Equilibrium

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. For the following three reactions (i), (ii) and (iii), equilibrium constants are given
(i) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}; K_1$
(ii) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}; K_2$
(iii) $CH_{4(g)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 4H_{2(g)}; K_3$
Which of the following relations is correct?
(a) $K_3 K_2^3 = K_1^2$
(b) $K_1 \sqrt{K_2} = K_3$
(c) $K_2 K_3 = K_1$
(d) $K_3 = K_1 K_2$

2. If K_1 and K_2 are the respective equilibrium constants for the two reactions,
$XeF_{6(g)} + H_2O_{(g)} \rightleftharpoons XeOF_{4(g)} + 2HF_{(g)}$
$XeO_{4(g)} + XeF_{6(g)} \rightleftharpoons XeOF_{4(g)} + XeO_3F_{2(g)}$
The equilibrium constant for the reaction,
$XeO_{4(g)} + 2HF_{(g)} \rightleftharpoons XeO_3F_{2(g)} + H_2O_{(g)}$ is
(a) K_1K_2
(b) K_1/K_2^2
(c) K_2/K_1
(d) K_1/K_2

3. For the reversible reaction,

$$A_{(s)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)},\ \Delta G^\circ = -350 \text{ kJ},$$

which one of the following statements is true?
(a) The reaction is thermodynamically nonfeasible.
(b) The entropy change is negative.
(c) Equilibrium constant is greater than one.
(d) The reaction should be instantaneous.

4. In a chemical equilibrium the rate constant of backward reaction is 3.2×10^{-2} and the equilibrium constant is 2^{-5}. The rate constant of forward reaction is
(a) 1×10^{-3}
(b) 2×10^{-2}
(c) 8×10^{-2}
(d) 4×10^{-2}

5. It is not possible to attain equilibrium in
(a) closed system
(b) isolated system
(c) open system
(d) none of these.

6. Conjugate base for Bronsted acids H_2O and HF are
(a) H_3O^+ and H_2F^+, respectively
(b) OH^- and H_2F^+, respectively
(c) H_3O^+ and F^-, respectively
(d) OH^- and F^-, respectively.

7. For the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at 300 K, the value of ΔG is $-690.9\ R$. The equilibrium constant value for the reaction at that temperature is (R is gas constant)
(a) 10 atm^{-1}
(b) 10 atm
(c) 10
(d) 1

8. The solubility product of aluminium sulphate is given by the expression
(a) $4s^3$
(b) $6912s^7$
(c) s^2
(d) $108s^5$

9. In a reversible chemical reaction at equilibrium, if the concentration of any one of the reactants is doubled, then the equilibrium constant will
(a) also be doubled
(b) be halved
(c) remain the same
(d) become one-fourth.

10. Identify a species which is 'NOT' a Bronsted acid but a Lewis acid.
(a) BF_3
(b) H_3O^+
(c) NH_3
(d) HCl

11. For the system $3A + 2B \rightleftharpoons C$,the expression for equilibrium constant K is
(a) $\dfrac{[3A] \times [2B]}{[C]}$
(b) $\dfrac{[A]^3 \times [B]}{[C]}$
(c) $\dfrac{C}{[A]^3 \times [B]^2}$
(d) $\dfrac{[C]}{[3A] \times [2B]}$

12. Among the following, the one which can act as both Bronsted acid as well as Bronsted base is
(a) H_3PO_4
(b) $AlCl_3$
(c) CH_3COO^-
(d) H_2O

13. The solubility of $Ca_3(PO_4)_2$ in water is y moles/litre. Its solubility product is
(a) $6y^4$
(b) $36y^4$
(c) $64y^5$
(d) $108y^5$

14. Which of the following is not a characteristic of equilibrium?
(a) Rate is equal in both directions.
(b) Measurable quantities are constant at equilibrium.

(c) Equilibrium occurs in reversible condition.

(d) Equilibrium occurs only in an open vessel at constant temperature

15. When the rate of formation of reactants is equal to the rate of formation of products, this is known as,

(a) chemical reaction

(b) chemical equilibrium

(c) chemical kinetics

(d) none of these.

16. Which of the following options will be correct for the stage of half completion of the reaction $X \rightleftharpoons Y$.

(a) $\Delta G^\circ = 0$ (b) $\Delta G^\circ > 0$

(c) $\Delta G^\circ < 0$ (d) $\Delta G^\circ = -RT \ln 2$

17. In Bronsted–Lowry concept of acid-base, H^+ donor is a/an

(a) acid

(b) basic

(c) exclusively amphoteric substance

(d) hydroxide acceptor.

18. In HS^-, I^-, $R - NH_2$, NH_3 order of proton accepting tendency will be

(a) $I^- > NH_3 > R - NH_2 > HS^-$

(b) $NH_3 > R - NH_2 > HS^- > I^-$

(c) $R - NH_2 > NH_3 > HS^- > I^-$

(d) $HS^- > R - NH_2 > NH_3 > I^-$

19. Equilibrium constants are given for the following reactions. Out of the following, which is farthest towards completion?

(a) $K = 100$ (b) $K = 0.1$

(c) $K = 0.01$ (d) $K = 1$

20. Of the following the incorrect relation is

(a) $\Delta G = \Delta G^\circ + RT\ln K$ (b) $\Delta G^\circ = -RT\ln K$

(c) $\Delta G^\circ = \Delta G + RT\ln K$ (d) $K = e^{-\Delta G/RT}$

21. Calculate K_c for the reversible process given below if $K_p = 167$ and $T = 800°C$.

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

(a) 1.95 (b) 1.85

(c) 1.89 (d) 1.60

22. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium,

$$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$$

would be

(a) 3.0×10^{-5} (b) 3.0×10^{-4}

(c) 3.0×10^{4} (d) 3.0×10^{5}

23. What will be the solubility product of AX_3?

(a) $27S^4$ (b) $4S^3$

(c) $36S^4$ (d) $9S^3$

24. Which of the following is a characteristic of reversible reaction?

(a) It never proceeds to completion.

(b) It can be influenced by a catalyst.

(c) It proceeds only in the forward direction.

(d) Number of moles of reactants and products are equal.

25. For the reaction, $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_p = K_c(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality)

(a) 1 (b) -1

(c) $-\frac{1}{2}$ (d) $\frac{1}{2}$

26. Which of these is least likely to act as a Lewis base?

(a) BF_3 (b) PF_3

(c) CO (d) F^-

27. Which of the following solutions will have pH close to 1.0?

(a) 100 mL of M/10 HCl + 100 mL of M/10 NaOH

(b) 55 mL of M/10 HCl + 45 mL of M/10 NaOH

(c) 10 mL of M/10 HCl + 90 mL of M/10 NaOH

(d) 75 mL of M/10 HCl + 25 mL of M/10 NaOH

28. Using the Gibbs' energy change, $\Delta G = +63.3$ kJ, for the following reaction,

$$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+_{(aq)} + CO^{2-}_{3(aq)}$$

the K_{sp} of $Ag_2CO_{3(s)}$ in water at 25°C is

($R = 8.314\ J\ K^{-1}\ mol^{-1}$)

(a) 3.2×10^{-26} (b) 8.0×10^{-12}

(c) 2.9×10^{-3} (d) 7.9×10^{-2}

29. Consider the general hypothetical reaction,

$$A_{(s)} \rightleftharpoons 2B_{(g)} + 3C_{(g)}$$

If the concentration of C at equilibrium is doubled, then after the equilibrium is re-established, the concentration of B will be

(a) two times the original value

(b) one half of its original value

(c) $1/2\sqrt{2}$ times the original value

(d) $2\sqrt{2}$ times the original value.

30. The pH of 10^{-4} M KOH solution will be

(a) 4
(b) 11
(c) 10.5
(d) 10

31. If the pH increases from 5 to 7, then acidic strength decreases _________ times.

(a) 2
(b) 20
(c) 10
(d) 100

32. The reaction quotient, Q_c is useful in predicting the direction of the reaction. Which of the following is incorrect?

(a) If $Q_c > K_c$, net reaction goes from right to left.
(b) If $Q_c < K_c$, net reaction goes from left to right.
(c) If $Q_c = K_c$, no net reaction occurs.
(d) If $Q_c > K_c$, net reaction goes from left to right.

33. $\frac{K_p}{K_c}$ for following reaction will be

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

(a) RT
(b) $\frac{1}{RT}$
(c) $\frac{1}{\sqrt{RT}}$
(d) $\frac{RT}{2}$

34. Buffer solutions have constant acidity and alkalinity because

(a) these give unionised acid or base on reaction with added acid or alkali
(b) acids and alkalies in these solutions are shielded from attack by other ions
(c) they have large excess of H^+ or OH^- ions
(d) they have fixed value of pH.

35. The equilibrium constant, K_p for the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \text{ is 1.6 at } 200°C.$$

The pressure at which PCl_5 will be 50% dissociated at 200°C is

(a) 3.2 atm
(b) 4.8 atm
(c) 2.4 atm
(d) 6.4 atm

36. In the reaction;

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-_{(aq)}$, if the concentration of OH^- ions is decreased by $\frac{1}{4}$ times, then the equilibrium concentration of Fe^{3+} will increase by

(a) 8 times
(b) 16 times
(c) 64 times
(d) 4 times.

37. The value of ΔH for the reaction

$X_{2(g)} + 4Y_{2(g)} \rightleftharpoons 2XY_{4(g)}$ is less than zero.

Formation of $XY_{4(g)}$ will be favoured at

(a) high temperature and high pressure
(b) low pressure and low temperature
(c) high temperature and low pressure
(d) high pressure and low temperature.

38. In which of the following equilibrium K_c and K_p are not equal?

(a) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$
(b) $SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$
(c) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
(d) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

39. Which will make basic buffer?

(a) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
(b) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH
(c) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
(d) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH

40. 4 moles of A are mixed with 4 moles of B, when 2 moles of C and D are formed at equilibrium according to the reaction,

$$A + B \rightleftharpoons C + D$$

the value of equilibrium constant is

(a) 4
(b) 1
(c) 1/2
(d) 1/4

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 41 to 45.

Le Chatelier's principle is also known as the equilibrium law, used to predict the effect of change on a system at chemical equilibrium. This principle states that equilibrium adjust the forward and backward reactions in such a way as to accept the change affecting the equilibrium condition. When factor like concentration, pressure, temperature, inert gas that affect equilibrium are changed, the equilibrium will shift in that direction where the effects that caused by these changes are nullified. This principle is also used to manipulate reversible reaction in order to obtain suitable outcomes.

41. Which one of the following conditions will favour maximum formation of the product in the reaction

$A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)}, \Delta_r H = -X$ kJ ?

(a) Low temperature and high pressure
(b) Low temperature and low pressure
(c) High temperature and high pressure
(d) High temperature and low pressure

42. In which one of the following equilibria will the point of equilibrium shift to left when the pressure of the system is increased?

(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
(b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
(c) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
(d) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$

43. For the reversible reaction,

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + \text{heat}$

The equilibrium shifts in forward direction

(a) by increasing the concentration of $NH_{3(g)}$
(b) by decreasing the pressure
(c) by decreasing the concentrations of $N_{2(g)}$ and $H_{2(g)}$
(d) by increasing pressure and decreasing temperature.

44. Favourable conditions for manufacture of ammonia by the reaction,

$N_2 + 3H_2 \rightleftharpoons 2NH_3; \Delta H = -21.9$ kcal are

(a) low temperature, low pressure and catalyst
(b) low temperature, high pressure and catalyst
(c) high temperature, low pressure and catalyst
(d) high temperature, high pressure and catalyst.

45. $X + Y \rightleftharpoons P + Q$

For the above equilibrium, the reactant concentration is doubled, what would happen then to equilibrium constant?

(a) Remains constant
(b) Be doubled
(c) Be halved
(d) Cannot be predicted

Case II : Read the passage given below and answer the following questions from 46 to 50.

Reactants and products coexist at equilibrium, so that the conversion of reactant to products is always less than 100%. Equilibrium reaction may involve the decomposition of a covalent (non-polar) reactant or ionization of ionic compound into their ions in polar solvents. Ostwald dilution law is the application of the law of mass action to the weak electrolytes in solution.

A binary electrolyte AB which dissociates into A^+ and B^- ions i.e.

$AB \rightleftharpoons A^+ + B^-$

for every weak electrolyte, Since $\alpha << 1$

$(1 - \alpha) = 1$

$$K = C\,\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}} \Rightarrow \alpha = \sqrt{KV}.$$

46. A monobasic weak acid solution has a molarity of 0.005 M and pH of 5. What is its percentage ionization in this solution?

(a) 2.0 (b) 0.2
(c) 0.5 (d) 0.25

47. Calculate ionisation constant for pyridinium hydrogen chloride. (Given that H^+ ion concentration is 3.6×10^{-4} M and its concentration is 0.02 M.)

(a) 6.48×10^{-2} (b) 6×10^{-6}
(c) 1.5×10^{-9} (d) 12×10^{-8}

48. The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 $K(K_w = 10^{-14})$ is

(a) 9.525×10^{-8} M (b) 1.0×10^{-8} M
(c) 1.0×10^{-6} M (d) 1.0525×10^{-7} M

49. Ostwald dilution law is applicable to

(a) weak electrolytes
(b) non-electrolyte
(c) strong electrolyte
(d) all type of electrolyte.

50. If α is the fraction of HI dissociated at equilibrium in the reaction :

$2HI \rightleftharpoons H_2 + I_2$

then starting with 2 mol of HI, the total number of moles of reactants and products at equilibrium are

(a) 1 (b) 2
(c) $1 + \alpha$ (d) $2 + 2\alpha$

Assertion & Reasoning Based MCQs

For question numbers 51-60, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

51. Assertion : At 25°C the pH of 10^{-7} M HCl is 6.69.

Reason : pH of acidic solution is always below 7 at 25°C.

52. Assertion : The value of K_w at 25°C is 1.0×10^{-14} mol^2 dm^{-6}.

Reason : K_w of water changes with change in temperature.

53. Assertion : K_P can be equal to, less than or greater than the value of K_c.

Reason : $K_p = K_c(RT)^{\Delta n}$ where Δn is the change in the number of moles of gaseous reactants and products.

54. Assertion : The active mass of pure solid is taken unity.

Reason : The active mass of pure solids depends on density and molecular mass. The density and molecular mass of pure solids are constant.

55. Assertion : H_3PO_4 is a stronger acid than $H_2PO_4^-$

Reason : pK_{a_1} is greater than pK_{a_2} for H_3PO_4.

56. Assertion : For the equilibrium mixture $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$ if the volume is decreased, reaction proceeds in the forward direction.

Reason : For the methanation reaction (above), decrease in volume causes $Q_c > K_c$.

57. Assertion : At constant temperature, the pressure of the gas is proportional to its concentration.

Reason : $K_P = K_c$ for all reactions.

58. Assertion : For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason : Equilibrium constant is independent of temperature.

59. Assertion : On dilution, the solubility of $BaSO_4$ increases.

Reason : On dilution, K_{sp} increases.

60. Assertion : The equilibrium constant does not change on addition of catalyst.

Reason : A catalyst provides an alternative path of lower activation energy for conversion of reactants to products.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. 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 $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

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

3. 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^-

4. 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.

5. 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.

6. Give two important characteristics of chemical equilibrium.

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

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

8. Give relation between $[A]$ and $[B]$ for the stage of half completion of the reaction $A \rightleftharpoons B$.

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

Short Answer Type Questions (SA-I)

10. Equilibrium constant for a reaction is 10. What will be the equilibrium constant for the reverse reaction?

11. Write the expression for the equilibrium constant K_c for the following equilibrium :

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

12. For the system $3A + 2B \rightleftharpoons C$,the expression for equilibrium constant K is?

13. Differentiate between homogeneous and heterogeneous equilibrium giving examples.

14. 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

15. Write expressions for K_p and K_c for the decomposition reaction of calcium carbonate.

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

17. Write the relation between Q_c and K_c for reverse reaction.

18. 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

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$

19. What will be the conjugate bases for the Bronsted acids: HF, H_2SO_4 and HCO_3^-?

Short Answer Type Questions (SA-II)

20. Calculate (a) ΔG and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K.

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}$$

where $\Delta_f G^\circ (NO_2) = 52.0$ kJ mol^{-1},
$\Delta_f G^\circ (NO) = 87.0$ kJ mol^{-1},
$\Delta_f G^\circ (O_2) = 0$ kJ mol^{-1}

21. 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?

22. In 1 L saturated solution of AgCl $[K_{sp} = 1.6 \times 10^{10}]$, 0.1 mol of CuCl $[K_{sp} = 1.0 \times 10^{-6}]$ is added. Find out the resultant concentration of Ag^+ in the solution.

23. Reaction between N_2 and O_2 takes place as follows :

$$2N_{2(g)} + O_{2(g)} \rightleftharpoons 2N_2O_{(g)}$$

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.

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

25. Define Le-Chatelier's Principle. What is the effect of :

(i) addition of H_2

(ii) removal of CO

on the equilibrium :

$$2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}?$$

26. The value of ΔG° for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of K_c at 298 K.

27. For the reaction,

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)};\ \Delta H_r = -92\ \text{kJ/mol}$$

predict the direction of the reaction when

(i) pressure is doubled

(ii) temperature is doubled.

28. What is the effect of increase of temperature on the pH of a buffer solution?

29. Equilibrium constant, K_c for the reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}\ \text{at 500 K is 0.061.}$$

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?

30. (i) Define Lewis acids and bases with example.

(ii) The value of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2×10^{-15} and 6×10^{-17}. Which salt is more soluble and why?

31. Which of the following combinations would result in the formation of a buffer solution?

(i) $NH_4Cl + NH_3$

(ii) $CH_3COOH + HCl$

(iii) $CH_3COONa + CH_3COOH$

(iv) $NH_3 + HCl$ in the molar ratio of 2 : 1

(v) HCl + NaOH

32. 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.

33. 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.

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

What will be the effect on K. if the total pressure at which the equilibrium is established, is increased without changing the temperature?

34. The solubility product of AgCl is 1.5×10^{-10}. Predict whether there will be any precipitation by mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M $AgNO_3$ solution.

35. What is the pH of 0.001 M aniline solution? The ionisation constant of aniline is 4.27×10^{-10}. Calculate the degree of ionisation of aniline in the solution. Also calculate the ionisation constant of the conjugate acid of aniline.

Long Answer Type Questions (LA)

36. (i) Point out the differences between ionic product and solubility product.

(ii) The solubility of AgCl in water at 298 K is 1.06×10^{-5} mole per litre. Calculate its solubility product at this temperature .

37. (i) Derive the relationship between pK_w, pH and pOH starting from ionisation constant of water, K_w. What is the numerical value of pK_w at 298 K?

(ii) If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of K^+ and OH^-. What is its pH? (Give atomic masses K = 39, O = 16, H = 1)

38. (i) What is common ion effect?

(ii) Write the K_{sp} expressions for Ag_2CrO_4 and zirconium phosphate.

(iii) Calculate the pH of 0.005 M HCl solution.

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

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)};\ \Delta_r H = 124.0\ \text{kJ mol}^{-1}$$

(a) Write an expression for K_c for the reaction.

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

(c) What would be the effect on K_c if

(i) the pressure is increased

(ii) the temperature is increased?

40. One mole of N_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (d) : $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

$$K_1 = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad \text{...(i)}$$

$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$

$$K_2 = \frac{[CO][H_2]^3}{[CH_4][H_2O]} \quad \text{...(ii)}$$

$CH_{4(g)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 4H_{2(g)}$

$$K_3 = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2} \quad \text{...(iii)}$$

From equations (i), (ii) and (iii) ; $K_3 = K_1 \times K_2$

2. (c) : $K_1 = \dfrac{[XeOF_4][HF]^2}{[XeF_6][H_2O]}$ ...(i)

$$K_2 = \frac{[XeOF_4][XeO_3F_2]}{[XeO_4][XeF_6]} \quad \text{...(ii)}$$

Dividing Eq. (ii) by (i) we have,

$$\frac{K_2}{K_1} = \frac{[XeO_3F_2][H_2O]}{[XeO_4][HF]^2} = K'$$

3. (c) : For a reversible reaction,

$A_{(s)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$, $\Delta G° = -350$ kJ

Standard free energy change can be thermodynamically calculated as,

when $\Delta G° < 0$, *i.e.*, negative, then $K_c > 1$. In this case forward reaction is feasible. The reaction is spontaneous reaction.

4. (a) : In a chemical equilibrium

Equilibrium constant,

$$K = \frac{\text{Rate constant of forward reaction, } k_f}{\text{Rate constant of backward reaction, } k_b}$$

$$\therefore \quad k_f = k_b \times K = 3.2 \times 10^{-2} \times 2^{-5} = \frac{3.2 \times 10^{-2}}{32} = 1 \times 10^{-3}$$

5. (c) : In open system equilibrium cannot be attained.

6. (d) :

Bronsted acid	Conjugate base
H_2O	OH^-
HF	F^-

7. (a) : $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$$\Delta G = -RT \ln K \Rightarrow -690.9\,R = -RT \ln K \text{ or } \frac{690.9}{300} = \ln K$$

$$2.303 = \ln K \Rightarrow 2.303 = 2.303 \log K,\ K = 10^1$$

$$K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}} \times \frac{atm^2}{atm^3} = atm^{-1}$$

$\therefore K_p = 10$ atm^{-1}

8. (d) : $Al_2(SO_4)_3 \rightleftharpoons \underset{2s}{2Al^{3+}} + \underset{3s}{3SO_4^{2-}}$

$K_{sp} = (2s)^2 (3s)^3 = 4 \times 27s^5 = 108s^5$

9. (c) : Equilibrium constant depends only on temperature.

10. (a) : Molecules having a central atom with incomplete octet, act as a Lewis acid not Brönsted acid (proton donor). In BF_3, B is having six electrons.

11. (c) : $K = \dfrac{[C]}{[A]^3[B]^2}$

12. (d) : H_2O can accept or give a proton hence, it acts both as Bronsted acid as well as Bronsted base.

$H_2O + H^+ \longrightarrow H_3O^+$, $H_2O \longrightarrow H^+ + OH^-$

13. (d) : $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

Concentrations of various species at equilibrium

$Ca^{2+} = 3y$, $PO_4^{3-} = 2y$

Solubility product $= (3y)^3 (2y)^2 = 27y^3 \times 4y^2 = 108y^5$

14. (d) : Equilibrium state can only be achieved if a reversible reaction is carried out in a closed vessel.

15. (b) : At equilibrium, rate of forward reaction is equal to rate of backward reaction.

16. (a) : $X \rightleftharpoons Y$

$\Delta G° = -RT \ln K$

At the stage of half completion of reaction $[X] = [Y]$.

Therefore, $K = 1$. Thus, $\Delta G° = 0$.

17. (a)

18. (c) : Proton accepting tendency is known as the strength of basicity.

In $R-\ddot{N}H_2$, N has lone pair of electrons which intensify due to electron releasing R group and increase the tendency to donate lone pair of electrons to H^+.

Secondly, as the size of the ion increases there is less attraction for H^+ to form weaker bonds with H – atom and are less basic. The order of the given series is: $RNH_2 > NH_3 > HS^- > I^-$.

19. (a) : Higher the value of equilibrium constant, the reaction is farther towards completion.

20. (c) : $\Delta G = \Delta G° + RT \ln K$

at equilibrium $\Delta G = 0$

$\Delta G^\circ = -RT \ln K$ and $K = e^{-\Delta G^\circ/RT}$

21. (c) : $K_p = K_c(RT)^{\Delta n}$; $\Delta n = n_p - n_r = 1$

$$K_p = K_c(0.0821 \times 1073) \Rightarrow K_c = \frac{167}{0.0821 \times 1073} = 1.891$$

22. (c) : Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.5\times10^{-5}$$

$HCN \rightleftharpoons H^+ + CN^-$

$$K_2 = \frac{[CN^-][H^+]}{[HCN]} = 4.5\times10^{-10}$$

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$

$$K = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$$

$$K = \frac{K_1}{K_2} = \frac{1.5\times10^{-5}}{4.5\times10^{-10}} \approx 0.3\times10^5 \text{ or } K = 3\times10^4$$

23. (a) : $AX_3 \rightleftharpoons \underset{S}{A^{3+}} + \underset{3S}{3X^-}$

$K_{sp} = [A^{3+}]\,[X^-]^3 = (S)\cdot(3S)^3 = 27S^4$

24. (a) : Reversible reaction never goes to completion, rather attains an equilibrium point.

25. (c) : For the reaction, $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$

Using formula, $K_p = K_c(RT)^{\Delta n_g}$

where, Δn_g = no. of products$_{(g)}$ – no. of reactants$_{(g)}$

$$= 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2} = x$$

26. (a) : BF_3 is Lewis acid (electron pair acceptor).

27. (d) : (a) is exact neutralisation. Hence pH = 7

(b) After neutralisation, M/10 HCl left = 10 mL

Total volume = 100 mL

Dilution = 10 times. ∴ $[H^+] = 10^{-2}$ or pH = 2

(c) After neutralisation, M/10 NaOH left = 80 mL

Total volume = 100 mL, pH > 7

(d) After neutralisation, M/10 HCl left = 50 mL

Total volume = 100 mL

Dilution = 2 times

$$\therefore\ [H^+] = \frac{1}{2\times10} = \frac{10^{-1}}{2}\text{ M or pH} = 1.3$$

28. (b) : $\Delta G^\circ = -2.303RT\log K_{sp}$

$63.3\times10^3\text{ J} = -2.303\times8.314\times298\log K_{sp}$

$63.3\times10^3\text{ J} = -5705.84\log K_{sp}$

$$\log K_{sp} = -\frac{63.3\times10^3}{5705.84} = -11.09$$

K_{sp} = antilog (–11.09) = 8.128×10^{-12}

29. (c) : $K = [B_{(g)}]^2[C_{(g)}]^3 = x^2y^3$.

If $[C_{(g)}]$ is doubled *i.e.* = 2*y*, suppose $[B_{(g)}]$ is *z*, then

$$K = z^2(2y)^3 = x^2y^3 \text{ or } z^2 = \frac{1}{8}x^2 \text{ or } z = \frac{1}{\sqrt{8}}x = \frac{1}{2\sqrt{2}}x$$

30. (d) : $\underset{10^{-4}\text{ M}}{KOH} \longrightarrow K^+ + \underset{10^{-4}\text{ M}}{OH^-}$

∴ $[OH^-] = 10^{-4}$ M

∴ $pOH = -\log_{10}[OH^-] = -\log_{10}(10^{-4}) = 4$

∴ pH = 14 – 4 = 10

31. (d) : pH = 5 ⇒ $[H^+] = 10^{-5}$

pH = 7 ⇒ $[H^+] = 10^{-7}$

∴ Acidic strength decreases 10^2 or 100 times.

32. (d)

33. (c) : $\Delta n_g = n_p - n_r = 1 - \frac{3}{2}$

$\Delta n_g = \frac{-1}{2}$. Hence $K_p = K_c(RT)^{-1/2}$

$$\frac{K_p}{K_c} = \frac{1}{(RT)^{1/2}} = \frac{1}{\sqrt{RT}}$$

34. (a)

35. (b) :

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
Initial moles	1	0	0
Moles at eqm.	0.5	0.5	0.5

Total moles at equilibrium = 1.5

Partial pressures $\frac{0.5}{1.5}P$ $\frac{0.5}{1.5}P$ $\frac{0.5}{1.5}P$

(where *P* is the total pressure.)

$$K_p = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} \text{ or } 1.6 = \frac{\left(\frac{0.5}{1.5}P\right)\left(\frac{0.5}{1.5}P\right)}{\left(\frac{0.5}{1.5}P\right)}$$

or $\frac{1}{3}P$ = 1.6 (Given) or *P* = 4.8 atm

36. (c) : $K_c = [x]\,[3x]^3$ ...(i)

When concentration of OH^- ions is decreased by $\frac{1}{4}$ times,

$$K_c = [x']\left[\frac{3x}{4}\right]^3 \qquad ...(ii)$$

Equating eq. (i) and (ii), $x\times(3x)^3 = x'\left(\frac{3x}{4}\right)^3 \Rightarrow 64x = x'$

37. (d) : $X_{2(g)} + 4Y_{2(g)} \rightleftharpoons 2XY_{4(g)}$

Δn_g = –ve and ΔH = –ve

The reaction is favoured in forward direction at low temperature and high pressure

38. (d) : K_p and K_c are related by the equation,

$K_p = K_c(RT)^{\Delta n_g}$ where, Δn_g = difference in the number of moles of products and reactants in the gaseous state.

For $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$, $\Delta n_g = 2 - (1) = 1 \neq 0$

39. (d) : Acid-base titration :

$\underset{10\text{ mmol}}{HCl} + \underset{20\text{ mmol}}{NH_4OH} \longrightarrow NH_4Cl$

∴ HCl is the limiting reagent.

Solution contains NH_4OH (weak base) and NH_4Cl (salt of strong acid and weak base). Therefore, a basic buffer will be formed.

40. (b)

41. (a) : On increasing the pressure and decreasing the temperature, equilibrium will shift in forward direction.

42. (b) : An increase in pressure applied to a system at equilibrium, favours the reaction in the direction that produces smaller no. of gaseous moles. Thus, only in the reaction, $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$ there are smaller no. of gaseous moles on left hand side.

43. (d) : As the forward reaction is exothermic and leads to lowering of pressure (produces lesser number of gaseous moles) hence, according to Le Chatelier's principle, at high pressure and low temperature, the given reversible reaction will shift in forward direction to form more product.

44. (b) : The formation of ammonia is favoured by high pressure which would shift the reaction in the forward direction. The reaction shifts in forward direction at low temperature and more product formation occurs.

Fe acts as a positive catalyst and also shifts the reaction in forward reaction.

45. (a) : Value of equilibrium constant is independent of initial concentration of reactants.

46. (b) : $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}, \quad pH = -\log[H^+]$$

$[H^+] = 10^{-5}$; $[H^+] = [A^-]$

$$K_a = \frac{10^{-5} \times 10^{-5}}{0.005} = 2 \times 10^{-8} \ ; \ \alpha = \sqrt{\frac{K_a}{C}} = 2 \times 10^{-3}$$

Percentage ionization = 0.2

47. (c) : Pyridinium hydrochloride is a salt of weak base and strong acid.

$pH = -\log[H^+] = -\log(3.6 \times 10^{-4}) = 3.44$

Now, $pH = -\frac{1}{2}[\log K_w - \log K_a + \log C)$

$\Rightarrow \quad 3.44 = -\frac{1}{2}[-14 - \log K_a + \log(2 \times 10^{-2})]$

$\Rightarrow \quad 6.88 = 14 + \log K_a + 1.70 \Rightarrow \log K_a = -8.82$

$\Rightarrow \quad K_a = \text{antilog}(-8.82) = 1.5 \times 10^{-9}$

48. (d) : 10^{-8} M HCl = 10^{-8} M H^+

Also from water, $[H^+] = 10^{-7}$ M

$\therefore \quad \text{Total } [H^+] = 10^{-7} + 0.10 \times 10^{-7} = 1.1 \times 10^{-7}$ M

49. (a)

50. (b) : $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

	$2HI_{(g)}$	$H_{2(g)}$	$I_{2(g)}$
Initial moles	2	0	0
At eqm.	$2(1-\alpha)$	α	α

Total number of moles = $2(1-\alpha) + \alpha + \alpha = 2$

51. (a) : Since HCl is a strong acid therefore, its pH should be less than 7. In this case we should also consider the $[H^+]$ which comes from water i.e.

$[H^+] = 10^{-7}$ M from H_2O + [Acid]

$= 10^{-7} + 10^{-7} = 2 \times 10^{-7}$

$pH = -\log[H^+] = -\log(2 \times 10^{-7}) = 6.69$

52. (b) : The value of K_w at 25°C is about 1.0×10^{-14} mol^2 dm^{-6}. Since in pure water, the concentration of H^+ and OH^- ions must be equal to one another *i.e.*, 1.0×10^{-7} mol dm^{-3}.

53. (a) : If $\Delta n = +$ ve, $K_p > K_c$

$\Delta n = -$ve, $K_p < K_c$

$\Delta n = 0, K_p = K_c$

54. (a)

55. (c) : $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; K_{a_1}

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; K_{a_2}

H^+ and $H_2PO_4^-$ are having stronger ion-pair attraction.

Hence, $K_{a_2} < K_{a_1}$ and $pK_{a_2} > pK_{a_1}$.

56. (c) : Volume is decreased, reaction proceeds in the forward direction because decrease in volume increases the number of moles per unit volume. In order to undo the effect the reaction shifts towards the direction which produces lesser number of moles. Concentration increases, Q_c must be lesser than K_c. Suppose volume is decreased to half, concentration becomes 2 times.

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

after decreasing $Q_c = \dfrac{[2CH_4]\cdot[2H_2O]}{[2CO][2H_2]^3}$

$$Q_c = \frac{K_c}{4}$$

57. (c) : $K_p \neq K_c$ for all reactions.

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

Δn = number of moles of gaseous products – number of moles of gaseous reactants in the balanced chemical equation.

So, if for a reaction $\Delta n = 0$, then $K_p = K_c$.

58. (c) : Equilibrium constant is temperature dependent.

59. (c) : K_{sp} remains constant at a particular temperature.

60. (b) : A catalyst increases the rate of forward and backward reactions by same factor hence, does not change the equilibrium constant.

SUBJECTIVE TYPE QUESTIONS

1. The reaction is :

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

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

$$= \frac{\left(\frac{8.13}{20}\text{ mol L}^{-1}\right)^2}{\left(\frac{1.57}{20}\text{ mol L}^{-1}\right)\left(\frac{1.92}{20}\text{ mol L}^{-1}\right)^3} = 2.38 \times 10^3$$

As $Q_c \neq K_c$, the reaction mixture is not in equilibrium.

As $Q_c > K_c$, the net reaction will be in the backward direction.

2. For the concentration of pure solid or pure liquid,

$$\text{Molar conc.} = \frac{\text{Moles of the substance}}{\text{Volume of the substance}}$$

$$= \frac{\text{Mass/Molar mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Molar mass}}$$

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

Since density of pure solid or liquid is constant at constant temperature and molar mass is also constant therefore, their molar concentrations are constant and are included in the equilibrium constant.

3. Conjugate acids of given bases are H_2O, ROH, CH_3COOH, HCl.

Their acidic strength is in the order

$$HCl > CH_3COOH > H_2O > ROH$$

Hence, basic strength is in the order

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

4. (a) : OH^- : OH^- is a Lewis base because it can donate lone pair of electrons.

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

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

(d) BCl_3 : BCl_3 is a Lewis acid because it is electron deficient and can accept a lone pair of electrons.

5. pH of solution $A = 6$

$[H^+] = 10^{-6}$ mol L^{-1}

pH of solution $B = 4$

$[H^+] = 10^{-4}$ mol L^{-1}

On mixing one litre of each solution

Total volume = 1 L + 1 L = 2 L

Total amount of H^+ in 2 L solution formed by mixing solutions A and $B = 10^{-6} + 10^{-4}$ mol

$$\text{Total }[H^+] = \frac{10^{-4}(1+0.01)}{2} = \frac{1.01\times10^{-4}}{2}$$

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

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

$$= -\log5 - (-5\log10) = -\log5 + 5$$

$$= 5 - \log5 = 5 - 0.6990 = 4.3010 = 4.3$$

6. Characteristics of chemical equilibrium are as follows **:**

(i) Chemical equilibrium is dynamic in nature.

(ii) A catalyst does not alter the state of equilibrium.

7.

$$\begin{array}{lccc} & 2ICl_{(g)} \rightleftharpoons & I_{2(g)} + & Cl_{2(g)};\ K_c = 0.14 \\ \text{Initial molar conc.} & 0.78 & 0 & 0 \\ \text{Eqm. molar conc.} & 0.78 - 2x & x & x \end{array}$$

Applying law of chemical equilibrium,

$$K_c = \frac{[I_2][Cl_2]}{[ICl]^2} \Rightarrow 0.14 = \frac{x \cdot x}{(0.78 - 2x)^2}$$

$$x^2 = 0.14(0.78 - 2x)^2$$

or $$\frac{x}{0.78 - 2x} = \sqrt{0.14} = 0.374$$

or $x = 0.292 - 0.748x$

or $1.748x = 0.292$ or $x = 0.167$

Hence at equilibrium, $[I_2] = [Cl_2] = 0.167$ M

$[ICl] = 0.78 - 2 \times 0.167 = 0.446$ M

8. $A \rightleftharpoons B$

At the stage of half completion of reaction $[A] = [B]$.

9. We know that pH = $-\log[H^+]$

$\therefore$ $[H^+]$ = antilog[–pH] = antilog(–3.76)

$= 1.738 \times 10^{-4}$ M

10. $$K'_c = \frac{1}{K_c} = \frac{1}{10} = 0.1$$

11. $$K_c = \frac{[H_{2(g)}]^4[Fe_3O_{4(s)}]}{[Fe_{(s)}]^3[H_2O_{(g)}]^4} = \frac{[H_{2(g)}]^4}{[H_2O_{(g)}]^4}$$

($\because$ concentration of solids is taken as unity)

12. $$K = \frac{[C]}{[A]^3[B]^2}$$

13. Equilibrium is said to be homogeneous if reactants and products are in same phase, *e.g.*,

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

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

Equilibrium is said to be heterogeneous if reactants and products are in different phases, *e.g.*,

$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

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

14. $H_2S \rightleftharpoons H^+ + HS^-$; K_{a_1}

$HS^- \rightleftharpoons H^+ + S^{2-}$; K_{a_2}

$H_2S \rightleftharpoons 2H^+ + S^{2-}$; K_{a_3}

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is $K_{a_3} = K_{a_1} \times K_{a_2}$.

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

$$K_c = \frac{[CaO_{(s)}][CO_{2(g)}]}{[CaCO_{3(s)}]}$$

Taking active masses of solids to be unity,

$K_c = [CO_{2(g)}]$, $K_p = p_{CO_2}$

16. $K_b = \dfrac{K_w}{K_a}$

For F^-, $K_b = \dfrac{10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$

For $HCOO^-$, $K_b = \dfrac{10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$

For CN^-, $K_b = \dfrac{10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$

17. $Q_c > K_c$, for reverse reaction.

18. $\Delta n = n_p - n_r = 2 - 0 = 2$

19.

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

20. $NO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}$

$$\Delta G^\circ = \Delta_f G^\circ(NO_2) - [\Delta_f G^\circ(NO) + \frac{1}{2}\Delta_f G^\circ(O_2)]$$

$$= 52.0 - 87.0 - \frac{1}{2} \times 0 = -35 \text{ kJ mol}^{-1}$$

Now, $\log K = -\dfrac{\Delta G^\circ}{2.303\,RT}$

$$= -\frac{-35 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1}\text{ mol}^{-1} \times 298\,K} = 6.314$$

or $K = 2.06 \times 10^6$

21. Higher the boiling point, lesser the vapour pressure hence the order of V.P. is

water < acetone < ether

22. Let the concentration of AgCl be x mol/litre and that of CuCl be y mol/litre

$$AgCl \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$$

$$\underset{y\,=\,0.1}{CuCl} \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-}$$

K_{sp} of AgCl = $[Ag^+][Cl^-] = x(x + y)$ ...(i)

K_{sp} of CuCl = $[Cu^+][Cl^-] = y(x + y)$ ...(ii)

On solving (i) and (ii), we get

$$\frac{K_{sp} \text{ of AgCl}}{K_{sp} \text{of CuCl}} = \frac{x}{y} \Rightarrow \frac{1.6 \times 10^{-10}}{1.0 \times 10^{-6}} = \frac{x}{0.1}$$

$\Rightarrow$ $x = 1.6 \times 10^{-5}$ mol/litre

23.

	$2N_{2(g)}$	+ $O_{2(g)}$ $\rightleftharpoons$	$2N_2O_{(g)}$
Initial moles :	0.482	0.933	0
Moles at eqm. :	$(0.482 - x)$	$(0.933 - x/2)$	x
Molar conc :	$\frac{0.482 - x}{10}$	$\frac{0.933 - (x/2)}{10}$	$\frac{x}{10}$

As $K_c = 2.0 \times 10^{-37}$ is very small, this means that the amount of N_2 and O_2 reacted (x) is very small. Hence, at equilibrium, we have

$[N_2] = 0.0482 \text{ mol L}^{-1}, [O_2] = 0.0933 \text{ mol L}^{-1}, [N_2O] = 0.1x \text{ mol L}^{-1}$

$$\therefore \quad K_c = \frac{(0.1x)^2}{(0.0482)^2(0.0933)} = 2.0 \times 10^{-37} \text{ (given)}$$

On solving this we get, $x \approx 6.6 \times 10^{-20}$

$\therefore$ $[N_2O] = 0.1x = 6.6 \times 10^{-21}$ mol L^{-1}

24. When equal volumes of sodium iodate and copper chlorate are mixed, the molar concentrations of both the solutes would be reduce to half *i.e.*, 0.001 M.

$$\underset{0.001\text{ M}}{NaIO_3} \longrightarrow \underset{0.001\text{ M}}{Na^+} + IO_3^-$$

$$\underset{0.001\text{ M}}{Cu(ClO_3)_2} \longrightarrow \underset{0.001\text{ M}}{Cu^{2+}} + 2ClO_3^-$$

$\therefore$ After mixing, $[IO_3^-] = [NaIO_3] = 0.001$ M

$[Cu^{2+}] = [Cu(IO_3)_2] = 0.001$ M

Solubility equilibrium for copper iodate may be written as,

$$Cu(IO_3)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2IO^-_{3\,(aq)}$$

Ionic product of copper iodate

$= [Cu^{2+}][IO_3^-]^2 = (0.001)(0.001)^2 = 1 \times 10^{-9}$

Since ionic product (1×10^{-9}) is less than $K_{sp}(7.4 \times 10^{-8})$, therefore, no precipitation will take place.

25. When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.

(i) When H_2 is added, the rate of forward reaction will increase.

(ii) Addition of CH_3OH will lead to increase in rate of backward reaction

26. $\Delta G^\circ = -RT \ln K_c$

$-13.8 \times 10^3 = 8.314 \times 298 \times \ln K_c$

$\therefore$ $\ln K_c = -5.569$

$K_c = e^{-5.569} \Rightarrow K_c = 3.81 \times 10^{-3}$

27. $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}; \Delta H_r^\circ = -92$ kJ/mol

(i) When pressure is doubled, equilibrium will shift in the direction where pressure decreases *i.e.*, forward direction.

(ii) As this is an exothermic reaction, so the equilibrium will shift in backward direction when the temperature is doubled.

28. pH of a buffer changes with temperature because concentration of H^+ ions increases, thus pH decreases with increase of temperature.

29. $$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$$

Given, $K_c = 0.061$

As $Q_c \neq K_c$, reaction is not in equilibrium.

As $Q_c < K_c$, reaction will proceed in the forward direction.

30. (i) Lewis acids are those which can accept a pair of electrons or negatively charged ions *e.g.*, BCl_3. Lewis bases can donate a pair of electrons or negatively charged ions *e.g.*, NH_3.

(ii) Given, K_{sp} of $Ni(OH)_2 = 2 \times 10^{-15}$

K_{sp} of $AgCN = 6 \times 10^{-17}$

i.e., $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$K_{sp} = [Ni^{2+}]\,[OH^-]^2 = 2 \times 10^{-15}$

$AgCN \rightleftharpoons Ag^+ + CN^-$

$K_{sp} = [Ag^+]\,[CN^-] = 6 \times 10^{-17}$

Suppose $[Ag^+] = [CN^-] = s_1$ and $[Ni^{2+}] = s_2$

Hence, $[OH^-] = 2s_2$

Since, $s_1^2 = 6 \times 10^{-17} \Rightarrow s_1 = \sqrt{60 \times 10^{-18}}$

$\Rightarrow \quad s_1 = 7.7 \times 10^{-9}$ M

Since, $s_2 \times (2s_2)^2 = 2 \times 10^{-15} \Rightarrow 4s_2^3 = 2 \times 10^{-15}$

$\Rightarrow \quad s_2^3 = 0.5 \times 10^{-15} \Rightarrow s_2^3 = 5 \times 10^{-16}$

$\Rightarrow \quad s_2^3 = 500 \times 10^{-18}$

$\Rightarrow \quad s_2 = \sqrt[3]{500 \times 10^{-18}} = 7.9 \times 10^{-6}$ M

$s_2 = 7.9 \times 10^{-6}$ M

Since $s_2 > s_1$, therefore $Ni(OH)_2$ is more soluble than AgCN.

31. (i), (iii), (iv) would result in the formation of a buffer solution.

32. $$\underset{S}{A_x^{p+}B_y^{q-}} \rightleftharpoons \underset{xS}{xA^{p+}} + \underset{yS}{yB^{q-}}$$

$K_{sp} = [A^{p+}]^x\,[B^{q-}]^y = (xS)^x\,(yS)^y = x^x \cdot y^y \cdot S^{(x+y)}$

$S^{(x+y)} = K_{sp}/x^x \cdot y^y$

33. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

According to Le Chatelier's principle, at constant temperature, the equilibrium composition will change but K will remain same.

34. On mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M $AgNO_3$ the total volume becomes 100 mL.

Therefore,

Conc. of NaCl in 100 mL = $\dfrac{0.01 \times 50}{100} = 0.005$ M

Conc. of $AgNO_3$ in 100 mL = $\dfrac{0.01 \times 50}{100} = 0.005$ M

Now $NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$

and $AgNO_{3(aq)} \rightleftharpoons Ag^+_{(aq)} + NO_3^-{}_{(aq)}$

$[Cl^-] = [NaCl] = 0.005$ M

$[Ag^+] = [AgNO_3] = 0.005$ M

$\therefore$ Ionic product of $[Ag^+]\,[Cl^-] = 0.005 \times 0.005$

$= 2.5 \times 10^{-5}$

Since, ionic product is greater than its solubility product, precipitation will occur.

35. $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$$K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{[OH^-]^2}{[C_6H_5NH_2]}$$

$[OH^-] = \sqrt{K_b[C_6H_5NH_2]}$

$= \sqrt{(4.27 \times 10^{-10})(10^{-3})}$

$= 6.534 \times 10^{-7}$ M

$pOH = -\log(6.534 \times 10^{-7}) = 6.18$

$\therefore \quad pH = 14 - 6.18 = 7.82$

$$\begin{array}{llll} & C_6H_5NH_2 + H_2O \rightleftharpoons & C_6H_5NH_3^+ & + OH^- \\ \text{Initial :} & C & 0 & 0 \\ \text{At. eqm. :} & C - C\alpha & C\alpha & C\alpha \end{array}$$

$$K_b = \frac{C\alpha . C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad (\because 1 >>> \alpha)$$

$$\therefore \quad \alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{4.27 \times 10^{-10}}{10^{-3}}} = 6.53 \times 10^{-4}$$

$pK_b = -\log(4.27 \times 10^{-10}) = 9.37$

$pK_a + pK_b = 14$

(for a pair of conjugate acid and base)

$\therefore \quad pK_a = 14 - 9.37 = 4.63$

i.e., $-\log K_a = 4.63$ or, $\log K_a = -4.63$

or, K_a = antilog $(-4.63) = 2.34 \times 10^{-5}$

36. (i) The term ionic product has a broad meaning since it is applicable to all types of solution, may be unsaturated or saturated. On the other hand, the solubility product has restricted meaning since it applies only to a saturated solution in which there exists a dynamic equilibrium between the undissolved salt and the ions present in solution. Thus, the solubility product is, in fact the ionic product for a saturated solution.

The solubility product of a salt is constant at constant temperature whereas ionic product depends upon the concentrations of ions in the solution.

(ii) The solubility equilibrium in the saturated solution is

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

The solubility of AgCl is 1.06×10^{-5} mole per litre.

$$[Ag^+_{(aq)}] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$[Cl^-_{(aq)}] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$K_{sp} = [Ag^+_{(aq)}]\,[Cl^-_{(aq)}]$$

$$= (1.06 \times 10^{-5} \text{ mol L}^{-1}) \times (1.06 \times 10^{-5} \text{ mol L}^{-1})$$

$$= 1.12 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$$

37. (i) Sorensen (1909) defined pH of a solution as negative logarithm of the hydrogen ion concentration of the solution.

Thus, $\text{pH} = -\log[H^+] = \log\dfrac{1}{[H^+]}$ or $[H^+] = 10^{-\text{pH}}$

Likewise, pOH of a solution

$$\text{pOH} = -\log[OH^-] = \log\frac{1}{[OH^-]} \text{ or } [OH^-] = 10^{-\text{pOH}}$$

$K_w = [H^+][OH^-]$ = Ionic product of water = 10^{-14} (mol/L)^2

$\text{p}K_w = -\log K_w$

$\text{p}K_w = \text{pH} + \text{pOH} = 14$

(ii) $\text{KOH} = \dfrac{0.561}{56} \times \dfrac{1000}{200} = 0.05 \text{ M}$

As, $\text{KOH} \longrightarrow K^+ + OH^-$

$[K^+] = [OH^-] = 0.05$ M

$[H^+] = K_w/OH^- = 10^{-14}/0.05$

$= 10^{-14}/(5 \times 10^{-2}) = 2.0 \times 10^{-13}$ m

$\text{pH} = -\log 2 \times 10^{-13} = 13 - \log 2 = 12.69$

38. (i) Common ion effect can be defined as the suppression of the degree of ionisation of a weak electrolyte by the addition of a strong electrolyte having an ion common with the weak electrolyte.

(ii) $Ag_2CrO_4 \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{CrO_4^{2-}}$

$K_{sp} = [Ag^+]^2\,[CrO_4{}^{2-}] = (2s)^2 \times s = 4s^3$

$Zr_3(PO_4)_4 \rightleftharpoons \underset{3s}{3Zr^{4+}} + \underset{4s}{4PO_4^{3-}}$

$K_{sp} = [Zr^{4+}]^3\,[PO_4{}^{3-}]^4 = (3s)^3 \times (4s)^4 = 6912s^7$

(iii) $\text{pH} = -\log[H_3O^+] = -\log(0.005) = 2.30$

39. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$; $\Delta_r H° = 124.0$ kJ mol^{-1}

(a) $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = 8.3 \times 10^{-3}$

(b) K_c for the reverse reaction

$$= \frac{1}{K_c \text{ for the forward reaction}}$$

$$= \frac{1}{8.3 \times 10^{-3}} = 120.48$$

(c) (i) When pressure increases, K_c remains unchanged.

(ii) K_c increases with increase in temperature because the reaction is endothermic.

40.

	$PCl_{5(g)}$	$\rightleftharpoons$	$PCl_{3(g)}$ +	$Cl_{2(g)}$
$t = 0$	3		0	0
t_{eqm}	$3(1 - x)$		$3x$	$3x$

where x = degree of dissociation of $PCl_{5(g)}$ at 227°C

Total no. of moles at equilibrium = $[(3 - 3x) + 3x + 3x + 1$ (molar concentration of N_2)$] = 4 + 3x$.

From gas equation : $PV = nRT$

Total pressure $(P) = \dfrac{(4+3x)}{100} \times 0.082 \times 500$ atm

= 2.05 atm (given)

Thus, $4 + 3x = 5.0$

or $3x = 1.0$

Hence, $x = \dfrac{1.0}{3} = 0.33$

Percentage dissociation = 33%

$$pPCl_5 = \frac{3-3x}{4+3x} \times P = \frac{(3-0.99)\times 2.05}{4+0.33\times 3} = \frac{2.01\times 2.05}{4.99} = 0.825$$

$$pPCl_3 = \frac{3x}{4+3x} \times P = \frac{3\times 0.33\times 2.05}{4.99} = \frac{2.03}{4.99} = 0.4067$$

$$pCl_2 = \frac{3x}{4+3x} \times P = \frac{3\times 0.33\times 2.05}{4.99} = \frac{2.03}{4.99} = 0.4067$$

Hence, $K_p = \dfrac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \dfrac{0.4067 \times 0.4067}{0.825} = 0.200$ atm.