CHEMICAL EQUILIBRIUM AND ACIDS-BASES

Short Answer Questions:

1. Write the Important Characteristics of Equilibrium?

Ans. The important characteristics of chemical equilibrium:

I) At equilibrium state, the rate of the forward reaction is equal to that of the reverse reaction.

ii) All the reactants and all the products of the reaction are present at equilibrium.

iii) Properties like concentration, pressure, intensity of colour remain unchanged with time after the equilibrium is established.

IV) The same equilibrium can be attained by carrying out the reaction starting with the reactants or starting with the products.

v) The equilibrium is not static. It is dynamic. Since forward and backward reactions are not ceased at equilibrium.

VI). Change in temperature, pressure or concentration of substances may change the position of equilibrium.

vii) Addition of a catalyst to the reaction does not alter the position of equilibrium. It only speeds up the attainment of equilibrium.

viii) At equilibrium change in free energy $\Delta G = 0$

2. State Lechatelier's principle. Apply the Lechatelier's principle in the manufacture of ammonia from the following equilibrium?

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g), \Delta H = -92kJ$$

Ans. Le Chatelier Principle: It states that "If a chemical reaction at equilibrium is subjected to any change in pressure or temperature or concentration then the equilibrium position shifts in the direction in which the applied change is reduced".

Application to manufacture of ammonia by Haber's process: The chemical equation denoting the synthesis of ammonia from its elements is,

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g), \Delta H = -92kJ$$

It is an exothermic reaction and in forward reaction number of moles decreases.

Effect of Concentration: According to Le Chatelier principle increase in the concentration of reactants (i.e. N_2 or H_2 or both) and removing product i.e. ammonia from the vessel from time to time favouring the formation of more ammonia.

Effect of Pressure: According to Le Chatelier principle, increase in pressure on a system at equilibrium will shift the equilibrium in the direction in which pressure is reduced or decrease in number of moles. Four moles of reactants produce two moles of products in Haber's synthesis. Since the moles is decreased, high pressure must favour the formation of ammonia and shifts the equilibrium state towards right.

Effect of Temperature: According to Le Chatelier principle low temperature is favourable for an exothermic reaction. As the formation of ammonia is exothermic low temperature favours the formation of ammonia and shifts the equilibrium state towards right. However, moderate temperature is used experimentally as the reaction is slow at low temperature.

Introduction of a catalyst iron at the reaction temperature, favours the reaction, as the catalyst helps increasing the rate of reaction and also makes the attainment of equilibrium fast.

Optimum conditions of Haber's ammonia synthesis are:

a) High pressure, 200 – 300 atm.

b) Low but an optimum temperature of 725 – 775K

c) Removal of ammonia by liquification

d) Use of iron as catalyst and molybdenum **or** mixture of K_2O and Al_2O_3 as promoter.

3.What is the relationship between K_P and K_C.Derive the relationship between K_P and K_C for the equilibrium reaction $N_2(g)+3H_2(g) \rightleftarrows 2NH_3(g)$ **.**

Ans. The relationship between K_P and K_C is $K_p = K_c(RT)^{\Delta n}$ where Δn=moles of gaseous products-moles of gaseous reactants.

Derivation of the relationship between K_P and K_C For $N_2(g)+3H_2(g) \rightleftarrows 2NH_3(g)$

Let $[N_2]$.$[H_2]$ and $[NH_3]$ are the molar concentrations of N_2, H_2 and NH_3at equilibrium respectively.

By applying law of mass action, the rate of forward reaction 'r_f is rf = $k_f [N_2] [H_2]^3$

And the rate of backward reaction 'r_b' is $r_b = k_b [NH_3]^2$

At equilibrium, $r_f = r_b$

Therefore $k_f [N_2]^1 [H_2]^3 = k_b [NH_3]^2$ or $\frac{k_f}{k_b} = \frac{[\mathbf{NH_3}]^2}{[N_2]\ [H_2]^3} = K_c$

According to ideal gas equation, PV = nRT, where P is the pressure, n is the number of moles, V is the volume of the vessel and T is the absolute temperature.

$P = \frac{n}{V} RT = []RT$, [ ] is the concentration

$P_{N2} = [N_2]$ RT , $P_{H2} = [H_2]$ RT and $P_{NH3} = [NH3]$ RT

Substituting the values in Kp expression. We get

$$K_P = \frac{P_{NH_3}{}^2}{P_{N_2} \times P_{H_2}{}^3} = \frac{[NH_3]^2 (RT)^2}{[N_2](RT)[H_2]^3 (RT)^3} = \frac{[NH_3]^2}{[N_2][H_2]^3}(RT)^{-2} = K_C (RT)^{-2}$$

$$\therefore K_P = K_C (RT)^{-2}$$

4. Derive the relationship between Kp and K_c For the equilibrium reaction

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

Ans. Let $[SO_2].[O_2]$ and $[SO_3]$ are the molar concentrations of SO_2, O_2 and SO_3at equilibrium respectively.

By applying law of mass action, the rate of forward reaction 'r_f' is $r_f = k_f [SO_2]^2[O_2]$

And the rate of backward reaction 'r_b' is $r_b = k_b [SO_3]^2$

At equilibrium, $r_f = r_b$

Therefore $k_f [SO_2]^2[O_2] = k_b [SO_3]^2$ or $\frac{k_f}{k_b} = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = K_c$

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

According to ideal gas equation, PV = nRT, where P is the pressure, n is the number of moles, V is the volume of the vessel and T is the absolute temperature.

$P = \frac{n}{V} RT = []RT$, [ ] is the concentration

$P_{so_2} = [SO_2]$ RT, $P_{o_2} = [O_2]$ RT and $P_{so_3} = [SO_3]$ RT

Substituting the values in Kp expression. We get

$$K_P = \frac{P_{SO_3}{}^2}{P_{SO_2}{}^2 \times P_{O_2}} = \frac{[SO_3]^2 (RT)^2}{[SO_2]^2 (RT)^2 [O_2](RT)} = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}(RT)^{-1} = K_C (RT)^{-1}$$

$$\therefore K_P = K_C (RT)^{-1}$$

5. What are homogeneous and heterogeneous equilibria? Give examples?

Ans. Homogeneous equilibrium: The equilibrium in which both reactants and products are in the same phase is called a homogeneous equilibrium.

Examples:

1. Thermal decomposition of ammonia.

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

2. Oxidation of sulphur dioxide to sulphur trioxide.

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

Heterogeneous Equilibrium: The equilibrium in which reactants and products are in two or more phases is called a heterogeneous equilibrium.

Examples:

1. Thermal decomposition of lime stone in a closed vessel.

   $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

2. Decomposition of ammonium bisulphide in a closed vessel.

   $NH_4HS_{(s)} \rightleftharpoons NH_{3\,(g)} + H_2S_{(g)}$.

6. **What is conjugate acid-base pair? Give four examples?**

Ans. An acid –base pair which differ structurally by a single proton is called a conjugate acid-base pair.

Acid $\rightleftharpoons$ Proton + Conjugate base

HCl $\rightleftharpoons$ Cl^- + Proton

$\therefore$ Cl^- is the Conjugate base of HCl

Ex; In the reaction **$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$,**

HCl and Cl^- are one conjugate acid-base pair & H_3O^+ and H_2O is another conjugate acid-base pair.

7. Define ionic product of water .What is its value at room temperature?

Ans. The product of molar concentration of proton (H^+) or H_3O^+ and hydroxyl ions (OH^-) present in pure water at a given temperature is called as ionic product of water (K_W).

$$K_W = [H^+][OH^-] \text{ or } K_W = [H_3O^+][OH^-]$$

The value of K_W at room temperature is 1×10^{-14} $mol^2\ L^{-2}$.

As the temperature increases the degree of ionisation of water increases and K_W increases.

Very Shot Answer Questions

1. **The equilibrium constant for the reaction, $2x + y \xrightleftharpoons{\Delta} x_2y$ is 10 L^2mol^{-2}. The rate constant for the backward reaction 28 s^{-1}. What is the rate constant of the forward reaction?**

Solution: Equilibrium constant, $K_c = \frac{K_f}{K_b}, \frac{K_f}{28} = 10$. $\therefore K_f = 10 X 28 = 280$

Hence the Forward rate constant, kf = 280 $Lit^2 mol^{-2} s^{-1}$.

2. **What is solubility product?**

Ans. The product of the concentrations of the caution and the anion present in a saturated solution of a sparingly soluble salt at room temperature is called as Solubility product. It is denoted by K_{sp}.

The expression of K_{sp} for

a. $AgCl \rightleftharpoons Ag^+ + Cl^-$; $K_{sp} = [Ag^+][Cl^-]$

b. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$; $K_{sp} = [Mg^{2+}][OH^-]^2$

3. What is common ion Effect?

Ans. The suppression of the dissociation of weak electrolyte by the addition of a strong electrolyte having some common ion is called common ion effect.

Ex: The dissociation of week acid CH_3COOH is decreased by the addition of HCl

(H^+ ion is common) or by the addition of CH_3COONa (CH_3COO^- is the common ion).

4. What are Lewis acids and bases?

Ans. Lewis Acid: It is a substance that can accept an electron pair to form a coordinate covalent bond with the donor.

E.g. BCl_3, BeF_2, $AlCl_3$,

Lewis base is a substance that can donate an electron pair to form a dative bond with electron pair acceptor acid.

Eg. NH_3, H_2O, F^-, Cl^-, I^-,

5. Define P^H. calculate the P^H of 0.05 M Ba $(OH)_2$.

Ans. The pH of a solution is defined as negative value of logarithm of H^+ ion concentration to base 10 at a given temperature.

$$p^H = -\log_{10}[H^+] \quad \text{or} \quad p^H = -\log_{10}[H_3O^+]$$

$[OH^-]$ = Normality of the strong base = acidity x M = 2 x 0.05 = 0.1=10^{-1}

$$P^{OH} = -\log[OH^-] = -\log\left[10^{-1}\right] = \log 10 = 1$$

$$P^H = 14 - P^{OH} = 14 - 1 = 13$$

6. The P^H of HCl solution 5.4. What is the Hydrogen ion concentration?

Solution: pH = – log $[H^+]$, log $[H^+]$ = –pH

Log $[H^+]$ = -5.4= -6+0.6

$[H^+]$ = antilog of 0.6 x 10^{-6} = 3.98 x 10^{-6} M

7. What is a buffer solution? Give the equation for P^H of acid buffer.

Ans. The Solution whose pH is almost constant when a small amount of acid or alkali is added is called buffer solution. Buffer solutions have reserve acidity or alkalinity. The P^H of an acid buffer is calculated by Henderson's equation i.e. $pH = pK_a + \log\frac{[salt]}{[acid]}$

8. What is meant by Salt Hydrolysis?

Ans. The phenomenon in which the anion or caution or both ions of a salt react with water producing excess of OH^- ions or H^+ ions or both in aqueous solutions is called as Salt hydrolysis .

Salt + water ⇌ acid + base

9. Give two examples of salts whose aqueous solutions are acidic?

Ans. Aqueous solution of a salt of strong acid and weak base is acidic due to cationic hydrolysis.

Eg. NH_4Cl, $CuSO_4$, $(NH_4)_2SO_4$, $MgSO_4$, $CaCl_2$, etc.

10. Give two examples of salts whose aqueous solutions are basic?

Ans. Aqueous solution of a salt of weak acid and strong base is basic due to anionic hydrolysis.

Eg. CH_3COONa, Na_2CO_3, KCN, Na_3PO_4, K_2SO_3, etc.