of NOBr are formed from $\frac{0.0518}{2}$ mol of Br, or

0.0259 mol of NO

The amount of NO and Br present initially is as follows:

[NO] = 0.087 mol $[Br_2]$ = 0.0437 mol

Therefore, the amount of NO present at equilibrium is:

[NO] = 0.087 – 0.0518

= 0.0352 mol

And, the amount of Br present at equilibrium is:

$[Br_2]$ = 0.0437 – 0.0259

= 0.0178 m

Question 7.10:

At 450 K, K_p= 2.0 × 10^{10}/bar for the given reaction at equilibrium.

$$2SO_{2(g)} + O_{2(g)} \longleftrightarrow 2SO_{3(g)}$$

What is K_c at this temperature?

- **Answer**

For the given reaction,

$\Delta n = 2 - 3 = -1$

$T = 450$ K

$R = 0.0831$ bar L bar K^{-1} mol^{-1}

$K_P = 2.0 \times 10^{10}$ bar $^{-1}$

We know that,

$$K_P = K_C\left(RT\right)\Delta n$$

$$\Rightarrow 2.0\times10^{10}\ \text{bar}^{-1} = K_C\left(0.0831\,\text{L bar K}^{-1}\text{mol}^{-1}\times450\,\text{K}\right)^{-1}$$

$$\Rightarrow K_C = \frac{2.0\times10^{10}\ \text{bar}^{-1}}{\left(0.0831\ \text{L bar K}^{-1}\text{mol}^{-1}\times450\text{K}\right)^{-1}}$$

$$= \left(2.0\times10^{10}\ \text{bar}^{-1}\right)\left(0.0831\,\text{L bar K}^{-1}\text{mol}^{-1}\times450\text{K}\right)$$

$$= 74.79\times10^{10}\ \text{L mol}^{-1}$$

$$= 7.48\times10^{11}\ \text{L mol}^{-1}$$

$$= 7.48\times10^{11}\ \text{M}^{-1}$$

Question 7.11:

A sample of HI $_{(g)}$ is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI $_{(g)}$ is 0.04 atm. What is K_p for the given equilibrium?

$$2\text{HI}(g) \longleftrightarrow \text{H}_2(g) + \text{I}_2(g)$$

- **Answer**

The initial concentration of HI is 0.2 atm. At equilibrium, it has a partial pressure of 0.04 atm. Therefore, a decrease in the pressure of HI is 0.2 – 0.04 = 0.16. The given reaction is:

	$2\text{HI}_{(g)}$	$\longleftrightarrow$	$\text{H}_{2(g)}$	+	$\text{I}_{2(g)}$
Initial conc.	0.2 atm		0		0
At equilibrium	0.04 atm		$\frac{0.16}{2}$ $= 0.08\,\text{atm}$		$\frac{2.15}{2}$ $= 0.08\,\text{atm}$

Therefore,

$$K_p = \frac{p_{\text{H}_2}\times p_{\text{I}_2}}{p^2_{\text{HI}}}$$

$$= \frac{0.08\times0.08}{\left(0.04\right)^2}$$

$$= \frac{0.0064}{0.0016}$$

$$= 4.0$$

Hence, the value of K_p for the given equilibrium is 4.0.

Question 7.12:

A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_2(g) + 3H_2(g) \longleftrightarrow 2NH_3(g)$ is 1.7×10^2

Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

- **Answer**

The given reaction is:

$$N_{2(g)} + 3H_{2(g)} \longleftrightarrow 2NH_{3(g)}$$

The given concentration of various species is

$$[N_2] = \frac{1.57}{20}\text{mol L}^{-1} \qquad [H_2] = \frac{1.92}{20}\text{mol L}^{-1}$$

$$[NH_3] = \frac{8.13}{20}\text{mol L}^{-1}$$

Now, reaction quotient Q_c is:

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

$$= \frac{\left(\frac{(8.13)}{20}\right)^2}{\left(\frac{1.57}{20}\right)\left(\frac{1.92}{20}\right)^3}$$

$$= 2.4\times10^3$$

Since $Q_C \neq K_C$, the reaction mixture is not at equilibrium.

Again, $Q_C > K_C$. Hence, the reaction will proceed in the reverse direction.

Question 7.13:

The equilibrium constant expression for a gas reaction is,

$$K_C = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

- **Answer**

The balanced chemical equation corresponding to the given expression can be written as:

$$4NO_{(g)} + 6H_2O_{(g)} \longleftrightarrow 4NH_{3(g)} + 5O_{2(g)}$$

Question 7.14:

One mole of H_2O and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation,

$$H_2O(g) + CO(g) \longleftrightarrow H_2(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

- **Answer**

The given reaction is:

$$\begin{array}{lccccccc}
 & H_2O_{(g)} & + & CO_{(g)} & \longleftrightarrow & H_{2(g)} & + & CO_{2(g)} \\
\text{Initial conc.} & \frac{1}{10}\text{M} & & \frac{1}{10}\text{M} & & 0 & & 0 \\
\text{At equilibrium} & \frac{1-0.4}{10}\text{M} & & \frac{1-0.4}{10}\text{M} & & \frac{0.4}{10}\text{M} & & \frac{0.4}{10}\text{M} \\
 & =0.06\text{M} & & =0.06\text{M} & & =0.04\text{M} & & =0.04\text{M}
\end{array}$$

Therefore, the equilibrium constant for the reaction,

$$\begin{aligned}
K_C &= \frac{[H_2][CO_2]}{[H_2O][CO]} \\
&= \frac{0.04 \times 0.04}{0.06 \times 0.06} \\
&= 0.444 \text{ (approximately)}
\end{aligned}$$

Question 7.15:

At 700 K, equilibrium constant for the reaction

$$H_{2(g)} + I_{2(g)} \longleftrightarrow 2HI_{(g)}$$

is 54.8. If 0.5 molL^{-1} of $HI_{(g)}$ is present at equilibrium at 700 K, what are the concentration of $H_{2(g)}$ and $I_{2(g)}$ assuming that we initially started with $HI_{(g)}$ and allowed it to reach equilibrium at 700 K?

- **Answer**

It is given that equilibrium constant K_C for the reaction

$H_{2(g)} + I_{2(g)} \longleftrightarrow 2HI_{(g)}$ is 54.8.

Therefore, at equilibrium, the equilibrium constant K'_C for the reaction

$2HI_{(g)} \longleftrightarrow H_{2(g)} + I_{2(g)}$ will be $\frac{1}{54.8}$.

$[HI] = 0.5\,molL^{-1}$

Let the concentrations of hydrogen and iodine at equilibrium be x $molL^{-1}$

$[H_2] = [I_2] = x\,mol\,L^{-1}$.

Therefore, $\frac{[H_2][I_2]}{[HI]^2} = K'_C$

$\Rightarrow \frac{x \times x}{(0.5)^2} = \frac{1}{54.8}$

$\Rightarrow x^2 = \frac{0.25}{54.8}$

$\Rightarrow x = 0.06754$

$x = 0.068\,molL^{-1}$ (approximately)

Hence, at equilibrium, $[H_2] = [I_2] = 0.068\,mol\,L^{-1}$.

Question 7.16:

What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?

$2ICl_{(g)} \longleftrightarrow I_{2(g)} + Cl_{2(g)}; \quad K_c = 0.14$

- **Answer**

The given reaction is:

	$2ICl_{(g)}$	$\longleftrightarrow$	$I_{2(g)}$	$Cl_{2(g)}$
Initial conc.	0.78 M		0	0
At equilibrium	$(0.78-2x)$ M		xM	xM

Now, we can write, $\frac{[I_2][Cl_2]}{[ICl]^2} = K_C$

$$\Rightarrow \frac{x \times x}{(0.78-2x)^2} = 0.14$$

$$\Rightarrow \frac{x^2}{(0.78-2x)^2} = 0.14$$

$$\Rightarrow \frac{x}{0.78-2x} = 0.374$$

$$\Rightarrow x = 0.292 - 0.748x$$

$$\Rightarrow 1.748x = 0.292$$

$$\Rightarrow x = 0.167$$

Hence, at equilibrium,

$$[H_2] = [I_2] = 0.167 \text{ M}$$

$$[HI] = (0.78 - 2 \times 0.167) \text{ M}$$

$$= 0.446 \text{M}$$

Question 7.17:

K_p = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

$$C_2H_6(g) \longleftrightarrow C_2H_4(g) + H_2(g)$$

- **Answer**

Let *p* be the pressure exerted by ethene and hydrogen gas (each) at equilibrium.

Now, according to the reaction,

	$C_2H_{6(g)}$	$\longleftrightarrow$ $C_2H_{4(g)}$	+ $H_{2(g)}$
Initial conc.	4.0atm	0	0
At equilibrium	$4.0 - p$	p	p

We can write,

$$\frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}} = K_p$$

$$\Rightarrow \frac{p \times p}{40 - p} = 0.04$$

$$\Rightarrow p^2 = 0.16 - 0.04p$$

$$\Rightarrow p^2 + 0.04p - 0.16 = 0$$

$$\text{Now, } p = \frac{-0.04 \pm \sqrt{(0.04)^2 - 4 \times 1 \times (-0.16)}}{2 \times 1}$$

$$= \frac{-0.04 \pm 0.80}{2}$$

$$= \frac{0.76}{2} \qquad \text{(Taking positive value)}$$

$$= 0.38$$

Hence, at equilibrium,

$$[C_2H_6] - 4 - p = 4 - 0.38$$

$$= 3.62 \text{ atm}$$

Question 7.18:

Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \longleftrightarrow CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

(i) Write the concentration ratio (reaction quotient), Qc, for this reaction (note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

- **Answer**

(i) Reaction quotient, $Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$

(ii) Let the volume of the reaction mixture be *V*. Also, here we will consider that water is a solvent and is present in excess.

The given reaction is:

$$\begin{array}{lcccc} & CH_3COOH_{(l)} + & C_2H_5OH_{(l)} \longleftrightarrow & CH_3COOC_2H_{5(l)} & + \ H_2O_{(l)} \\ \text{Initial conc.} & \frac{1}{V}\text{M} & \frac{0.18}{V}\text{M} & 0 & 0 \\ \text{At equilibrium} & \frac{1-0.171}{V} & \frac{0.18-0.171}{V} & \frac{0.171}{V}\text{M} & \frac{0.171}{V}\text{M} \\ & =\frac{0.829}{V}\text{M} & =\frac{0.009}{V}\text{M} & & \end{array}$$

Therefore, equilibrium constant for the given reaction is:

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{\frac{0.171}{V} \times \frac{0.171}{V}}{\frac{0.829}{V} \times \frac{0.009}{V}} = 3.919$$

$$= 3.92 (\text{approximately})$$

(iii) Let the volume of the reaction mixture be *V*.

$$\begin{array}{lcccc} & CH_3COOH_{(l)} + & C_2H_5OH_{(l)} \longleftrightarrow & CH_3COOC_2H_{5(l)} & + \ H_2O_{(l)} \\ \text{Initial conc.} & \frac{1.0}{V}\text{M} & \frac{0.5}{V}\text{M} & 0 & 0 \\ \text{After some time} & \frac{10-0.214}{V} & \frac{0.5-0.214}{V} & \frac{0.214}{V}\text{M} & \frac{0.214}{V}\text{M} \\ & =\frac{0.786}{V}\text{M} & =\frac{0.286}{V}\text{M} & & \end{array}$$

Therefore, the reaction quotient is,

$$Q_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{\frac{0.214}{V} \times \frac{0.214}{V}}{\frac{0.786}{V} \times \frac{0.286}{V}}$$

$$= 0.2037$$

$$= 0204 \ (\text{approximately})$$

Since $Q_C < K_C$, equilibrium has not been reached.

Question 7.19:

A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?

$$PCl_5\ (g) \longleftrightarrow PCl_3\ (g) + Cl_2(g)$$

- **Answer**

Let the concentrations of both PCl_3 and Cl_2 at equilibrium be x molL^{-1}. The given reaction is:

$$\begin{array}{lcccccc} & PCl_{5(g)} & \longleftrightarrow & PCl_{3(g)} & + & Cl_{2(g)} \\ \text{At equilibrium} & 0.5\times10^{-1}\text{mol L}^{-1} & & x\,\text{mol L}^{-1} & & x\,\text{mol L}^{-1} \end{array}$$

It is given that the value of equilibrium constant , K_C is 8.3×10^{-3}.

Now we can write the expression for equilibrium as:

$$\frac{[PCl_2][Cl_2]}{[PCl_5]} = K_C$$

$$\Rightarrow \frac{x\times x}{0.5\times10^{-1}} = 8.3\times10^{-3}$$

$$\Rightarrow x^2 = 4.15\times10^{-4}$$

$$\begin{aligned} \Rightarrow x &= 2.04\times10^{-2} \\ &= 0.0204 \\ &= 0.02\,(\text{approximately}) \end{aligned}$$

Therefore, at equilibrium,

$$[PCl_3] = [Cl_2] = 0.02 \text{ mol L}^{-1}.$$

Question 7.20:

One of the reactions that take place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2.

FeO (s) + CO (g) $\longleftrightarrow$ Fe (s) + CO_2 (g); K_p= 0.265 at 1050 K.

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are: p_{CO} = 1.4 atm and p_{CO_2} = 0.80 atm?

- **Answer**

For the given reaction,

$$\begin{array}{llllll} FeO_{(g)} & + & CO_{(g)} & \longleftrightarrow & Fe_{(s)} + & CO_{2(g)} \\ \text{Initialy,} & & 1.4 \text{ atm} & & & 0.80 \text{ atm} \end{array}$$

$$\begin{aligned} Q_P &= \frac{p_{CO_2}}{p_{CO}} \\ &= \frac{0.80}{1.4} \\ &= 0.571 \end{aligned}$$

It is given that $K_P = 0.265$.

Since $Q_P > K_P$, the reaction will proceed in the backward direction.

Therefore, we can say that the pressure of CO will increase while the pressure of CO_2 will decrease.

Now, let the increase in pressure of CO = decrease in pressure of CO_2 be *p*.

Then, we can write,

$$\begin{aligned} &K_P = \frac{p_{CO_2}}{p_{CO}} \\ &\Rightarrow 0.265 = \frac{0.80 - p}{1.4 + p} \\ &\Rightarrow 0.371 + 0.265\,p = 0.80 - p \\ &\Rightarrow 1.265\,p = 0.429 \\ &\Rightarrow p = 0.339 \text{ atm} \end{aligned}$$

Therefore, equilibrium partial of $CO_2, p_{CO_2} = 0.80 - 0.339 = 0.461$ atm.

And, equilibrium partial pressure of $CO, p_{CO} = 1.4 + 0.339 = 1.739$ atm.

Question 7.21:

Equilibrium constant, K_c for the reaction

$N_2(g) + 3H_2(g) \longleftrightarrow 2NH_3(g)$ ***at 500 K is 0.061.***

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

- **Answer**

The given reaction is:

$$\begin{array}{lccc} & N_{2(g)} \quad + & 3H_{2(g)} \longleftrightarrow & 2NH_{3(g)} \\ \text{At a particular time:} & 3.0\,\text{mol L}^{-1} & 2.0\,\text{mol L}^{-1} & 0.5\,\text{mol L}^{-1} \end{array}$$

Now, we know that,

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

$$= \frac{(0.5)^2}{(3.0)(2.0)^3}$$

$$= 0.0104$$

It is given that $K_C = 0.061$.

Since $Q_C \neq K_C$, the reaction is not at equilibrium.

Since $Q_C < K_C$, the reaction will proceed in the forward direction to reach equilibrium.

Question 7.22:

Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium:

$$2BrCl\,(g) \longleftrightarrow Br_2\,(g) + Cl_2\,(g)$$

for which K_c= 32 at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} $molL^{-1}$, what is its molar concentration in the mixture at equilibrium?

- **Answer**

Let the amount of bromine and chlorine formed at equilibrium be *x*. The given reaction is:

$$\begin{array}{lcccc} & 2BrCl_{(g)} & \longleftrightarrow & Br_{2(g)} \quad + & Cl_{2(g)} \\ \text{Initial conc.} & 3.3\times10^{-3} & & 0 & 0 \\ \text{At equilibrium} & 3.3\times10^{-3} - 2x & & x & x \end{array}$$

Now, we can write,

$$\frac{[Br_2][Cl_2]}{[BrCl]^2} = K_C$$

$$\Rightarrow \frac{x \times x}{\left(3.3\times10^{-3} - 2x\right)^2} = 32$$

$$\Rightarrow \frac{x}{3.3\times10^{-3} - 2x} = 5.66$$

$$\Rightarrow x = 18.678\times10^{-3} - 11.32x$$

$$\Rightarrow 12.32x = 18.678\times10^{-3}$$

$$\Rightarrow x = 1.5\times10^{-3}$$

Therefore, at equilibrium,

$$\begin{aligned}[BrCl] &= 3.3\times10^{-3} - \left(2\times1.5\times10^{-3}\right)\\ &= 3.3\times10^{-3} - 3.0\times10^{-3}\\ &= 0.3\times10^{-3}\\ &= 3.0\times10^{-4}\ \text{molL}^{-1}\end{aligned}$$

Question 7.23:

At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass

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

Calculate K_c for this reaction at the above temperature.

- **Answer**

Let the total mass of the gaseous mixture be 100 g.

Mass of CO = 90.55 g

And, mass of CO_2 = (100 – 90.55) = 9.45 g

Now, number of moles of CO, $n_{CO} = \frac{90.55}{28} = 3.234\ \text{mol}$

Number of moles of CO_2, $n_{CO_2} = \frac{9.45}{44} = 0.215\ \text{mol}$

Partial pressure of CO,

$$p_{CO} = \frac{n_{CO}}{n_{CO} + n_{CO_2}} \times p_{total}$$
$$= \frac{3.234}{3.234 + 0.215} \times 1$$
$$= 0.938 \text{ atm}$$

Partial pressure of CO_2,

$$p_{CO_2} = \frac{n_{CO_2}}{n_{CO} + n_{CO_2}} \times p_{total}$$
$$= \frac{0.215}{3.234 + 0.215} \times 1$$
$$= 0.062 \text{ atm}$$

$$\text{Therefore, } K_P = \frac{[CO]^2}{[CO_2]}$$
$$= \frac{(0.938)^2}{0.062}$$
$$= 14.19$$

For the given reaction,

$\Delta n = 2 – 1 = 1$

We know that,

$$K_P = K_C (RT)^{\Delta n}$$
$$\Rightarrow 14.19 = K_C (0.082 \times 1127)^1$$
$$\Rightarrow K_C = \frac{14.19}{0.082 \times 1127}$$
$$= 0.154 (\text{approximately})$$

Question 7.24:

Calculate a) $\Delta G°$and b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K

$$NO (g) + ½ O_2 (g) \longleftrightarrow NO_2 (g)$$

where $\Delta_f G°$ (NO_2) = 52.0 kJ/mol

$\Delta_f G°$ (NO) = 87.0 kJ/mol

$\Delta_f G°$ (O_2) = 0 kJ/mol

- **Answer**

(a) For the given reaction,

$\Delta G° = \Delta G°$(Products) – $\Delta G°$(Reactants)

$\Delta G° = 52.0 - \{87.0 + 0\}$

$= -35.0 \text{ kJ mol}^{-1}$

(b) We know that,

$\Delta G° = \text{RT} \log K_c$

$\Delta G° = 2.303 \text{ RT} \log K_c$

$$K_c = \frac{-35.0\times10^{-3}}{-2.303\times8.314\times298}$$
$$= 6.134$$
$$\therefore K_c = \text{antilog}\left(6.134\right)$$
$$= 1.36\times10^{6}$$

Hence, the equilibrium constant for the given reaction K_c is 1.36×10^6

Question 7.25:

Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

(a) $PCl_5\ (g) \longleftrightarrow PCl_3\ (g) + Cl_2\ (g)$

(b) $CaO\ (s) + CO_2\ (g) \longleftrightarrow CaCO_3\ (s)$

(c) $3Fe\ (s) + 4H_2O\ (g) \longleftrightarrow Fe_3O_4\ (s) + 4H_2\ (g)$

- **Answer**

(a) The number of moles of reaction products will increase. According to Le Chatelier’s principle, if pressure is decreased, then the equilibrium shifts in the direction in which the number of moles of gases is more. In the given reaction, the number of moles of gaseous products is more than that of gaseous reactants. Thus, the reaction will proceed in the forward direction. As a result, the number of moles of reaction products will increase.

(b) The number of moles of reaction products will decrease.

(c) The number of moles of reaction products remains the same

Question 7.26:

Which of the following reactions will get affected by increasing the pressure?

Also, mention whether change will cause the reaction to go into forward or backward direction.

(i) $COCl_2\ (g) \longleftrightarrow CO\ (g) + Cl_2\ (g)$

(ii) $CH_4\ (g) + 2S_2\ (g) \longleftrightarrow CS_2\ (g) + 2H_2S\ (g)$

(iii) $CO_2\ (g) + C\ (s) \longleftrightarrow 2CO\ (g)$

(iv) $2H_2\ (g) + CO\ (g) \longleftrightarrow CH_3OH\ (g)$

(v) $CaCO_3\ (s) \longleftrightarrow CaO\ (s) + CO_2\ (g)$

(vi) $4\ NH_3\ (g) + 5O_2\ (g) \longleftrightarrow 4NO\ (g) + 6H_2O(g)$

- **Answer**

The reactions given in (i), (iii), (iv), (v), and (vi) will get affected by increasing the pressure.

The reaction given in (iv) will proceed in the forward direction because the number of moles of gaseous reactants is more than that of gaseous products.

The reactions given in (i), (iii), (v), and (vi) will shift in the backward direction because the number of moles of gaseous reactants is less than that of gaseous products.

Question 7.27:

The equilibrium constant for the following reaction is 1.6 ×10^5 at 1024 K.

$H_2(g) + Br_2(g) \longleftrightarrow 2HBr(g)$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

- **Answer**

Given,

K_P for the reaction i.e., $H_{2(g)} + Br_{2(g)} \longleftrightarrow 2HBr_{(g)}$ is 1.6×10^5.

Therefore, for the reaction $2HBr_{(g)} \longleftrightarrow H_{2(g)} + Br_{2(g)}$, the equilibrium constant will be,

$$K'_P = \frac{1}{K_P}$$
$$= \frac{1}{1.6 \times 10^5}$$
$$= 6.25 \times 10^{-6}$$

Now, let p be the pressure of both H_2 and Br_2 at equilibrium.

	$2HBr_{(g)}$	$\longleftrightarrow$	$H_{2(g)}$	$+$	$Br_{2(g)}$
Initial conc.	10		0		0
At equilibrium	$10 - 2p$		p		p

Now, we can write,

$$\frac{p_{HBr} \times p_{\ \ 2}}{p^2_{HBr}} = K'_P$$

$$\frac{p \times p}{(10 - 2p)^2} = 6.25 \times 10^{-6}$$

$$\frac{p}{10 - 2p} = 2.5 \times 10^{-3}$$

$$p = 2.5 \times 10^{-2} - \left(5.0 \times 10^{-3}\right) p$$

$$p + \left(5.0 \times 10^{-3}\right) p = 2.5 \times 10^{-2}$$

$$\left(1005 \times 10^{-3}\right) p = 2.5 \times 10^{-2}$$

$$p = 2.49 \times 10^{-2}\,\text{bar} = 2.5 \times 10^{-2}\,\text{bar}\,(\text{approximately})$$

Therefore, at equilibrium,

$$[H_2] = [Br_2] = 2.49 \times 10^{-2}\ \text{bar}$$
$$[HBr] = 10 - 2 \times (2.49 \times 10^{-2})\,\text{bar}$$
$$= 9.95\,\text{bar} = 10\,\text{bar}\,(\text{approximately})$$

Question 7.28:

Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$$CH_4\ (g) + H_2O\ (g) \longleftrightarrow CO\ (g) + 3H_2\ (g)$$

(a) Write as expression for K_p for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by

(i) Increasing the pressure

(ii) Increasing the temperature

(iii) Using a catalyst?

- **Answer**

(a) For the given reaction,

$$K_p = \frac{p_{CO} \times p_{H_2}^3}{p_{CH_4} \times p_{H_2O}}$$

(b) (i) According to Le Chatelier's principle, the equilibrium will shift in the backward direction.

(ii) According to Le Chatelier's principle, as the reaction is endothermic, the equilibrium will shift in the forward direction.

(iii) The equilibrium of the reaction is not affected by the presence of a catalyst. A catalyst only increases the rate of a reaction. Thus, equilibrium will be attained quickly.

Question 7.29:

Describe the effect of:

a) Addition of H_2

b) Addition of CH_3OH

c) Removal of CO

d) Removal of CH_3OH

on the equilibrium of the reaction:

$$2H_2(g) + CO(g) \longleftrightarrow CH_3OH(g)$$

- **Answer**

(a) According to Le Chatelier's principle, on addition of H_2, the equilibrium of the given reaction will shift in the forward direction.

(b) On addition of CH_3OH, the equilibrium will shift in the backward direction.

(c) On removing CO, the equilibrium will shift in the backward direction.

(d) On removing CH_3OH, the equilibrium will shift in the forward direction.

Question 7.30:

At 473 K, equilibrium constant K_c for decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If decomposition is depicted as,

$PCl_5\,(g) \longleftrightarrow PCl_3\,(g) + Cl_2\,(g)$ $\Delta_r H° = 124.0\ kJmol^{-1}$

a) Write an expression for K_c for the reaction.

b) What is the value of K_c for the reverse reaction at the same temperature?

c) What would be the effect on K_c if (i) more PCl_5 is added (ii) pressure is increased? (iii) The temperature is increased?

- **Answer**

(a) $$K_c \frac{[PCl_{3(g)}][Cl_{2(g)}]}{[PCl_{5(g)}]}$$

(b) Value of K_c for the reverse reaction at the same temperature is:

$$K'_c = \frac{1}{K_c}$$
$$= \frac{1}{8.3 \times 10^{-3}} = 1.2048 \times 10^2$$
$$= 120 - 48$$

(c) (i) K_c would remain the same because in this case, the temperature remains the same.

(ii) K_c is constant at constant temperature. Thus, in this case, K_c would not change.

(iii) In an endothermic reaction, the value of K_c increases with an increase in temperature. Since the given reaction in an endothermic reaction, the value of K_c will increase if the temperature is increased.

Question 7.31:

Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction

involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction,

$$CO\ (g) + H_2O\ (g) \longleftrightarrow CO_2\ (g) + H_2\ (g)$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{CO} = p_{H_2O} =$ 4.0 bar, what will be the partial pressure of H_2 at equilibrium? Kp= 10.1 at 400°C

- **Answer**

Let the partial pressure of both carbon dioxide and hydrogen gas be *p*. The given reaction is:

	$CO_{(g)}$	+	$H_2O_{(g)}$	$\longleftrightarrow$	$CO_{2(g)}$	+	$H_{2(g)}$
Initial conc.	4.0 bar		4.0 bar		0		0
At equilibrium	$4.0 - p$		$4.0 - p$		p		p

It is given that $K_p = 10.1$.

Now,

$$\frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} = K_p$$

$$\Rightarrow \frac{p \times p}{(4.0 - p)(4.0 - p)} = 10.1$$

$$\Rightarrow \frac{p}{4.0 - p} = 3.178$$

$$\Rightarrow p = 12.712 - 3.178p$$

$$\Rightarrow 4.178p = 12.712$$

$$\Rightarrow p = 3.04$$

Hence, at equilibrium, the partial pressure of H_2 will be 3.04 bar.

Question 7.32:

Predict which of the following reaction will have appreciable concentration of reactants and products:

a) $Cl_2\ (g) \longleftrightarrow 2\ Cl\ (g)\ ; \quad K_c = 5 \times 10^{-39}$

b) $Cl_2\ (g) + 2\ NO\ (g) \longleftrightarrow 2\ NOCl\ (g)\ ; \quad K_c = 3.7 \times 10^8$

c) $Cl_2\ (g) + 2\ NO_2\ (g) \longleftrightarrow 2\ NO_2Cl\ (g)\ ; \quad K_c = 1.8$

- **Answer**

If the value of K_c lies between 10^{-3} and 10^3, a reaction has appreciable concentration of reactants and products. Thus, the reaction given in (c) will have appreciable concentration of reactants and products.

Question 7.33:

The value of K_c for the reaction

$3O_2\ (g) \longleftrightarrow 2O_3\ (g)$

is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?

- **Answer**

The given reaction is:

$$3O_{2(g)} \longleftrightarrow 2O_{3(g)}$$

$$\text{Then, } K_C = \frac{\left[O_{3(g)}\right]^2}{\left[O_{2(g)}\right]^3}$$

It is given that $K_C = 2.0 \times 10^{-50}$ and $\left[O_{2(g)}\right] = 1.6 \times 10^{-2}$.

Then, we have,

$$2.0 \times 10^{-50} = \frac{\left[O_{3(g)}\right]^2}{\left[1.6 \times 10^{-2}\right]^3}$$

$$\Rightarrow \left[O_{3(g)}\right]^2 = 2.0 \times 10^{-50} \times \left(1.6 \times 10^{-2}\right)^3$$

$$\Rightarrow \left[O_{3(g)}\right]^2 = 8.192 \times 10^{-56}$$

$$\Rightarrow \left[O_{3(g)}\right] = 2.86 \times 10^{-28}\ \text{M}$$

Hence, the concentration of O_3 is 2.86×10^{-28} M.

Question 7.34:

The reaction, $CO(g) + 3H_2(g) \longleftrightarrow CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration

of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

- **Answer**

Let the concentration of methane at equilibrium be *x*.

$$\begin{array}{lccccccc} & CO_{(g)} & + & 3H_{2(g)} & \longleftrightarrow & CH_{4(g)} & + & H_2O_{(g)} \\ \text{At equilibrium} & \frac{0.3}{1}=0.3\text{M} & & \frac{0.1}{1}=0.1\text{M} & & x & & \frac{0.02}{1}=0.02\text{M} \end{array}$$

It is given that $K_c = 3.90$.

Therefore,

$$\frac{\left[CH_{4(g)}\right]\left[H_2O_{(g)}\right]}{\left[CO_{(g)}\right]\left[H_{2(g)}\right]^3} = K_c$$

$$\Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} = 3.90$$

$$\Rightarrow x = \frac{3.90 \times 0.3 \times (0.1)^3}{0.02}$$

$$= \frac{0.00117}{0.02}$$

$$= 0.0585\,\text{M}$$

$$= 5.85 \times 10^{-2}\ \text{M}$$

Hence, the concentration of CH_4 at equilibrium is 5.85×10^{-2} M.

Question 7.35:

What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

$HNO_2, CN^-, HClO_4, F^-, OH^-, CO_3^{2-}, \text{and}\ S^-$

- **Answer**

A conjugate acid-base pair is a pair that differs only by one proton.

The conjugate acid-base for the given species is mentioned in the table below.

Species	**Conjugate acid-base**
HNO_2	NO_2^- (base)
CN^-	HCN (acid)

$HClO_4$	ClO_4^- (base)
F^-	HF (acid)
OH^-	H_2O (acid) /O^{2-} (base)
CO_3^{2-}	HCO_3^- (acid)
S^{2-}	HS^- (acid)

Question 7.36:

Which of the followings are Lewis acids? H_2O, BF_3, H^+, and NH_4^+

- **Answer**

Lewis acids are those acids which can accept a pair of electrons. For example, BF_3, H^+, and NH_4^+ are Lewis acids.

Question 7.37:

What will be the conjugate bases for the Brönsted acids: HF, H_2SO_4 and HCO_3?

- **Answer**

The table below lists the conjugate bases for the given Bronsted acids.

Bronsted acid	**Conjugate base**
HF	F^-
H_2SO_4	HSO_4^-
HCO_3^-	CO_3^{2-}

Question 7.38:

Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

- **Answer**

The table below lists the conjugate acids for the given Bronsted bases.

Bronsted base	**Conjugate acid**
NH_2^-	NH_3
NH_3	NH_4^+
$HCOO^-$	HCOOH

Question 7.39:

The species: H_2O, HCO_3^-, HSO_4^-, and NH_3 can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base.

- **Answer**

The table below lists the conjugate acids and conjugate bases for the given species.

Species	**Conjugate acid**	**Conjugate base**
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

Question 7.40:

Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH^- (b) F^- (c) H^+ (d) BCl_3.

- **Answer**

(a) OH^- is a Lewis base since it can donate its lone pair of electrons.

(b) F^- is a Lewis base since it can donate a pair of electrons.

(c) H^+ is a Lewis acid since it can accept a pair of electrons.

(d) BCl_3 is a Lewis acid since it can accept a pair of electrons.

Question 7.41:

The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. what is its pH?

- **Answer**

Given,

$$\left[H^+\right] = 3.8 \times 10^{-3}\ M$$

$\therefore$ pH value of soft drink

$$= -\log\left[H^+\right]$$

$$= -\log\left(3.8 \times 10^{-3}\right)$$
$$= -\log 3.8 - \log 10^{-3}$$
$$= -\log 3.8 + 3$$
$$= -0.58 + 3$$
$$= 2.42$$

Question 7.42:

The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Question 7.43:

The ionization constant of HF, HCOOH and HCN at 298K are 6.8 × 10^{-4}, 1.8 × 10^{-4} and 4.8 × 10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.

- **Answer**

It is known that,

$$K_b = \frac{K_w}{K_a}$$

Given,

K_a of HF = 6.8 × 10^{-4}

Hence, K_b of its conjugate base F^-

$$= \frac{K_w}{K_a}$$

$$= \frac{10^{-14}}{6.8 \times 10^{-4}}$$
$$= 1.5 \times 10^{-11}$$

Given,

K_a of HCOOH = 1.8 × 10^{-4}

Hence, K_b of its conjugate base $HCOO^-$

$$= \frac{K_w}{K_a}$$

$$= \frac{10^{-14}}{1.8 \times 10^{-4}}$$

$$= 5.6 \times 10^{-11}$$

Given,

K_a of HCN = 4.8×10^{-9}

Hence, K_b of its conjugate base CN^-

$$= \frac{K_w}{K_a}$$

$$= \frac{10^{-14}}{4.8 \times 10^{-9}}$$

$$= 2.08 \times 10^{-6}$$

Question 7.44:

The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate?

- **Answer**

Ionization of phenol:

$$\begin{array}{lcccc} & C_6H_5OH + H_2O & \longleftrightarrow & C_6H_5O^- & + H_3O^+ \\ \text{Initial conc.} & 0.05 & & 0 & 0 \\ \text{At equilibrium} & 0.05 - x & & x & x \end{array}$$

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

$$K_a = \frac{x \times x}{0.05 - x}$$

As the value of the ionization constant is very less, x will be very small. Thus, we can ignore x in the denominator.

$$\therefore x = \sqrt{1 \times 10^{-10} \times 0.05}$$

$$= \sqrt{5 \times 10^{-12}}$$

$$= 2.2 \times 10^{-6} \text{M} = [H_3O^+]$$

Since $[H_3O^+] = [C_6H_5O^-]$,

$[C_6H_5O^-] = 2.2 \times 10^{-6}$M.

Now, let α be the degree of ionization of phenol in the presence of 0.01 M C_6H_5ONa.

$$\begin{array}{lccc} & C_6H_5ONa \longrightarrow & C_6H_5O^- & + Na^+ \\ \text{Conc.} & & 0.01 & \end{array}$$

Also,

$$\begin{array}{lccccccc} & C_6H_5OH & + & H_2O & \longleftrightarrow & C_6H_5O^- & + & H_3O^+ \\ \text{Conc.} & 0.05-0.05\alpha & & & & 0.05\alpha & & 0.05\alpha \end{array}$$

$$[C_6H_5OH] = 0.05 - 0.05\alpha \; ; \; 0.05 \text{ M}$$

$$[C_6H_5O^-] = 0.01 + 0.05\alpha \; ; \; 0.01\text{M}$$

$$[H_3O^+] = 0.05\alpha$$

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

$$K_a = \frac{(0.01)(0.05\alpha)}{0.05}$$

$$1.0 \times 10^{-10} = .01\alpha$$

$$\alpha = 1 \times 10^{-8}$$

Question 7.45:

The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

- **Answer**

(i) To calculate the concentration of HS^- ion:

Case I (in the absence of HCl):

Let the concentration of HS^- be x M.

$$\begin{array}{llll} & H_2S \longleftrightarrow & H^+ + & HS^- \\ C_i & 0.1 & 0 & 0 \\ C_f & 0.1-x & x & x \end{array}$$

$$\text{Then,}\quad K_{a_1} = \frac{\left[H^+\right]\left[HS^-\right]}{\left[H_2S\right]}$$

$$9.1\times10^{-8} = \frac{(x)(x)}{0.1-x}$$

$$\left(9.1\times10^{-8}\right)(0.1-x) = x^2$$

Taking $0.1-x\,\text{M}\ ;\ 0.1\text{M}$, we have $\left(9.1\times10^{-8}\right)(0.1) = x^2$.

$$9.1\times10^{-9} = x^2$$

$$x = \sqrt{9.1\times10^{-9}}$$

$$= 9.54\times10^{-5}\,\text{M}$$

$$\Rightarrow \left[HS^-\right] = 9.54\times10^{-5}\,\text{M}$$

Case II (in the presence of HCl):

In the presence of 0.1 M of HCl, let $\left[HS^-\right]$ be *y* M.

$$\begin{array}{llll} \text{Then,} & H_2S \longleftrightarrow & HS^- + & H^+ \\ C_i & 0.1 & 0 & 0 \\ C_f & 0.1-y & y & y \end{array}$$

$$\begin{array}{lll} \text{Also,}\quad HCl \longleftrightarrow & H^+ + & Cl^- \\ & 0.1 & 0.1 \end{array}$$

$$\text{Now,}\quad K_{a_1} = \frac{\left[HS^-\right]\left[H^+\right]}{\left[H_2S\right]}$$

$$K_{a_1} = \frac{[y](0.1+y)}{(0.1-y)}$$

$$9.1\times10^{-8} = \frac{y\times0.1}{0.1} \qquad (\because 0.1 - y\ ;\ 0.1\text{M})$$

$$(\text{and}\ 0.1 + y\ ;\ 0.1\text{M})$$

$$9.1\times10^{-8} = y$$

$$\Rightarrow \left[HS^-\right] = 9.1\times10^{-8}$$

(ii) To calculate the concentration of $\left[S^{2-}\right]$:

Case I (in the absence of 0.1 M HCl):

$$HS^- \longleftrightarrow H^+ + S^{2-}$$

$\left[\mathrm{HS}^-\right] = 9.54\times10^{-5}\,\mathrm{M}$ (From first ionization, case I)

Let $\left[\mathrm{S}^{2-}\right]$ be X.

Also, $\left[\mathrm{H}^+\right] = 9.54\times10^{-5}\,\mathrm{M}$ (From first ionization, case I)

$$K_{a_2} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{S}^{2-}\right]}{\left[\mathrm{HS}^-\right]}$$

$$K_{a_2} = \frac{\left(9.54\times10^{-5}\right)(X)}{9.54\times10^{-5}}$$

$$1.2\times10^{-13} = X = \left[\mathrm{S}^{2-}\right]$$

Case II (in the presence of 0.1 M HCl):

Again, let the concentration of HS^- be X' M.

$\left[\mathrm{HS}^-\right] = 9.1\times10^{-8}\,\mathrm{M}$ (From first ionization, case II)

$\left[\mathrm{H}^+\right] = 0.1\,\mathrm{M}$ (From HCl, case II)

$\left[\mathrm{S}^{2-}\right] = X'$

$$\text{Then, } K_{a_2} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{S}^{2-}\right]}{\left[\mathrm{HS}^-\right]}$$

$$1.2\times10^{-13} = \frac{(0.1)(X')}{9.1\times10^{-8}}$$

$$10.92\times10^{-21} = 0.1X'$$

$$\frac{10.92\times10^{-21}}{0.1} = X'$$

$$X' = \frac{1.092\times10^{-20}}{0.1}$$

$$= 1.092\times10^{-19}\,\mathrm{M}$$

$$\Rightarrow K_{a_1} = 1.74\times10^{-5}$$

Question 7.46:

The ionization constant of acetic acid is 1.74 × 10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

- **Answer**

1) $CH_3COOH \longleftrightarrow CH_3COO^- + H^+ \quad K_a = 1.74 \times 10^{-5}$

2) $H_2O + H_2O \longleftrightarrow H_3O^+ + OH^- \quad K_w = 1.0 \times 10^{-14}$

Degree of dissociation,

$$\alpha = \sqrt{\frac{K_a}{c}}$$

c = 0.05 M

$K_a = 1.74 \times 10^{-5}$

$$\text{Then, } \alpha = \sqrt{\frac{1.74 \times 10^{-5}}{.05}}$$

$$\alpha = \sqrt{34.8 \times 10^{-5}}$$

$$\alpha = \sqrt{3.48} \times 10^{-4}$$

$$\alpha = 1.8610^{-2}$$

$$CH_3COOH \longleftrightarrow CH_3COO^- + H^+$$

Thus, concentration of CH_3COO^- = c.α

$$= .05 \times 1.86 \times 10^{-2}$$

$$= .093 \times 10^{-2}$$

$$= .00093\,\text{M}$$

$$\text{Since } \left[\text{oAc}^-\right] = \left[H^+\right],$$

$$\left[H^+\right] = .00093 = .093 \times 10^{-2}.$$

$$\text{pH} = -\log\left[H^+\right]$$

$$= -\log\left(.093 \times 10^{-2}\right)$$

$$\therefore \text{pH} = 3.03$$

Hence, the concentration of acetate ion in the solution is 0.00093 M and its Ph is 3.03.

Question 7.47:

It has been found that the pH of a 0.01M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK$_a$.

- **Answer**

Let the organic acid be HA.

$\Rightarrow HA \longleftrightarrow H^{+} + A^{-}$

Concentration of HA = 0.01 M

pH = 4.15

$$-\log\left[H^{+}\right] = 4.15$$
$$\left[H^{+}\right] = 7.08 \times 10^{-5}$$

Now, $K_a = \dfrac{\left[H^{+}\right]\left[A^{-}\right]}{[HA]}$

$$\left[H^{+}\right] = \left[A^{-}\right] = 7.08 \times 10^{-5}$$
$$[HA] = 0.01$$

Then,

$$K_a = \frac{\left(7.08 \times 10^{-5}\right)\left(7.08 \times 10^{-5}\right)}{0.01}$$
$$K_a = 5.01 \times 10^{-7}$$
$$pK_a = -\log K_a$$
$$= -\log\left(5.01 \times 10^{-7}\right)$$
$$pK_a = 6.3001$$

Question 7.48:

Assuming complete dissociation, calculate the pH of the following solutions:

(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

- **Answer**

(i) 0.003MHCl:

$$H_2O + HCl \longleftrightarrow H_3O^{+} + Cl^{-}$$

Since HCl is completely ionized,

$$\left[H_3O^{+}\right] = [HCl].$$
$$\Rightarrow \left[H_3O^{+}\right] = 0.003$$

Now,

$$pH = -\log\left[H_3O^{+}\right] = -\log(.003)$$
$$= 2.52$$

Hence, the pH of the solution is 2.52**.**

(ii) 0.005MNaOH:

$$NaOH_{(aq)} \longleftrightarrow Na^+_{(aq)} + HO^-_{(aq)}$$

$$\left[HO^-\right] = \left[NaOH\right]$$
$$\Rightarrow \left[HO^-\right] = .005$$
$$pOH = -\log\left[HO^-\right] = -\log(.005)$$
$$pOH = 2.30$$
$$\therefore pH = 14 - 2.30$$
$$= 11.70$$

Hence, the pH of the solution is 11.70.

(iii) 0.002 HBr:

$$HBr + H_2O \longleftrightarrow H_3O^+ + Br^-$$

$$\left[H_3O^+\right] = \left[HBr\right]$$
$$\Rightarrow \left[H_3O^+\right] = .002$$
$$\therefore pH = -\log\left[H_3O^+\right]$$
$$= -\log(0.002)$$
$$= 2.69$$

Hence, the pH of the solution is 2.69.

(iv) 0.002 M KOH:

$$KOH_{(aq)} \longleftrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

$$\left[OH^-\right] = \left[KOH\right]$$
$$\Rightarrow \left[OH^-\right] = .002$$
$$\text{Now, } pOH = -\log\left[OH^-\right]$$
$$= 2.69$$
$$\therefore pH = 14 - 2.69$$
$$= 11.31$$

Hence, the pH of the solution is 11.31.

Question 7.49:

Calculate the pH of the following solutions:

a) 2 g of TlOH dissolved in water to give 2 litre of solution.

b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.

c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.

d) 1mL of 13.6 M HCl is diluted with water to give 1 litre of solution.

- **Answer**

(a) For 2g of TlOH dissolved in water to give 2 L of solution:

$$\left[\mathrm{TlOH}_{(aq)}\right] = \frac{2}{2}\,\mathrm{g/L}$$
$$= \frac{2}{2} \times \frac{1}{221}\,\mathrm{M}$$
$$= \frac{1}{221}\,\mathrm{M}$$

$$\mathrm{TlOH}_{(aq)} \longrightarrow \mathrm{Tl}^{+}_{(aq)} + \mathrm{OH}^{-}_{(aq)}$$

$$\left[\mathrm{OH}^{-}_{(aq)}\right] = \left[\mathrm{TlOH}_{(aq)}\right] = \frac{1}{221}\,\mathrm{M}$$

$$K_w = \left[\mathrm{H}^+\right]\left[\mathrm{OH}^-\right]$$

$$10^{-14} = \left[\mathrm{H}^+\right]\left(\frac{1}{221}\right)$$

$$221 \times 10^{-14} = \left[\mathrm{H}^+\right]$$

$$\Rightarrow \mathrm{pH} = -\log\left[\mathrm{H}^+\right] = -\log\left(221 \times 10^{-14}\right)$$
$$= -\log\left(2.21 \times 10^{-12}\right)$$
$$= 11.65$$

(b) For 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution:

$$\mathrm{Ca(OH)_2} \longrightarrow \mathrm{Ca}^{2+} + 2\mathrm{OH}^-$$

$$\left[\mathrm{Ca(OH)_2}\right] = 0.3 \times \frac{1000}{500} = 0.6\mathrm{M}$$

$$\left[\mathrm{OH}^-{}_{aq}\right] = 2 \times \left[\mathrm{Ca(OH)}_{2aq}\right] = 2 \times 0.6$$
$$= 1.2\mathrm{M}$$

$$\left[\mathrm{H}^+\right] = \frac{K_w}{\left[\mathrm{OH}^-{}_{aq}\right]}$$
$$= \frac{10-14}{1.2}\,\mathrm{M}$$
$$= 0.833 \times 10^{-14}$$

$$
\begin{aligned}
\text{pH} &= -\log\left(0.833\times10^{-14}\right)\\
&= -\log\left(8.33\times10^{-13}\right)\\
&= \left(-0.902+13\right)\\
&= 12.098
\end{aligned}
$$

(c) For 0.3 g of NaOH dissolved in water to give 200 mL of solution:

$$\text{NaOH} \longrightarrow \text{Na}^{+}_{(aq)} + \text{OH}^{-}_{(aq)}$$

$$[\text{NaOH}] = 0.3\times\frac{1000}{200} = 1.5\text{M}$$

$$\left[\text{OH}^{-}{}_{aq}\right] = 1.5\text{M}$$

$$
\begin{aligned}
\text{Then,}\left[\text{H}^{+}\right] &= \frac{10^{-14}}{1.5}\\
&= 6.66\times10^{-13}
\end{aligned}
$$

$$
\begin{aligned}
\text{pH} &= -\log\left(6.66\times10^{-13}\right)\\
&= 12.18
\end{aligned}
$$

(d) For 1mL of 13.6 M HCl diluted with water to give 1 L of solution:

13.6 × 1 mL = M_2 × 1000 mL

(Before dilution) (After dilution)

$13.6 \times 10^{-3} = M_2 \times 1\text{L}$

$M_2 = 1.36 \times 10^{-2}$

$[H^+] = 1.36 \times 10^{-2}$

$\text{pH} = -\log(1.36 \times 10^{-2})$

$= (-0.1335 + 2)$

= 1.866 □ 1.8

Question 7.50:

The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK$_a$ of bromoacetic acid.

- **Answer**

Degree of ionization, □ = 0.132

Concentration, *c* = 0.1 M

Thus, the concentration of H_3O^+ = *c*.□

= 0.1 × 0.132

= 0.0132

$$\begin{aligned} \mathrm{pH} &= -\log\left[\mathrm{H}^{+}\right] \\ &= -\log(0.0132) \\ &= 1.879 : 1.88 \end{aligned}$$

Now,

$$\begin{aligned} K_a &= C\alpha^2 \\ &= 0.1\times(0.132)^2 \\ K_a &= .0017 \\ pK_a &= 2.75 \end{aligned}$$

Question 7.51:

The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pK_b.

- **Answer**

c = 0.005

pH = 9.95

pOH = 4.05

pH = – log (4.105)

$$\begin{aligned} 4.05 &= -\log\left[\mathrm{OH}^{-}\right] \\ \left[\mathrm{OH}^{-}\right] &= 8.91\times10^{-5} \\ c\alpha &= 8.91\times10^{-5} \\ \alpha &= \frac{8.91\times10^{-5}}{5\times10^{-3}} = 1.782\times10^{-2} \end{aligned}$$

$$\begin{aligned} \text{Thus, } K_b &= c\alpha^2 \\ &= 0.005\times(1.782)^2\times10^{-4} \\ &= 0.005\times3.1755\times10^{-4} \\ &= 0.0158\times10^{-4} \\ K_b &= 1.58\times10^{-6} \\ Pk_b &= -\log K_b \\ &= -\log\left(1.58\times10^{-6}\right) \\ &= 5.80 \end{aligned}$$

Question 7.52:

What is the pH of 0.001 M aniline solution? The ionization constant of aniline can be taken from Table 7.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

- **Answer**

$K_b = 4.27 \times 10^{-10}$

$c = 0.001\text{M}$

pH =?

α=?

$$
\begin{aligned}
&k_b = c\alpha^2 \\
&4.27\times10^{-10} = 0.001\times\alpha^2 \\
&4270\times10^{-10} = \alpha^2 \\
&65.34\times10^{-5} = \alpha = 6.53\times10^{-4} \\
&\text{Then, } [\text{anion}] = c\alpha = .001\times65.34\times10^{-5} \\
&\qquad\qquad\qquad = .065\times10^{-5} \\
&\text{pOH} = -\log\left(.065\times10^{-5}\right) \\
&\qquad = 6.187 \\
&\text{pH} = 7.813 \\
&\text{Now,} \\
&K_a\times K_b = K_w \\
&\therefore 4.27\times10^{-10}\times K_a = K_w \\
&K_a = \frac{10^{-14}}{4.27\times10^{-10}} \\
&\quad = 2.34\times10^{-5}
\end{aligned}
$$

Thus, the ionization constant of the conjugate acid of aniline is 2.34×10^{-5}.

Question 7.53:

Calculate the degree of ionization of 0.05M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01 M (b) 0.1 M in HCl?

- **Answer**

$$c = 0.05 \text{ M}$$
$$pK_a = 4.74$$
$$pK_a = -\log(K_a)$$
$$K_a = 1.82 \times 10^{-5}$$
$$K_a = c\alpha^2 \qquad \alpha = \sqrt{\frac{K_a}{c}}$$
$$\alpha = \sqrt{\frac{1.82 \times 10^{-5}}{5 \times 10^{-2}}} = 1.908 \times 10^{-2}$$

When HCl is added to the solution, the concentration of H^+ ions will increase. Therefore, the equilibrium will shift in the backward direction i.e., dissociation of acetic acid will decrease.

Case I: When 0.01 M HCl is taken.

Let *x* be the amount of acetic acid dissociated after the addition of HCl.

	$CH_3COOH \longleftrightarrow$	H^+	$+ \; CH_3COO^-$
Initial conc.	0.05 M	0	0
After dissociation	$0.05 - x$	$0.01 + x$	x

As the dissociation of a very small amount of acetic acid will take place, the values i.e., 0.05 – *x* and 0.01 + *x* can be taken as 0.05 and 0.01 respectively.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$
$$\therefore K_a = \frac{(0.01)x}{0.05}$$
$$x = \frac{1.82 \times 10^{-5} \times 0.05}{0.01}$$
$$x = 1.82 \times 10^{-3} \times 0.05 \text{ M}$$

Now,

$$\alpha = \frac{\text{Amount of acid dissociated}}{\text{Amount of acid taken}}$$
$$= \frac{1.82 \times 10^{-3} \times 0.05}{0.05}$$
$$= 1.82 \times 10^{-3}$$

Case II: When 0.1 M HCl is taken.

Let the amount of acetic acid dissociated in this case be *X*. As we have done in the first case, the concentrations of various species involved in the reaction are:

$$[\mathrm{CH_3COOH}] = 0.05 - X \; ; \; 0.05\,\mathrm{M}$$

$$[\mathrm{CH_3COO^-}] = X$$

$$[\mathrm{H^+}] = 0.1 + X \; ; \; 0.1\mathrm{M}$$

$$K_a = \frac{[\mathrm{CH_3COO^-}][\mathrm{H^+}]}{[\mathrm{CH_3COOH}]}$$

$$\therefore K_a = \frac{(0.1)X}{0.05}$$

$$x = \frac{1.82\times10^{-5}\times0.05}{0.1}$$

$$x = 1.82\times10^{-4}\times0.05\,\mathrm{M}$$

Now,

$$\alpha = \frac{\text{Amount of acid dissociated}}{\text{Amount of acid taken}}$$

$$= \frac{1.82\times10^{-4}\times0.05}{0.05}$$

$$= 1.82\times10^{-4}$$

Question 7.54:

The ionization constant of dimethylamine is 5.4 × 10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH?

- **Answer**

$$K_b = 5.4\times10^{-4}$$

$$c = 0.02\ \mathrm{M}$$

$$\text{Then, } \alpha = \sqrt{\frac{K_b}{c}}$$

$$= \sqrt{\frac{5.4\times10^{-4}}{0.02}}$$

$$= 0.1643$$

Now, if 0.1 M of NaOH is added to the solution, then NaOH (being a strong base) undergoes complete ionization.

$$\underset{}{\mathrm{NaOH}_{(aq)}} \longleftrightarrow \underset{0.1\ \mathrm{M}}{\mathrm{Na^+}_{(aq)}} + \underset{0.1\ \mathrm{M}}{\mathrm{OH^-}_{(aq)}}$$

And,

$$\begin{array}{lcccccc}(CH_3)_2NH & + & H_2O & \longleftrightarrow & (CH_3)_2NH_2^+ & + & \bar{O}H \\ (0.02-x) & & & & x & & x \\ ;\ 0.02\,M & & & & & & ;\ 0.1\,M\end{array}$$

Then, $\left[(CH_3)_2NH_2^+\right] = x$

$\left[OH^-\right] = x + 0.1\ ;\ 0.1$

$$\Rightarrow K_b = \frac{\left[(CH_3)_2NH_2^+\right]\left[OH^-\right]}{\left[(CH_3)_2NH\right]}$$

$$5.4\times10^{-4} = \frac{x\times0.1}{0.02}$$

$x = 0.0054$

It means that in the presence of 0.1 M NaOH, 0.54% of dimethylamine will get dissociated.

Question 7.55:

Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

(a) Human muscle-fluid, 6.83

(b) Human stomach fluid, 1.2

(c) Human blood, 7.38

(d) Human saliva, 6.4.

- **Answer**

(a) Human muscle fluid 6.83:

pH = 6.83

pH = – log [H^+]

6.83 = – log [H^+]

[H^+] =1.48 × 10^{-7} M

(b) Human stomach fluid, 1.2:

pH =1.2

1.2 = – log [H^+]

[H^+] = 0.063

(c) Human blood, 7.38:

pH = 7.38 = – log [H^+]

$[H^+] = 4.17 \times 10^{-8}$ M

(d) Human saliva, 6.4:

pH = 6.4

$6.4 = -\log [H^+]$

$[H^+] = 3.98 \times 10^{-7}$

Question 7.56:

The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

- **Answer**

The hydrogen ion concentration in the given substances can be calculated by using the given relation:

$pH = -\log [H^+]$

(i) pH of milk = 6.8

Since, $pH = -\log [H^+]$

$6.8 = -\log [H^+]$

$\log [H^+] = -6.8$

$[H^+] = \text{anitlog}(-6.8)$

$= 1.5 \times 10^{-7}$ M

(ii) pH of black coffee = 5.0

Since, $pH = -\log [H^+]$

$5.0 = -\log [H^+]$

$\log [H^+] = -5.0$

$[H^+] = \text{anitlog}(-5.0)$

$= 10^{-5}$ M

(iii) pH of tomato juice = 4.2

Since, $pH = -\log [H^+]$

$4.2 = -\log [H^+]$

$\log [H^+] = -4.2$

$[H^+]$ = anitlog(–4.2)

= 6.31×10^{-5} M

(iv) pH of lemon juice = 2.2

Since, pH = –log $[H^+]$

2.2 = –log $[H^+]$

log $[H^+]$ = –2.2

$[H^+]$ = anitlog(–2.2)

= 6.31×10^{-3} M

(v) pH of egg white = 7.8

Since, pH = –log $[H^+]$

7.8 = –log $[H^+]$

log $[H^+]$ = –7.8

$[H^+]$ = anitlog(–7.8)

= 1.58×10^{-8} M

Question 7.57:

If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

- **Answer**

$$\left[\mathrm{KOH}_{aq}\right]=\frac{0.561}{\frac{1}{5}}\mathrm{g}/L$$

$$=2.805\,\mathrm{g}/L$$

$$=2.805\times\frac{1}{56.11}\ \mathrm{M}$$

$$=.05\ \mathrm{M}$$

$$\mathrm{KOH}_{(aq)}\rightarrow \mathrm{K}^{+}{}_{(aq)}+\mathrm{OH}^{-}{}_{(aq)}$$

$$\left[\mathrm{OH}^{-}\right]=.05\ \mathrm{M}=\left[\mathrm{K}^{+}\right]$$

$$\left[\mathrm{H}^{+}\right]\left[\mathrm{H}^{-}\right]=K_{\mathrm{w}}$$

$$\left[\mathrm{H}^{+}\right]\frac{K_{\mathrm{w}}}{\left[\mathrm{OH}^{-}\right]}$$

$$=\frac{10^{-14}}{0.05}=2\times10^{-13}\ \mathrm{M}$$

$$\therefore\ \mathrm{pH}=12.70$$

Question 7.58:

The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

- **Answer**

Solubility of $Sr(OH)_2$ = 19.23 g/L

Then, concentration of $Sr(OH)_2$

$$=\frac{19.23}{121.63}\ \mathrm{M}$$

$$=0.1581\ \mathrm{M}$$

$$\mathrm{Sr}\left(\mathrm{OH}\right)_{2(aq)}\longrightarrow \mathrm{Sr}^{2+}{}_{(aq)}+2\left(\mathrm{OH}^{-}\right)_{(aq)}$$

$$\therefore\left[\mathrm{Sr}^{2+}\right]=0.1581\ \mathrm{M}$$

$$\left[\mathrm{OH}^{-}\right]=2\times0.1581\ \mathrm{M}=0.3126\ \mathrm{M}$$

Now,

$$K_w=\left[\mathrm{OH}^{-}\right]\left[\mathrm{H}^{+}\right]$$

$$\frac{10^{-14}}{0.3126}=\left[\mathrm{H}^{+}\right]$$

$$\Rightarrow\left[\mathrm{H}^{+}\right]=3.2\times10^{-14}$$

$$\therefore \mathrm{pH}=13.495\ ;\ 13.50$$

Question 7.59:

The ionization constant of propanoic acid is 1.32 × 10^{-5}. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also?

- **Answer**

Let the degree of ionization of propanoic acid be □.

Then, representing propionic acid as HA, we have:

$$\begin{array}{lllll} \mathrm{HA} & + \quad \mathrm{H_2O} & \longleftrightarrow & \mathrm{H_3O^+} & + \quad \mathrm{A^-} \\ (.05-0.0\alpha)\approx .05 & & & .05\alpha & \quad .05\alpha \end{array}$$

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{A^-}\right]}{[\mathrm{HA}]}$$

$$= \frac{(.05\alpha)(.05\alpha)}{0.05} = .05\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{.05}} = 1.63\times10^{-2}$$

$$\text{Then,}\left[\ \mathrm{H_3O^+}\right] = .05\alpha = .05\times1.63\times10^{-2} = K_b.15\times10^{-4}\ \mathrm{M}$$

$$\therefore\ \mathrm{pH} = 3.09$$

In the presence of 0.1M of HCl, let □′ be the degree of ionization.

$$\text{Then,}\left[\ \mathrm{H_3O^+}\right] = 0.01$$

$$\left[\mathrm{A^-}\right] = 005\alpha'$$

$$[\mathrm{HA}] = .05$$

$$K_a = \frac{0.01\times.05\alpha'}{.05}$$

$$1.32\times10^{-5} = .01\times\alpha'$$

$$\alpha' = 1.32\times10^{-3}$$

Question 7.60:

The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

- **Answer**

c = 0.1 M

pH = 2.34

$-\log[H^+] = pH$

$-\log[H^+] = 2.34$

$[H^+] = 4.5\times10^{-3}$

Also,

$[H^+] = c\alpha$

$4.5\times10^{-3} = 0.1\times\alpha$

$$\frac{4.5\times10^{-3}}{0.1} = \alpha$$

$\alpha = 45\times10^{-3} = .045$

Then,

$$\begin{aligned} K_a &= c\alpha^2 \\ &= 0.1\times\left(45\times10^{-3}\right)^2 \\ &= 202.5\times10^{-6} \\ &= 2.02\times10^{-4} \end{aligned}$$

Question 7.61:

The ionization constant of nitrous acid is 4.5 × 10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

- **Answer**

$NaNO_2$ is the salt of a strong base (NaOH) and a weak acid (HNO_2).

$$NO_2^- + H_2O \longleftrightarrow HNO_2 + OH^-$$

$$K_h = \frac{[HNO_2][OH^-]}{[NO_2^-]}$$

$$\Rightarrow \frac{K_w}{K_a} = \frac{10^{-14}}{4.5\times10^{-4}} = .22\times10^{-10}$$

Now, If *x* moles of the salt undergo hydrolysis, then the concentration of various species present in the solution will be:

$$\left[\mathrm{NO_2^-}\right] = .04 - x\ ;\ 0.04$$

$$\left[\mathrm{HNO_2}\right] = x$$

$$\left[\mathrm{OH^-}\right] = x$$

$$K_h = \frac{x^2}{0.04} = 0.22 \times 10^{-10}$$

$$x^2 = .0088 \times 10^{-10}$$

$$x = .093 \times 10^{-5}$$

$$\therefore \left[\mathrm{OH^-}\right] = 0.093 \times 10^{-5}\ \mathrm{M}$$

$$\left[\mathrm{H_3O^+}\right] = \frac{10^{-14}}{.093 \times 10^{-5}} = 10.75 \times 10^{-9}\ \mathrm{M}$$

$$\Rightarrow\ \mathrm{pH} = -\log\left(10.75 \times 10^{-9}\right)$$

$$= 7.96$$

Therefore, degree of hydrolysis

$$= \frac{x}{0.04} = \frac{.093 \times 10^{-5}}{.04} = 2.325 \times 10^{-5}$$

Question 7.62:

A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine

- **Answer**

pH = 3.44

We know that,

pH = – log [H^+]

$$\therefore \left[\mathrm{H^+}\right] = 3.63 \times 10^{-4}$$

$$\text{Then, } K_h = \frac{\left(3.63 \times 10^{-4}\right)^2}{0.02} \qquad (\because \text{concentration} = 0.02\ \mathrm{M})$$

$$\Rightarrow K_h = 6.6 \times 10^{-6}$$

$$\text{Now, } K_h = \frac{K_w}{K_a}$$

$$\Rightarrow K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{6.6 \times 10^{-6}}$$

$$= 1.51 \times 10^{-9}$$

Question 7.63:

Predict if the solutions of the following salts are neutral, acidic or basic:

$NaCl$, KBr, $NaCN$, NH_4NO_3, $NaNO_2$ and KF

- **Answer**

(i) NaCl:

$$NaCl + H_2O \longleftrightarrow \underset{\text{Strong base}}{NaOH} + \underset{\text{Strong acid}}{HCl}$$

Therefore, it is a neutral solution.

(ii) KBr:

$$KBr + H_2O \longleftrightarrow \underset{\text{Strong base}}{KOH} + \underset{\text{Strong acid}}{HBr}$$

Therefore, it is a neutral solution.

(iii) NaCN:

$$NaCN + H_2O \longleftrightarrow \underset{\text{Weak acid}}{HCN} + \underset{\text{Strong base}}{NaOH}$$

Therefore, it is a basic solution.

(iv) NH_4NO_3

$$NH_4NO_3 + H_2O \longleftrightarrow \underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HNO_3}$$

Therefore, it is an acidic solution.

(v) $NaNO_2$

$$NaNO_2 + H_2O \longleftrightarrow \underset{\text{Strong base}}{NaOH} + \underset{\text{Weak acid}}{HNO_2}$$

Therefore, it is a basic solution.

(vi) KF

$$KF + H_2O \longleftrightarrow \underset{\text{Strong base}}{KOH} + \underset{\text{Weak acid}}{HF}$$

Therefore, it is a basic solution.

Question 7.64:

The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1M acid and its 0.1M sodium salt solution?

- **Answer**

It is given that K_a for $ClCH_2COOH$ is 1.35×10^{-3}.

$$\Rightarrow K_a = c\alpha^2$$

$$\therefore \alpha = \sqrt{\frac{K_a}{c}}$$

$$= \sqrt{\frac{1.35\times10^{-3}}{0.1}} \qquad (\because \text{ concentration of acid } = 0.1\text{m})$$

$$\alpha = \sqrt{1.35\times10^{-2}}$$

$$= 0.116$$

$$\therefore \left[H^+\right] = c\alpha = 0.1\times0.116$$

$$= .0116$$

$$\Rightarrow pH = -\log\left[H^+\right] = 1.94$$

$ClCH_2COONa$ is the salt of a weak acid i.e., $ClCH_2COOH$ and a strong base i.e., NaOH.

$$ClCH_2COO^- + H_2O \longleftrightarrow ClCH_2COOH + OH^-$$

$$K_h = \frac{[ClCH_2COOH][OH^-]}{[ClCH_2COO^-]}$$

$$K_h = \frac{K_w}{K_a}$$

$$K_h = \frac{10^{-14}}{1.35 \times 10^{-3}}$$

$$= 0.740 \times 10^{-11}$$

$$\text{Also, } K_h = \frac{x^2}{0.1} \qquad (\text{where } x \text{ is the concentration of } OH^- \text{and } ClCH_2COOH)$$

$$0.740 \times 10^{-11} = \frac{x^2}{0.1}$$

$$0.074 \times 10^{-11} = x^2$$

$$\Rightarrow x^2 = 0.74 \times 10^{-12}$$

$$x = 0.86 \times 10^{-6}$$

$$[OH^-] = 0.86 \times 10^{-6}$$

$$\therefore [H^+] = \frac{K_w}{0.86 \times 10^{-6}}$$

$$= \frac{10^{-14}}{0.86 \times 10^{-6}}$$

$$[H^+] = 1.162 \times 10^{-8}$$

$$pH = -\log[H^+]$$

$$= 7.94$$

Question 7.65:

Ionic product of water at 310 K is 2.7 × 10^{-14}. What is the pH of neutral water at this temperature?

- **Answer**

Ionic product,

$K_w = [H^+][OH^-]$

$\text{Let}[H^+] = x.$

$\text{Since}[H^+] = [OH^-], K_w = x^2.$

$\Rightarrow K_w \text{ at } 310\text{K is } 2.7 \times 10^{-14}.$

$\therefore 2.7 \times 10^{-14} = x^2$

$\Rightarrow x = 1.64 \times 10^{-7}$

$\Rightarrow [H^+] = 1.64 \times 10^{-7}$

$\Rightarrow \text{pH} = -\log[H^+]$

$= -\log[1.64 \times 10^{-7}]$

$= 6.78$

Hence, the pH of neutral water is 6.78.

Question 7.66:

Calculate the pH of the resultant mixtures:

a) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1M HCl

b) 10 mL of 0.01M H_2SO_4 + 10 mL of 0.01M $Ca(OH)_2$

c) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH

- **Answer**

(a) $\text{Moles of } H_3O^+ = \frac{25 \times 0.1}{1000} = .0025\,\text{mol}$

$\text{Moles of } OH^- = \frac{10 \times 0.2 \times 2}{1000} = .0040\,\text{mol}$

Thus, excess of OH^- = .0015 mol

$[OH^-] = \frac{.0015}{35 \times 10^{-3}}\,\text{mol/L} = .0428$

$\text{pOH} = -\log[OH]$

$= 1.36$

$\text{pH} = 14 - 1.36$

$= 12.63 \qquad (\text{not matched})$

(b) $\text{Moles of } H_3O^+ = \frac{2 \times 10 \times 0.01}{1000} = .0002\,\text{mol}$

$\text{Moles of } OH^- = \frac{2 \times 10 \times .01}{1000} = .0002\,\text{mol}$

Since there is neither an excess of H_3O^+ or OH^-, the solution is neutral. Hence, pH = 7.

(c) $\text{Moles of } H_3O^+ = \frac{2\times 10\times 0.1}{1000} = .002\text{ mol}$

$\text{Moles of } OH^- = \frac{10\times 0.1}{1000} = 0.001\text{ mol}$

Excess of H_3O^+ = .001 mol

$$\text{Thus, } \left[H_3O^+\right] = \frac{.001}{20\times 10^{-3}} = \frac{10^{-3}}{20\times 10^{-3}} = .05$$

$\therefore\ pH = -\log(0.05)$

= 1.30

Question 7.67:

Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 7.9 (page 221). Determine also the molarities of individual ions.

- Answer

(1) Silver chromate:

$Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$

Then,

$K_{sp} = \left[Ag^+\right]^2\left[CrO_4^{2-}\right]$

Let the solubility of Ag_2CrO_4 be s.

$\Rightarrow \left[Ag^+\right]2s \text{ and} \left[CrO_4^{2-}\right] = s$

Then,

$K_{sp} = (2s)^2 .s = 4s^3$

$\Rightarrow 1.1\times 10^{-12} = 4s^3$

$.275\times 10^{-12} = s^3$

$s = 0.65\times 10^{-4}\ \text{M}$

Molarity of Ag^+ = 2s = 2 × 0.65 × 10^{-4} = 1.30 × 10^{-4} M

Molarity of CrO_4^{2-} = s = 0.65 × 10^{-4} M

(2) Barium chromate:

$$BaCrO_4 \longrightarrow Ba^{2+} + CrO_4^{2-}$$

$$\text{Then, } K_{sp} = \left[Ba^{2+}\right]\left[CrO_4^{2-}\right]$$

Let s be the solubility of $BaCrO_4$.

Thus, $\left[Ba^{2+}\right]$ = s and $\left[CrO_4^{2-}\right]$ = s

$$\Rightarrow K_{SP} = s^2$$

$$\Rightarrow 1.2 \times 10^{-10} = s^2$$

$$\Rightarrow s = 1.09 \times 10^{-5} \text{ M}$$

Molarity of Ba^{2+} = Molarity of $CrO_4^{2-} = s = 1.09 \times 10^{-5}$ M

(3) Ferric hydroxide:

$$Fe(OH)_3 \longrightarrow Fe^{2+} + 3OH^-$$

$$K_{sp} = \left[Fe^{2+}\right]\left[OH^-\right]^3$$

Let s be the solubility of $Fe(OH)_3$.

$$\text{Thus,}\left[Fe^{3+}\right] = s \text{ and } \left[OH^-\right] = 3s$$

$$\Rightarrow K_{sp} = s.(3s)^3$$

$$= s.27s^3$$

$$K_{sp} = 27s^4$$

$$1.0 \times 10^{-38} = 27s^4$$

$$.037 \times 10^{-38} = s^4$$

$$.00037 \times 10^{-36} = s^4 \qquad \Rightarrow 1.39 \times 10^{-10} \text{ M} = S$$

Molarity of $Fe^{3+} = s = 1.39 \times 10^{-10}$ M

Molarity of $OH^- = 3s = 4.17 \times 10^{-10}$ M

(4) Lead chloride:

$$PbCl_2 \longrightarrow Pb^{2+} + 2Cl^-$$

$$K_{SP} = \left[Pb^{2+}\right]\left[Cl^-\right]^2$$

Let K_{SP} be the solubility of $PbCl_2$.

$\left[PB^{2+}\right] = s \text{ and } \left[Cl^-\right] = 2s$

$\text{Thus, } K_{sp} = s.(2s)^2$

$= 4s^3$

$\Rightarrow 1.6 \times 10^{-5} = 4s^3$

$\Rightarrow 0.4 \times 10^{-5} = s^3$

$4 \times 10^{-6} = s^3 \Rightarrow 1.58 \times 10^{-2} \text{M} = \text{S.1}$

Molarity of $PB^{2+} = s = 1.58 \times 10^{-2} \text{M}$

Molarity of chloride $= 2s = 3.16 \times 10^{-2} \text{M}$

(5) Mercurous iodide:

$Hg_2I_2 \longrightarrow Hg^{2+} + 2I^-$

$K_{sp} = \left[Hg_2^{2+}\right]^2 \left[I^-\right]^2$

Let s be the solubility of Hg_2I_2.

$\Rightarrow \left[Hg_2^{2+}\right] = s \text{ and} \left[I^-\right] = 2s$

$\text{Thus, } K_{sp} = s(2s)^2 \Rightarrow K_{sp} = 4s^3$

$4.5 \times 10^{-29} = 4s^3$

$1.125 \times 10^{-29} = s^3$

$\Rightarrow s = 2.24 \times 10^{-10} \text{ M}$

Molarity of $Hg_2^{2+} = s = 2.24 \times 10^{-10} \text{ M}$

Molarity of $I^- = 2s = 4.48 \times 10^{-10} \text{ M}$

Question 7.68:

The solubility product constant of Ag_2CrO_4 and AgBr are 1.1 × 10^{-12} and 5.0 × 10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

- **Answer**

Let *s* be the solubility of Ag_2CrO_4.

$\text{Then, } Ag_2CrO_4 \longleftrightarrow Ag^{2+} + 2CrO_4^-$

$K_{sp} = (2s)^2.s = 4s^3$

$1.1 \times 10^{-12} = 4s^3$

$s = 6.5 \times 10^{-5} \text{ M}$

Let *s*´ be the solubility of AgBr.

$$AgBr_{(s)} \longleftrightarrow Ag^+ + Br^-$$

$$K_{sp} = s'^2 = 5.0 \times 10^{-13}$$

$$\therefore s' = 7.07 \times 10^{-7}\ M$$

Therefore, the ratio of the molarities of their saturated solution is

$$\frac{s}{s'} = \frac{6.5 \times 10^{-5} M}{7.07 \times 10^{-7} M} = 91.9.$$

Question 7.69:

Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$).

- **Answer**

When equal volumes of sodium iodate and cupric chlorate solutions are mixed together, then the molar concentrations of both solutions are reduced to half i.e., 0.001 M.

Then,

$$\begin{array}{ccccc} Na10_3 & \rightarrow & Na^+ & + & 10_3^- \\ 0.001M & & & & 0.001M \end{array}$$

$$\begin{array}{ccccc} Cu(ClO_3)_2 & \rightarrow & Cu^{2+} & + & 2ClO_3^- \\ 0.001M & & & & 0.001M \end{array}$$

Now, the solubility equilibrium for copper iodate can be written as:

$$Cu(10_3)_2 \quad \rightarrow \quad Cu^{2+}_{(aq)} \quad + \quad 210^-_{3(aq)}$$

Ionic product of copper iodate:

$$= [Cu^{2+}][10_3^-]^2$$

$$= (0.001)(0.001)^2$$

$$= 1 \times 10^{-9}$$

Since the ionic product (1×10^{-9}) is less than K_{sp} (7.4×10^{-8}), precipitation will not occur.

Question 7.70:

The ionization constant of benzoic acid is 6.46 × 10^{-5} and K_{sp} for silver benzoate is 2.5 × 10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

- **Answer**

Since pH = 3.19,

$$\left[H_3O^+\right] = 6.46 \times 10^{-4}\ \text{M}$$

$$C_6H_5COOH + H_2O \longleftrightarrow C_6H_5COO^- + H_3O$$

$$K_a \frac{\left[C_6H_5COO^-\right]\left[H_3O^+\right]}{\left[C_6H_5COOH\right]}$$

$$\frac{\left[C_6H_5COOH\right]}{\left[C_6H_5COO^-\right]} = \frac{\left[H_3O^+\right]}{K_a} = \frac{6.46 \times 10^{-4}}{6.46 \times 10^{-5}} = 10$$

Let the solubility of C_6H_5COOAg be x mol/L.

Then,

$$\left[Ag^+\right] = x$$

$$\left[C_6H_5COOH\right] + \left[C_6H_5COO^-\right] = x$$

$$10\left[C_6H_5COO^-\right] + \left[C_6H_5COO^-\right] = x$$

$$\left[C_6H_5COO^-\right] = \frac{x}{11}$$

$$K_{sp}\left[Ag^+\right]\left[C_6H_5COO^-\right]$$

$$2.5 \times 10^{-13} = x\left(\frac{x}{11}\right)$$

$$x = 1.66 \times 10^{-6}\ \text{mol/L}$$

Thus, the solubility of silver benzoate in a pH 3.19 solution is 1.66 × 10^{-6} mol/L.

Now, let the solubility of C_6H_5COOAg be x' mol/L.

$$\text{Then, } \left[Ag^+\right] = x'\text{M and } \left[CH_3COO^-\right] = x'\text{M.}$$

$$K_{sp} = \left[Ag^+\right]\left[CH_3COO^-\right]$$

$$K_{sp} = (x')^2$$

$$x' = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7}\ \text{mol/L}$$

$$\therefore \frac{x}{x'} = \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32$$

Hence, C_6H_5COOAg is approximately 3.317 times more soluble in a low pH solution.

Question 7.71:

What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).

- **Answer**

Let the maximum concentration of each solution be x mol/L. After mixing, the volume of the concentrations of each solution will be reduced to half i.e., $\frac{x}{2}$.

$$\therefore [FeSO_4] = [Na_2S] = \frac{x}{2}M$$

$$\text{Then, } \left[Fe^{2+}\right] = [FeSO_4] = \frac{x}{2}M$$

$$\text{Also, } \left[S^{2-}\right] = [Na_2S] = \frac{x}{2}M$$

$$FeS_{(s)} \longleftrightarrow Fe^{2+}{}_{(aq)} + S^{2-}{}_{(aq)}$$

$$K_{sp} = \left[Fe^{2+}\right]\left[S^{2-}\right]$$

$$6.3 \times 10^{-18} = \left(\frac{x}{2}\right)\left(\frac{x}{2}\right)$$

$$\frac{x^2}{4} = 6.3 \times 10^{-18}$$

$$\Rightarrow x = 5.02 \times 10^{-9}$$

If the concentrations of both solutions are equal to or less than 5.02×10^{-9} M, then there will be no precipitation of iron sulphide

Question 7.72:

What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, K_{sp} is 9.1×10^{-6}).

- **Answer**

$$CaSO_{4(s)} \longleftrightarrow Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

Let the solubility of $CaSO_4$ be s.

$$\text{Then, } K_{sp} = s^2$$

$$9.1\times10^{-6} = s^2$$

$$s = 3.02\times10^{-3} \text{ mol/L}$$

Molecular mass of $CaSO_4$ = 136 g/mol

Solubility of $CaSO_4$ in gram/L = $3.02 \times 10^{-3} \times 136$

= 0.41 g/L

This means that we need 1L of water to dissolve 0.41g of $CaSO_4$

Therefore, to dissolve 1g of $CaSO_4$ we require $= \frac{1}{0.41}\text{L} = 2.44\text{L}$ of water.

Question 7.73:

The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. in which of these solutions precipitation will take place?

- **Answer**

Given K_{sp} for $FeS = 6.3\times10^{-18}$, $MnS = 2.5\times10^{-13}$, $ZnS = 1.6\times10^{-24}$,

$CdS = 8.0\times10^{-27}$

For precipitation to take place, it is required that the calculated ionic product exceeds the K_{sp} value.

Before mixing:

$$[S^{2-}] = 1.0\times10^{-19}\text{ M} \quad [M^{2+}] = 0.04\text{M}$$

$$\text{volume} = 10 \text{ mL} \qquad \text{volume} = 5 \text{ mL}$$

After mixing:

$\left[S^{2-}\right] = ?$ $\left[M^{2+}\right] = ?$

volume $= (10 + 5) = 15$ mL volume $= 15$ mL

$$\left[S^{2-}\right] = \frac{1.0 \times 10^{-19} \times 10}{15} = 6.67 \times 10^{-20}\ \text{M}$$

$$\left[M^{2+}\right] = \frac{0.04 \times 5}{15} = 1.33 \times 10^{-2}\ \text{M}$$

$$\begin{aligned}\text{Ionic product} &= \left[M^{2+}\right]\left[S^{2-}\right]\\ &= \left(1.33 \times 10^{-2}\right)\left(6.67 \times 10^{-20}\right)\\ &= 8.87 \times 10^{-22}\end{aligned}$$

This ionic product exceeds the K_{sp} of ZnS and CdS. Therefore, precipitation will occur in $CdCl_2$ and $ZnCl_2$ solutions.

*********************************THE END*************************