CHAPTER-7

EQUILIBRIUM

ONE MARK QUESTIONS WITH ANSWERS.

CHAPTER WEIGHTAGE: 13

1. What is a reversible reaction?

Ans. The reaction in which both forward and backward reaction takes place simultaneously is called as reversible reaction.

2. Give an example for a reversible process.

Ans.
$$H_2O(s) \leftrightarrows H_2O(l)$$

3. What is an irreversible process?

Ans. It is a process in which the products obtained does not give back the reactants.

4. Give an example for an irreversible process.

Ans. NaCl(aq) + AgNO₃(aq)
$$\leftrightarrows$$
 AgCl(s) + NaNO₃(aq)

5. Define equilibrium state.

Ans. It is a state in a reversible reaction at which both forward and backward reaction takes place in same rate.

6. What is the freezing point of water?

Ans.
$$273 \text{K or } 0^{\circ} \text{C}$$

7. Give the boiling point of water at sea level.

Ans.
$$373 \text{K or } 100^{\circ} \text{C}$$

8. Write an example for solid-liquid equilibrium

Ans.
$$H_2O(s) \leftrightarrows H_2O(l)$$

9. Give an example for liquid-gas equilibrium.

Ans.
$$H_2O(I) \leftrightarrows H_2O(g)$$

10. Give an example for solid-gas equilibrium.

Ans.
$$I_2(s) \leftrightarrows I_2(g)$$

11. State law of mass action.

Ans. It states that "rate of a reaction is directly proportional to active masses of the reactants at constant temperature."

12. What is equilibrium constant Kc?

13. Write the relationship between Kp and Kc.

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

14. Given an example for a reaction in which Kp = Kc

Ans.
$$H_{2(g)} + I_{2(g)} \leftrightarrows 2HI(g)$$

15. Write the relationship between Kp and Kc for the reaction

CS₂(g) + 4H₂(g)
$$\leftrightarrows$$
 CH₄ (g) + 2H₂S (g)
Ans. n_p = 1 + 2 = 3, n_R = 1 + 4 = 5, $\Delta n = n_p - n_R$ = 3-5 = -2
∴ $K_p = K_c (RT)^{\Delta n}$, $K_p = K_c (RT)^{-2}$

$$\therefore K_{p} = \underbrace{K_{c}}_{(RT)^{2}} \Rightarrow K_{c} > K_{p}$$

16. Write Kc expression for the reaction $N_2(g) + 3H_2(g) \stackrel{\leftarrow}{\rightarrow} 2NH_3(g)$

Ans.
$$Kc = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

17. The equilibrium constant for the reaction A+B $\stackrel{\leftarrow}{\rightarrow}$ C + D is 10. If the initial concentration of A and B is doubled then what is the value of equilibrium constant?

Ans. It remains same.

18. Write K_P expression for the reaction $2SO_3(g) = 2SO_2(g) + O_2(g)$.

Ans.
$$P_{SO_{2}}^{2} \times P_{O}$$

$$K_{P} = \frac{P_{SO_{2}}^{2}}{P_{SO_{2}}^{2}}$$

19. What is the effect of catalyst on the equilibrium in a reversible reaction?

Ans. Catalyst has no effect.

20. What is reaction quotient?

21. In a reversible reaction $K = Q_c$, what does it signify?

Ans. The reaction is at equilibrium.

22. In a reversible reaction $Q_c > K$, predict the direction in which the reaction proceeds?

Ans. Net reaction goes from right to left i.e., towards backward direction.

23. Give the relationship Gibb's free energy change and equilibrium constant

Ans.
$$\Delta G^{\circ} = -2.303 \text{ RTlogK}$$

24. What happens to the rate of forward reaction when the pressure increases

$$COCl_2(g) \leftrightarrows CO(g) + Cl_2(g)$$
?

Ans. Increase in pressure decreases the rate of forward reaction.

25. The rate constant values of a certain reaction is 7.2×10^{-10} and 3.9×10^{-7} at 600K and 800K. predict whether reaction is exothermic or endothermic?

Ans. Since rate constant values are increasing with temperature, the reaction is endothermic.

26. In a certain chemical reaction change in pressure does not influence the equilibrium state. What does it signify?

Ans.The number of moles of gaseous products and reactants are same in the reaction.

27. For the reaction $2SO_2(g) + O_2(g) \stackrel{\leftarrow}{\rightarrow} 2SO_2(g) \Delta H = -qkJ$. State whether rate of forward reaction increases or decreases when temperature is decreased.

Ans. Rate of forward reaction increases.

28. What happens to rate of forward reaction

 $N_2(g) + O_2(g) \implies 2NO(g) \Delta H = +qkJ$, when pressure is increased?

Ans. Rate of the reaction remains same.

29. What is a strong electrolyte?

Ans. It is an electrolyte which ionizes almost completely in aqueous solution.

30. What is a weak electrolyte?

Ans. It is an electrolyte which ionizes partially in an aqueous solution.

31. Give two examples for a strong electrolyte.

Ans. NaCl, HCl.

32. Write two examples for a weak electrolyte.

Ans. CH₃COOH, NH₄OH.

33. What is hydronium ion?

Ans. Hydrated proton or H⁺₃O.

34. Give the conjugate acid of H₂O, CO₃², HSO₄, O² and CH₃COO.

Ans.

35. Write the conjugate base of H₂O, NH⁺₄, H₂CO₃, HS⁻, HCl.

Ans. a)
$$H_2O$$
 --- OH^-

36. OH is a Lewis base. Why?

Ans. Since it can donate a pair of electrons.

37. What is the value of ionic product of water at 298K?

Ans. $10^{-14} (\text{mol/dm}^3)^2$.

38. What is the P^H of 10⁻² M HCl solution?

Ans. $P^{H} = 2$.

39. The pKa values of acids x, y and z are 4.2, 9.8 and 6.1 respectively. Which among the above acid is strongest?

Ans. X

40.An aqueous solution of NH₄Cl is acidic. Why?

Ans. NH₄Cl upon hydrolysis gives ammonium hydroxide, a weak base and strong acid HCl.

41. A small amount of NH₄Cl is added to NH₄OH, what happens to ionization of NH₄OH?

Ans. Ionisation of NH₄OH decreases.

42. Write solubility product expression of Ag₂CrO₄.

Ans.
$$Ag_2CrO_4 \implies 2Ag^+(aq) + CrO_4^{2-}(aq)$$

 $Ksp = (2s)^2 x s \qquad Ksp = 4s^3.$

43. What is the effect of addition of noble gas on equilibrium?

Ans. Equilibrium remains undisturbed.

44. Define pH.

Ans. It is defined as negative logarithm to the base 10 of molarity of hydrogen ion.

i.e.,
$$pH = -log[H^{\dagger}]$$

45. what is the significance of Ka/Kb?

Ans. At given temperature Ka/Kb is a measure of strength of acid/base. Larger the value of Ka/Kb, stronger is the acid/base.

TWO MARKS QUESTIONS WITH ANSWERS.

1. Write any two characteristics of equilibrium?

Ans. a) Equilibrium is possible only in a closed system at constant temperature.

b) All measurable properties of the system remain constant.

2. Explain solid –liquid equilibrium with an example?

Ans. Solid –liquid equilibrium is a stage in a reversible reaction at which the rate of transfer of molecules from solid state to liquid state and rate of transfer of molecules from liquid state to solid state are equal at atmospheric pressure and at freezing point / melting point of the substance.

Example: $H_2O(s) \leftrightarrows H_2O(l)$

3) Explain liquid-vapour equilibrium with an example?

Ans. Liquid –vapour equilibrium is a stage in a reversible reaction which rate of evaporation is equal to rate of condensation at the boiling point of liquid and at atmospheric pressure.

Example: $H_2O(I) \leftrightarrows H_2O(vap)$

4) Explain solid –vapour equilibrium with an example?

Ans. It is a stage at which rate of sublimation is equal to rate of condensation of a solid at given temperature

Example: I_2 (solid) $\leftrightarrows I_2$ (vap)

5) Explain solid –solution equilibrium with an example?

Ans. It is a stage at which rate of dissolution of solid is equal to rate of crystallization of solid in a saturated solution at given temperature.

Example: NaCl(s) \leftrightarrows NaCl (in solution)

6) Explain gas –solution equilibrium with an example?

Ans. It is a stage of equilibrium between the gas dissolved in solution and vapours of the gas above the liquid surface at given temperature.

Example: $CO_2(g) \leftrightarrows CO_2(in solution)$

7) Sate Henry's law?

Ans. It states that the mass of a gas dissolved in a given mass of solvent is proportional to pressure of the gas above the solvent at given temperature.

8) What is homogeneous equilibrium? given an example

Ans. It is an equilibrium in which all the reactants and products are in same phase.

Example: $H_2(g)+I_2(g) \leftrightarrows 2HI(g)$

9) What is heterogeneous equilibrium? given an example

Ans. It is an equilibrium in which reactants and products are in different phases.

Example: $CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$

10) State law of chemical equilibrium

Ans. "The ratio of product of concentration of products to the product of concentration of reactants all the concentration terms are raised to respective stoichiometric co-efficient in the balanced chemical equation is a constant at given temperature" is called law of chemical equilibrium.

11) Chemical equilibrium is dynamic. Explain

Ans. At equilibrium the concentration of reactants and products remains constant, but rates of forward and backward reactions are equal. Hence the equilibrium said to be dynamic.

12) Given an example for the reaction in which a) $K_p > K_c$ b) $K_p < K_c$

Ans. a) $PCl_5(g) \leftrightarrows PCl_3(g) + Cl_2(g)$

b) $N_2(g)+3H_2(g) \leftrightarrows 2NH_3(g)$

13) Write the significance of reaction quotient?

Ans. 1.If Q_c<K_c net reaction goes from left to right (towards forward direction)

- 2. If Q_c>K_c net reaction goes from right to left (towards backward direction)
- 3. If Q_c=K_c no net reaction occurs (reaction is at equilibrium)

14) State le Chatelier's principle?

Ans. If a system under equilibrium is subjected to change in temperature, pressure or concentration then the equilibrium shifts itself in such a way so as to neutralize the effect of the change.

15) Discuss the effect of increase in temperature on the rate an exothermic reversible reaction.

Ans. Increase in temperature decrease the rate of forward reaction which is exothermic. The rate of backward reaction increases on increasing temperature since the reverse reaction is endothermic.

16) What is the effect of a)addition of NH_3 b) addition of H_2 on the reaction $N_2(g) + 3H_2(g) \implies 2NH_3(g)$?

Ans: a) The increase in concentration of ammonia increases the rate of backward reaction. b)The increase in concentration of hydrogen increases the rate of forward reaction.

17) Discuss the effect of pressure on the reaction $PCl_5(g) \hookrightarrow PCl_3(g) + Cl_2(g)$

Ans. Increase in pressure increases rate of backward reaction in which there is decrease in no. of gaseous components. Decrease in pressure increases rate of forward reaction in which there is increase in no. of moles of gaseous components.

18) Explain Arrhenius concept of acid and base with an example?

Ans. According to Arrhenius, acid is a substance that dissociates in water to give H⁺ ions and base is substance that produce OH⁻ (hydroxyl) ions.

Example:
$$HCI \rightarrow H^+ + CI^-$$
(acid)
 $NaOH \rightarrow Na^+ + OH^-$
(Base)

19) With an example explain Bronsted Lowry concept of acid and base?

Ans. Consider a reaction $CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3^+O$

In the above example acetic acid donates a proton hence it is an acid and water accepts a proton and it is a base.

20) Explain Lewis concept of acid and base with an example?

Ans. According to Lewis "acid is an electron pair acceptor and base is electron pair donor".

$$F_3B$$
 + :NH₃ ------ \rightarrow F_3B \leftarrow :NH₃ Acid base

In the above example boron trifluoride is an acid and ammonia is a base

21) What are conjugate acid-base pairs? Explain with an example.

Ans. A pair of acid and base which differ by a proton is called conjugate acid-base pairs.

Example:
$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3^+O$$

In the Above example acetic acid and acetate ion act as a pair of conjugate acid-base.

22) Explain amphoteric substance with an example?

Ans. Substance which act as acid in presence of a base and base in presence of an acid is called amphoteric substance.

Example:
$$CH_3COOH + H_2O \implies CH_3COO^- + H_3^+O$$

Base
 $NH_3 + H_2O \implies NH_4^+ + OH^-$
Acid

23) What is ionic product of water?

Ans. It is the product of molar concentration of H^+ and OH^- ions in water or in any aqueous solution is a constant at constant temperature. i.e., $K_w = [H^+]$ [OH-]

24) Show that pH + pOH = 14 at 298K

Ans. WKT,
$$[H^+][OH^-] = 10^{-14}$$
 at 298K
Taking negative logarithm on both sides
-log $[H^+]$ -log $[OH^-]$ = -log 10^{-14}
pH +pOH = -(-14)log10
Therefore pH+ pOH = 14

25) Explain common ion effect with an example.

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

Example: the ionization of acetic acid [weak electrolyte] is suppressed by addition of sodium acetate [strong electrolyte] containing common acetate ion.

26) Define solubility product.

Ans. The product of molar concentrations of constituent ions, each raised to the power of its stoichiometric co-efficient in the equilibrium equation of the electrolyte at given temperature, is called as solubility product.

27) What is a buffer solution? Give an Example.

Ans. It is a solution that has ability to resist change in p^Hupon addition of small amount of acid or base.

Example: Mixture of acetic acid and sodium acetate.

28) Is Cl⁻ a strong base or weak base of conjugate acid HCl? Why?

Ans. It is a weak base because HCl is a strong Bronsted acid its conjugate base is weak.

29) What is hydrolysis of salt? Give an Example.

Ans. The interaction of cations and anions of salt with water to give acidic or basic or neutral solution is called hydrolysis.

Example: when sodium acetate undergoes hydrolysis in water it gives basic solution due to formation of strong base NaOH and weak acid CH₃COOH.

30) The aqueous solution of K_2CO_3 is it acidic or basic or neutral? Explain.

Ans. K_2CO_3 is a salt obtained by neutralization of weak acid H_2CO_3 and strong base KOH. Hence the aqueous solution of the salt has more OH^- than H^+ ions and resultant solution is basic.

31) An aqueous solution of NH₄Cl is acidic. Why?

Ans. NH_4Cl is a salt obtained by neutralization of strong acid HCl and weak base NH_4OH . The aqueous solution of the salt has more H^+ ions than OH^- hence the solution is acidic.

32) Write applications of equilibrium constant.

- Ans. 1) If the value of Kc is very large $[>10^3]$ the reaction proceeds nearly to completion.
 - 2) If the value of Kc is small $[<10^{-3}]$ the reaction proceeds rarely.
 - 3) If the value of Kc is in range of 10^{-3} to 10^{3} , the appreciable concentrations of both reactants and products are present.

33) Explain ionic equilibrium with an example.

Ans. It is the equilibrium established betweens ions and unionized molecules in an aqueous solution of the weak electrolyte.

Ex. $CH_3COOH(aq) \Rightarrow CH_3COO^-(aq) + H^+(aq)$

34) Ka₁ of polyprotic acid is higher than Ka₂. Why?

Ans. Ka_1 of polyprotic acid is higher than Ka_2 because it difficult to remove an H^+ ion from a negative ion due to electrostatic forces of attraction.

4 Marks questions with answers

1) Explain the Effect of pressure concentration and temperature on reaction

 $N_2(g) + 3H_2(g) \implies 2NH_3(g) \Delta H = -xkJ using Le Chatelier's principle?$

- **Ans.** a) Effect of pressure: increase in pressure increases rate of forward reaction since it is accompanied by decrease in no. of gaseous moles; hence equilibrium shifts to right side decrease in pressure increases rate of backward reaction.
- b) <u>Effect of concentration:</u> Increase in concentration of reactants increase rate of forward reaction. Addition of ammonia or decrease in concentration of reactants increase rate of backward reaction.
- c) <u>Effect of temperature:</u> Increase in temperature increases rate of endothermic reaction that is backward reaction. Decrease in temperature increases rate of exothermic reaction that is forward reaction.

2) For the equilibrium $4NH_3$ (g) $+5O_2$ (g) \Rightarrow 4NO (g) $+6H_2O$ (g) Discuss the effect of

- a) Addition of NH₃
- b) Addition of oxygen

c) Addition of H₂O

- d) Removal of H₂O
- Ans. a) Addition of NH_3 : Addition of ammonia (reactant) increases the concentration of product that is rate of forward reaction increases.
- b) <u>Addition of oxygen:</u> Addition of oxygen increases the concentration of product that is rate of forward reaction increases.

- c) <u>Addition of water</u>: Addition of water (product) increases the concentration of reactant that is rate of backward reaction increases.
- d) <u>Removal of water</u>: Removal of water (product) decreases the concentration of reactant i.e. rate of forward reaction increases.

3) Mention four conditions by which the concentration of sulphur trioxide can be increased in the following reaction. $2SO_2(g) + O_2(g) = 2SO_3(g) + heat$.

- **Ans.** a) Addition of any of the reactants SO₂or O₂ increases the concentration of products
- b) Removal of sulphur trioxide increases the rate of forward reaction. i .e. Product concentration increases.
- c) Increase of pressure increases concentration of SO₃, because forward reaction is accompanied by decrease in no. of moles.
- d) Decrease of temperature increases the rate of forward reaction hence the product concentration.
- 4) Which of the following reactions is affected by increase in pressure? Also mention the change in direction of equilibrium.

a) $CO_2(g) + C(s) = 2CO(g)$

b) C_2H_4 (g) $+H_2$ (g) $-C_2H_6$ (g)

c) $COCl_2(g) \hookrightarrow CO(g) + Cl_2(g)$

d) $H_2(g) + Br_2(g) + 2HBr(g)$

Ans. a) Increase in pressure increases rate of backward reaction because $n_P(2) > n_R(1)$

- b) Increase in pressure increases rate of forward reaction because $n_R(2) > n_P(1)$
- c) Increase in pressure increases rate of backward reaction because $n_P(2) < n_R(1)$
- d) Increase in pressure has no effect on effect on the reaction because $n_{\text{P}}(2) = n_{\text{R}}(2)$
- 5) Write conjugate acid and base for following amphoteric species

a) H₂O

b) NH₃

c) HSO₄

d) HCO₃

Ans.

Conjugate acid	Species			Conjugate base
H ₃ ⁺ O	+H⁺ ←	H ₂ O	→ -H ⁺	OH ⁻
NH ₄ ⁺	+H⁺ ←	NH ₃	→ -H ⁺	H ₂ N ⁻
H ₂ SO ₄	+H⁺ ←	HSO ₄	→ -H ⁺	SO ₄ ²⁻
H ₂ CO ₃	+H ⁺ ←	HCO ₃	→ -H ⁺	CO ₃ ²⁻

6) Write any four characteristics of equilibrium constants Kc/Kp.

- **Ans.** a) The value of equilibrium constant is independent of initial concentrations of reactants and products
- b) Equilibrium constant depends on temperature. It is constant for a given reaction at constant temperature.
- c) The equilibrium constant for the reverse reaction is equal to inverse of equilibrium constant for the forward reaction is $K_{rev} = 1/Kc$
- d) Equilibrium constant is applicable only when concentrations of reactants and products have attained equilibrium.

7) Explain the factors affecting acidic strength of acids.

Ans. The important factors affecting acidic strengths are

- 1)The bond strength of H-A: The strength of H-A bond is weak in case of strong acids hence cleavage of bond becomes easier, whereas the strength of H-A bond is high in case of weak acids.
- 2) Polarity of H-A bond: In case of strong acids the electronegativity difference between H and A is large, hence H-A bond become more polar therefore cleavage of bond becomes easier, where as polarity of H-A bond is less in case of weak acids.

8) Derive an expression for ionization constant K_a of weak acid.

Initial concentration

Ans. Consider a weak acid HX which partially ionizes in aqueous solution as

$$\text{HX(aq)} \leftrightarrows \quad \text{H}^+\text{(aq)} \quad + \quad \text{X}^-\text{(aq)}$$
 Initial concentration
$$C \qquad \qquad 0 \qquad \qquad 0$$
 Equilibrium concentration
$$C\text{-}C\alpha \qquad C\alpha \qquad C\alpha$$

Where C is the initial concentration in mol/L of the acid, $\boldsymbol{\alpha}$ is the extent of ionization. The ionization constant of the acid is given by

$$Ka = [H^+] [X^-]/[HX] = C\alpha \cdot C\alpha / C - C\alpha$$

 $Ka = C\alpha^2 / 1 - \alpha$

The above expression is called as mathematical form of Ostwald's dilution law.

2 Marks Problems

1) The K_c for a certain reaction is 4.5 x 10^7 at 750K, what is K_c for the reverse reaction?

Ans.
$$K_c^1 = 1/K_c = 1/4.5 \times 10^7 = 0.2222 \times 10^{-7}$$

 $K_c^1 = 2.222 \times 10^{-8}$

2) For a reversible reaction $PCl_3(g) + Cl_2(g) \leftrightarrows PCl_5(g)$ K_c is 3.0 at 270° C find the value of K_p ?

Ans. Given
$$t=270^{0}\text{C} \qquad \qquad \text{For the above reaction} \\ T=t+273 \qquad \qquad \qquad n_{P}=1 \text{ , } n_{R}=2 \\ =270+273=543\text{K} \qquad \qquad \Delta n=n_{P}-n_{R}=1-2=-1 \\ \text{R=0.0831barlitre/mol K} \qquad \qquad W.K.T \qquad K_{P}=K_{c}(RT)^{\Delta n} \\ \text{K}_{c}=3.0 \qquad \qquad \qquad K_{p}=3.0x(0.0831x543)^{-1} \\ \text{K}_{P}=3.0/0.0831x543 = 0.06648} \\ \end{cases}$$

For the synthesis of ammonia $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$ the K_P value is 41 at 400K. 3) Calculate K_C for the reaction?

Ans. Given For the above reaction
$$K_P = 41 \qquad \qquad n_P = 2 \ , \ n_R = 4$$

$$T = 400K \qquad \qquad \Delta n = n_P - n_R = 2 - 4 = -2$$

$$R = 0.0831 bar \ litre \ / \ mol \ K \qquad \qquad W.K.T \quad K_P = K_c (RT)^{\Delta n}$$

$$Kc = Kp/(RT)^{\Delta n} \qquad \qquad \qquad 41/(0.0831x400)^{-2}$$

$$K_C = 41x(0.0831x400)^2 = \qquad 45300.8$$

For the reaction 2NOCl(g) $\stackrel{\leftarrow}{\rightarrow}$ 2NO(g) + Cl₂(g), The equilibrium constant is 3.75 X 10⁻⁶ 4) at 1069K. What is equilibrium constant for the reaction $2NO(g) + Cl_2(g) \Rightarrow 2NOCl(g)$?

Ans. Given
$$K_{c} = 3.75 \times 10^{-6}$$

W.K.T $K_{C}^{1} = 1/K_{c} = 1/3.75 \times 10^{-6}$
 $= 0.2666 \times 10^{6} = 2.666 \times 10^{+5}$

5) The equilibrium concentrations of ammonia, hydrogen and Nitrogen for synthesis of ammonia are $1.2 \times 10^{-2} M$, $3 \times 10^{-2} M$ and $1.5 \times 10^{-2} M$ respectively, at given temperature calculate equilibrium constant K_c .

Ans. Given
$$[NH_3] = 1.2x10^{-2}M$$
 $N_2 + 3H_2 \leftrightarrows 2NH_3(g)$ $[H_2] = 3x10^{-2}M$ $K_c = [NH_3]^2/[N_2][H_2]^3$ $= (1.2x10^{-2})^2/(1.5x10^{-2})x(3x10^{-2})^3$ $= 0.03556x10^{-4+2+6}$ $= 0.03556x10^{-4+2+6}$

6) The equilibrium concentrations of hydrogen iodide and hydrogen for the reaction $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$ are $5.86 \times 10^{-2} M$ and $0.86 \times 10^{-2} M$ respectively. At given temperature calculate equilibrium constant K_c .

Ans. Given
$$[HI] = 5.86 \times 10^{-2}$$
 $K_c = [HI]^2 / [H_2] [I_2]$ $[H_2] = [I_2] = 0.86 \times 10^{-2}$ $= (5.86 \times 10^{-2})^2 / 0.86 \times 10^{-2} \times 0.86 \times 10^{-2}$ $= 42.43 \times 10^{-4+2+2}$ $= 42.43$

7) For the reaction $2NO(g) + Br_2(g) \leftrightarrows 2NOBr(g)$ the equilibrium concentrations of Nitric oxide, bromine and nitrosyl bromide are 0.0352M, 0.0178M and 0.0518M respectively at constant temperature, calculate equilibrium constant K_c .

Ans. Given [NO] =
$$0.0352$$
 $K_C = [NOBr]^2/[NO]^2[Br_2]$ [Br₂] = 0.0178 $K_C = (0.0518)^2/(0.0352)^2(0.0178)$ [NOBr] = 0.0518 = 121.66

8) The equillibricum partial pressure of HI , H_2 and I_2 for the reaction $2HI(g) \leftrightarrows I_2(g) + H_2(g)$ are 0.04 atm , 0.08 atm respectively, Calculate equilibrium constant K_P for the reaction.

Ans. Given
$$P_{HI} = 0.04$$
atm $K_P = P_{H2}xP_{12}/P_{HI}^2$
 $P_{I2} = 0.08$ atm $= 0.08x0.08/(0.04)^2$
 $P_{H2} = 0.08$ atm $= 0.16$

9) For the reaction A+3B \leftrightarrows 4C,the partial pressure of B and C are 0.8atm and 0.4 atm respectively. The equilibrium constant K_P for the reaction is 24, what is the partial pressure of A at equilibrium?

Ans. Given
$$K_P = 24$$
 $K_P = P_c^4/P_A.P_B^3$ $P_B = 0.8 \text{tm}$ $P_A = P_c^4/K_P.P_B^3$ $P_C = 0.4 \text{atm}$ $P_A = ?$ $P_A = 0.00208 \text{atm}$

10) The equilibrium constant K_C for a reaction is 1.3×10^2 at 300K. Calculate standard free energy change for the reaction. State whether the reaction is spontaneous or non-spontaneous.

Ans. Given
$$R = 8.314 \text{J mol}^{-1} \text{ K}^{-1}$$
 $\Delta G^0 = -2.303 \text{RT log K}_{\text{C}}$ $= -2.302 \times 8.314 \text{J K}^{-1} \text{mol}^{-1} \times 300 \text{K log } 1.3 \times 10^2$ $= -5744.14 (2 + \log 1.3)$ $\Delta G^0 = -12142.54 \text{ J mol}^{-1}$

Since ΔG^0 is negative the reaction is spontaneous

11) standard free energy change for a reaction is 12 KJ at 300K. Calculate equilibrium constant for the reaction at same temperature.

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Ans. Given \Delta G^0 = 12 \text{KJ} = 12 \text{x} 10^3 \text{J} \Delta G^0 = -2.303 \text{RT} \log K_C T = 300 \text{K} \log K_C = -\Delta G^0/2.303 \text{RT} R = 8.314 \text{Jmol}^{-1} \text{K}^{-1} \log K_C = -12000 \text{J}/2.303 \text{x} 8.314 \text{JK}^{-1} \text{mol}^{-1} \text{x} 300 \text{K} \log K_C = -2.0891 K_C = \text{antilog}[+1-1-2.0891] = \text{antilog}[3.9109] K_C = 8.145 \text{x} 10^{-3}
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12) Calculate the pH of 10⁻³M NaOH solution at 298K

Ans.
$$[OH^{-}] = 10^{-3}M$$

 $pOH = -log[OH^{-}]$
 $pOH = -log 10^{-3} = -(-3log 10) = 3$
W.K.T $pH + pOH = 14$ at 298K
 $pH = 14-3 = 11$

13) Find the pH of 0.025M HCl solution.

Ans.
$$[H^+]$$
 = 0.025 =25x10⁻³
pH = -log[H⁺]
pH = -log[25 x 10⁻³]
= -[log25 - 3log10] = +3-1.3979
pH = 1.6021

14) Calculate pH of 0.02M H₂SO₄ solution.

Ans. Since
$$H_2SO_4$$
 is a dibasic acid $[H^+]$ =2 x 0.02 = 0.04 = 4 x 10^{-2}
pH = $-log[H^+]$
pH = $-log[4 \times 10^{-2}]$
= $-[log4 - 2log10]$ = +2 - 0.6021
pH = 1.3979

15) Calculate the hydrogen ion concentration of a sample of milk of pH 6.4.

16) Calculate the hydroxyl ion concentration of a sample of soft drink of pH 3.2 at 298K.

Ans.
$$pOH = 14 - pH = 14 - 3.2 = 11.8$$

 $pOH = -log[OH]$
 $11.8 = -log[OH]$
 $[OH^-] = Antilog[-11.8]$
 $[OH^-] = Antilog[+1 - 1 - 11.8]$
 $[OH^-] = Antilog[12.2]$
 $[OH^-] = 1.585 \times 10^{-12}$

17) The ionization constant 0.05M propanoic acid is 1.3×10^{-5} . Calculate degree of ionization.

Ans. Given
$$K_a = 1.3 \times 10^{-5}$$
 C = 0.05M

$$\alpha = \sqrt{K_a/C} = \sqrt{1.3 \times 10^{-5}/0.05} = \sqrt{26 \times 10^{-5}}$$
$$= \sqrt{2.6 \times 10^{-4}}$$
$$\alpha = 1.61 \times 10^{-2} = 0.0161$$

18) calculate the percentage of ionization of 0.05M ammonia solution if ionization constant is 1.75×10^{-5}

Ans. Given
$$K_b = 1.75 \times 10^{-5}$$
 $\alpha = \sqrt{K_b / C} = \sqrt{1.75 \times 10^{-5} /_{0.05}} = \sqrt{35 \times 10^{-5}}$ $C = 0.05 M$ $\alpha = \sqrt{3.5 \times 10^{-4}} = 1.87 \times 10^{-2}$

Percentage of ionization is $1.87 \times 10^{-2} \times 100 = 1.87$

19) Hydrogen ion concentration of a solution is 4.5×10^{-6} mol/L, what is the hydroxyl ion concentration at 298K.

Ans. W.K.T
$$[H^{+}][OH^{-}] = 10^{-14}$$
 at 298K $[OH^{-}] = 10^{-14}/[H^{+}] = 10^{-14}/4.5 \times 10^{-6}$ $[OH^{-}] = 0.2222 \times 10^{-14+6} = 0.2222 \times 10^{-8} \text{mol/L}$

20) The pK_a of acetic acid and pK_b of ammonium hydroxide are 5.75 and 5.70 respectively. Calculate the pH of ammonium acetate solution.

Ans. pH =
$$7 + \frac{1}{2}[pK_a + pK_b] = 7 + \frac{1}{2}[5.75 - 5.70]$$

= $7 + \frac{1}{2} \times 0.05 = 7 + 0.025 = 7.025$

21) The solubility of A_2X in water is 1.1×10^{-5} mol/L calculate the solubility product of the electrolyte.

Ans.
$$S = 1.1 \times 10^{-5}$$
 $A_2X \rightarrow 2A^+ + X^{2-}$ $Ksp = [A^+]^2[X^{2-}] = (2s)^2 \cdot s = 4s^3$ $= 4 \times (1.1 \times 10^{-5})^3$ $= 5.324 \times 10^{-15} (mol/L)^3$

22) The solubility product of silver bromide is 5.0×10^{-13} at 298K. find its solubility.

Ans.
$$K_{sp} = 5 \times 10^{-13}$$
 AgBr \rightarrow Ag⁺ + Br⁻ $K_{sp} = [Ag^+][Br^-]$ $K_{sp} = s \cdot s$ $5 \times 10^{-13} = s^2$ $s = \sqrt{5 \times 10^{-13}} = 0.7071 \times 10^{-6} \text{mol/L}$

3 Marks Problems

1) For the reaction $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$, The partial pressures of N_2 and H_2 are 0.8 and 0.4 atmosphere respectively at equilibrium. The total pressure of the system is 2.80 atmospheres. What is K_P for the above reaction?

Ans. Given
$$P_{N2} = 0.8$$
atm $P_{N2} + P_{H2} + P_{NH3} = P$

$$P_{H2} = 0.4$$
atm $0.8 + 0.4 + P_{NH3} = 2.8$

$$P = 2.8$$
atm $P_{NH3} = 2.8 - 1.2 = 1.6$ atm $P_{NH3} = 2.8 - 1.2 = 1.6$

2) The equilibrium constant at 298K for the reaction $Cu(s) + 2Ag^{+}(aq) + Cu^{2}(aq) + 2Ag(s)$ is 2.0×10^{15} . The concentration of Cu^{2+} and Ag^{+} in solution are 1.8×10^{-2} mol/L and 3.0×10^{-9} mol/L respectively. Predict the direction in which reaction proceed.

Ans. Given[Cu²⁺] =
$$1.8 \times 10^{-2}$$
 mol/L $Q_c = [Cu^{2+}(aq)][Ag(s)] / [Cu(s)][Ag^{+}(aq)]^2$ [Ag⁺] = 3.0×10^{-9} mol/L $= 1.8 \times 10^{-2} / (3.0 \times 10^{-9})^2$ $= 0.2 \times 10^{-2+18} = 2 \times 10^{15}$ By convention [Ag(s)] = 1 and [Cu(s)] = 1

 $Q_c = K_P = 2 \times 10^{15}$, hence reaction is at equilibrium

2 moles of N_2O_4 taken in a flask of 10L capacity is heated to 350K. At equilibrium 50% of N_2O_4 was found to be dissociated to give NO_2 . Find the equilibrium constant for the reaction.

Ans. Initial concentration of
$$N_2O_4 = 2/10 \text{ mol/L}$$
 $50\% \text{ of } 2N_2O_4 \text{ is dissociated implies, } x = 50/100 = 0.5$
 $N_2O_4 \iff 2NO_2$
Initial concentration $2/10 = 0$
Equilibrium concentration $2(1-x)/10 = 2(2x)/10$
 $2(1-0.5)/10 = 0.1 = 2(2x0.5)/10 = 0.2$
 $K_c = [NO_4]^2/[N_2O_4]$
 $= (0.2)^2/0.1 = 0.4$

4) Calculate the pK $_a$ value of 0.1M weak mono basic acid whose degree of ionisation 1.52 x 10^{-2}

Ans. Given
$$\alpha = 1.52 \times 10^{-2}$$
 $K_a = C\alpha^2$
$$C = 0.1 M = 0.1 \times (1.52 \times 10^{-2})^2 = 0.2310 \times 10^{-4}$$

$$= 2.310 \times 10^{-5}$$

$$pK_a = -log K_a$$

$$= -log[2.310 \times 10^{-5}] = -[log2.310 - (5)log10]$$

$$= +5 - log2.310 = +5 - 0.3636 = 4.6364$$

5) Calculate the hydrogen ion concentration of 0.1M weak mono basic acid whose dissociation constant is 4×10^{-10} at 298K.

Ans. Given
$$C = 0.1M$$
 $\alpha = \sqrt{\frac{K_{\alpha}}{C}} = \sqrt{\frac{4 \times 10^{-10}}{0.1}} = 6.324 \times 10^{-5}$

$$K_{a} = 4 \times 10^{-10}$$

$$Wkt [H^{+}] = C\alpha = 0.1 \times 6.324 \times 10^{-5} = 0.6324 \times 10^{-5}M$$

6) Find the pH of 0.05M acid which is 10% ionised at 298K.

Ans. Given
$$c = 0.05$$

 $\alpha = 10\% = 10/100 = 0.1$
wkt $[H^+] = C\alpha = 0.05 \times 0.1 = 0.005 = 5 \times 10^{-3} M$

$$pH = -log [H^+] = -log 5 \times 10^{-3}$$

$$= -[log 5 - 3log 10] = [3 - 0.6990]$$

$$pH = 2.301$$

4 Marks Problems

- 1) The initial molar concentration of reactants A and B are 0.1 M and 0.2M respectively in the reaction A +B \rightleftharpoons 2C at equilibrium. The concentration of A in the mixture was found to be 0.06m. Calculate the equilibrium constant.
- **Ans.** Initial concentration of A = 0.1M

Concentration of A at equilibrium = 0.06M

Concentration of A reacted = 0.1 - 0.06m = 0.04M

$$A + B \iff 2C$$

Initial concentration 0.1 0.2

Equilibrium concentration 0.1 - 0.04 0.2 - 0.04 $2 \times 0.04 = 0.08$

$$=0.06 = 0.16$$

$$K_c = [C]^2/[A][B] = (0.08)^2/0.06 \times 0.16 = 0.6667$$

- 2) 2 moles of HI when heated in a closed container, at equilibrium 20% of HI found to be dissociated. Calculate the equilibrium constant for the reaction $2HI(g) \leftrightarrows H_2(g) + I_2(g)$
- **Ans.** Initial concentration of HI = 2 moles

20 moles of HI are dissociated out of 100 moles at equilibrium

⇒ ? moles of HI are dissociated out of 2 moles

Concentration of dissociated HI = $2 \times 20 / 100 = 4/10 = 0.4$ moles

Initial concentration 2 0

Equilibrium concentration
$$2 - 0.4 = 1.6$$
 $1.6/2 = 0.8$ $1.6/2 = 0.8$

$$K_C = [H_2][I_2]/[HI]^2 = 0.8 \times 0.8/(1.6)^2 = 0.25$$

3) What is the equilibrium concentration of each of the substances in equilibrium when the initial concentration of ICl was 0.78M for the reaction $2|C| \leftrightarrows I_2 + CI_2$, $K_C = 0.14$.

Ans. Let x mol be the equilibrium concentration of I2 and Cl2

2ICI
$$\leftrightarrows$$
 $I_2 + CI_2$

Initial concentration 0.78

Equilibrium concentration $0.78 - 2x \times x$

$$K_C = [I_2][CI_2]/[ICI]^2$$

$$0.14 = X \cdot X/(0.78 - 2X)^2$$

$$0.14[0.78 - 2X]^2 = X^2$$

Taking the square root both sides

$$[0.14]^{1/2}[0.78-2X] = X$$

$$0.374 \times 0.78 - 0.374 \times 2X = X$$

$$0.2917 = X + 0.748X$$

 $0.2917=1.748X$
 $X = 0.2917/1.748 = 0.1668$
 $[Cl_2] = [l_2] = X = 0.1668M$
 $[ICl] = 0.78-2X=0.78-2 \times 0.1668$
 $[ICl] = 0.78-0.3336 = 0.446M$

4) Calculate the degree of ionisation and K_a of 0.025M ammonia solution, if the ionisation constant of ammonia is 1.77 x 10^{-5} at 298K.

Ans. Given
$$K_b = 1.77 \times 10^{-5}$$
 $\alpha = \sqrt{K_b/C}$
$$C = 0.025 \qquad = \sqrt{1.77 \times 10^{-5}/0.025}$$

$$\alpha = 2.66 \times 10^{-2}$$
 WKT, $K_a \times K_b = K_w$
$$K_a = K_w/K_b = 10^{-14}/1.77 \times 10^{-5} = 0.5649 \times 10^{-9}$$

5) The K_{sp} values of BaSO₄ and PbSO₄ are 1.1 x 10⁻¹⁰ and 1.6 x 10⁻⁸ respectively. Which salt is more soluble?

Ans. Let solubility of BaSO₄ is s_1 and solubility of PbSO₄ is s_2 BaSO₄ \leftrightarrows Ba²⁺ + SO₄²⁻

Ksp = [Ba²⁺] [SO₄²⁻]

1.1 x 10⁻¹⁰ = $s_1.s_1$ S₁ = $\sqrt{1.1 \times 10^{-10}}$ = 1.0489 x 10⁻⁵mol/L

PbSO₄ \leftrightarrows Pb²⁺ + SO₄²⁻

K_{sp} = [Pb²⁺][SO₄²⁻]

1.6 x 10⁻⁸ = s_2 . s_2 S₂ = $\sqrt{1.6 \times 10^{-8}}$ = 1.2649 x 10⁻⁴mol/L

S₂ > s_1 hence PbSO₄ is more soluble than BaSO₄