KD EDUCATION ACADEMY (9582701166

Time : 3 Hour 20 Minute

STD 11 Science Chemistry
kd 90+ ch-6 equilibrium

Total Marks : 230

*** Choose The Right Answer From The Given Options.[1 Marks Each] [69]**

1. 0.10M CH_3COOH is 1.34% ionised, calculate its K_a:

(A) 1.8×10^{-5} (B) 1.8×10^{-4} (C) 5×10^{-4} (D) 4×10^{-5}

Ans. :

a. 1.8×10^{-5}

Explanation:

$$K_a = C\alpha^2 = 0.1 \times \frac{1.34}{100} \times \frac{1.34}{100} = 1.795 \times 10^{-5}$$

2. "An acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+".
The above statement is justified by

(A) Arrhenius concept. (B) Bronsted-Lowry theory.

(C) Lewis concept. (D) All of the above.

Ans. :

b. Bronsted-Lowry theory.

3. What will be the conjugate bases for the following Bronsted acids?
$HF, H_2SO_4 \text{ and } HCO_3^-$

(A) $F^-, SO_4^{2-} \text{ and } CO_3^{2-}$ (B) $F^-, SO_4^{2-} \text{ and } H_2CO_3$

(C) $F^-, HSO_4^- \text{and } H_2CO_3$

(D) $F^-, HSO_4^- \text{ and } CO_3^{2-}$

Ans. :

d. $F^-, HSO_4^- \text{ and } CO_3^{2-}$

Explanation:

The conjugate bases should have one proton less in each case and therefore, the corresponding conjugate bases are $F^-, HSO_4^- \text{ and } CO_3^{2-}$ respectively.

4. What will be the molar solubility S of a solid salt with general formula $M_x^{p+}X_y^{q-}$?

(A) $\left(\frac{K_{sp}}{x^y.y^x}\right)^{\frac{1}{x+y}}$ (B) $\left(\frac{K_{sp}}{x^x.y^y}\right)^{x+y}$ (C) $\left(\frac{K_{sp}}{x^x.y^y}\right)^{\frac{1}{x+y}}$ (D) $\left(\frac{K_{sp}}{x^y.y^x}\right)^{x+y}$

Ans. :

c. $\left(\frac{K_{sp}}{x^x.y^y}\right)^{\frac{1}{x+y}}$

5. The pH of boiling water is 6.4. This implies that boiling water is:

(A) Slightly basic. (B) Slightly acidic.

(C) Neutral. (D) Amphoteric.

Ans. :

c. Neutral.

Explanation:

The ph of boiling water is 6.4. This implies that boiling water is neutral. When water is boiled, both hydrogen ion and hydroxide ion concentration increases to same extent. Hence it is neutral. With increase in the hydrogen ion concentration, pH decreases from 7 to 6.4. Also, the value of Kw also increases as the degree of dissociation of water increases with increase in temperature.

6. The equilibrium constant of a reaction at 298K and 1000K is 5×10^{-3} and 2×10^{-3} respectively. The $\triangle \mathrm{H}$ for the reaction is:

(A) Positive. (B) Negative.

(C) Either positive or negative. (D) Zero.

Ans. :

b. Negative.

Explanation:

With the increase in temperature from 298K to 1000K, the value of the equilibrium constant decreases from 5×10^{-3} to 2×10^{-3}.

Thus, as the temperature increases, the equilibrium shifts to the left direction. This is possible for an exothermic reaction.

7. The mass of acetic acid present in 500ml of solution in which it is 1% ionised (Ka of $CH_3COOH = 1.8 \times 10^{-5}$)

(A) 5.4g (B) 12.6g (C) 6.4g (D) 10.8g

Ans. :

a. 5.4g

8. Which among the following factors changes the value of ionic product of water?

(A) Change in temperature. (B) Addition of acid.

(C) Addition of base. (D) Addition of either acid and base.

Ans. :

a. Change in temperature.

Explanation:

Ionic product depends only on temperature.

9. In which condition, the reaction proceeds in the forward direction?

(A) $\mathrm{Q_C = K_C}$ (B) $\mathrm{Q_C > K_C}$ (C) $\mathrm{Q_C < K_C}$ (D) $\mathrm{Q_C \neq K_C}$

Ans. :

c. $\mathrm{Q_C < K_C}$

Explanation:

When $Q_C < K_C$ then the reaction proceeds in the forward direction.

10. The strength of acid is highest in:

(A) $pK_a = 6$ (B) $pK_a = 5$ (C) $pK_a = 10$ (D) $pK_a = 1$

Ans. :

d. $pK_a = 1$

Explanation:

$pK_a = -\log K_a$

Higher the Ka, higher is the strength of the acid.

For higher Ka, pKa value is smaller.

11. 0.1M CH_3COOH and 1.01CH_3COONa are mixed togethere, what will be pH of buffer solution if $\mathrm{pK_a} = 4.75[\log 10 - 1 = -1]$

(A) 3.75 (B) 4.75 (C) 5.75 (D) 6.75

Ans. :

a. 3.75

Explanation:

$$\mathrm{pH} = \mathrm{pK_a} + \log \frac{(\mathrm{Salt})}{(\mathrm{Acid})}$$
$$= 4.75 + \log \frac{10^{-2}}{10^{-1}}$$
$$= 4.75 - 1 = 3.75$$

12. Cottrell precipitator acts on which of the following principle?

(A) Hardy-Schulze rule.

(B) Distribution law.

(C) Le Chatelier's principle.

(D) Neutralization of charge on the colloidal particles.

Ans. :

d. Neutralization of charge on the colloidal particles.

Explanation:

It is related with neutralisation of charge on colloidal particlr.

13. A solution which maintains constant pH when small amounts of acid or alkali are added is known as ____.

(A) Indicator (B) Buffer

(C) Amphoteric (D) Neutral

Ans. :

b. Buffer

Explanation:

A buffer solution is one which resists changes in pH when small quantities of an acid or an alkali are added to it.

14. The pH value of blood does not appreciably change by a small addition of an acid or a base, because the blood:

(A) Is a body fluid.

(B) Can be easily coagulated.

(C) Contains iron as a part of the molecule.

(D) Contains serum protein which acts as buffer.

Ans. :

d. Contains serum protein which acts as buffer.

Explanation:

The buffer system present in serum is H_2CO_3 + $NaHCO_3$ and as we know that a buffer solution resist the change in pH therefore pH value of blood does not change by a small addition of an acid or a base.

15. Addition of HCl will not suppress the ionization of:

(A) Acetic acid
(B) Benzoic acid
(C) H_2S
(D) Sulphuric acid

Ans. :

d. Sulphuric acid

Explanation:

Any acid weaker than HCl will be suppressed by HCl. Hence, among the given options, only sulphuric acid is an acid with comparable acidity strength to HCl. The same can also be verified using Ka values from the data.

16. The solubility product K_{sp} of the sparingly soluble salt Ag_2CrO_4 is 4×10^{-12}. The molar solubility of the salt is:

(A) 1.0×10^{-4} mol L^{-1}
(B) 2×10^{-6} mol L^{-1}
(C) 1.0×10^{-5} mol L^{-1}
(D) 2×10^{-12} mol L^{-1}

Ans. :

a. 1.0×10^{-4} mol L^{-1}

17. Which of the following species is amphoteric in nature.

(A) $\mathrm{H_3O^+}$
(B) $\mathrm{Cl^-}$
(C) $\mathrm{HSO_4^-}$
(D) $\mathrm{CO_3^{2-}}$

Ans. :

b. $\mathrm{Cl^-}$

Explanation:

$\mathrm{HSO_3^-}$ because if can gain H^+ as well as lose H^+.

18. The ionic product of water ______ if a few drops of acid or base are added to it.

(A) Increases.
(B) Decreases.
(C) Remains the same.
(D) Can not predict.

Ans. :

c. Remains the same.

Explanation:

The ionic product of water at a particular temperature is constant and has no effect of acid or base addition.

19. A buffer solution is a solution whose pH value on keeping in the air:

(A) Increases rapidly.
(B) Decreases rapidly.
(C) May increase or decrease.
(D) Does not change.

Ans. :

d. Does not change.

20. In the reaction,
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 180.7$ kJ,
on increasing the temperature, the production of NO:

(A) Increases.
(B) Decreases.
(C) Remains same.
(D) Cannot be predicted.

Ans. :

a. Increases.

Explanation:

Given $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) = 180.7$ kJ

For this reaction, $\triangle H = +180.7$ kJ

Positive value of $\triangle H$ shows that the reaction is endothermic.

According to Le-Chatelier's principle, in case of endothermic reaction, increase in temperature, shifts the reaction towards product side.

21. Calculate the molar solubility (S) of a salt like zirconium phosphate of molecular formula $(\mathrm{Zr}^{4+})_3(\mathrm{PO}_4^{3-})_4$.

(A) $\left(\frac{\mathrm{K_{sp}}}{9612}\right)^{\frac{1}{8}}$ (B) $\left(\frac{\mathrm{K_{sp}}}{6912}\right)^{\frac{1}{7}}$ (C) $\left(\frac{\mathrm{K_{sp}}}{5348}\right)^{\frac{1}{6}}$ (D) $\left(\frac{\mathrm{K_{sp}}}{8435}\right)^{\frac{1}{7}}$

Ans. :

b. $\left(\frac{\mathrm{K_{sp}}}{6912}\right)^{\frac{1}{7}}$

Explanation:

$$[\mathrm{Zr}^{4+}] = 3\,\mathrm{S} \text{ and } [\mathrm{PO}_4^{3-}] = 4\mathrm{S}$$

$$\text{and } \mathrm{K_{sp}} = (3\mathrm{S})^3(4\mathrm{S})^4 = 6912(\mathrm{S})^7$$

$$\text{or } \mathrm{S} = \left\{\frac{\mathrm{K_{sp}}}{(3^3 \times 4^4)}\right\}^{\frac{1}{7}}$$

$$= \left(\frac{\mathrm{K_{sp}}}{6912}\right)^{\frac{1}{7}}$$

22. Strong electrolyte of the following is?

(A) 01M HAc (B) 0.1M HCl

(C) 0.1M KCl (D) 0.1M NaCl

Ans. :

b. 0.1M HCl

23. In the presence of a common ion (incapable of forming complex ion), the solubility of salt _______ in solution.

(A) Increases. (B) Decreases.

(C) Remains the same. (D) Cannot predict.

Ans. :

b. Decreases.

Explanation:

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

$BC \rightarrow B^+ + C^-$

Since B^+ is incapable of forming a complex salt it tends to decrease the solubility by Le-Chatelier's principle.

24. In a reversible reaction $H_2 + I_2 \leftrightharpoons 2HI$, if the concentration of H_2 and I_2 are increased, the value of Kc:

(A) Decreases. (B) Increases.

(C) Remains the same. (D) Changes exponentially.

Ans. :

c. Remains the same.

Explanation:

The magnitude of the equilibrium constant is not affected by the changes in concentrations of reactants and products, pressure and volume. Thus, when the concentrations of hydrogen and iodine are increased, the value of the equilibrium constant remains the same.

25. Given the chemical equilibrium, $A \rightleftharpoons B + C$, where ΔH_{rxn} is negative, what effect increasing the temperature (at constant pressure) would have on the system at equilibrium?

(A) No change.

(B) Shift to the left.

(C) Shift to the right.

(D) Shift to the left for K<1 and to the right for K>1.

Ans. :

b. Shift to the left.

Explanation:

$A \rightarrow B + C; \triangle H < 0$

Here, forward reaction is exothermic. So, if temperature is increased then as per Le Chatelier's principle, the equilibrium shifts to left side (backward direction).

26. 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

(A) 7.005

(B) 4.75

(C) 7.0

(D) Between 6 and 7

Ans. :

c. 7.0

Explanation:

Ammonium acetate is a salt of weak acid and weak base.

$$\mathrm{pH} = \frac{1}{2}\left[\mathrm{pK_w} + \mathrm{pK_a} + \mathrm{pK_b}\right]$$

$$= \frac{1}{2}\left[14 - \log(1.8 \times 10^{-5}) + \log(1.8 \times 10^{-5})\right] = 7.0$$

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

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

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

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

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

Ans. :

c. 0.1mol dm^{-3} NH_4OH and 0.05mol dm^{-3} HCl.

Explanation:

In (c), all HCl will be neutralized and NH_4Cl will be formed. Also some NH_4OH will be left unneutralized. Thus, the final solution will contain NH_4OH and NH_4Cl and hence will form a buffer.

28. Which one does not give a buffer solution?

(A) Ammonia and sodium hydroxide in water.

(B) Sodium acetate and acetic acid in water.

(C) Ammonia and ammonium chloride in water.

(D) Sodium acetate and hydrochloric acid in water.

Ans. :

a. Ammonia and sodium hydroxide in water.

Explanation:

Buffer solution is a mixture of weak acid and its conjugate base or weak base and its conjugate acid. So ammonia(strong base) and sodium hydroxide does not give a buffer.

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

(A) Arrhenius concept.

(B) Bronsted Lowry concept.

(C) Lewis concept.

(D) Bronsted Lowry as well as Lewis concept.

Ans. :

c. Lewis concept.

Explanation:

According to Lewis concept, a positively charged or an electron deficient species acts as Lewis acid. BF_3 is an electron deficient compound with B having 6 electrons only.

30. Strong acid dissociates completely in water, the resulting base formed would be very weak. The reason is that:

(A) Strong acids have strong conjugate bases.

(B) Strong acids have strong conjugate acids.

(C) Strong acids have very weak conjugate bases.

(D) Strong acids have very weak conjugate acids.

Ans. :

c. Strong acids have very weak conjugate bases.

31. $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$. If the concentration of A and B are equal at equilibrium and concentration of D will be twice that of A, then what will be the equilibrium constant of the reaction?

(A) 4 (B) 6 (C) $\frac{4}{5}$ (D) $\frac{6}{7}$

Ans. :

a. 4

32. 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.

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

(A) $\Delta\mathrm{H} > 0$ for the reaction.

(B) $\Delta H < 0$ for the reaction.

(C) $\Delta H = 0$ for the reaction.

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

Ans. :

a. $\Delta H > 0$ for the reaction.

Explanation:

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

33. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ shifts forward if:

(A) Catalyst is used.

(B) An adsorbent is used to remove SO_3 as soon as it is formed.

(C) Large amount of products are used.

(D) Small amount of reactants are used.

Ans. :

b. An adsorbent is used to remove SO_3 as soon as it is formed.

Explanation:

Removal of any product or adding of reactants favours forward reaction i.e., SO_3 formation. This is according to Le- Chatelier's principle.

34. The addition of NaCl to AgCl decreases the solubility of AgCl because:

(A) Solubility product decreases.

(B) Solubility product remains constant.

(C) Solution becomes unsaturated.

(D) Solution becomes supersaturated.

Ans. :

b. Solubility product remains constant.

Explanation:

$[Cl^-]$ increases but $K_{sp} = [Ag^+][Cl^-]$remains constant. So, $[Ag^+]$ decreases.

35. In the equilibrium, $AB \rightleftharpoons A + B$ if the equilibrium concentration of A is double, then equilibrium concentration of B will be:

(A) Half (B) twice (C) $\frac{1}{4}$th (D) $\frac{1}{8}$th

Ans. :

a. Half

Explanation:

$AB \rightleftharpoons A + B$

or $K = \frac{[A][B]}{[AB]}$

If concentration of A is doubled, the equilibrium concentration of B becomes half to maintain K constant.

36. Equal volume of following Ca^{2+} and F solution are mixed. In which of the Solutions will precipitation occur? [K_{SP} of $CaF_2 = 1.7 \times 10^{-10}$

(A) $10^{-2}M\ Ca^{2+} + 10^{-5}MF^-$

(B) $10^{-3}\mathrm{M\ Ca}^{2+}$ and $10^{-3}\mathrm{MF}^{-}$

(C) $10^{-2}\mathrm{M\ Ca}^{2+}+10^{-3}\mathrm{MF}^{-}$

(D) $10^{-3}\mathrm{M\ Ca}^{2+}$ and $10^{-5}\mathrm{MF}^{-}$

Ans. :

c. $10^{-2}\mathrm{M\ Ca}^{2+}+10^{-3}\mathrm{MF}^{-}$

Explanation:

$\because \mathrm{I.P} = (\mathrm{Ca}^{2+})(\mathrm{F}^{-})^2$

$= 10^{-2} \times (10^{-3})^2 = 10^{-8} > \mathrm{K_{SP}}$

$\therefore$ precipitation will occur.

37. $SO_2 + O_2 \rightleftharpoons 2SO_3$ + Heat

The equilibrium reaction proceeds in forward direction by:

(A) Addition of O_2

(B) Removal of O_2

(C) Addition of inert gas

(D) Cannot proceed

Ans. :

a. Addition of O_2

Explanation:

According to Le-Chatelier's principle, equilibrium shift towards forward direction by addition of reactant.

38. An equimolar solution of $NaNO_2$ and HNO_2 can act as a:

(A) Strong reductant.

(B) Strong oxidant.

(C) Buffer solution.

(D) None of these.

Ans. :

c. Buffer solution.

Explanation:

HNO_2 is a weak acid.

$NaNO_2$ is a salt of weak acid HNO_2 with strong base NaOH.

39. In the gaseous equilibrium A + 2B $\rightleftharpoons$ C + Heat, the forward reaction is favoured:

(A) Low P, High T

(B) Low P, Low T

(C) High P, Low T

(D) High P, High T

Ans. :

c. High P, Low T

Explanation:

A + 2B $\rightleftharpoons$ C + Heat

The equation shows, that it is exothermic reaction.

Since the heat is released in the reaction, so the reaction is favoured in forward direction at low temperature.

$\Delta n = 1 - (2 + 1) = -2$

40. The solubility product of $CaSO_4$ is 6.4×10^{-5}. The solubility of salt in mol L^{-1} is:

(A) 8.10^{-16}

(B) 8.10^{-2}

(C) 8.10^{-3}

(D) 1.6^{-3}

Ans. :

b. 8.10^{-2}

Explanation:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

$$\Rightarrow 6.4 \times 10^{-5} \times = s \times s$$

$$\Rightarrow s^2 = \sqrt{64 \times 10^{-6}}$$

$$\Rightarrow s = 8 \times 10^{-3} mol\ L^{-1}$$

41. Buffer Solution is prepared by mixing ________________.

(A) Weak acid and its salt of strong base.

(B) Strong acid + its salt of strong base.

(C) Weak acid + its salt of weak base.

(D) Strong base + its salts of strong acid.

Ans. :

a. Weak acid and its salt of strong base.

Explanation:

A solution that resists change in pH value upon addition of a small amount of strong acid or base (less than 1 %) or when the solution is diluted is called buffer solution.

An acidic buffer solution consists of
a solution of a weak acid and its salt with a strong base. while basic buffer solution consists of a mixture of a weak base and its salt with strong acid.

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

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

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

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

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

Ans. :

d. The equilibrium will remain unaffected in all the three cases.

Explanation:

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

43. 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.

(A) 1.8 × 10^{3}mol L^{-1}

(B) 1.8 × 10^{-3}

(C) 1.8 × 10^{-3}L mol^{-1}

(D) 0.55 × 10^{4}

Ans. :

b. 1.8 × 10^{-3}

Explanation:

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

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{1.2 \times 10^{-3} \times 1.2 \times 10^{-3}}{0.8 \times 10^{-3}}$$

$= 1.8 \times 10^{-3}]\mathrm{moL\ L^{-1}}$

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

(A) K = 0 (B) K > 1 (C) K = 1 (D) K < 1

Ans. :

d. K < 1

45. We know that the relationship between K_c and K_p is $\mathrm{K_p = K_c(RT)^{\Delta n}}$ What would be the value of Δn for the reaction $\mathrm{NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)}$

(A) 1 (B) 0.5 (C) 1.5 (D) 2

Ans. :

d. 2

Explanation:

The relationship between K_p and K_c is

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

Where Δn = (number of moles of gaseous products) - (number of moles of gaseous reactants)

For the reaction,

$$\mathrm{NH_4C1(s) \leftrightarrows NH_3(g) + HCl(g)}$$

$$\Delta n = 2 - 0 = 2$$

46. 1mL of $\frac{N}{100}\mathrm{HCl}$ is added to 1L of buffer having pH = 5. The pH of the solution will be:

(A) Become 7 (B) Become 3

(C) Become 6 (D) Remain unaffected.

Ans. :

d. Remain unaffected.

47. 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?

(A) Normal melting point. (B) Equilibrium temperature.

(C) Boiling point. (D) Freezing point.

Ans. :

a. Normal melting point.

d. Freezing point.

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.

For example:

it is 4°C in case of water. The system here is in dynamic equilibrium

48. The chemical equilibrium of reversible reaction is not influenced by:

(A) Pressure. (B) Catalyst.

(C) Concentration of the reactants.

(D) Temperature.

Ans. :

b. Catalyst.

Explanation:

Chemical equilibrium of reversible reaction is not influenced by the catalyst. Catalyst decreases the activation barrier for a reaction so the reaction proceeds fast. In the presence of the catalyst, the equilibrium reaches faster but it doesn't affect the thermodynamic properties.

49. The dissociation constant of water is represented by $K = \frac{[H_3O^+][OH^-]}{[H_2O]}$

$\text{or } = [H^+][OH^-]K_w$ is called:

(A) Ionic product of salts.

(B) Ionic product of water.

(C) Ionisation constant of water.

(D) Ionisation constant of acid and base.

Ans. :

b. Ionic product of water.

Explanation:

The dissociation constant is represented by,

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[H_2O)$ is incorporated within the equilibrium constant to give a new constant, K_w, which is called the ionic product of water,

$$K_w = [H^+][OH^-]$$

50. The equibrium constant K_c for the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ at } 700K \text{ is } 49$

The 'K' for reaction $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$.

(A) 49

(B) 0.02

(C) $\frac{1}{7}$

(D) 1.43

Ans. :

c. $\frac{1}{7}$

Explanation:

$$K = \frac{[KI^2]}{[H_2][I_2]} = 49$$

$$\Rightarrow K' = \frac{[H_2]^{\frac{1}{2}}[I^2]^{\frac{1}{2}}}{[HI]}$$

$$= \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{49}} = \frac{1}{7}$$

51. Production of ammonia according to the reaction,

$N_2(g) + 3H_2(g)2NH_3(g);$

$$\Delta H = -92.38 \text{kJ mol}^{-1}$$

is an exothermic process. At low temperature, the reaction shifts in:

(A) Forward direction.

(B) Backward direction.

(C) Either forward or backward direction.

(D) None of the above.

Ans. :

a. Forward direction.

52. Which buffer solution comprising of the following has its pH value greater than 7?

(A) $CH_3COOH + CH_3COONa$

(B) $HCOOH + HCOOK$

(C) CH_3COONH_4

(D) $NH_4OH + NH_4Cl$

Ans. :

d. $NH_4OH + NH_4Cl$

53. 1M NaCl and 1M HCl are present in an aqueous solution . The solution is:

(A) Not a buffer solution with $pH < 7$

(B) Not a buffer solution with $pH > 7$

(C) A buffer solution with $pH < 7$

(D) A buffer solution with $pH > 7$

Ans. :

a. Not a buffer solution with $pH < 7$

Explanation:

Buffer can accept and donate protons at the same time and HC1is an acid. So, it has $pH < 7$.

So, this is not a buffer and the solution will be acidic.

54. It accepts a proton. It is called as:

(A) A Bronsted acid.

(B) A Bronsted base.

(C) A strong acid.

(D) A weak base.

Ans. :

a. A Bronsted acid.

Explanation:

A Bronsted acid can accept a proton (H^+). For example a basic salt, such as $Na^{\oplus}H^{\ominus}$, can take up a H^+ from H_2O to form $OH^{\ominus}$ ions.

$F^{\ominus}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{\oplus}(aq)$

55. The addition of HCl will not suppress the ionisation of:

(A) Acetic acid

(B) Sulphuric acid

(C) H_2S

(D) Benzoic acid

Ans. :

b. Sulphuric acid

56. 100mL of a solution contains $0.1MNH_4OH$ and $0.1MNH_4Cl$. The pH of the solution will not change on adding:

(A) 20mL of 0.1M NH_4OH solution.

(B) 20mL of 0.1M NH_4Cl solution.

(C) 10mL of 0.1M NaOH solution.

(D) 10mL of distilled water.

Ans. :

d. 10mL of distilled water.

Explanation:

pH of buffer does not change on adding distilled water as there are no ions present in it.

57. A 0.2 molar solution of formic acid is 3.2% ionised. Its ionisation constant is:

(A) 9.6×10^{-3} (B) 2.1×10^{-4}

(C) 1.25×10^{-6} (D) 4.8×10^{-5}

Ans. :

b. 2.1×10^{-4}

Explanation:

$$\mathrm{K} = \mathrm{C}\alpha^2 = 0.2 \times (0.032)^2$$
$$= 2.1 \times 10^{-4}$$

58. What will be pH of 0.01M CH_3COOH?

($K_a = 1.80 \times 10^{-5}$)

(A) 3.4 (B) 3.6 (C) 3.9 (D) 3.0

Ans. :

a. 3.4

Explanation:

$$\mathrm{pH} = -\log(\mathrm{H}^+)$$
$$= -\log\sqrt{\mathrm{K}_1 \times \mathrm{C}}$$
$$= -\log\sqrt{1.80 \times 10^{-5} \times 10^{-2}}$$
$$= -\log\sqrt{18 \times 10^{-8}}$$
$$= -\log 4.24 = 0.62$$
$$\mathrm{pH} = -\log 4.24 - \log 10^{-4}$$
$$= 0.62 + 4.00 = 3.38 \simeq 3.4$$

59. Buffer solution can be obtained by mixing aqueous solution of _______.

(A) Sodium acetate and excess of HCl.

(B) Sodium acetate and acetic acid.

(C) Sodium chloride and HCl.

(D) Acetic acid and excess of NaOH.

Ans. :

b. Sodium acetate and acetic acid.

Explanation:

A mixture of acetic acid (a weak acid) and sodium acetate (its salt with strong base sodium hydroxide) acts as acidic buffer.

Option A, C and D does not contain weak acid/ weak base and its salt thus it does not form buffer solution.

60. The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3}M. What is its pH?

(A) 4.32 (B) 5.12 (C) 3.31 (D) 2.42

Ans. :

d. 2.42

61. Addition of water to this solution will not change $[H_3O^+]$.

(A) Chemical pH indicator.
(B) Acid/ base buffer.
(C) Anhydrous solution.
(D) Hypotonic solution.

Ans. :

b. Acid/ base buffer.

Explanation:

Addition of water to X solution does not change the pH of the solution, which means the concentration of the species present changes in such a way that the pH remains the same. This is possible for acid/base buffer.

$$\mathrm{pH} = \mathrm{pk_a} + \log \frac{[\mathrm{acid}]}{[\mathrm{salt}]}$$

Since the volume changes the same for both salt and acid, the ratio $\frac{[\mathrm{salt}]}{[\mathrm{acid}]}$ remains the same and hence pH also remains the same. Same in the case of basic buffer solution.

62. The solubility of AgI in NaI solutions is less than that in pure water because:

(A) AgI forms complex with NaI.
(B) Of common ion effect.
(C) Solubility product of AgI is less than that of NaI.
(D) The temperature of the solution decreases.

Ans. :

b. Of common ion effect.

Explanation:

$AgI \rightleftharpoons Ag^{+} + I^{-}$

$NaCl \rightarrow Na^{+} + I^{-}$

Sodium iodide is a strong electrolyte and is completely dissociated. This increases the iodide ion concentration in solution and suppresses the ionization of AgI.

63. The solubility product of a sparingly soluble salt AB at room temperature is 1.21×10^{-6}, its molar solubility is:

(A) 1.21 × 100M.
(B) 1.1×10^{-4}M.
(C) 1.1×10^{-3}M.
(D) None of these.

Ans. :

c. 1.1×10^{-3}M.

Explanation:

$$\mathrm{S} = \sqrt{\mathrm{K_{sp}}}$$
$$= \sqrt{1.21 \times 10^{-6}}$$
$$= 1.1 \times 10^{-3}\mathrm{M}.$$

64. 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.

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

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

(A) K will remain same.

(B) K will decrease.

(C) K will increase.

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

Ans. :

a. K will remain same.

Explanation:

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

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

65. The solubility of CO_2 in water increases with:

(A) Increase in temperature.

(B) Reduction of gas pressure.

(C) Increase in gas pressure.

(D) Increase in volume.

Ans. :

c. Increase in gas pressure.

Explanation:

When carbon dioxide reacts with water it forms carbonic acid. Increasing the pressure of carbon dioxide makes the reaction feasible in the forward direction and hence solubility of CO_2 increases.

66. Which is not a buffer solution:

(A) $NH_4Cl + NH_4OH$

(B) $CH_3COOH + CH_3COONa$

(C) CH_3COONH_4

(D) NH_4NO_3

Ans. :

c. CH_3COONH_4

Explanation:

A buffer solution either is a mixture of a weak acid and its salt with strong base or a mixture of a weak base and its salt with strong acid. Hence, clearly CH_3COONH_4 is not a buffer solution.

67. 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?

(A) Equal to 7.0

(B) Greater than 7.0

(C) Less than 7.0

(D) Equal to zero.

Ans. :

c. Less than 7.0

Explanation:

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

As $[H^+] = [OH^-]$

or $[H^+]^2 = 10^{-14}$

or $[H^+] > 10^{-7}M$

pH < 7

68. What is pH of resulting solution when equal volume when equal of 0.1M NaOH and 0.01M HCl are mixed? $[\log 4.5 = 0.65]$

(A) 7 (B) 1.04 (C) 12.65 (D) 2.0

Ans. :

c. 12.65

Explanation:

Number of mole of $[\mathrm{OH}^-] = \frac{0.1}{2} = 0.05$ on mixing

$[\mathrm{H}^+] = \frac{0.01}{2} = 0.005$

No. of mole of [OH$^-$] left = 0.05 - 0.005 = 0.045

$\mathrm{pOH} = -\log 4.5 \times 10 - 2$

= -0.65 + 2.00 = 1.35

pH = 14 - 135 = 12.65

69. Which of the following is the example of a reversible reaction?

(A) $\mathrm{Pb(NO_3)_2(aq)} + \mathrm{2NaI(aq)} \longrightarrow \mathrm{PbI_2(s)} + \mathrm{2NaNO_3(aq)}$

(B) $\mathrm{2Na(s)} + \mathrm{2H_2O(l)} \longrightarrow \mathrm{2NaOH(aq)} + \mathrm{H_2(g)}$

(C) $\mathrm{AgNO_3(aq)} + \mathrm{HCl(aq)} \longrightarrow \mathrm{AgCl(s)} + \mathrm{HNo_3(aq)}$

(D) $\mathrm{KNO_3(aq)} + \mathrm{NaCl(aq)} \longrightarrow \mathrm{KCl(aq)} + \mathrm{NaNO_3(aq)}$

Ans. :

d. $\mathrm{KNO_3(aq)} + \mathrm{NaCl(aq)} \longrightarrow \mathrm{KCl(aq)} + \mathrm{NaNO_3(aq)}$

*** a statement of Assertion (A) is followed by a statement of Reason (R). [2] Choose the correct option.**

70. **Note:** 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.

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. :

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

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.

71. **Note:** 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.

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

Explanation:

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

* Answer The Following Questions In One Sentence.[1 Marks Each] [25]

72. What is Kc for the following equilibrium when the equilibrium concentration of each substance is:

$[SO_2]$= 0.60M, $[O_2]$ = 0.82M and $[SO_3]$ = 1.90M?

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

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

Applying law of chemical equilibrium.

73. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

Human blood, 7.38

Ans. : Human blood, 7.38:

$$\mathrm{pH} = 7.38 = -\log[\mathrm{H}^+]$$

$$\therefore\ [\mathrm{H}^+] = 4.17 \times 10^{-8}\mathrm{M}$$

74. The equilibrium constant expression for a gas reaction is,

$$\mathrm{K_c} = \frac{[\mathrm{NH_3}]^4[\mathrm{O_2}]^5}{[\mathrm{NO}]^4[\mathrm{H_2O}]^6}$$

Write the balanced chemical equation corresponding to this expression.

Ans. : Balanced chemical equation for the reaction is 4

$$\mathrm{4NO\ (g) + 6H_2O\ (g) \rightleftharpoons 4NH_3\ (g) + 5O_2\ (g)}$$

75. Write the conjugate acids for the following Brönsted bases: $\mathrm{NH_2^-}$, NH_3 and $HCOO^-$.

Ans. : The table below lists the conjugate acids for the given Bronsted bases.

Bronsted base	Conjugate acid
$\mathrm{NH_2^-}$	$\mathrm{NH_3}$
$\mathrm{NH_3}$	$\mathrm{NH_4^+}$
$\mathrm{HCOO^-}$	HCOOH

76. Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.

$$\mathrm{CH_4\ (g) + 2S_2\ (g) \rightleftharpoons CS_2\ (g) + 2H_2S\ (g)}$$

Ans. : Only those reactions will be affected by increasing the pressure in which the number of moles of the gaseous reactants and products are different ($n_p \neq n_r$) (gaseous). With the exception of the reaction (1); all the reamaining five reactions will get affected by increasing the pressure. In general,

- The reaction will go to the left if $n_p > n_r$.
- The reaction will go to the right if $n_r > n_p$.
  Keeping this in mind,

Increase in pressure will favour backward reaction because n_p (2) > n_r (1)

77. Write the expression for the equilibrium constant, K_c for each of the following reactions:

$$\mathrm{Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(S)}$$

Ans. : $\mathrm{K_c = \frac{[Fe(OH)_3(S)]}{[Fe^{3+}(aq)][OH^-(aq)]^3}}$

$= \frac{1}{\mathrm{[Fe^{3+}(aq)][OH^-(aq)]^3}}$

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

$$\mathrm{PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)\ \Delta_rH^\ominus = 124.0\ kJ\ mol^{-1}}$$

what is the value of K_c for the reverse reaction at the same temperature?

Ans. : $\mathrm{PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}}$

$\therefore\ \mathrm{K_c'} = \frac{\mathrm{[PCl_{5(g)}]}}{\mathrm{[PCl_{3(g)}][Cl_{2(g)}]}} = \frac{1}{8.3\times10^{-3}} = 120.48$

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

$$\mathrm{PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)\ \Delta_rH^\ominus = 124.0\ kJ\ mol^{-1}}$$

what would be the effect on Kc if

i. more PCl5 is added
ii. pressure is increased
iii. the temperature is increased?

Ans. : $\mathrm{PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}}$

i. If more $\mathrm{PCl_5}$ is added, then $\mathrm{Q_c}$ becomes less than $\mathrm{K_{c'}}$ the reaction will shift in the forward direction.
ii. If the pressure is increased, the reaction will shift towards backward direction as it contains less number of gaseous species. $\mathrm{K_c}$ remains constant.
iii. As the reaction is endothermic, the increase in temperature will favour the forward reaction. More $\mathrm{PCl_5}$ will dissociate to form $\mathrm{PCl_3}$ and $\mathrm{Cl_2}$. $\mathrm{K_c}$ increases.

80. Describe the effect of:
addition of H2
on the equilibrium of the reaction:

$$\mathrm{2H_2\ (g) + CO\ (g) \rightleftharpoons CH_3OH\ (g)}$$

Ans. : According to Le Chatelier's principle, on addition of H_2, the equilibrium of the given reaction will shift in the forward direction.

81. Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward

direction.

$$CO_2\ (g) + C\ (S) \rightleftharpoons 2CO\ (g)$$

Ans. : Only those reactions will be affected by increasing the pressure in which the number of moles of the gaseous reactants and products are different ($n_p \neq n_r$) (gaseous). With the exception of the reaction (1); all the reamaining five reactions will get affected by increasing the pressure. In general,

- The reaction will go to the left if $n_p > n_r$.
- The reaction will go to the right if $n_r > n_p$.

  Keeping this in mind,

Increase in pressure will favour backward reaction because n_p (10) > n_r (9)

82. Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?

$$CaO\ (S) + CO_2\ (g) \rightleftharpoons CaCO_3\ (S)$$

Ans. : The number of moles of reaction products will decrease.

83. Predict if the solutions of the following salts are neutral, acidic or basic:

KB$_r$

Ans. :

$$\mathrm{KBr} \quad + \quad \mathrm{H_2O} \quad \leftrightarrow \quad \underset{\text{Strong base}}{\mathrm{KOH}} \quad + \quad \underset{\text{Strong acid}}{\mathrm{HBr}}$$

Therefore, it is a neutral solution.

84. Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:

Human stomach fluid, 1.2

Ans. : Human stomach fluid, 1.2:

$$\mathrm{pH} = 1.2$$

$$1.2 = -\log[\mathrm{H}^+]$$

$$\therefore\ [\mathrm{H}^+] = 0.063$$

85. Describe the effect of:

removal of CH_3OH

on the equilibrium of the reaction:

$$2H_2\ (g) + CO\ (g) \rightleftharpoons CH_3OH\ (g)$$

Ans. : On removing CH_3OH, the equilibrium will shift in the forward direction.

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

Ans. : The table below lists the conjugate bases for the given Bronsted acids.

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

87. For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000K

$\mathrm{NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)}$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c, for the reverse reaction?

Ans. : For the reverse reaction $\mathrm{K_c = \frac{1}{K_c} = \frac{1}{6.3 \times 10^{14}} = 1.59 \times 10^{-15.}}$

88. If $Q_c < K_c$, in which direction reaction will proceed?

Ans. : If $Q_c < K_c$, the reaction will proceed in the direction of products.

89. What happens to ionic product of water if some acid is added to it?

Ans. : Ionic product will remain unchanged.

90. Classify the following as Lewis acid or Lewis base:

$\mathrm{NH_4^+ \text{ and } NH_3}$

Ans. : $\mathrm{NH_4^+}$ Lewis acid, whereas NH_3 is Lewis base.

91. $\mathrm{SO_3^{2-}}$ is Bronsted base or acid and why?

Ans. : $\mathrm{SO_3^{2-}}$ is Bronsted base because it can accept H^+.

92. Why pH of our blood remains constant at 7.4 through we quite often eat spicy food?

Ans. : Blood contains basic buffer which keep its pH constant.

93. What is the effect of temperature on solubility product (K_{sp})?

Ans. : K_{sp} increases with increase in temperature because solubility increases.

94. Write K_p in terms of K_c for the following chemical reaction:

$\mathrm{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}$

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

$\mathrm{\Delta n = 2 - 3 = -1}$

$\mathrm{K_c(RT)^{-1}}$

95. Which of the following is weakest acid?

$\mathrm{HClO_4, HClO_3, HCl_2, HClO}$

Ans. : HCl_4O is weakest acid because Cl is in +1 oxidation state, i.e., lowest oxidation state.

96. For Tribasic acid $K_{a1} > K_{a2} > K_{a3}$ what will happen to the acid strength of polyprotic acids if protons are lost?

Ans. : Acid strength will decrease because K_{a2}, is less than K_{a1} and K_{a3} is less than K_{a2}

* Given Section consists of questions of 2 marks each. [66]

97. A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
How do rates of evaporation and condensation change initially?

Ans. : On increasing the volume of the container, the rate of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decrease on increasing the volume, therefore, the rate of condensation will decrease initially.

98. Assuming complete dissociation, calculate the pH of the following solutions:
0.002 M KOH

Ans. : 0.002 M KOH:

$\mathrm{KOH_{(aq)}} \leftrightarrow \mathrm{K_{(aq)}} + \mathrm{OH^-_{(aq)}}$

$[\mathrm{OH^-}] = [\mathrm{KOH}]$

$\Rightarrow [\mathrm{OH^-}] = .002$

Now, $\mathrm{pOH} = -\log[\mathrm{OH^-}]$

$= 2.69$

$\therefore \mathrm{pH} = 14 - 2.69$

$= 11.31$

Hence, the pH of the solution is 11.31.

99. Assuming complete dissociation, calculate the pH of the following solutions:
0.003M HCl

Ans. : 0.003M HCl:

$\mathrm{H_2O} + \mathrm{HCl} \leftrightarrow \mathrm{H_3O^+} + \mathrm{Cl^-}$

Since HCl is completely ionized,

$[\mathrm{H_3O^+}] = [\mathrm{HCl}]$.

$\Rightarrow [\mathrm{H_3O^+}] = 0.003$

Now,

$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(.003)$

$= 2.52$

Hence, the pH of the solution is 2.52**.**

100. Assuming complete dissociation, calculate the pH of the following solutions:
0.002 M HBr

Ans. : 0.002 M HBr

$\mathrm{HBr} + \mathrm{H_2O} \leftrightarrow \mathrm{H_3O^+} + \mathrm{Br^-}$

$[\mathrm{H_3O^+}] = [\mathrm{HBr}]$

$\Rightarrow [\mathrm{H_3O^+}] = .002$

$\therefore \mathrm{pH} = -\log[\mathrm{H_3O^+}]$

$= -\log(0.002)$

$= 2.69$

Hence, the pH of the solution is 2.69.

101. Calculate the pH of the resultant mixtures:
10mL of 0.01M H_2SO_4 + 10mL of 0.01M $Ca(OH)_2$

Ans. : $\text{Moles of } \mathrm{H_3O^+} = \frac{2\times10\times0.1}{1000} = .0002\text{mol}$

$\text{Moles of } \mathrm{OH^-} = \frac{2\times10\times.01}{1000} = .0002\text{mol}$

Since there is neither an excess of $\mathrm{H_3O^+}$ or $\mathrm{OH^-}$,the solution is neutral. Hence, pH = 7.

102.

A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

What happens when equilibrium is restored finally and what will be the final vapour pressure?

Ans. : Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

103. Assuming complete dissociation, calculate the pH of the following solutions:
0.005 M NaOH

Ans. : 0.005M NaOH

$$\mathrm{NaOH_{(aq)}} \leftrightarrow \mathrm{Na_{(aq)}} + +\mathrm{HO^-_{(aq)}}$$
$$[\mathrm{HO^-}] = [\mathrm{NaOH}]$$
$$\Rightarrow [\mathrm{HO^-}] = .005$$
$$\mathrm{pOH} = -\log[\mathrm{HO^-}] = -\log(.005)$$
$$\mathrm{pOH} = 2.30$$
$$\therefore \mathrm{pH} = 14 - 2.30$$
$$= 11.70$$

Hence, the pH of the solution is 11.70.

104. Calculate the pH of the resultant mixtures:
10mL of 0.1M H_2SO_4 + 10mL of 0.1M KOH

Ans. : $\text{Moles of } \mathrm{H_3O^+} = \frac{2\times10\times0.1}{1000} = .002\mathrm{mol}$

$$\text{Moles of } \mathrm{OH^-} = \frac{10\times.01}{1000} = 0.001\mathrm{mol}$$

Excess of $\mathrm{H_3O^+} = .001\mathrm{mol}$

Thus, $[\mathrm{H_3O^+}] = \frac{.001}{20\times10^{-3}} = \frac{10^{-3}}{20\times10^{-3}} = .05$

$$\therefore \ \mathrm{pH} = -\log(0.05)$$
$$= 1.30$$

105. $\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$;
$\mathrm{K} = 0.50 \text{ at } 673\mathrm{K}.$
Write the equilibrium expression and equilibrium constant for reverse reaction.

Ans. : $\mathrm{2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)}$

$\mathrm{K_c'} = \frac{[\mathrm{N_2}][\mathrm{H_2}]^3}{[\mathrm{NH_3}]^2}$ for reverse reaction

$$\mathrm{K_c} = 0.50$$
$$\Rightarrow \mathrm{K_c'} = \frac{1}{\mathrm{K_c}} = \frac{1}{0.50} = 2$$

106. 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.

Ans. : Concentration 10^{-8}mol dm^{-3} indicates that the solution is very dilute. So, we cannot neglect the contribution of H_3O^+ ions produced from H_2O in the solution. Total [H_3O^+] =

$10^{-8} + 10^{-7}$M. From this we get the value of pH close to 7 but less than 7 because the solution is acidic.

From calculation, it is found that pH of 10^{-8}mol dm^{-3} solution of HCl is equal to 6.96.

107. Which of the following is strongest acid?
$\mathrm{HCl, HClO_3, HNO_3, H_2SO_4, HClO_4}$

Ans. : $HClO_4$ is strongest acid because 'Cl' is in +7 oxidation state. Higher the oxidation state, stronger will be acid.

108. The K_{sp} of Ag_2CrO_4 AgCl, AgBr and AgI are respectively, 1.1×10^{-12}, 1.8×10^{-10}, 5.0×10^{-13}, 8.3×10^{-17}, which one of the following salts will precipitate first $AgNO_3$ solution is adding to a solution containing equal mole of NaCl, NaBs, NaI and Na_2CrO_4.

Ans. : AgI will precipitate first because K_{sp} of AgI is lowest, therefore, ionic product will exceed the solubility products easily.

109. At what temperature the solid and liquid are in equilibrium under 1 atm pressure?

Ans. : Melting point or freezing point is a temperature at which solid and liquid are in equilibrium.

110. What will be effect on boiling point of liquid if pressure is increased?

Ans. : The boiling point of liquid will increase because the vapour pressure of liquid will become equal to external pressure at higher temperature.

111. How does a catalyst affect the equilibrium constant? Explain.

Ans. : The equilibrium constant is not affected by catalyst. Catalyst increases the rate of forward as well as backward reaction equally and equilibrium is attained faster.

112. Mention the conditions of temperature and pressure when gas will dissolve in liquid to maximum extent with decrease in volume and absorption of heat.

Ans. : Since decrease in volume takes place, high pressure is favourable for gas to dissolve. Since absorption of heat takes place, high temperature will be suitable to dissolve maximum amount of gas.

113. The value of Kc for the reaction $\mathrm{2HI(g) \rightleftharpoons H_2(g) + I_2(g)}$ is 1×10^{-4}
At a given time, the composition of reaction mixture is [HI] = 2×10^{-5}mol, [H_2] = 1×10^{-5}mol and [I_2] = 1×10^{-5}mol In which direction will the reaction proceed?

Ans. : $\mathrm{Q} = \frac{[\mathrm{H}^2][\mathrm{I}^2]}{[\mathrm{HI}]^2} = \frac{1\times10^{-5}\times1\times10^{-5}}{(2\times10^{-5})^2}$
$= \frac{1}{4} = 0.25 = 2.5 \times 10^{-1}$
Value of $\mathrm{K_c} = 1 \times 10^{-4}$
Since $\mathrm{Q} > \mathrm{K_c}$, the reaction will proceed in backward direction.

114. $\mathrm{CaCl_2(s) + aq \rightleftharpoons CaCl_2(aq) + Heat}$
Discuss the solubility if temperature is increased.

Ans. : The solubility will decrease with increase in temperature because dissolution of $CaCl_2$ is exothermic process.

115.

One millilitre solution of 0.01M HCl is added to 1L of sodium chloride solution. What will be the pH of the resulting solutions?

Ans. : NaCl is neutral, it simply dilutes the HCl solution from 1mL to 1000mL so that

$$[\mathrm{H^+}] = \frac{0.01}{1000} = 10^{-5}\mathrm{M}$$

$$\mathrm{pH} = -\log(10^{-5}) = 5$$

116. Consider the following equilibrium:

$$\mathrm{CO_2(g) + C\ (graphite) \rightleftharpoons 2CO(g)}$$

Write the equilibrium expression for K_c and calculate its units.

Ans. : $\mathrm{K_c} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}]} = \frac{(\mathrm{mol\ L^{-1}})^2}{\mathrm{mol\ L^{-1}}} = \mathrm{mol\ L^{-1}}$

$\therefore [\mathrm{C\ (graphite)}] = 1$

$\because$ Graphite is pure solid.

117. Will AgCl be more soluble in aqueous solution or NaCl solution and why?

Ans. : In NaCl solution, the Cl^- ions will increase. Since solubility product, $K_{sp} = [Ag^+][Cl^-]$ remains constant. $[Ag^+]$ will decrease. Therefore, solubility of AgCl will be less in NaCl solution than in water.

118. What is the effect of reducing volume on the following system?

$$\mathrm{2C(s) + O_2 \rightleftharpoons 2CO(g)}$$

Ans. : On reducing volume, pressure will increase. According to Le-Chatelier principle, equilibrium will shift to the side where number of moles of gas can be increased. In the above reaction, equilibrium will shift in forward direction.

119. $\mathrm{C(diamond) \rightleftharpoons C(graphite)}$

$\mathrm{d = 3.5g\ cm^{-3}} \quad \mathrm{d = 2.3g\ cm^{-3}}$

What will be effect of increasing pressure in this equilibrium?

Ans. : It will shift to backward direction because high pressure will load to formation more denser diamond.

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

$$\mathrm{OH^-,\ RO^-,\ CH_3COO^-,\ Cl^-}$$

Ans. : Conjugate acids of given bases are:

$$\mathrm{H_2O,\ ROH,\ CH3COOH,\ HCl.}$$

Their acidic strength is in the order.

$\mathrm{HCl > CH_3COOH > H_2O > ROH}$ Hence, basic strength is in the order

$$\mathrm{RO^- > OH^- > CH_3COO \longrightarrow Cl^- >}$$

121. pK_a value of acids A, B, C, D are 1.5, 3.5, 2.0 and 5.0. Which of them is strongest acid?

Ans. : Acid A with $pK_a = 1.5$ is strongest acid, lower the value of pK_a stronger will be the acid.

122. What could be temperature 15°C or 100°C for $K_w = 7.5 \times 10^{-14}$. What happens to ionic product if some acid is added to it?

Ans. : Temperature will be 100°C. K_w increases with increase in temperature K_w (ionic product) does not change if same acid is added to it.

123. What will be the pH of 1M Na_2SO_4 solution?

Ans. : Na_2SO_4 is salt of strong acid and strong base, thus its aqueous solution will be neutral. Therefore, its pH will be 7.

124. What is the relation between K_p and K_c?

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

where R = 0.0821L atm K^{-1} mol^{-1}

$\Delta n =$ number of moles of gaseous products - number of moles of gaseous reactants.

125. What is the effect of increasing pressure on the equilibrium?

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

Ans. : On increasing pressure on the equilibrium:

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

The reaction will shift in the forward direction, i.e. towards lesser number of moles because number of moles are decreasing from reactants to products.

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

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

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?

Ans. :

Greater is the ionization constant (K_b) of a base, greater is the ionization of the base. Order of extent of ionization at equilibrium is dimethylamine > ammonia > pyridine > urea. Dimethylamine is the strongest base due to maximum value of K_b.

127. At 0°C, ice and water are present in equilibrium.
What will happen on increasing the pressure?

Ans. : On increasing the pressure, ice melts to form water (because water has lesser volume than ice).

128. Why do we sweat more on humid day?

Ans. : It is because on humid day Water vapours are more in air, therefore sweat does not get evaporated easily and therefore we sweat more.

129. Write conjugate acid and conjugate base of H_2O.

Ans. : Conjugate acid is H_3O^+ and conjugate base is OH^-. Add H^+ to get conjugate acid and remove H^+ to get conjugate base.

*** Given Section consists of questions of 3 marks each. [60]**

130.

What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species:

$$\mathrm{HNO_2, CN^-, HClO_4, F^-, OH^-, CO_3^{2-} and\ S^{2-}}$$

Ans. : A conjugate acid-base pair is a pair that differs only by one proton. The conjugate acid-base for the given species is mentioned in the table below.

Species	Conjugate acid-base
$\mathrm{HNO_2}$	$\mathrm{NO_2^-}$ (base)
$\mathrm{CN-}$	HCN(acid)
$\mathrm{HClO_4}$	$\mathrm{ClO_4^-}$ (base)
$\mathrm{F-}$	HF(acid)
$\mathrm{OH-}$	$\mathrm{H_2O}$(acid)/$\mathrm{O^{2-}}$(base)
$\mathrm{CO_3^{2-}}$	$\mathrm{HCO_3^-}$ (acid)
$\mathrm{S^{2-}}$	$\mathrm{HS^-}$ (acid)

131. The value of K_c for the reaction $3O_2\ (g) \rightleftharpoons 2O_3\ (g)$ is 2.0 $\times 10^{-50}$ at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6 $\times 10^{-2}$, what is the concentration of O_3?

Ans. : The given reaction is: $3O_{2(g)} \leftrightarrow 2O_{3(g)}$

Then, $K_c = \frac{[O_{3(g)}]^2}{[O_{2(g)}]^3}$

It is given that $K_C = 2.0 \times 10^{-50}$ and $[O_{2(g)}] = 1.6 \times 10^{-2}$.

Then, we have,

$$2.0 \times 10^{-50} = \frac{[O_{3(g)}]^2}{[1.6 \times 10^{-2}]^3}$$

$$\Rightarrow [O_{3(g)}]^2 = 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3$$

$$\Rightarrow [O_{3(g)}]^2 = 8.192 \times 10^{-56}$$

$$\Rightarrow [O_{3(g)}] = 2.86 \times 10^{-28}\ \mathrm{M}$$

Hence, the concentration of O_3 is 2.86×10^{-28} M.

132. Find out the value of K_c for each of the following equilibria from the value of K_p:

$$2\mathrm{CaCO_3\ (S) \rightleftharpoons CaO(S) + CO_2\ (g);\ k_p = 167\ at\ 1073K}$$

Ans. : The relation between K_p and K_c is given as:

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

Here,

$$\Delta n = 2 - 1 = 1$$

$$R = 0.0831\ \mathrm{bar\ L\ mol^{-1} K^{-1}}$$

$$T = 1073K$$

$$K_p = 167$$

Now,

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

$$\Rightarrow 167 = K_c(0.0831 \times 1073)^{\Delta n}$$

$\Rightarrow K_c = \frac{167}{0.0831 \times 1073}$

$= 1.87(\text{approximately})$

133. The reaction, $CO\ (g) + 3H_2\ (g) \rightleftharpoons CH_4\ (g) + H_2O\ (g)$ is at equilibrium at 1300K in a 1L flask. It also contain 0.30mol of CO, 0.10molof H_2 and 0.02mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.

Ans. : Let the concentration of methane at equilibrium be x.

	$CO_{(g)}$	+	$3H_{2(g)}$	$\leftrightarrow$	$CH_{4(g)}$	+	$H_2O_{(g)}$
At equilibrium	$\frac{0.3}{1}$ $= 0.3M$		$\frac{0.1}{1}$ $= 0.1M$		x		$\frac{0.02}{1}$ $= 0.02M$

It is given that $K_c = 3.90$.

Therefore,

$\frac{[CH_{4(g)}][H_2O_{(g)}]}{[CO_{(g)}][H_{2(g)}]} = K_c$

$\Rightarrow \frac{x \times 0.02}{0.3 \times (0.1)^3} = 3.90$

$\Rightarrow x = \frac{3.90 \times 0.3 \times (0.1)^3}{0.02}$

$= \frac{0.00117}{0.02}$

$= 0.0585M$

$= 5.85 \times 10^{-2}M$

Hence, the concentration of CH_4 at equilibrium is $5.85 \times 10^{-2}M$

134. The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.

Ans. : Degree of ionization, α = 0.132

Concentration, c = 0.1M

Thus, the concentration of H_3O^+ = c.α

= 0.1 × 0.132

= 0.0132

$pH = -\log[H^+]$

$= -\log(0.0132)$

$= 1.879 : 1.88$

Now,

$K_a = C\alpha^2$

$= 0.1 \times (0.132)^2$

$K_a = .0017$

$pK_a = 2.75$

135. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Ans. : Given,

pH = 3.76

It is known that,

$$pH = -\log[H^+]$$
$$\Rightarrow \log[H^+] = -pH$$
$$\Rightarrow [H^+] = \text{antilog}(-pH)$$
$$= \text{antilog}(-3.76)$$
$$= 1.74 \times 10^{-4} M$$

Hence, the concentration of hydrogen ion in the given sample of vinegar is 1.74×10^{-4}M.

136. If $K_w = 49 \times 10^{-14}$, what will be neutral pH of H_2O?

Ans. : $K_w = 49 \times 10 - 14[H_3O^+][OH^-]$
$$= 49 \times 10^{-14}$$
$$[H_3O^+] = [OH^-]$$
$$\Rightarrow [H_3O^+]^2 = 49 \times 10^{-14}$$
$$\Rightarrow [H_3O^+] = 7 \times 10^{-7} \text{ mol L}^{-1}$$
$$pH = -\log[H_3O^+]$$
$$= -\log 7 \times 10^{-7}$$
$$= -\log 7 - \log 10^{-7}$$
$$= -\log 7 + 7 \log 10$$
$$pH = -0.8451 + 7.000$$
$$= 6.1549$$

137. Why do we pass H_2S gas in acidic medium in group 2?

Ans. : It is done so as to reduce concentration of [SP^{2-}] by common ion effect so that only group 2 radicals get precipitated whereas higher group radicals do not as K_{sp} of group II sulphides is low as compared to K_{sp} of sulphides of higher groups.

138. The K_{sp} values of two slightly soluble salts AB and PQ_2 are each equal to 4.0×10^{-18}. Which salt is more soluble?

Ans. : For AB salt, $K_{sp} = [A^+]\,[B^-]$ If x is the solubolity, then

$x^2 = 4.0 \times 10^{-18}$

or $x = 2.0 \times 10^{-9}$

For PQ_2 salt, $K_{sp} = [P^{2+}]\,[Q^-]^2$

If y is the solubility, then

$4y^3 = K_{sp} = 4.0 \times 10^{-18}$

or $y = 1.0 \times 10^{-6}$

Since y is more than x, PQ_2 salt has more solubility.

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

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

Ans. :

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

140. 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: $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Ans. : $\Delta G = \Delta G^{\ominus} + RT\ InQ$

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

ΔG = Standard free energy change.

Q = Reaction quotient.

R = Gas constant.

T = Absolute temperature.

Since $\Delta G^{\ominus} = -RT\ InK$

$\therefore \Delta G = -RT\ InK + RT\ InQ = RT\ In\frac{Q}{K}$

If $Q < K, \Delta G$ 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 $Q < K$ and hence the reaction proceeds in forward direction.]

141. Urine has a pH of 6.0. If a patient eliminates 1300mL of urine per day, how many gram equivalents of the acid he eliminates per day?

Ans. : $\because$ pH = 6.0

$\therefore [H_3O^+] = 10^{-6}M$

i.e. [Acid] = $10^{-6}M = 10^{-6}N$

Thus, 1000mL of the urine contain acid = 10^{-6}g e.q

$\therefore$ 1300mL pf the urine will contain acid = 1.3×10^{-6}g eq.

142.

Calculate the molar solubility of $Ni(OH)_2$ in 0.10M NaOH. The ionic product of $Ni(OH)_2$ is 2.0×10^{-15}.

Ans. : $\mathrm{Ni(OH)\_2} \longrightarrow \mathrm{Ni^{2+}} + 2\mathrm{OH^-}$

Ionic product = $[Ni^{2+}]\,[OH^-]^2$

$[OH^-] = 0.1M$, $[Ni^{2+}] = ?$

$2.0 \times 10^{-15} = [Ni^{2+}]\,(0.1)^2$

$$\Rightarrow [\mathrm{Ni^{2+}}] = \frac{2\times10^{-15}}{10^{-2}}$$

$$= 2 \times 10^{-13}\mathrm{M}$$

Solubility of $Ni(OH)_2$ will be equal to $[Ni^{2+}] = 2 \times 10^{-13}M$.

143. For the reaction, $\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$, the partial pressures of N_2 and H_2 are 0.80 and 0.40 atmosphere respectively at equilibrium. The total pressure of the system is 2.80 atmosphere. What is K_p for the above reaction?

Ans. : $\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$,

Given, at equilibrium, $\mathrm{p_{N_2}} = 0.80$ atmosphere,

$\mathrm{p_{H_2}} = 0.40$ atmosphere

$\mathrm{p_{N_2} + p_{H_2} + p_{NH_3}} = 2.80$ atmosphere

$\therefore \mathrm{p_{NH_3}} = 2.80 - (0.80 + 0.40) = 1.60$ atmosphere

From, $\mathrm{K_p} = \frac{\mathrm{p^2_{NH_3}}}{\mathrm{p_{N_3} \times p^3_{H_2}}}$

$$= \frac{(1.60)^2}{0.80 \times (0.40)^3} = 50.0$$

144.
- i. Why is NH_4Cl added before addition of NH_4OH in qualitative analysis of 3rd group?
- ii. Which will be added to precipitate soap (RCOONa)? NaCl or KCl and why?'

Ans. :
- i. It is done so as to decrease conc. of OH^- due to common ion effect so that only group 3 radicals get precipitated and higher group radicals do not.
- ii. NaCl will be added to precipitate soap.

$$\mathrm{RCOO^- + Na^+ \rightleftharpoons RCOONa}$$

$$\mathrm{Na^+ + Cl^- \rightleftharpoons NaCl}$$

Due to common ion effect of Na^+, soap (RCOONa) will get precipitated completely.

145. Solid $Ba(NO_3)$, is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form.(K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)

Ans. : $\mathrm{BaCO_3(s) \rightleftharpoons Ba^{2+} + CO_3^{2-}}$

$$\mathrm{Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}}$$

$$[\mathrm{Na_2CO_3}] = 1.0 \times 10^{-4}\mathrm{M}$$

$$\mathrm{K_{sp}} = [\mathrm{Ba^{2+}}][\mathrm{CO_3^{2-}}]$$

$$5.1 \times 10^{-9} = [\mathrm{Ba^{2+}}][1 \times 10^{-4}\mathrm{M}]$$

$$[\mathrm{Ba}^{2+}] = \frac{5.1\times10^{-9}}{1\times10^{-4}}$$
$$= 5.1 \times 10^{-5}\mathrm{M}$$

At 5.1 × 10^{-5}M concentration of [Ba^{2+}], I.P(ionic product) will become equal to K_{sp} and precipitate will begin to from.

146. A certain buffer is made by mixing sodium formate and formic acid in water. With the help of equations explain how this buffer neutralizes addition of a small amount of an acid or a base?

Ans. : $\mathrm{HCOONa} \longrightarrow \mathrm{HCOO}^- + \mathrm{Na}^+$

$$\mathrm{HCOOH} \rightleftharpoons \mathrm{HCOO}^- + \mathrm{H}^+$$

HCOO^- is common ion in the above acidic buffer. When small amount of H^+ ions is added, these H^+ ions combine with HCOO^- which are in excess to form HCOOH back and [H^+]remains practically same, so pH remains constant. When small amount of OH^- ions are added, OH^- ions will take up H^+ and association of HCOOH will increase so as to maintain concentration of H^+ ions. So, pH is not affected.

147. MY and NY_3 two nearly insoluble salts, have same K_{sp} values 6.2 × 10^{-3} of non temperature. Calculate solubility of each salt. Which has more solubility.

Ans. : $\mathrm{MY} \rightleftharpoons \mathrm{M}^+ + \mathrm{Y}^-$

$$\quad\ \mathrm{'s'} \qquad \mathrm{'s'} \qquad \mathrm{'s'}$$
$$\mathrm{K_{sp}} = [\mathrm{M}^+][\mathrm{Y}^-] = \mathrm{s}^2$$
$$\Rightarrow \mathrm{s} = \sqrt{\mathrm{K_{sp}}}$$
$$= \sqrt{6.2\times10^{-13}}$$
$$= \sqrt{62\times10^{-14}}$$
$$= 7.9\times10^{-7}\mathrm{mol\ L}^{-1}$$
$$[\because \sqrt{62} = 7.9 \text{ and } \sqrt{10^{-14}} = 10^{-7}]$$
$$\mathrm{NY_3} \rightleftharpoons \mathrm{M}^{+3} + 3\mathrm{Y}^-$$
$$\mathrm{'s'} \qquad \mathrm{'s'} \qquad \mathrm{'3s'}$$
$$\mathrm{K_{sp}} = [\mathrm{M}^+][\mathrm{Y}^-]$$
$$= \mathrm{s}\times(3\mathrm{s})^3 = 27\mathrm{s}^4$$
$$\mathrm{s}^4 = 4\sqrt{\frac{\mathrm{K_{sp}}}{27}}$$
$$= 4\sqrt{\frac{62\times10^{-14}}{24}}$$
$$= 4\sqrt{2.296\times10^{-14}}$$
$$4\sqrt{229.6\times10^{-16}}$$
$$3.85\times10^{-4}\mathrm{mol\ L}^{-1}$$

148. What is the effect of temperature on the reactions? Give reason.

i. $\mathrm{N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g) + Heat}$

ii. $\mathrm{N_2(g)+O_2(g) \rightleftharpoons 2NO(g) + Heat}$

Ans. :

i. The increase in temperature will favour backward reaction because the reaction is exothermic. On increasing temperature, equilibrium will shift in opposite direction to counter balance the effect of increasing temperature, i.e., backward reaction.

ii. The increase in temperature favours forward reaction because the reaction is endothermic.

149. i. Give the relationship between K_a, c and $('\alpha')$ where 'K_a' is acid dissociation constant, 'c' is molar concentration, $'\alpha'$ is degree of dissociation.

ii. If the solubility of $Ca(IO_3)_2$ in water at 18°C is 2.1g/ litre. Calculate the value of solubility product.

[Molecular mass of $Ca(IO_3)_2$ = 390]

Ans. :

i. $\mathrm{K_a} = \frac{\mathrm{c}\alpha^2}{1-\alpha}$ if $\alpha <<<< 1$ then $\mathrm{K_a} = \mathrm{c}\alpha^2$

$\because 1-\alpha = 1$

ii. Solubility in mol L^{-1} $= \frac{2.1\mathrm{g\ L^{-1}}}{390\mathrm{g\ mol^{-1}}}$

$$= 5.4 \times 10^{-3}\mathrm{mol\ L^{-1}}$$

$$\mathrm{Ca(IO_3)_2} \rightleftharpoons \mathrm{Ca^{2+}} + 2\mathrm{IO_3^-}$$

$$\mathrm{K_{sp}} = [\mathrm{Ca^{2+}}][\mathrm{IO_3^-}]^2$$

$$\mathrm{K_{sp}} = (5.4\times10^{-3})(2\times5.4\times10^{-3})^2$$

$$\mathrm{K_{sp}} = -629.856\times10^{-9}\mathrm{mol^3L^{-3}}$$

$$= 6.6\times10^{-7}\mathrm{mol^3L^{-3}}$$

* Case study based questions [8]

150. Read the passage given below and answer the following questions from (i) to (v).

Predicting the Direction of the Reaction- The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the reaction quotient Q. The reaction quotient, Q (Qc with molar concentrations and QP with partial pressures) is defined in the same way as the equilibrium constant Kc except that the concentrations in Qc are not necessarily equilibrium values. For a general reaction:

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

$$\mathrm{Qc} = \frac{[\mathrm{C}]^\mathrm{c}[\mathrm{D}]^\mathrm{d}}{[\mathrm{A}]^\mathrm{a}[\mathrm{B}]^\mathrm{b}}$$

Then,

If Qc > Kc, the reaction will proceed in the direction of reactants (reverse reaction).

If Qc < Kc, the reaction will proceed in the direction of the products (forward reaction).

If Qc = Kc, the reaction mixture is already at equilibrium. Consider the gaseous reaction of H_2 with I_2 ,

$$\mathrm{H_{2(g)} + l_{2(g)} \rightleftharpoons 2Hl_{(g)}; kc = 57.0at700k.}$$

Suppose we have molar concentrations $[H_2]$t =0.10M, $[I_2]$t = 0.20 M and [HI]t = 0.40 M. (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium). Thus, the reaction quotient, Qc at this stage of the reaction is given by,

$$\mathrm{Qc} = \frac{[\mathrm{Hl}]\mathrm{t}^2}{[\mathrm{H}]^2]_\mathrm{t}[\mathrm{l}_2]_\mathrm{t}} = \frac{(0.40)_2}{(0.10)\times(0.20)} = 8.0$$

Now, in this case, Qc (8.0) does not equal Kc (57.0), so the mixture of $H_{2\ (g)}$, $I_{2\ (g)}$ and $HI_{(g)}$ is not at equilibrium; that is, more $H_{2\ (g)}$ and $I\ 2_{\ (g)}$ will react to form more $HI_{(g)}$ and their concentrations will decrease till Qc = Kc. The reaction quotient, Qc is useful in predicting the direction of reaction by comparing the values of Qc and Kc.Thus, we can make the following generalisations concerning the direction of the reaction

If Qc < Kc, net reaction goes from left to right

If Qc > Kc, net reaction goes from right to left.

If Qc = Kc, no net reaction occurs.

Calculating Equilibrium Concentrations In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1) Write the balanced equation for the reaction.

Step 2) Under the balanced equation, make a table that lists for each substance involved in the reaction: (a) the initial concentration, (b) the change in concentration on going to equilibrium, and (c) the equilibrium concentration. In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3) Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4) Calculate the equilibrium concentrations from the calculated value of x.

Step 5) Check your results by substituting them into the equilibrium equation.

Relationship between equilibrium constant K, reaction quotient Q and gibbs energy G The value of Kc for a reaction does not depend on the rate of the reaction. However, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, $\triangle \mathrm{G}.$ If,

$\triangle \mathrm{G}$ is negative, then the reaction is spontaneous and proceeds in the forward direction.

$\triangle \mathrm{G}$ is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative $\triangle \mathrm{G},$ the products of the forward reaction shall be converted to the reactants.

$\triangle \mathrm{G}$ is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction. A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation:

$$\triangle \mathrm{G} = \triangle \mathrm{G}^{\phi} + \mathrm{RTlnQ}$$

where, $\triangle \mathrm{G}^{\phi}$ is standard Gibbs energy. At equilibrium, when $\triangle \mathrm{G} = 0$ and Q = Kc, the equation becomes,

$$\triangle \mathrm{G} = \mathrm{G}^{\phi} + \mathrm{RTlnk} = 0$$

$$\triangle \mathrm{G}^{\phi} = -\mathrm{RTlnk}$$

$$\mathrm{Ink} = \frac{-\triangle \mathrm{G}^{\phi}}{\mathrm{RT}}$$

Taking antilog of both sides, we get,

$$\mathrm{K} = \mathrm{e} - \frac{\triangle \mathrm{G0}}{\mathrm{RT}}$$

Hence, using the equation, the reaction spontaneity can be interpreted in terms of the value of $\triangle \mathrm{G}^{\phi}$.

If $\triangle \mathrm{G}^{\phi} > 0$ then $\frac{-\triangle \mathrm{G}^{\phi}}{\mathrm{RT}}$ is positive, and >1, making K > 1, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.

If $\triangle \mathrm{G}^{\phi} > 0,$ then $\frac{-\triangle \mathrm{G}^{\phi}}{\mathrm{RT}}$ is negative, and < 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.

Factors affecting equilibria One of the principal goals of chemical synthesis is to maximise the conversion of the reactants to products while minimizing the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N_2 and H_2, the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tones, primarily for use as fertilizers. Equilibrium constant, Kc is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium we use Le Chatelier’s principle. It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change. This is applicable to all physical and chemical equilibria.

Effect of Concentration Change In general, when equilibrium is disturbed by the addition/removal of any reactant/ products, Le Chatelier’s principle predicts that:

The concentration stress of an added reactant/product is relieved by net reaction in the direction that consumes the added substance.

The concentration stress of a removed reactant/product is relieved by net reaction in the direction that replenishes the removed substance. or in other words, “When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes”. Let us take the reaction,

$$\mathrm{H}_{2(\mathrm{g})} + \mathrm{l}_{2(\mathrm{g})} \rightleftharpoons 2\mathrm{Hl}_{(\mathrm{g})}$$

If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H_2 is consumed, i.e., more of H_2 and I_2 react to form HI and finally the equilibrium shifts in right (forward) direction. This is in accordance with the Le Chatelier’s principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture. The same point can be explained in terms of the reaction quotient, Qc,

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$$\mathrm{Qc} = \frac{[\mathrm{HI}]^2}{[\mathrm{H}]_2[\mathrm{I}]_2}$$

Addition of hydrogen at equilibrium results in value of Qc being less than Kc. Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Qc at a value less than Kc and reaction continues to move in the forward direction.

i. If … the reaction will proceed in the direction of reactants (reverse reaction).
   a. Qc > Kc
   b. Qc < Kc
   c. Qc = Kc
   d. None of above

ii. If … the reaction will proceed in the direction of the products (forward reaction).
   a. Qc > Kc
   b. Qc < Kc
   c. Qc = Kc
   d. None of above

iii. If … the reaction mixture is already at equilibrium. Consider the gaseous reaction.
   a. Qc > Kc
   b. Qc < Kc
   c. Qc = Kc
   d. All of above

iv. If $\triangle G$ is …. then the reaction is spontaneous and proceeds in the forward direction.
   a. Zero
   b. Positive
   c. Negative
   d. None of above

v. $\triangle G$ is … reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.
   a. Zero
   b. Positive
   c. Negative
   d. None of above

Ans. :

i. (a) Qc > Kc
ii. (b) Qc < Kc
iii. (c) Qc = Kc
iv. (c) Negative
v. (a) Zero

151. Read the passage given below and answer the following questions from (i) to (v).

When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached equilibrium state at this stage. However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at equilibrium, the rate of evaporation is equal to the rate of condensation. It may be represented by

$$\mathrm{H_2O_{(l)} \rightleftharpoons H_2O_{(vap)}}$$

The double half arrows indicate that the processes in both the directions are going on simultaneously. The mixture of reactants and products in the equilibrium state is called an equilibrium mixture.

Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the dynamic equilibrium

The chemical equilibrium may be classified in three groups.

1. The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally.
2. The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.
3. The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

The equilibrium involving ions in aqueous solutions which is called as ionic equilibrium.

Solid-Liquid Equilibrium Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K. It is obvious that 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 and we can infer the following:

1. Both the opposing processes occur simultaneously.
2. Both the processes occur at the same rate so that the amount of ice and water remains constant.

Solid – Vapour Equilibriu*m* Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,

$$\mathrm{l_2(solid) \rightleftharpoons l_2(vapour)}$$

Other examples showing this kind of equilibrium are,

$$\mathrm{Camphor\,_{(solid)} \rightleftharpoons Camphor\,_{(vapour)}}$$

$$\mathrm{NH_4CI_{(solid)} \rightleftharpoons NH_4CI_{(vapour)}}$$

The equilibrium Involving Dissolution of Solid in Liquids Only a limited amount of salt or sugar can dissolves in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution: Sugar (solution) Sugar (solid), and the rate of dissolution of sugar = rate of crystallisation of sugar. Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non- radioactive molecules in the solution increases till it attains a constant value.

i. Which of the following symbol represents equilibrium.
  a. ⇌
  b. ⇆
  c. ⇼
  d. ↑↓
ii. When there is no change in the concentrations of either of the reactants or products, this stage of the system is the …
  a. Static equilibrium
  b. Dynamic equilibrium
  c. Physical equilibrium
  d. Chemical equilibrium
iii. A … solution means no more of solute can be dissolved in it at a given temperature.
  a. Unsaturated
  b. Supersaturated
  c. Saturated
  d. None of these.
iv. The equilibrium involving ions in aqueous solutions which is called as …
  a. Static equilibrium
  b. Dynamic equilibrium
  c. Physical equilibrium
  d. Ionic equilibrium
v. The concentration of the solute in a saturated solution depends upon the …
  a. Solvent
  b. Pressure
  c. Temperature
  d. System

Ans. :

i. (a) ⇌
ii. (b) Dynamic equilibrium
iii. (c) Saturated
iv. (d) Ionic equilibrium
v. (c) Temperature

----- Stay away from those people who try to disparage your ambitions. … -----