

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



- (i) 1 (ii) 0.5
(iii) 1.5 (iv) 2

Ans. (iv)

Explanation: $\Delta n = \text{no. of moles of product} - \text{no. of moles of reactant}$.

2. For the reaction $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$, 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) $K < 1$

Ans. (iv)

Explanation: $\Delta G^\ominus = -RT \ln K$

If $\Delta G^\ominus > 0$, then $-\Delta G^\ominus/RT$ is negative, and $e^{-\Delta G^\ominus/RT} < 1$. That is $K < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

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.

Ans. (iii)

Explanation: Both the opposing processes occur at the same rate and there is a 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 $0.8 \times 10^{-3} \text{ mol L}^{-1}$, $1.2 \times 10^{-3} \text{ mol L}^{-1}$ and $1.2 \times 10^{-3} \text{ mol L}^{-1}$ respectively. The value of K_c for the reaction $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$ will be

- (i) $1.8 \times 10^3 \text{ mol L}^{-1}$ (ii) 1.8×10^{-3}
(iii) $1.8 \times 10^{-3} \text{ L mol}^{-1}$ (iv) 0.55×10^4

Ans. (ii)

$$\text{Explanation: } K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{1.2 \times 10^{-3} \times 1.2 \times 10^{-3}}{0.8 \times 10^{-3}} = 1.8 \times 10^{-3}.$$

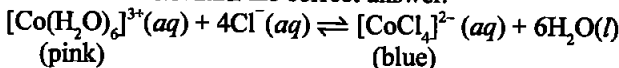
5. Which of the following statements is incorrect?

- (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.

Ans. (ii)

Explanation: Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), reacts with Fe^{3+} ions to form the stable complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, thus decreasing the concentration of free $\text{Fe}^{3+}(\text{aq})$. Because the concentration of $[\text{Fe}(\text{SCN})]^{2+}$ decreases, the intensity of red colour decreases.

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.



- (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.

Ans. (i)

Explanation: On cooling the mixture reaction moves towards backward direction it means it is an endothermic reaction i.e., $\Delta H > 0$.

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

Ans. (iii)

Explanation: As K_w increases $[\text{H}^+][\text{OH}^-] > 10^{-14}$

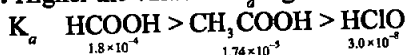
$$\begin{aligned} \text{As } [\text{H}^+] &= [\text{OH}^-] \\ \text{or } [\text{H}^+]^2 &= 10^{-14} \\ \text{or } [\text{H}^+] &> 10^{-7} \text{ M} \\ \text{pH} &< 7 \end{aligned}$$

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?

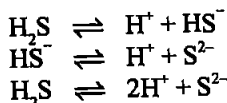
- (i) acetic acid > hypochlorous acid > formic acid
 (ii) hypochlorous acid > acetic acid > formic acid
 (iii) formic acid > hypochlorous acid > acetic acid
 (iv) formic acid > acetic acid > hypochlorous acid

Ans. (iv)

Explanation: Higher the value of K_a higher will be the acidic strength.



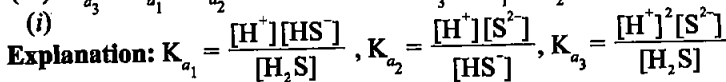
9. K_{a_1} , K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.



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

Ans.



For dibasic acid, $K_{a_3} = K_{a_1} \times K_{a_2}$

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.

Ans. (iii)

Explanation: BF_3 is an electron deficient species that is why it is a Lewis acid. (all Lewis acid can accept a pair of electrons)

11. Which of the following will produce a buffer solution when mixed in equal volumes?
- (i) $0.1 \text{ mol dm}^{-3} \text{NH}_4\text{OH}$ and $0.1 \text{ mol dm}^{-3} \text{HCl}$
 (ii) $0.05 \text{ mol dm}^{-3} \text{NH}_4\text{OH}$ and $0.1 \text{ mol dm}^{-3} \text{HCl}$
 (iii) $0.1 \text{ mol dm}^{-3} \text{NH}_4\text{OH}$ and $0.05 \text{ mol dm}^{-3} \text{HCl}$
 (iv) $0.1 \text{ mol dm}^{-3} \text{CH}_3\text{COONa}$ and $0.1 \text{ mol dm}^{-3} \text{NaOH}$

Ans. (iii)

Explanation: A mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25.

12. In which of the following solvents is silver chloride most soluble?
- (i) $0.1 \text{ mol dm}^{-3} \text{AgNO}_3$ solution
 (ii) $0.1 \text{ mol dm}^{-3} \text{HCl}$ solution
 (iii) H_2O
 (iv) Aqueous ammonia

Ans. (iv)

Explanation: Aqueous ammonia will absorb chloride ions and thus the equilibria will shift in forward direction and solubility of silver chloride will increase.

13. What will be the value of pH of $0.01 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$?

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

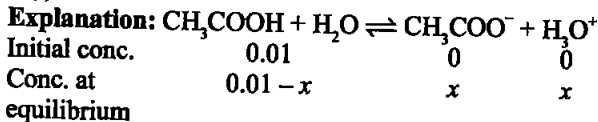
(i) 3.4

(ii) 3.6

(iii) 3.9

(iv) 3.0

Ans. (i)



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.74 \times 10^{-5} = \frac{x^2}{0.01}$$

$$x = \sqrt{1.74 \times 10^{-5} \times 0.01}$$

$$-\log x = 3.37$$

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

Ans. (iii)

Explanation: $\text{CH}_3\text{COONH}_4$ is a salt of weak acid and weak base.

$$\text{pH} = 7 + \frac{1}{2}(\text{p}K_a - \text{p}K_b)$$

$$\therefore \text{pH} = 7 + 0 = 7$$

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

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

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

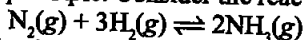
(iii) $\Delta G^\ominus < 0$

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

Ans. (i)

Explanation: At the stage of half completion of reaction $[\text{A}] = [\text{B}]$. Therefore, $K = 1$. Thus, $\Delta G^\ominus = 0$.

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.



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

Ans. (i)

Explanation: Equilibrium constant K will remain same if temperature is not changed.

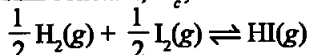
17. What will be the correct order of vapour pressure of water, acetone and ether at 30°C. Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

- (i) Water < ether < acetone (ii) Water < acetone < ether
(iii) Ether < acetone < water (iv) Acetone < ether < water

Ans. (ii)

Explanation: Greater the boiling point, lower will be the vapour pressure.

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



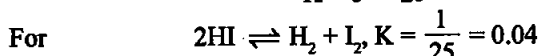
What would be the equilibrium constant K_c for the reaction



- (i) 0.04 (ii) 0.4
(iii) 25 (iv) 2.5

Ans. (i)

Explanation: If the equation is multiplied by 2, the equilibrium constant for the new equation is the square of K and on reversing the reaction the value of the equilibrium constant is inversed.



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

- (i) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
(ii) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
(iii) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
(iv) The equilibrium will remain unaffected in all the three cases.

Ans. (iv)

Explanation: At constant volume equilibrium remains unaffected with the addition of inert gas.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

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

20. For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, 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 $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are mixed at 400 K at partial pressures 20 bar and 2 bar respectively, more $\text{N}_2\text{O}_4(\text{g})$ will be formed.
(iv) The entropy of the system increases.

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

Explanation: K increases with increase in temperature.

K increases, it shows that the reaction must be endothermic.

No. of molecules increases thus, there is increase in entropy.

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?

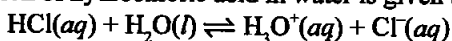
- (i) Normal melting point (ii) Equilibrium temperature
(iii) Boiling point (iv) Freezing point

Ans. (i) and (iv)

Explanation: Ice and water are in equilibrium only at particular temperature and pressure. For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance. The system here is in dynamic equilibrium.

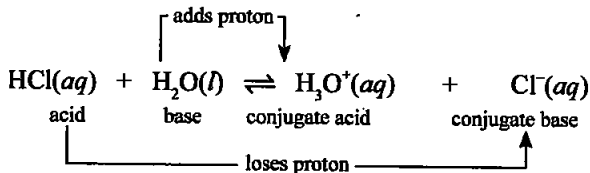
III. SHORT ANSWER TYPE

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



Label two conjugate acid-base pairs in this ionisation.

Ans.

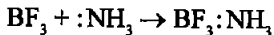


23. The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionisation and how is it affected by concentration of sodium chloride?

Ans. Conductance depends upon no. of ions present in the solution since sodium chloride (NaCl) ionizes completely in aqueous solution. Hence, the solution conducts electricity.

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?

Ans. BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by



Coordinate bond is formed between BF_3 and NH_3 .

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

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

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

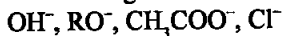
Base	Dimethylamine	Urea	Pyridine	Ammonia
K_b	5.4×10^{-4}	1.3×10^{-14}	1.77×10^{-9}	1.77×10^{-5}

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

Ans. K_b Dimethylamine > Ammonia > Pyridine > Urea
 5.4×10^{-4} 1.77×10^{-5} 1.77×10^{-9} 1.3×10^{-14}

Higher the value of K_b , stronger will be the base. Among the given bases, the strongest base is Dimethylamine.

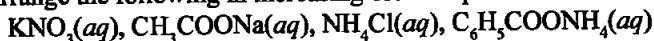
26. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?



Ans. $\text{RO}^- > \text{OH}^- > \text{CH}_3\text{COO}^- > \text{Cl}^-$

Strongest the acid, weak will be its conjugate base.

27. Arrange the following in increasing order of pH.



Ans. $\text{NH}_4\text{Cl} < \text{C}_6\text{H}_5\text{COONH}_4 < \text{KNO}_3 < \text{CH}_3\text{COONa}$

Salts of strong acid and strong base do not hydrolyse and form neutral solution thus, pH will be nearly 7 of KNO_3 . In sodium acetate, acetic acid remains unionised this results in increase in OH^- concentration and pH will be more than 7. NH_4Cl formed from weak base, NH_4OH and strong acid, HCl , in water dissociates completely. aq. ammonium ions undergo hydrolysis with water to form NH_4OH and H^+ ions resulting in less pH value.

28. The value of K_c for the reaction $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ is 1×10^{-4}

At a given time, the composition of reaction mixture is

$$[\text{HI}] = 2 \times 10^{-5} \text{ mol}, [\text{H}_2] = 1 \times 10^{-5} \text{ mol and } [\text{I}_2] = 1 \times 10^{-5} \text{ mol}$$

In which direction will the reaction proceed?

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

$$\begin{aligned} Q &= \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \\ &= \frac{1 \times 10^{-5} \times 1 \times 10^{-5}}{(2 \times 10^{-5})^2} = \frac{1}{4} \\ &= 0.25 = 2.5 \times 10^{-1} \end{aligned}$$

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

Ans. Here concentration of water cannot be neglected since the solution is very dilute. pH will be less than 7.0.

$$[\text{H}_3\text{O}^+] = 10^{-8} + 10^{-7} \text{ M}$$

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?

Ans. pH = 5

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

On 100 times dilution

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

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

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

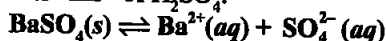
$$= \left[\begin{array}{l} \text{Contribution of } H_3O^+ \text{ ion} \\ \text{concentration of acid} \end{array} \right] + \left[\begin{array}{l} \text{Contribution of } H_3O^+ \text{ ion} \\ \text{concentration of water} \end{array} \right]$$

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

$$\text{pH} = 2 \times 10^{-7} = 7 - \log 2 = 7 - 0.3010 = 6.6990$$

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 $8 \times 10^{-4} \text{ mol dm}^{-3}$, calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4 .

Ans.



At $t = 0$

$$1 \qquad 0 \qquad 0$$

At equilibrium in water

$$1-S \qquad 0 \qquad 0$$

At equilibrium in the presence

$$1-S \qquad S \qquad (S + 0.01)$$

of sulphuric acid

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

But

$$S = 8 \times 10^{-4} \text{ mol dm}^{-3}$$

\therefore

$$K_{sp} = (8 \times 10^{-4})^2 = 64 \times 10^{-8} \qquad \dots(1)$$

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

$$K_{sp} = (S)(S + 0.01) \qquad \dots(2)$$

Since, value of K_{sp} will not change in the presence of sulphuric acid.

Therefore, from (1) and (2), we have,

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

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

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

\Rightarrow

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

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

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

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

$$\begin{aligned}
 &= \frac{-0.01 \pm 10^{-2} \sqrt{1.256}}{2} \\
 &= \frac{-10^{-2} + (1.12 \times 10^{-2})}{2} \\
 &= \frac{(-1 + 1.12) \times 10^{-2}}{2} = \frac{0.12}{2} \times 10^{-2} \\
 &= 6 \times 10^{-4} \text{ mol dm}^{-3}
 \end{aligned}$$

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

Ans. pH of HOCl = 2.85

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

$\therefore -2.85 = \log [\text{H}^+]$

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

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

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

$$\begin{aligned}
 \Rightarrow K_a &= \frac{[\text{H}^+]^2}{C} = \frac{(1.413 \times 10^{-3})^2}{0.08} \\
 &= 24.957 \times 10^{-6} = 2.4957 \times 10^{-5}
 \end{aligned}$$

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.

Ans. pH of solution A = 6

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

pH of solution B = 4

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

On mixing one litre of each solution, total volume = $1\text{L} + 1\text{L} = 2\text{L}$.

Amount of H^+ ions in 1L of solution A = concentration \times volume V
 $= 10^{-6} \text{ mol} \times 1\text{L}$

Amount of H^+ ions in 1L of solution B = $10^{-4} \text{ mol} \times 1\text{L}$.

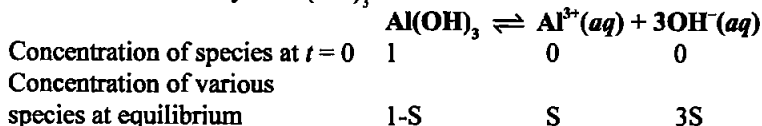
\therefore Total amount of H^+ ions in the solution formed by mixing solutions A and B is $(10^{-6} \text{ mol} + 10^{-4} \text{ mol})$.

This amount is present in 2L solution.

$$\begin{aligned}
 \therefore \text{Total } [\text{H}^+] &= \frac{10^{-4}(1 + 0.01)}{2} = \frac{1.01 \times 10^{-4}}{2} \text{ mol L}^{-1} \\
 &= \frac{1.01 \times 10^{-4}}{2} \text{ mol L}^{-1} = 0.5 \times 10^{-4} \text{ mol L}^{-1} = 5 \times 10^{-5} \text{ mol L}^{-1} \\
 \text{pH} &= -\log[\text{H}^+] = -\log(5 \times 10^{-5}) \\
 &= -[\log 5 + (-5 \log 10)] \\
 &= -\log 5 + 5 \\
 &= 5 - \log 5 \\
 &= 5 - 0.6990 \\
 &= 4.3010 = 4.3
 \end{aligned}$$

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

Ans. Let S be the solubility of $\text{Al}(\text{OH})_3$



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

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

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

- (i) **Solubility of $\text{Al}(\text{OH})_3$** : Molar mass of $\text{Al}(\text{OH})_3$ is 78 g. Therefore, Solubility of $\text{Al}(\text{OH})_3$ in $\text{g L}^{-1} = 1 \times 10^3 \times 78 \text{g L}^{-1} = 78 \times 10^{-3} \text{g L}^{-1} = 7.8 \times 10^{-2} \text{g L}^{-1}$

- (ii) **pH of the solution** : $\text{S} = 1 \times 10^{-3} \text{ mol L}^{-1}$

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

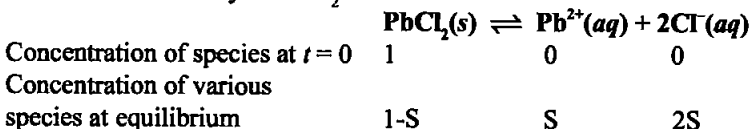
$$\text{p}[\text{OH}] = 3 - \log 3$$

$$\text{pH} = 14 - \text{pOH} = 11 + \log 3 = 11.4771$$

35. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. (K_{sp} of $\text{PbCl}_2 = 3.2 \times 10^{-8}$, atomic mass of Pb = 207 u).

Ans. K_{sp} of $\text{PbCl}_2 = 3.2 \times 10^{-8}$

Let S be the solubility of PbCl_2



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

$$K_{sp} = 4\text{S}^3$$

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

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

$$\text{Molar mass of } \text{PbCl}_2 = 278$$

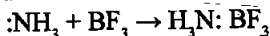
$$\begin{aligned} \therefore \text{Solubility of } \text{PbCl}_2 \text{ in } \text{g L}^{-1} &= 2 \times 10^{-3} \times 278 \text{ g L}^{-1} \\ &= 556 \times 10^{-3} \text{ g L}^{-1} \\ &= 0.556 \text{ g L}^{-1} \end{aligned}$$

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

0.1 g PbCl_2 is dissolved in $\frac{0.1}{0.556} \text{ L} = 0.1798 \text{ L}$ 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.

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



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

Ans. $:\text{NH}_3$ is Lewis base while BF_3 is Lewis acid. Lewis electronic theory of acids and bases explains it.

Hybridisation state: N in NH_3 is sp^3 hybridised and Boron in BF_3 is sp^2 hybridised.

37. Following data is given for the reaction: $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$

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

$$\Delta_f H^\ominus [\text{CO}_2(g)] = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\ominus [\text{CaCO}_3(s)] = -1206.9 \text{ kJ mol}^{-1}$$

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

Ans. $\Delta_r H^\ominus = \Delta_f H^\ominus [\text{CaO}(s)] + \Delta_f H^\ominus [\text{CO}_2(g)] - \Delta_f H^\ominus [\text{CaCO}_3(s)]$

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

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

IV. MATCHING TYPE

38. 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

Ans. (i) \rightarrow (b); (ii) \rightarrow (d); (iii) \rightarrow (c); (iv) \rightarrow (a)

39. For the reaction : $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

$$\text{Equilibrium constant } K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

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) $2\text{N}_2(g) + 6\text{H}_2(g) \rightleftharpoons 4\text{NH}_3(g)$	(a) $2K_c$
(ii) $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$	(b) $\frac{1}{K_c^2}$
(iii) $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$	(c) $\frac{1}{K_c}$
	(d) K_c^2

Ans. (i) \rightarrow (d); (ii) \rightarrow (c); (iii) \rightarrow (b)

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) $K < 1$

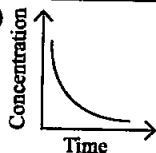
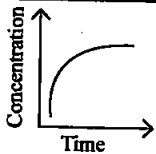
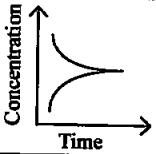
Ans. (i) \rightarrow (d); (ii) \rightarrow (a); (iii) \rightarrow (b)

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

Ans. (i) \rightarrow (b); (ii) \rightarrow (e); (iii) \rightarrow (c); (iv) \rightarrow (d)

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.

Ans. (i) \rightarrow (c); (ii) \rightarrow (a); (iii) \rightarrow (b)

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) $\Delta G < 0$, $K > 1$

Ans. (i) \rightarrow (c); (ii) \rightarrow (d); (iii) \rightarrow (a)

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 $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

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.

Ans. (i)

Explanation: H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases.

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.

Ans. (i)

Explanation: The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called buffer solutions.

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.

Ans. (ii)

Explanation: In presence of H^+ ion, equilibrium shifts in backward direction.

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.

Ans. (iii)

Explanation: • The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.

• The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

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.

Ans. (i)

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.

Ans. (iii)

Explanation: Salt of weak acid and weak base can form buffer solution.

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.

Ans. (iii)

Explanation: If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed.

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.

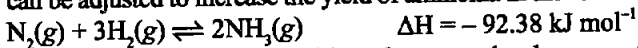
(iii) No net reaction occurs.

Ans. (i) As $Q_c < K_c$, the reaction proceeds in the forward direction.

(ii) If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

(iii) If $Q_c = K_c$, 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:



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

Ans. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia since it is an exothermic reaction. In other words, low temperature and high pressure is favourable for high yield of ammonia. There will be no change in equilibria on addition of argon.

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.

Ans. $A_x^{p+} B_y^{q-} \rightleftharpoons xA^{p+}(\text{aq}) + yB^{q-}(\text{aq})$

S moles of $A_x B_y$ dissolve to give xS moles of A^{p+} and yS moles of B^{q-} .

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

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 : $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$.

Ans. (a) $\Delta G = \Delta G^\ominus + RT \ln Q$

ΔG^\ominus = Change in free energy as the reaction proceeds

ΔG = Standard free energy change

Q = Reaction quotient

R = Gas constant

T = Absolute temperature

Since $\Delta G^\ominus = -RT \ln K$

$$\therefore \Delta G = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K}$$

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

If $Q = K$, $\Delta G = 0$, reaction is in equilibrium and no net reaction is there.

(b) On increasing the pressure equilibrium will shift in forward direction it means $Q < K$.

□□□