Unit 7

EQUILIBRIUM

I. Multiple Choice Questions (Type-I)

1. We know that the relationship between K_c and K_p is

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

What would be the value of Δn for the reaction

$NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$

(i) 1

(ii) 0.5

(iii) 1.5

(iv) 2

2. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$, the standard free energy is $\Delta G^{\ominus} > 0$. The equilibrium constant (K) would be __________.

(i) $K = 0$

(ii) $K > 1$

(iii) $K = 1$

(iv) $K < 1$

3. Which of the following is **not** a general characteristic of equilibria involving physical processes?

(i) Equilibrium is possible only in a closed system at a given temperature.

(ii) All measurable properties of the system remain constant.

(iii) All the physical processes stop at equilibrium.

(iv) The opposing processes occur at the same rate and there is dynamic but stable condition.

4. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1} respectively. The value of K_c for the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$ will be

(i) 1.8×10^3 mol L^{-1}

(ii) 1.8×10^{-3}

(iii) 1.8×10^{-3} L mol^{-1}

(iv) 0.55×10^4

5. Which of the following statements is incorrect?

(i) In equilibrium mixture of ice and water kept in perfectly insulated flask mass of ice and water does not change with time.

(ii) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.

(iii) On addition of catalyst the equilibrium constant value is not affected.

(iv) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases.

6. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

$$\underset{\text{(pink)}}{[Co\,(H_2O)_6]^{3+}}\,(aq) + 4Cl^-\,(aq) \rightleftharpoons \underset{\text{(blue)}}{[CoCl_4]^{2-}}\,(aq) + 6H_2O\,(l)$$

(i) $\Delta H > 0$ for the reaction

(ii) $\Delta H < 0$ for the reaction

(iii) $\Delta H = 0$ for the reaction

(iv) The sign of ΔH cannot be predicted on the basis of this information.

7. The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C?

(i) Equal to 7.0

(ii) Greater than 7.0

(iii) Less than 7.0

(iv) Equal to zero

8. The ionisation constant of an acid, K_a, is the measure of strength of an acid. The K_a values of acetic acid, hypochlorous acid and formic acid are 1.74×10^{-5}, 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of pH of 0.1 mol dm^{-3} solutions of these acids is correct?

(i) acetic acid > hypochlorous acid > formic acid

(ii) hypochlorous acid > acetic acid > formic acid

(iii) formic acid > hypochlorous acid > acetic acid

(iv) formic acid > acetic acid > hypochlorous acid

9. K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.

$H_2S \rightleftharpoons H^+ + HS^-$

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

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is

(i) $K_{a_3} = K_{a_1} \times K_{a_2}$

(ii) $K_{a_3} = K_{a_1} + K_{a_2}$

(iii) $K_{a_3} = K_{a_1} - K_{a_2}$

(iv) $K_{a_3} = K_{a_1} / K_{a_2}$

10. Acidity of BF_3 can be explained on the basis of which of the following concepts?

(i) Arrhenius concept

(ii) Bronsted Lowry concept

(iii) Lewis concept

(iv) Bronsted Lowry as well as Lewis concept.

11. Which of the following will produce a buffer solution when mixed in equal volumes?

(i) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(ii) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(iii) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl

(iv) 0.1 mol dm^{-3} CH_4COONa and 0.1 mol dm^{-3} NaOH

12. In which of the following solvents is silver chloride most soluble?

(i) 0.1 mol dm^{-3} $AgNO_3$ solution

(ii) 0.1 mol dm^{-3} HCl solution

(iii) H_2O

(iv) Aqueous ammonia

13. What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH ($K_a = 1.74 \times 10^{-5}$)?

(i) 3.4

(ii) 3.6

(iii) 3.9

(iv) 3.0

14. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5} . The pH of ammonium acetate will be

(i) 7.005

(ii) 4.75

(iii) 7.0

(iv) Between 6 and 7

15. Which of the following options will be correct for the stage of half completion of the reaction A $\rightleftharpoons$ B.

(i) $\Delta G^{\ominus} = 0$

(ii) $\Delta G^{\ominus} > 0$

(iii) $\Delta G^{\ominus} < 0$

(iv) $\Delta G^{\ominus} = -RT \ln 2$

16. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction.

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

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(i) K will remain same

(ii) K will decrease

(iii) K will increase

(iv) K will increase initially and decrease when pressure is very high

17. What will be the correct order of vapour pressure of water, acetone and ether at 30°C. Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

(i) Water < ether < acetone

(ii) Water < acetone < ether

(iii) Ether < acetone < water

(iv) Acetone < ether < water

18. At 500 K, equilibrium constant, K_c , for the following reaction is 5.

$$\frac{1}{2} H_2 (g) + \frac{1}{2} I_2 (g) \rightleftharpoons HI (g)$$

What would be the equilibrium constant K_c for the reaction

$$2HI (g) \rightleftharpoons H_2 (g) + I_2 (g)$$

(i) 0.04

(ii) 0.4

(iii) 25

(iv) 2.5

19. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?

(i) $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

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

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

(iv) The equilibrium will remain unaffected in all the three cases.

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

20. For the reaction $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$, the value of K is 50 at 400 K and 1700 at 500 K. Which of the following options is correct?

(i) The reaction is endothermic

(ii) The reaction is exothermic

(iii) If NO_2 (g) and N_2O_4 (g) are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more N_2O_4 (g) will be formed.

(iv) The entropy of the system increases.

21. At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist in equilibrium. Which of the following term defines this temperature?

(i) Normal melting point

(ii) Equilibrium temperature

(iii) Boiling point

(iv) Freezing point

III. Short Answer Type

22. The ionisation of hydrochloric in water is given below:

$HCl(aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Cl^-\ (aq)$

Label two conjugate acid-base pairs in this ionisation.

23. The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionisation and how is it affected by concentration of sodium chloride?

24. BF_3 does not have proton but still acts as an acid and reacts with NH_3. Why is it so? What type of bond is formed between the two?

25. Ionisation constant of a weak base MOH, is given by the expression

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Values of ionisation constant of some weak bases at a particular temperature are given below:

Base	**Dimethylamine**	**Urea**	**Pyridine**	**Ammonia**
K_b	5.4×10^{-4}	1.3×10^{-14}	1.77×10^{-9}	1.77×10^{-5}

Arrange the bases in decreasing order of the extent of their ionisation at equilibrium. Which of the above base is the strongest?

26. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

OH^-, RO^-, CH_3COO^-, Cl^-

27. Arrange the following in increasing order of pH.

KNO_3 (*aq*), CH_3COONa (*aq*), NH_4Cl (*aq*), $C_6H_5COONH_4$ (*aq*)

28. The value of K_c for the reaction $2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$ is 1×10^{-4}

At a given time, the composition of reaction mixture is

$[HI] = 2 \times 10^{-5}$ mol, $[H_2] = 1 \times 10^{-5}$ mol and $[I_2] = 1 \times 10^{-5}$ mol

In which direction will the reaction proceed?

29. On the basis of the equation $pH = -\log [H^+]$, the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.

30. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution a 100 times?

31. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution (Q_{sp}) becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.

32. pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its ionisation constant.

33. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

34. The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in gL^{-1} and also find out pH of this solution. (Atomic mass of Al = 27 u).

35. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207 u).

36. A reaction between ammonia and boron trifluoride is given below:

$:NH_3 + BF_3 \longrightarrow H_3N:BF_3$

Identify the acid and base in this reaction. Which theory explains it? What is the hybridisation of B and N in the reactants?

37. Following data is given for the reaction: $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$

$$\Delta_f H^\ominus\,[CaO(s)] = -\,635.1\ \text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus\,[CO_2(g)] = -\,393.5\ \text{kJ mol}^{-1}$$

$$\Delta_f H^\ominus\,[CaCO_3(s)] = -\,1206.9\ \text{kJ mol}^{-1}$$

Predict the effect of temperature on the equilibrium constant of the above reaction.

IV. Matching Type

38. Match the following equilibria with the corresponding condition

(i)	Liquid $\rightleftharpoons$ Vapour	(a)	Saturated solution
(ii)	Solid $\rightleftharpoons$ Liquid	(b)	Boiling point
(iii)	Solid $\rightleftharpoons$ Vapour	(c)	Sublimation point
(iv)	Solute (s) $\rightleftharpoons$ Solute (solution)	(d)	Melting point
		(e)	Unsaturated solution

39. For the reaction : $N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{Equilibrium constant } K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Some reactions are written below in Column I and their equilibrium constants in terms of K_c are written in Column II. Match the following reactions with the corresponding equilibrium constant

	Column I (Reaction)		**Column II (Equilibrium constant)**
(i)	$2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$	(a)	$2K_c$
(ii)	$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	(b)	$K_c^{\frac{1}{2}}$
(iii)	$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$	(c)	$\frac{1}{K_c}$
		(d)	K_c^2

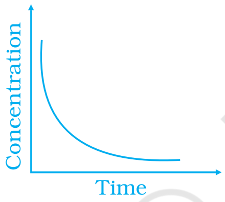
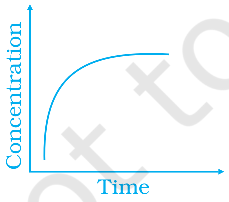
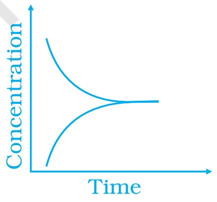
40. Match standard free energy of the reaction with the corresponding equilibrium constant

(i)	$\Delta G^{\ominus} > 0$	(a)	$K > 1$
(ii)	$\Delta G^{\ominus} < 0$	(b)	$K = 1$
(iii)	$\Delta G^{\ominus} = 0$	(c)	$K = 0$
		(d)	$K < 1$

41. Match the following species with the corresponding conjugate acid

	Species		**Conjugate acid**
(i)	NH_3	(a)	CO_3^{2-}
(ii)	HCO_3^-	(b)	NH_4^+
(iii)	H_2O	(c)	H_3O^+
(iv)	HSO_4^-	(d)	H_2SO_4
		(e)	H_2CO_3

42. Match the following graphical variation with their description

	A		**B**
(i)		(a)	Variation in product concentration with time
(ii)		(b)	Reaction at equilibrium
(iii)		(c)	Variation in reactant concentration with time

43. Match Column (I) with Column (II).

	Column I		Column II
(i)	Equilibrium	(a)	$\Delta G > 0$, $K < 1$
(ii)	Spontaneous reaction	(b)	$\Delta G = 0$
(iii)	Non spontaneous reaction	(c)	$\Delta G^{\ominus} = 0$
		(d)	$\Delta G < 0$, $K > 1$

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

44. ***Assertion (A) :*** Increasing order of acidity of hydrogen halides is HF < HCl < HBr < HI

Reason (R) : While comparing acids formed by the elements belonging to the same group of periodic table, H–A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

(i) Both A and R are true and R is the correct explanation of A.
(ii) Both A and R are true but R is not the correct explanation of A.
(iii) A is true but R is false.
(iv) Both A and R are false.

45. ***Assertion (A) :*** A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.

Reason (R) : A solution containing a mixture of acetic acid and sodium acetate acts as a buffer solution around pH 4.75.

(i) Both A and R are true and R is correct explanation of A.
(ii) Both A and R are true but R is not the correct explanation of A.
(iii) A is true but R is false.
(iv) Both A and R are false.

46. ***Assertion (A):*** The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.

Reason (R) : Hydrogen sulphide is a weak acid.

(i) Both A and R are true and R is correct explanation of A.
(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is true but R is false

(iv) Both A and R are false

47. ***Assertion (A):*** For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R) : Equilibrium constant is independent of temperature.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

48. ***Assertion (A) :*** Aqueous solution of ammonium carbonate is basic.

Reason (R) : Acidic/basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b value of the acid and the base forming it.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

49. ***Assertion (A):*** An aqueous solution of ammonium acetate can act as a buffer.

Reason (R) : Acetic acid is a weak acid and NH_4OH is a weak base.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is false but R is true.

(iv) Both A and R are false.

50. ***Assertion (A):*** In the dissociation of PCl_5 at constant pressure and temperature addition of helium at equilibrium increases the dissociation of PCl_5 .

Reason (R) : Helium removes Cl_2 from the field of action.

(i) Both A and R are true and R is correct explanation of A.

(ii) Both A and R are true but R is not correct explanation of A.

(iii) A is true but R is false.

(iv) Both A and R are false.

VI. Long Answer Type

51. How can you predict the following stages of a reaction by comparing the value of K_c and Q_c?

(i) Net reaction proceeds in the forward direction.

(ii) Net reaction proceeds in the backward direction.

(iii) No net reaction occurs.

52. On the basis of Le Chatelier principle explain how temperature and pressure can be adjusted to increase the yield of ammonia in the following reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.38 \text{ kJ mol}^{-1}$

What will be the effect of addition of argon to the above reaction mixture at constant volume?

53. A sparingly soluble salt having general formula $A_x^{p+}B_y^{q-}$ and molar solubility S is in equilibrium with its saturated solution. Derive a relationship between the solubility and solubility product for such salt.

54. Write a relation between ΔG and Q and define the meaning of each term and answer the following :

(a) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$.

(b) Explain the effect of increase in pressure in terms of reaction quotient Q. for the reaction : $CO\ (g) + 3H_2\ (g) \rightleftharpoons CH_4\ (g) + H_2O\ (g)$

ANSWERS

I. Multiple Choice Questions (Type-I)

1. (iv) 2. (iv) 3. (iii) 4. (ii) 5. (ii) 6. (i)

7. (iii) 8. (iv) 9. (i) 10. (iii) 11. (iii) 12. (iv)

13. (i) 14. (iii)

15. (i) $\Delta G^{\ominus} = 0$

Justification : $\Delta G^{\ominus} = -RT \ln K$

At the stage of half completion of reaction [A] = [B], Therefore, $K = 1$.

Thus, $\Delta G^{\ominus} = 0$

16. (i), *Justification*: According to Le-Chatelier's principle, at constant temperature, the equilibrium composition will change but K will remain same.

17. (ii)

18. (i)

19. (iv)

II. Multiple Choice Questions (Type-II)

20. (i), (iii) and (iv)

Justification : (i) K increases with increase in temperature.

(iii) $Q_c > K$, Therefore, reaction proceeds in the backward direction.

(iv) $\Delta n > 0$, Therefore, $\Delta S > 0$.

21. (i) and (iv)

III. Short Answer Type

22. HCl Cl^-
acid   conjugate base
H_2O H_3O^+
base   conjugate acid

23.
- Sugar does not ionise in water but NaCl ionises completely in water and produces Na^+ and Cl^- ions.
- Conductance increases with increase in concentration of salt due to release of more ions.

24. BF_3 acts as a Lewis acid as it is electron deficient compound and coordinate bond is formed as given below :

$H_3N : \rightarrow BF_3$

25. - Order of extent of ionisation at equilibrium is as follows :

    Dimethylamine > Ammonia > Pyridine > Urea

    - Since dimethylamine will ionise to the maximum extent it is the strongest base out of the four given bases.

26. $RO^- > OH^- > CH_3COO^- > Cl^-$

27. $NH_4Cl < C_6H_5COONH_4 < KNO_3 < CH_3COONa$

28. At a given time the reaction quotient Q for the reaction will be given by the expression.

$$Q = \frac{[H_2][I_2]}{[HI]^2}$$

$$= \frac{1 \times 10^{-5} \times 1 \times 10^{-5}}{(2 \times 10^{-5})^2} = \frac{1}{4}$$

$$= 0.25 = 2.5 \times 10^{-1}$$

As the value of reaction quotient is greater than the value of K_c i.e. 1×10^{-4} the reaction will proceed in the reverse direction.

29. Concentration of 10^{-8} mol dm^{-3} indicates that the solution is very dilute. Hence, the contribution of H_3O^+ concentration from water is significant and should also be included for the calculation of pH.

30. (i) pH = 5

$[H^+] = 10^{-5}$ mol L^{-1}

On 100 times dilution

$[H^+] = 10^{-7}$ mol L^{-1}

On calculating the pH using the equation pH = – log $[H^+]$, value of pH comes out to be 7. It is not possible. This indicates that solution is very dilute. Hence,

Total hydrogen ion concentration = $[H^+]$

= Contribution of H_3O^+ ion concentration of acid + Contribution of H_3O^+ ion concentration of water

= $10^{-7} + 10^{-7}$.

pH = 2×10^{-7} = 7 – log 2 = 7 – 0.3010 = 6.6990

31.

	$\mathbf{BaSO_4\,(s)}$ $\rightleftharpoons$	$\mathbf{Ba^{2+}}$ **(*aq*)** +	$\mathbf{SO_4^{2-}}$ **(*aq*)**
At t = 0	1	0	0
At equilibrium in water	1–S	S	S
At equilibrium in the presence of sulphuric acid	1–S	S	(S+0.01)

K_{sp} for $BaSO_4$ in water = $[Ba^{2+}]\,[SO_4^{2-}]$ = (S) (S) = S^2

But S = 8×10^{-4} mol dm^{-3}

$\therefore\ K_{sp} = (8\times10^{-4})^2 = 64 \times 10^{-8}$ ... (1)

The expression for K_{sp} in the presence of sulphuric acid will be as follows :

K_{sp} = (S) (S + 0.01) ... (2)

Since value of K_{sp} will not change in the presence of sulphuric acid, therefore from (1) and (2)

$(S)\,(S + 0.01) = 64 \times 10^{-8}$

$S^2 + 0.01\,S = 64 \times 10^{-8}$

$S^2 + 0.01\,S - 64 \times 10^{-8} = 0$

$$S = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4 \times 64 \times 10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4} + (256 \times 10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4}\,(1 + 256 \times 10^{-2})}}{2}$$

$$= \frac{-0.01 \pm\ 10^{-2}\sqrt{1 + 0.256}}{2}$$

$$= \frac{-0.01 \pm\ 10^{-2}\sqrt{1.256}}{2}$$

$$= \frac{-10^{-2} + (1.12 \times 10^{-2})}{2}$$

$$= \frac{(-1+1.12)\ \times\ 10^{-2}}{2} = \frac{0.12}{2} \times 10^{-2}$$

$$= 6 \times 10^{-4}\ \text{mol dm}^{-3}$$

32. pH of HOCl = 2.85

But, – pH = log $[H^+]$

$\therefore$ – 2.85 = log $[H^+]$

$\bar{3}.15 = \log [H^+]$

$[H^+] = 1.413 \times 10^{-3}$

For weak mono basic acid $[H^+] = \sqrt{K_a \times C}$

$$K_a = \frac{[H^+]^2}{C} = \frac{(1.413 \times 10^{-3})^2}{0.08}$$

$$= 24.957 \times 10^{-6} = 2.4957 \times 10^{-5}$$

33. pH of Solution A = 6

Therefore, concentration of $[H^+]$ ion in solution A = 10^{-6} mol L^{-1}

pH of Solution B = 4

Therefore, Concentration of $[H^+]$ ion concentration of solution B = 10^{-4} mol L^{-1}

On mixing one litre of each solution, total volume = 1L + 1L = 2L

Amount of H^+ ions in 1L of Solution A= Concentration × volume V

= 10^{-6} mol × 1L

Amount of H^+ ions in 1L of solution B = 10^{-4} mol × 1L

$\therefore$ Total amount of H^+ ions in the solution formed by mixing solutions A and B is (10^{-6} mol + 10^{-4} mol)

This amount is present in 2L solution.

$$\therefore \text{ Total } [H^+] = \frac{10^{-4}(1+0.01)}{2} = \frac{1.01 \times 10^{-4}}{2} \text{mol L}^{-1} = \frac{1.01 \times 10^{-4}}{2} \text{ mol L}^{-1}$$

$$= 0.5 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 5 \times 10^{-5} \text{ mol L}^{-1}$$

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

$$= -[\log 5 + (-5 \log 10)]$$

$$= -\log 5 + 5$$

$$= 5 - \log 5$$

$$= 5 - 0.6990$$

$$= 4.3010 = 4.3$$

34. Let S be the solubility of $Al(OH)_3$.

	$Al(OH)_3$ ⇌	**Al^{3+} (aq) +**	**$3OH^-$ (aq)**
Concentration of species at t = 0	1	0	0
Concentration of various species at equilibrium	1–S	S	3S

$K_{sp} = [Al^{3+}]\,[OH^-]^3 = (S)\,(3S)^3 = 27\,S^4$

$$S^4 = \frac{K_{sp}}{27} = \frac{27 \times 10^{-11}}{27 \times 10} = 1 \times 10^{-12}$$

$S = 1 \times 10^{-3}\ \text{mol L}^{-1}$

(i) **Solubility of $Al(OH)_3$**

Molar mass of Al $(OH)_3$ is 78 g. Therefore,

Solubility of Al $(OH)_3$ in g $L^{-1} = 1 \times 10^{-3} \times 78\ \text{g L}^{-1} = 78 \times 10^{-3}\ \text{g L}^{-1}$

$= 7.8 \times 10^{-2}\ \text{g L}^{-1}$

(ii) **pH of the solution**

$S = 1 \times 10^{-3}\ \text{mol L}^{-1}$

$[OH^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$

pOH = 3 – log 3

pH = 14 – pOH = 11 + log 3 = 11.4771

35. K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$

Let S be the solubility of $PbCl_2$.

	$PbCl_2$ (s) ⇌	**Pb^{2+} (aq) +**	**$2Cl^-$ (aq)**
Concentration of species at t = 0	1	0	0
Concentration of various species at equilibrium	1–S	S	2S

$K_{sp} = [Pb^{2+}]\,[Cl^-]^2 = (S)\,(2S)^2 = 4S^3$

$K_{sp} = 4S^3$

$$S^3 = \frac{K_{sp}}{4} = \frac{3.2 \times 10^{-8}}{4}\ \text{mol L}^{-1} = 8 \times 10^{-9}\ \text{mol L}^{-1}$$

$$S = \sqrt[3]{8 \times 10^{-9}} = 2 \times 10^{-3}\ \text{mol L}^{-1} \quad \therefore\ S = 2 \times 10^{-3}\ \text{mol L}^{-1}$$

Molar mass of $PbCl_2$ = 278

$\therefore$ Solubility of $PbCl_2$ in g $L^{-1} = 2 \times 10^{-3} \times 278$ g L^{-1}

$= 556 \times 10^{-3}$ g L^{-1}

$= 0.556$ g L^{-1}

To get saturated solution, 0.556 g of $PbCl_2$ is dissolved in 1 L water.

0.1 g $PbCl_2$ is dissolved in $\dfrac{0.1}{0.556}$ L = 0.1798 L water.

To make a saturated solution, dissolution of 0.1 g $PbCl_2$ in 0.1798 L $\approx$ 0.2 L of water will be required.

37. $\Delta_r H^{\ominus} = \Delta_f H^{\ominus}[CaO(s)] + \Delta_f H^{\ominus}[CO_2(g)] - \Delta_f H^{\ominus}[CaCO_3(s)]$

$\therefore$ $\Delta_r H^{\ominus} = 178.3$ kJ mol^{-1}

The reaction is endothermic. Hence, according to Le-Chatelier's principle, reaction will proceed in forward direction on increasing temperature.

IV. Matching Type

38. (i) → (b) (ii) → (d) (iii) → (c) (iv) → (a)
39. (i) → (d) (ii) → (c) (iii) → (b)
40. (i) → (d) (ii) → (a) (iii) → (b)
41. (i) → (b) (ii) → (e) (iii) → (c) (iv) → (d)
42. (i) → (c) (ii) → (a) (iii) → (b)
43. (i) → (b) and (c) (ii) → (d) (iii) → (a)

V. Assertion and Reason Type

44. (i) 45. (i) 46. (ii) 47.(iii) 48. (i) 49. (iii)

50. (iv)

VI. Long Answer Type

51. (i) $Q_c < K_c$

(ii) $Q_c > K_c$

(iii) $Q_c = K_c$

where, Q_c is reaction quotient in terms of concentration and K_c is equilibrium constant.

53. [**Hint :** $A_x^{p+}B_y^{q-} \rightleftharpoons x\,A^{p+}\,(aq) + y\,B^{q-}\,(aq)$

S moles of A_xB_y dissolve to give x S moles of A^{p+} and y S moles of B^{q-}.]

54. $\Delta G = \Delta G^{\ominus} + RT\ln Q$

$\Delta G^{\ominus}$ = Change in free energy as the reaction proceeds

ΔG = Standard free energy change

Q = Reaction quotient

R = Gas constant

T = Absolute temperature

Since $\Delta G^{\ominus} = -\mathrm{R}T\ln K$

$$\therefore \quad \Delta G = -RT\ln K + \mathrm{R}T\ln Q = \mathrm{RT}\ \ln\frac{Q}{K}$$

If $Q < K$, ΔG will be negative. Reaction proceeds in the forward direction.

If $Q = K$, $\Delta G = 0$, no net reaction.

[**Hint:** Next relate Q with concentration of CO, H_2, CH_4 and H_2O in view of reduced volume (increased pressure). Show that $Q < \mathrm{K}$ and hence the reaction proceeds in forward direction.]