Chapter 7. Equilibrium

Question-1

Why is vapour pressure independent of initial amount?

Solution:

Vapour pressure of liquid is defined as pressure exerted by liquid at equilibrium at a given temperature. Different amounts of liquids exert same equilibrium pressure at a given temperature.

At equilibrium, rate of evaporation = rate of condensation

Different amounts of liquid will give same ratio of amount of evaporation to amount of condensation.

Question-2

Write K_p for $CaCO_3$ decomposition.

Solution:

$$\underset{(s)}{CaCO_3} \overset{\Delta}{\rightleftharpoons} \underset{(s)}{CaO} + \underset{(g)}{CO_2}$$

Kp = p CO_2 where pCO_2 - Partial vapor pressure.

Question-3

At 500 k, 1.04 g of hydrogen, and 12,060 g of I_2 are in equilibrium with 5.058 g of hydrogen iodide in a vessel of capacity 1lit. Calculate the equilibrium constant.

Solution:

$[H_2] = \frac{1.04}{2}$ g/mole $[H\ I] = \frac{5.058}{128}$ g/mole ($H_2 = 2$; $I_2 = 254$; $HI = 128$)

$[I_2] = \frac{12060}{254}$ g/mole $H_2 + I_2 \rightleftharpoons 2HI$

$$K_c = \frac{[HI]^2}{[H_2[I_2]]} = \left(\frac{5.058}{128}\right)^2 \Bigg/ \left(\frac{1.04}{2}\right)\left(\frac{12060}{254}\right) = 6.48$$

$K_c = 6.48$.

Question-4

If the value of Kc be 50.21, for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ how much HI would be present at the equilibrium, if we start with 5.30 mol of I_2 and 7.94 mol of H_2?

Solution:

At equilibrium of 2x mol HI is formed, x mol H_2 and x mole of I_2 should be consumed.

At equilibrium $[HI] = 2x$; $[H_2] = [7.94 - x]$

$[I_2] = [5.30 - x]$

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

$50.21 = \frac{[2x]^2}{[7.94 - x][5.30 - x]}$

$4x^2 = 2112.93 - 664.78x + 50.21\,x^2$

$46.21\,x^2 - 664.78\,x -+ 2112.93 = 0;$

$x^2 - 14.3\,x + 46 = 0$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$x = \frac{14.3 \pm \sqrt{205 - 184}}{2}$

$x = \frac{14.3 \pm 4.58}{2}$

$2x = 9.72$ moles

At equilibrium $[HI] = 9.72$ moles.

Question-5

K_c for $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ is 61. What is K_c for $2NH_3 \rightleftharpoons N_2(g) + 3H_2\,(g)$?

Solution:

Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward reaction.

K'_c for $2NH_3 \rightleftharpoons N_2\,(g) + 3H_2\,(g)$ is $\frac{1}{61}$.

Question-6

For the equilibrium N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) K_p is 6.8 ×10^5 at 298 K. What is the K_c value for the same equilibrium?

Solution:

For the reaction $\Delta n = 2 - (1 + 3) = -2$

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

$6.8 \times 10^5 = K_c \times (0.0831\times298)^{-2}$

$6.8 \times 10^5 = K_c \times \frac{1}{(0.0831\times 298)^2}$

(i.e.) $K_c = 6.8 \times 10^5 \times (0.0831\times298)^2 = 4170.1 \times.$

Question-7

If the reaction between iron and steam proceeds as: $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$ and the partial pressure of steam be 50 mm and of hydrogen 940 mm at 250^o. Calculate the pressure of steam at equilibrium when the partial pressure of hydrogen is 1800 mm.

Solution:

$3Fe$ (s) + $4H_2O$ (g) $\rightleftharpoons$ Fe_3O_4 (s) + $4H_2$ (g)

$K_p = \frac{(pH_2)^4}{(pH_2O)^4} = \frac{(940)^4}{(50)^4}$

When pH_2 = 1800 mm

$K_p = \frac{(940)^4}{(50)^4} = \frac{(1800)^4}{x^4}$ where x is pH_2O

$x = \frac{50\times 1800}{940} = 95.7.$

∴Partial preesure of steam is 95.7 mm.

Question-8

Why is NaCl precipitated by passing HCl gas in a NaCl saturated solution?

Solution:

$NaCl \rightleftharpoons Na^+ Cl^-$, when HCl is passed, $[Cl^-]$ is more. To decrease the concentration of Cl^- backward reaction takes place. Hence NaCl is precipitated. This could also be attributed to common ion effect.

Question-9

What is effect of pressure for the following equilibrium?
(i) $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$; $K_c = 1.7 \times 10^{26}$
(ii) $C\ (s) + CO_2\ (g) \rightleftharpoons 2CO\ (g)$

Solution:

(i) $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3$

|When equilibrium pressure is increased, to annul the effect, the reaction in which pressure is consumed will take place. Pressure is used to decrease the volume (i.e.) forward reaction will take place where 3 moles are reduced to 2 moles. The equilibrium is shifted to forward direction.

(ii) $C\ (s) + CO_2\ (g) \rightleftharpoons 2CO\ (g)$

When pressure increased the reaction in which number of moles reduced will take place. (i.e.) equilibrium is shifted to reverse direction.

Question-10

N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) ; ΔH^o = -92.38 kJ mole^{-1}, what happens temp is increased at equilibrium?

Solution:

When temperature is increased at equilibrium, the reaction in which heat is consumed will take place to annul the effect of increase in temperature. Backward reaction is a heat consuming reaction. Hence, decomposition of ammonia takes decomposition when temp is increased.

Question-11

Explain the dynamic equilibrium between ice and water.

Solution:

The dynamic equilibrium consists of a forward reaction in which ice melts to give water and a reverse reaction in which water solidifies to ice.

Ice $\rightleftharpoons$ water,

At 273K, both ice and water are in equilibrium. Both forward and backward reactions occur at the same rate. At T > 273K, more water is present and $\Delta G < 0$. At T < 273K, more ice is present and $\Delta G > 0$.

Question-12

Explain why the equilibrium constant for a gaseous reaction can be written in terms of partial pressures instead of concentrations.

Solution:

The molar concentration of a gas is directly proportional to its partial pressure at a fixed temperature. Therefore, it is convenient to express the composition of a gaseous reaction mixture in terms of the partial pressures of the components rather than in terms of their molar concentrations.

Question-13

The equilibrium constant of a reaction decrease with increase in temperature. Is the reaction exothermic or endothermic?

Solution:

Exothermic because with increase in temperature, the equilibrium shifts in the backward direction.

Question-14

(a) Predict the direction of reaction when chlorine gas is added to an equilibrium mixture of PCl_3, PCl_5 and Cl_2. The reaction is
$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(b) What is the direction of reaction when chlorine gas is removed from an equilibrium mixture of these gases?

Solution:

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

(a) When Cl_2 is added to the reaction mixture, increasing its concentration, the reaction goes in the forward direction (more PCl_5 is formed).

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

(b) When Cl_2 is removed from the reaction mixture, lowering its concentration, the reaction goes in the reverse direction (more PCl_5 dissociates to PCl_3 and Cl_2) to partially restore the Cl_2 that was removed.

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

Question-15

What is the effect of reducing the volume on the system described below?
$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

Solution:
The forward reaction is accompanied by increase in volume. Hence according to Le-Chatelier's principle, reducing the volume will shift the equilibrium in the forward direction.

Question-16

Consider the reaction:
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 189.4\ kJ$
Indicate the direction in which the equilibrium will shift when
(i) a catalyst is added

(ii) pressure is decreased

Solution:
(i) A catalyst is added: The equilibrium will not shift in any direction because both the forward and backward rates are increased to the same extent.
(ii) Pressure is decreased: The equilibrium will shift to the left to produce more number of moles of the reactants.

Question-17

What is the effect of catalyst on the equilibrium? Give an example.

Solution:

A catalyst is a substance that increases the rate of a reaction but is not consumed by it. However, the presence of a catalyst speeds the reverse reaction as well as the forward reaction, leaving the equilibrium constant unchanged For example,

$N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3(g)$

Question-18

Classify conjugate pairs among the following:

Q. HCl, HS^-, HSO_4^{2-}, H_2O, HCO_3^-, H_2S, HPO_4^{2-}, NH_3, Cl^-, H_3O^+, NH_4^+, SO_4^{2-}.

Solution:

HCl and Cl^-, H_2S and HS^-, HSO_4^{2-} & SO_4^{2-}, H_3O^+ and H_2O.

Question-19

The solubility of magnesium oxalate, MgC_2O_4, in water is 00093 mol/L. Calculate K_{sp}.

Solution:

$Mg_2C_2O_4(s) \rightleftharpoons Mg^{+2}(aq) + C_2O_4^{-2}(aq)$

Starting 0 0

Equilibrium 9.3×10^{-3} 9.3×10^{-3}

$[Mg^{+2}] = 9.3 \times 10^{-3}$ mol L^{-3}. $[C_2O_4^{-2}] = 9.3 \times 10^{-3}$ mol L^{-1}

$K_{sp} = [Mg^{+2}][C_2O_4^{-2}] = (9.3 \times 10^{-3})(9.3 \times 10^{-3}) = 8.65 \times 10^{-5}\ M^2$.

Question-20

What is the solubility of strontium sulphate, $SrSO_4$, in 0.15 M sodium sulphate, Na_2SO_4? K_{sp} of $SrsO_4 = 2.5 \times 10^{-7}$

Solution:

The equation for the dissolving $SrSO_4$ is

$SrSO_4(s) \rightleftharpoons Sr^{+2}(aq) + SO_4^{-2}(aq)$

In this solution there are two sources of SO_4^{-2}(aq). The soluble Na_2SO_4 is completely dissociated into Na^+ ions and SO_4^{-2}(aq) ions, and the small amount of $SrSO_4$ that dissolves also provides SO_4^{-2}(aq) ions. The SO_4^{-2}(aq) ion is common to both the insoluble electrolyte $SrSO_4$ and the soluble salt Na_2SO_4. There is, however, only one source of Sr^{+2} ions, namely the dissolution of solid $SrSO_4$

Let

S = molar solubility of $SrSO_4$ in 0.15 M Na_2SO_4

Then, $[Sr^{+2}] = S$ and $[SO_4^{-2}] = 0.15 + S$

$K_{sp}(SrSO_4) = [Sr^{+2}]\,[SO_4^{-2}] = S(0.15 + S)$

$2.5 \times 10^{-7} = 0.15S + S^2$

Assuming S to be small compared to 0.15 and that

$\therefore 2.5 \times 10^{-7} = 0.15S$

or $S = 1.67 \times 10^{-6}$ M.

Question-21

The solubility product of $Fe(OH)_3$ is 1×10^{-36}. What is the minimum concentration of OH^- ions required to precipitate $Fe(OH)_3$ from a 0.001 M solution of $FeCl_3$?

Solution:

$K_w = [Fe^{3+}]\,[OH^-]^3$

Precipitation will occur when ionic product, $[Fe^{3+}]\,[OH^{-3}]$ becomes greater than K_s

$[Fe^{3+}] = [FeCl_3] = 0.001M$

The concentration of OH^- ions required to start the precipitation is

$[OH^-]^3 = \frac{K_{sp}}{[Fe^{3+}]} = \frac{1 \times 10^{-36}}{0.001} = 1 \times 10^{-11}$

$\therefore [OH^-] = (1 \times 10^{-33})^{1/3} = 1 \times 10^{-11}$ $molL^{-1}$.

Question-22

Calculate the pH of 0.5 molar solution of sulphuric acid.

Solution:

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{-2}$

In a 0.5 m H_2SO_4 solution

$[H^+] = 2 \times 0.5 \text{ mol L}^{-1} = 1 \text{ mol L}^{-1}$

$\therefore$ pH = - log $[H^+]$ = -log (1) = 0

Question-23

The pH of 0.05M aqueous solution of diethyl amine is 12.0 calculate its K_b.

Solution:

pH = 12.0; pOH = 14 − 12.00 = 2.00

$[OH^-] = 10^{-2}M$; $K_b = \frac{x^2}{c}$

$kb = \frac{(10^{-2})(10^{-2})}{5 \times 10^{-2}} = 0.2 \times 10^{-2} = 2 \times 10^{-3}$.

Question-24

The solubility of lead iodide in water is 0.63 gm/litre. Calculate the solubility product of lead iodide (At mass of Pb = 207; I = 127).

Solution:

Solubility of lead iodide in moles / litre

$= \frac{0.63}{461} = \frac{630 \times 10^{-3}}{461} = 1.36 \times 10^{-3}$ moles / litres

$PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$

$K_{SP} = [Pb^{2+}][I^-]^2$

$= [1.36 \times 10^{-3}][2 \times 1.36 \times 10^{-3}]^2$

$= 4 \times (1.36 \times 10^{-3})^3$

$= 4 \times (10^{-3})^3 (1.36)^3$

$= 4 \times 10^{-9} \times 1.4 \times 1.4 \times 1.4$

$= 4 \times 10^{-9 \times} 1.4 \times 1.4 \times 1.4$

$= 10.9 \times 10^{-9}$

KSP = 1.09×10^{-8} mol^{-3} L^{-3}.

Question-25

How many moles of AgBr ($K_{SP} = 5 \times 10^{-13}$ mol^{-2} L^{-2}) will dissolve in 0.01M NaBr solution?

$AgBr \rightleftharpoons [Ag^+] [Br^-]$

$K_{SP} = [x] [x + 0.01]$ where x = solubility of Ag^+ or Br^-.

Solution:

$5 \times 10^{-13} \equiv (x) (10^{-2})$ (compare to 0.01, x is small)

(i.e.) $x = \frac{5 \times 10^{-3}}{10^{-2}} = 5 \times 10^{-1}$ mol L^{-1}.

Question-26

Two moles of HI when heated at 44.4^{0}C until equilibrium is reached, were found to be 22% dissociated. Calculate the equilibrium constant for the reaction.

Solution:

$2HI \rightleftharpoons H_2 + I_2$

$x = 22\%$ (i.e.) that $\frac{22}{100} = 0.22$

$2\,HI \rightleftharpoons H_2 + I_2$

0.22 dissociate to give 0.11 moles of H_2 and 0.11 mole of I_2

Equilibrium concentration = (1 – 0.22) = 0.11 moles / litre

Equilibrium concentration of HI = 0.78 moles / litre.

$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.11 \times 0.11}{(0.78)^2}$

$K_c = 0.0198.$

Question-27

How does the solubility of AgCl change in the presence of NaCl solution? (S = 1.3 × 10^{-5}M)

Solution:

$AgCl(S) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$K_{SP} = [Ag^+][Cl^-]$

Addition of NaCl to saturated solution of AgCl increases the concentration of Cl^- ions. According to Le Chatelier's AgCl(s), there by reducing the Ag^+ concentration by precipitating AgCl. Thus solubility of AgCl in NaCl solution is lower than water, due to common ion effect.

Question-28

A 50.0 L reaction vessel contains 1.00 mol N_2, 3.00 mol H_2, and 0.055 mol NH_3. Will more ammonia, (NH_3), be formed or will it dissociate when the mixture goes to equilibrium at 400^0C? The equation is $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ K_c is 0.500 at 400^0 C.

Solution:

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

Concentrations $\frac{1.00}{50.0}\ \frac{3.00}{50.0}\ \frac{0.055}{50.0}$ = 0.0200 M, 0.0600 M, 0.0011 M

$\therefore Q_c = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.0011)^2}{(0.0600)^3(0.0200)} = 0.2801$

Because Q_c = 23.1 is greater than K_c = 0.500, the reaction will go to the left as it approaches equilibrium. Therefore, ammonia will dissociate.

Question-29

Consider the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas-phase.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

At 900 K, K_p for this reaction is 40.5 atm^{-1} and Δ H = -198 kJ

(a) Write the expression for the equilibrium constant for this reaction.

(b) Will the equilibrium constant for this reaction at room temperature (-300 K) be greater than, less than, or equal to the equilibrium constant at 900 K? Explain your answer.

(c) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant: what happens?

(d) What is the effect of adding one mole of He(g) to a flask containing SO_2 , O_2 and SO_3 at equilibrium at constant temperature?

Solution:

(a) $K_p = \frac{P^2_{SO_3}}{P^2_{SO_2} P_{O_2}}$

(b) The equilibrium constant at 300 K will be greater than the equilibrium constant at 900 K. This is an exothermic reaction. If we decrease the temperature from 900 to 300 K, the equilibrium will be displaced to the right, releasing heat, more SO_3 is produced and SO_2 and O_2 are used up. The equilibrium constant increases.

(c) Decreasing the volume of the vessel will increase the partial pressure of each gas and therefore increase the total pressure. The system will shift to the side with fewer numbers of moles of gas. Since there are two moles of gas on the right, but three on the left, the system will shift to the right. More SO_3 will be produced, and some SO_2 and O_2 will be used up.

(d) Adding He(g) has no effect at all. The partial pressures of SO_2 and O_2 and SO_3 are unchanged by the addition of helium. The total pressure in the container increases, but as the partial pressure of the gases involved in the equilibrium are unaffected, the equilibrium does not shift.

Question-30

Suppose we mix 25.0 cm^3 of 0.001 M $AgNO_3(aq)$ with 75.0 cm^3 of 0.001 M $Na_2CO_3(aq)$. Does a precipitate of Ag_2CO_3 form? The K_{sp} of Ag_2CO_3 is 6.2 × 10^{-12} at 298 K.

Solution:

At the instant of mixing,

Conc. Of $[Ag^+] = \frac{(0.025L)(0.001M)}{(0.100L)} = 2.5 \times 10^{-4}$ M

Conc. Of $[CO^{-2}_3] = \frac{(0.075L)(0.001M)}{(0.100L)} = 7.5 \times 10^{-4}$ M

We are considering the reaction

$AgCO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{-2}$

$K_i = [Ag^+]^2 [CO_3^{-2}] = (2.5 \times 10^{-4})^2 (7.5 \times 10^{-4})$

$K_i = 4.69 \times 10^{-11}$

Since, $K_i > K_{sp}$, the solution is saturated and Ag_2CO_3 will form.

Question-31

Which of the following are Lewis bases?

H_2O, BF_3, H^+, Ag^+, NH_3 & CO.

Solution:

H_2O, NH_3 and CO are Lewis bases as they have lone pairs of electrons to donate to Lewis acids.

Question-32

Which of the following act both as Bronsted acids and bases?

HSO_4^-, NH_3, CO, H_2O, SO_4^-.

Solution:

HSO_4^-, NH_3, H_2O can donate as well as accept a proton. Hence these can act as Bronsted acids and bases.

CO, SO_4^{2-} can only accept proton, hence they are Bronsted's bases.

Question-33

A solution has a hydroxide concentration of 1.0 $\times 10^{-5}$ M at 25° C. Is the solution acidic, natural or basic?

Solution:

$[OH^-] = 1.0 \times 10^{-5}$ M;

$[H^+][OH^-] = 1 \times 10^{-14}$;

$[H^+] = \frac{1\times 10^{-14}}{1\times 10^{-5}} = 1.0 \times 10^{-9}$ M

as $[H^+]$ is less than 1×10^{-7} M, the solution is basic.

Question-34

Calculate the pH value of mixture containing 50cc M-Hcl and 30cc M-NaOH solution assuming both to be completely ionised.

Solution:

Total volume after mixing = 50 + 30 = 80 cc

Molarity of HCl after mixing = $\frac{50}{80}$ M

Molarity of NaOH after mixing = $\frac{30}{80}$ M

Net molarity of HCl after mixing = $\frac{50}{80} - \frac{30}{80} = 0.25$ M

$[H^+] = 0.25 = 2.5 \times 10^{-1}$

$pH = -\log(2.5 \times 10^{-1}) = 0.6021.$

Question-35

The dissociation constant of an acid HA is 1.6 × 10^{-5}. Calculate H_3O+ ion concentration of its 0.01 M solution.

Solution:

$Ka = \frac{C\alpha^2}{1-\alpha}$; $Ka = C\,\alpha^2$

$\alpha = \sqrt{\frac{Ka}{C}}$

$\alpha = \sqrt{\frac{1.6\times 10^{-5}}{1\times 10^{-2}}} = \sqrt{1.6\times 10^{-3}} = \sqrt{10^{-4}\times 16} = 4 \times 10^{-2}$

$[H^+] = a \times C = (4 \times 10^{-2}) \times 10^{-2} = 4 \times 10^{-4}$ mol. L^{-1}.

Question-36

Calculate the concentration of H_3O+ ion in a mixture of 0.02 m acetic acid and 0.2 m sodium acetate. (Given Ka for acetic acid is 1.8×10^{-5})

Solution:

$CH_3COOH \overset{+H_2O}{\rightleftharpoons} CH_3COO^- + H_3O^+$

$\therefore Ka = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

$CH_3COO^- = 0.2\ M + x \approx 0.2\ M$

$[CH_3COOH] = 0.02\ M - x \equiv 0.02\ M$

$1.8 \times 10^{-5} = \frac{[H_3O^+][0.2]}{[0.02]}$

(i.e.) $H_3O^+ = \frac{1.8 \times 10^{-5} \times 0.02}{0.2} = 1.8 \times 10^{-6}$ mol. L^{-1}.

Question-37

Calculate pH of features 10^{-2} M H_2SO_4.

Solution:

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

One mole of H_2SO_4 gives 2 moles of $H^+_{(aq)(aq)}$ ions.

$[H^+] = 2[H_2SO_4]$

$[H^+] = 2[10^{-2}\ M]$

$pH = -\log [2 \times 10^{-2}]$

$= 2 - \log 2 = 2 - 0.3010$

$pH = 1.699$.

Question-38

Calculate pH of 0.001 M Ba $(OH)_2$.

Solution:

$Ba(OH)_2 \xrightarrow{} Ba^{2+} + 2OH^-$

Each mole of $Ba(OH)_2$ gives $2[OH^-]$ moles.

∴0.001 m $Ba(OH)_2$ gives $2 \times [0.001\ m]\ OH^{-1}$ ions

$[H^+] = \frac{10^{-14}}{2 \times 10^{-3}} = \frac{10^{-11}}{2} = 0.5 \times 10^{-11}$

$[H^+] = 5 \times 10^{-12}$

$pH = -\log_{10}[5 \times 10^{-12}]$

$pH = -[\log_{10} 5 + \log 10^{-12}]$

$= -(-12) \log 10 - \log 5$

$= 12 \times 1 - 0.6990$

$pH = 11.301.$

Question-39

How many grams of NaOH must be dissolved in one litre of solution to give it a pH of 12?

Solution:

PH = 12; $-\log[H^+] = 12$; $[H^+]$ = antilog of $-12 = 1 \times 10^{-12}$.

$[OH^-] = \frac{KW}{[H^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 1 \times 10^{-2} = 0.01$ moles/litre

We know, weight per litre ≡ molarity ×m.wt.

= 0.01 ×40 = 0.4 gms/litre.

∴Weight of NaOH present = 0.4 gms/litre.

Question-40

A buffer solution is prepared by mixing 6 g. of acetic acid and 13.6 g of sodium acetate $CH_3COONa.3H_2O$ and making the total volume 250 ml. Calculate the

(i) pH of the solution and

(ii) pH change on addition of 1 ml of 1m HCl to it. Ka = 1.8×10^{-5}.

Solution:

$[CH_3COOH] = \frac{wt}{mwt} = \frac{6}{60} = 0.1$ moles ; 0.1/.250 = 0.004

$[CH_3COONa] = \frac{wt}{mwt} = \frac{13.6}{136} = 0.1$ moles = 0.004

$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]}$

$pKa = -\log_{10} Ka = -\log 1.8 \times 10^{-5} \equiv 5 - 0.2553 = 4.74$

$pH = 4.74 + \log [0.004]/[0.004]$

$pH = 4.74 + \log_{10} 1 = 4.74 + 0 = 4.74.$

Question-41

Calculate the amount of $(NH_4)_2\ SO_4$ in gms which must be added to 500 ml of 0.200 MNH_3 to yield a solution with pH 9.35 (Kb for $NH_3 = 1.78 \times 10^{-5}$)

Solution:

$pOH = pKb + \log \frac{[Salt]}{[Base]}$

pH = 9.35

pOH = 14 - 9.35 = 4.65; Kb = 1.78×10^{-5}

pKb = 4.7447

Number of moles of NH_3 added: one litre of 0.2 M NH_3 contain 0.2 mole

500 ml contains $0.2 \times \frac{1}{2} = 0.1$ mole

Moles of $(NH_4)_2\ SO_4 = x$

$\therefore 4.65 = 4.7447 + \log \left(\frac{x}{0.1}\right)$

$\log \left(\frac{x}{0.1}\right) = -0.0947$ or $\log \left(\frac{0.1}{x}\right) = 0.0947$

$\frac{0.1}{x} = 1.2436$; $x = \frac{0.1}{1.2436} = 0.08$ mole

M. wt. of $(NH_4)_2\ SO_4$ = mole ×m.wt = 0.08 ×132 = 10.56 grams.

Question-43

What would be the pH of a solution that contains 100 ml of 0.1 N HCl and 9.9 ml of 1 N NaOH solution?

Solution:

9.9 ml of 1 N solution of NaOH should be converted into 0.1 N NaOH

$9.9 \times 1\ \text{N} \equiv x \times 0.1$; (i.e.) $x = \frac{9.9 \times 1}{0.1} = 99$ ml.

9.9 ml of 1.0 N NaOH = 99 ml of 0.1 N, NaOH

Volume of HCl left unneutralised ≡ (100 - 99 ml) of 0.1 N ≡ 1 ml of 0.1 N

Total volume of solution after mixing ≡ 100 + 9.9 = 109.9 ml ≡ 110 ml (app)

Conc. HCl after mixing ≡ $\frac{0.1}{110} = 9.09 \times 10^{-4}$ m

$[H^+] = 9.09 \times 10^{-4}$

$\text{pH} = -\log[9.09 \times 10^{-4}] = 4 - 0.9546 = 3.0454.$

Question-44

Calculate the degree of hydrolysis of 0.1M solution of sodium acetate at 25^0 C ; Ka=1.8×10^{-5}.

Solution:

Since sodium acetate is a salt of strong base and weak acid

$Kb = \frac{kw}{ka} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$

Since solution is 0.1, $h = \sqrt{\frac{kb}{c}}$

$= \sqrt{\frac{5.5 \times 10^{-10}}{0.1}} = 7.452 \times 10^{-5}.$

Question-45

Ka for butyric acid is 2.0×10^{-5}. Calculate pH and hydroxyl ion concentration of 0.2 M aqueous solution of sodium butyrate.

Solution:

For salt of a weak acid with strong base

$$pH = \tfrac{1}{2}pKw + \tfrac{1}{2}pKa + \tfrac{1}{2}\log C$$

$$= \tfrac{1}{2}\times 14 + \tfrac{1}{2}\log\left(\frac{1}{2\times 10^{-5}}\right) + \tfrac{1}{2}\log 0.2$$

$$= 7 + 2.3494 - 0.3494$$

$$= 9$$

$$pOH = 14 - 9 = 5$$

$[OH^-] = 10^{-5}$ M.

Question-46

The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 ml sample of blood which is 2 M in H_2CO_3 in order to maintain a pH of 7. 4? Ka for H_2CO_3 in blood is 7.8×10^{-7}.

Solution:

Let the amount of $NaHCO_3$ mixed = x ml

Number of moles of $NaHCO_3$ in x ml of 5 m $NaHCO_3$ = $\frac{5\times x}{1000}$ = 0. 005 x

Number of moles of H_2CO_3 in 10 ml of 2 m H_2CO_3 = $\frac{2\times 10}{1000}$ = 0. 02

$$pH = -\log Ka + \log\frac{[Salt]}{[Acid]}$$

$$7.4 = -\log 7.8\times 10^{-7} + \log\left(\frac{0.005x}{0.02}\right)$$

x = 78.36 ml.

Question-47

To a buffer solution containing 0. 02 mole of propionic acid and 0.015 mole of sodium propionate per litre, 0.01 mole / litre of HCl is added. What is the pH of the solution? Ka propionic acid = 1.34 × 10^{-5}.

Solution:

[propionic acid] = (0.02 + 0.01)M

[propionate] = (0.015 + 0.010)M

pH = pka + log [salt] / [Acid]

pH = - log (1.34×10^{-5}) + log $\frac{0.025}{0.03}$ = 4.9528.

Question-48

A buffer solution of acetic acid and sodium acetate of 1 M concentration was prepared. Calculate pH of the system when 0.01 mole of NaOH is added per litre of the above solution. Ka = 1.8 × 10^{-5}.

Solution:

NaOH ionises fully: Hence OH^- ions added will react with CH_3COOH of the buffer system.

Molar conc. before adding NaOH

$$\overset{1}{CH_3COOH} + \overset{0}{OH} \rightarrow \overset{1}{CH_3COO^-} + H_2O$$

Molar conc. after adding 0.01 mole of (1 - 0.01) = 0.99

PH = pKa + log $\frac{[Salt]}{[Acid]}$

= - log 1.8×10^{-5} + log $\frac{[1.01]}{[0.99]}$

= 4.74 + 0.01= 4.75.

Question-49

The solubility product of AgCl in water is 1.5 × 10^{-10}. Calculate its solubility in 0.01 M NaCl aqueous.

Solution:

Let the solubility of AgCl in 0.01 M NaCl solution = x g mole L^{-1}

$[Ag^+]$ in NaCl solution = x mol L^{-1}

$[Cl^-]$ in 0.01 M NaCl solution ≡ x + 0.01 M L^{-1}

$\therefore [Ag^+] [Cl^-] = Ksp$

$(x) (x + 0.01) = 1.5 \times 10^{-10}$

$0.01 x + x^2 = 1.5 \times 10^{-10}$

Since value of x is small x^2 is neglected.

$0.01 x = 1.5 \times 10^{-10}$

$x = 1.5 \times 10^{-8}$ mol L^{-1}.