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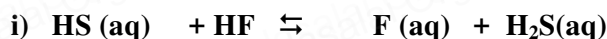**+2 CHEMISTRY**   **Dr. C. ARUL JOSEPH RAJ**

UNIT - 8 . IONIC EQUILIBRIUM

1. What are lewis acids and bases? Give two example for each.

Lewis acid is a species that accepts an electron pair while base is a species that donates an electron pair. We call such species as Lewis acids and bases. BF_3, $AlCl_3$
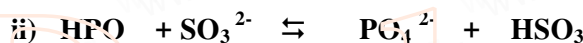
A Lewis acid is a positive ion (or) an electron deficient molecule and a Lewis base is a anion (or) neutral molecule with at least one lone pair of electrons NH_3 ,$H_2 O$,

2. Discuss the Lowery – Bronsted concept of acids and bases.

An acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton form other substance. In other words, an acid is a proton donor and a base is a proton acceptor.

**3. Indentify the conjugate acid base pair for the following reaction in aqueous solution.**

i) $HS (aq)$ $+ HF$ $\rightleftharpoons$ $F (aq)$ $+ H_2S(aq)$

     acid1   base2   acid2   base1

ii) HPO $+ SO_3^{2-}$ $\rightleftharpoons$ PO_4^{2-} $+$ HSO_3

    acid 1   base2   acid2   base1

iii) NH_4^{+} $+$ CO_3^{2-} $\rightleftharpoons$ NH_3 $+$ HCO_3

     acid 1   base2   acid2   base1

4. Account for the acidic nature of $HClO_4$. In terms of Bronsted – Lowry theory, identify

  its conjugate base.

Lowry – Bronsted (acid – base) reaction is represented as

Acid +Base   Acid +Base
   1   **2**   **2**   **1**

$HClO_4$ $\rightleftharpoons$ **H^{+} $+$ ClO_4^{-}**
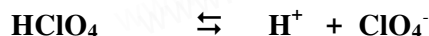
5. When aqueous ammonia is added to $CuSO_4$ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, $[Cu(H_2O)_2] + 4NH_3 (aq) [Cu(NH_3)_4]^{2-}$ (aq) among $H_2 O$ and NH_3 Which is stronger Lewis base.

✓ H_2O has two nonbonding electron pairs and is, therefore, a stronger Lewis base than NH_3 which only has one.

✓ H_2O is a stronger Lewis base because the extra hydrogen in NH_3 shields the lone pair of the central nitrogen atom. H_2O should be a stronger Lewis base because oxygen is more electronegative than nitrogen.

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6. The concentration of hydroxide ion in a water sample is found to be

2.5 x10^{-6} M. Identify the nature of the solution.

P^{OH} = - log [OH$^-$]

P^{OH} = - [log **2.5 x10^{-6}**]

P^{OH} = - [log **2.5 -6** log**10**]

P^{OH} = [- log **2.5 + 6**]

         = [**6** - log **2.5**]

   = [**6** – 0.3979]

 P^{OH} **= 5.6**

P^{H} = 14- 5.6 = 8.4   It is basic in nature

7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas

25oC to get a solution with [H $_2$O] = 4 x 10 $^{-5}$ M Is the solution neutral (or) acidic (or)

basic.

$$HCl \overset{H_2O}{\rightleftharpoons} H_3O^+ + Cl^-$$

[H$_3$O$^+$] = 10^{-7} (from water) + [H$_3$O$^+$] (from acid) = 4 x 10 $^{-5}$

pH = - log [H$_3$ O$^+$] = 4 x 10 $^{-5}$

P^{H} = - [log **4 x10^{-5}**]

P^{H} = - [log **4 - 5** log**10**]

P^{H} = [- log **4 + 5**]

     = [**5** - log **4**]

   = [**4** – 0.6020]

 P^{H} **= 3.398**

The solution is acidic

8. Calculate the pH of 0.04 M HNO3 Solution.

Concentration of   HNO3   = 0.04M

[H$_3$ O$^+$] =   0.04 mol / dm^3

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pH=-log[H O]
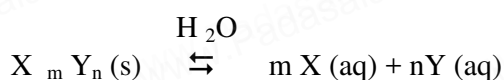
= - log (0.04)

= - log (4×10^{-2})

= 2-log4

= 2 - 0.6021

=1.3979 = 1.40

9. Define solubility product

To understand the precipitation, let us consider the solubility equilibria that exist between the undissociated sparingly soluble salt and its constituent ions in solution.

For a general salt $X_m Y_n$

$$X_m Y_n (s) \overset{H_2O}{\rightleftharpoons} m X (aq) + nY (aq)$$

The equilibrium constant for the above is

$$K = \frac{[X^n]^m \ [Y^m]^n}{[X_m Y_m]}$$

In solubility equilibria, the equilibrium constant is referred as solubility product constant (or) Solubility product.

In such heterogeneous equilibria, the concentration of the solid is a constant and it is omitted in the above expression

$$K_{sp} = [X^{n+}]^m \ [Y^{m-}]^n$$

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co– efficient in a balanced equilibrium equation.

10. Define ionic product of water. Give its value at room temperature.

✓ when an acidic or a basic substance is dissolved in water, depending upon its nature, it can either donate (or) accept a proton.

✓ In addition to that the pure water itself has a little tendency to dissociate. i.e, one water molecule donates a proton to an another water molecule.

✓ This is known as auto ionisation of water and it is represented as below.

$$HO-H + H_2O \rightleftharpoons H_3O^+ + OH^-$$
   acid1   base2   acid2   base1
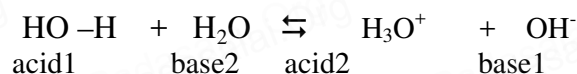
One water molecule acts as an acid while the another water molecule acts as a base.

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The dissociation constant for the above ionisation is given by the following expression

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

The concentration of pure liquid water is one. i.e, $[HO]^2 = 1$

$$K_w = [H_3O^+][OH^-]$$

Here, Kw represents the ionic product (ionic product constant) of water

✓ It was experimentally found that the concentration of H_3O^+ in pure water is 1×10^{-7} at 25oC

✓ Since the dissociation of water produces equal number of H_3O^+ and OH^-, the concentration of OH^- is also equal to 1×10 at 25° C

✓ Therefore, the ionic product of water at 25^oC is

$$K_w = [H_3O^+] \; [OH^-]$$
$$K_w = (1 \times 10^{-7}) \; (1 \times 10^{-7}) = 1 \times 10^{-14}$$

✓ The dissociation of water is an endothermic reaction.

✓ With the increase in temperature, the concentration of H_3O^+ and OH^- also increases, and hence the ionic product also increases

✓ Like all equilibrium constants, Kw is also a constant at a particular temperature.

✓ The dissociation of water is an endothermic reaction. With the increase in temperature, the concentration of H_3O^+ and OH^- also increases, and hence the ionic product also increases.

11. Explain common ion effect with an example.

When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid is suppressed further. For example, the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case, CH_3COOH and CH_3COONa have the common ion,CH_3COO.

Let us analyse why this happens. Acetic acid is a weak acid. It is not completely dissociated in aqueous solution and hence the following equilibrium exists.

$$CH COOH(aq) \rightleftharpoons H(aq) + CH COO (aq)$$

However, the added salt, sodium acetate, completely dissociates to produce Na+ and CH_3COO^- ion.

$CH_3 COONa(aq) \rightarrow Na(aq) + CH_3 COO(aq)$

Hence, the overall concentration of CH_3COO^- is increased, and the acid dissociation equilibrium is disturbed. the equilibrium will shift towards the left. In other words, the dissociation of $CH_3 COOH$ 3 is suppressed

12. Derive an expression for Ostwald's dilution law.

Ostwald's dilution law relates the dissociation constant of the weak acid (K_a) with its degree of dissociation (α) and the concentration (c).

Degree of dissociation (α) is the fraction of the total number of moles of a substance that dissociates at equilibrium.

$$\alpha = \frac{\text{total number of moles}}{\text{Number of moles dissociated}}$$

We shall derive an expression for ostwald's law by considering a weak acid, i.e. acetic acid ($CH_3 COOH$) . The dissociation of acetic acid can be represented as

$$CH_3 COOH \rightleftharpoons H^+ + CH_3 COO^-$$

The dissociation constant of acetic acid is,

$$k_a = \frac{[H^+][CH_3 COO^-]}{[CH_3COOH]} \quad --------(1)$$

	CH_3 COOH	H^+	CH_3 COO^-
Initial No. of moles	1	-	-
Degree of dissociation of CH_3 COOH	α	-	-
No. of moles at equilibrium	1- α	α	α
Equilibrium concentration	(1- α)C	αC	αC

Substituting the equilibrium concentration in equation (1)

$$k = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C}$$

$$k = \frac{\alpha^2 C}{1 - A} \quad ---(2)$$

We know that weak acid dissociates only to a very small extent compared to one, α is so small and hence in the denominator $(1 - \alpha) = 1$. The above expression (2) now becomes,

$$K_a = \alpha^2 C$$

$$\Rightarrow \alpha^2 = \frac{K_a}{C}$$

$$\alpha^2 = \sqrt{\frac{K_a}{C}} \quad ----(3)$$

When dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law.

13. Define pH

P^H of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$pH = -\log [H_3O^+]$$

14. Calculate the pH of $1.5 \times 10^{-3}M$ solution of Ba (OH)₂

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

$$1.5 \times 10 \, M \quad 2 \times 1.5 \times 10^{-3}M.$$

$$[OH^-] = 3 \times 10^{-3} \, M$$

$$[\, pH + pOH = 14$$

$$pH = 14 - pOH$$

$$pH = 14 \, (-\log [OH^-])$$

$$= 14 + \log [OH^-]$$

$$= 14 + \log(3 \times 10^{-3})$$

$$= 14 + \log 3 + \log 10^{-3}$$

$$= 14 + 0.4771 - 3$$

$$= 11 + 0.4771$$

$$pH = 11.48$$

15. 50ml of 0.05M HNO₃ is added to 50ml of 0.025M KOH . Calculate the pH of the resultant solution.

Number of moles of HNO_3 $= \quad 0.05 \times 50 \times 10^{-3}$

$= \quad 2.5 \times 10^{-3}$

Number of moles of KOH $= \quad 0.025 \times 50 \times 10^{-3}$

$= \quad 1.25 \times 10^{-3}$

concentration of HNO^3 $= \quad \dfrac{\text{Number of moles of HNO3 after mixing}}{\text{Volume is litre}}$

After mixing, total volume = 100 ml = 100×10^{-3} L

$= \quad 2.5 \times 10^{-3} - 1.5 \times 10^{-3}$

$[H^+] = \dfrac{1.25 \times 10^{-3}}{100 \times 10^{-3} \text{ L}}$

$= \quad 1.25 \; 10 \text{ moles L}^{-1}$

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

pH $= -\log(1.25 \times 10^{-2}) = 2 - 0.0969$

$= 1.9031$

16. The Ka value for HCN is 10⁻⁹ . What is the pH of 0.4M HCN solution?

Given

$K = 10^{-9}$

$C = 0.4M$

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

$[H^+] = \sqrt{K_a \times C}$

$= \sqrt{10^{-9} \times 0.4}$

$= 2 \times 10^{-3}$

pH $= -\log(2 \times 10^{-5})$

$= 5 - 0.3010 = 4.699$

17. Calculate the extent of hydrolysis and the pH of 0.1 M ammonium acetate Given that

Ka $= K_b = 1.8 \; 10^{-5}$

$$h = \sqrt{K_b} = \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}}$$

$$h = \sqrt{K_b} = \sqrt{\frac{1}{1.8}} \times 10^{-14} = \sqrt{0.5555 \times 10^{-4}}$$

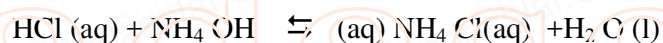$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$

Given that $K_a = K_b = 1.8 \ 10^{-5}$

If $K_a = K_b$ then $pK_a = pK_b$

$\therefore pH = = \frac{1}{2} pK_w = \frac{1}{2} (14) = 7$

18. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base.

Let us consider the reactions between a strong acid, HCl, and a weak base, NH4 OH , to produce a salt, NH4 Cl, and water

$$HCl \ (aq) + NH_4 \ OH \ \leftrightharpoons \ (aq) \ NH_4 \ Cl(aq) + H_2 O \ (l)$$

$$NH_4 \ Cl(aq) \ \rightarrow \ NH_4^+ + Cl^- \ (aq)$$

NH_4^+ is a strong conjugate acid of the weak base $NH_4 OH$ and it has a tendency to react with OH^- from water to produce unionised NH_4OH shown below.

$$NH_4^+ \ (aq) + H_2 O(l) \ \leftrightharpoons \ NH_4 \ OH \ (aq) + H^+ \ (aq)$$

There is no such tendency shown by Cl^- and therefore $[H^+] > [OH^-]$ the solution is acidic and the pH is less than 7.

Let us find a relation between the equilibrium constant for the hydrolysis reaction (hydrolysis constant) and the dissociation constant of the base.

$$K_h = \frac{[NH_4 \ OH][H^+]}{[NH_4^+][H_2 O]}$$

$$K_h = \frac{[NH_4 \ OH][H^+]}{[NH_4^+]} \qquad -------(1)$$

$$NH_4 \ OH(aq) \ \leftrightharpoons \ NH_4^+ \ (aq) + OH^- \ (aq)$$

$$[NH_4^+][OH^-]$$

K_b = --------------------   ....(2)

[$NH_4 OH$]

(1) x (2)

$K_h . K_b$ =   [H^+][OH^-]

we know that [H^+][OH^-] = K_w

we can establish a relationship between the K_h and K_b as

$K_h . K_b$ = K_w

Let us calculate the K_h value in terms of degree of hydrolysis (h) and the concentration

of salt (C) for the equilibrium can be obtained as in the case of ostwald's dilution law.

K_h = $h^2 C$ and   [H^+] = $\sqrt{K_h . C}$

$$[H^+] = \sqrt{\frac{K_w}{K_b} . C}$$

P^H = - log [H^+]

$$= - \log \left[\frac{K_w \ C}{K_b} \right]^{1/2}$$

$$= - \ 1/2 \log K_w \ – 1/2 \ \log C + ½ \ \log K_b$$

P^H = 7 –   ½ P^{K_b} – ½ log C

19. Solubility product of Ag Cr_2O_4 is 1 x 10^{-12} . What is the solubility of $Ag_2 CrO_4$ in 0.01M $AgNO_3$ solution?

Given that K_{sp} =1 x 10^{-12}

$Ag_2 CrO_4$ (s) $\leftrightarrows$ 2 Ag^+ (aq)   + CrO_4^{2-}

$AgNO_3$ (s) $\leftrightarrows$ Ag^+ (aq) + NO_3^- (aq)   [Ag^+] =2s +0.01
0.01M   0.01M   0.01M   0.01>> 2s

[Ag^+] = 0.01

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$$[CrO_4^{2-}] = 2s$$
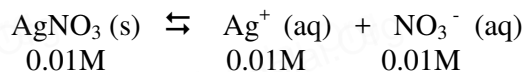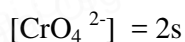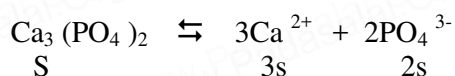
$$Ksp = [Ag^+]^2 \ [CrO_4^{2-}]$$

$$1 \times 10^{-12} = (0.01)^2 \ (s)$$

$$(s) = \frac{1 \times 10^{-12}}{(0.01)^2} = 1 \times 10^{-8} \ M$$

20. Write the expression for the solubility product of Ca₃ (PO₄)₂

$$Ca_3 (PO_4)_2 \ \rightleftharpoons \ 3Ca^{2+} + 2PO_4^{3-}$$
$$\quad S \qquad\qquad\qquad 3s \qquad\quad 2s$$

$$K_{sp} = [Ca^{2+}]^3 [PO]$$

$$K_{sp} = (3s) (2s)$$

$$K_{sp} = 27s \cdot 4s$$

$$K_{sp} = 108s^5$$

21. A saturated solution, prepared by dissolving 2 CaF₂ (s) in water, has

$$[Ca^{2+}] = 3.3 \times 10^{-4} \ M \ \ \text{What is the Ksp of } CaF_2 ?$$

$$CaF_2 \ _{(s)} \ \rightleftharpoons \ Ca^{2+} (aq) + 2F (aq)$$
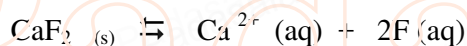
$$[F] = 2 [Ca^{2+}] = 2 \times 3.3 \times 10^{-4} \ M$$

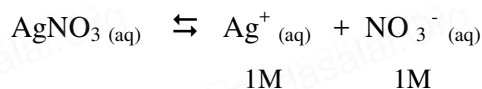$$= 6.6 \times 10 \ M$$

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

$$= (3.3 \times 10^{-4}) (6.6 \times 10^{-4})^2$$

$$= 1.44 \times 10^{-10}$$

22. K$_{sp}$ of AgCl is 1.8×10^{-10} .   Calculate molar solubility in 1 M AgNO$_3$

$$AgCl(s) \ \rightleftharpoons \ Ag^+(aq) + Cl^- (aq)$$
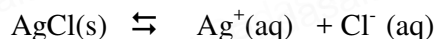
x= solubility of AgCl in 1M AgNO₃

$$AgNO_{3 \ (aq)} \ \rightleftharpoons \ Ag^+ \ _{(aq)} + NO_3^- \ _{(aq)}$$
$$\qquad\qquad\qquad\quad 1M \qquad\qquad 1M$$

$$[Ag^+] = x + 1 = +1 \qquad\qquad x <<1$$

$$[Cl^-] = x$$

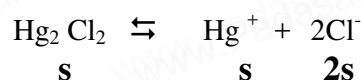$$K_{sp} = [Ag] \ [Cl]$$

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1.8×10^{-10} = (1) (x)

$\quad$ X = 1.8×10^{-10} M

23. A particular saturated solution of silver chromate Ag_2CrO_4 has $[Ag^+]$ = 5 x 10^{-5} and $[CrO_4^{2-}]$ = 4.4 x10^{-4} M. What is the value of K_{sp} for Ag_2CrO_4?

$\quad\quad Ag_2CrO_4$ (s) $\leftrightharpoons$ $2Ag^+$ (aq) $+CrO_4^{2-}$ (aq)

$\quad K_{sp}$ = $[Ag^+] [CrO_4^{2-}]$

$\quad\quad\quad$ = $(5\times10^{-5})^2$ (4.4×10)

$\quad\quad\quad$ = 1.1×10^{-4}

24. Write the expression for the solubility product of Hg_2Cl_2 .

$Hg_2Cl_2 \leftrightharpoons$ $Hg^+ + 2Cl^-$
$\quad$ **s** $\quad\quad\quad\quad$ **s** $\quad$ **2s**

$\quad K_{sp}$ = $[Hg^{+2}] [Cl^-]$

$\quad\quad\quad$ = $(s) (2s)^2$

$\quad K_{sp}$ = $4s^3$

25. K_{sp} of Ag CrO$_2$ 4 is 1.1×10^{-12} . what is solubility of Ag_2CrO_4 in 0.1M K_2CrO_4.

$\quad\quad Ag_2CrO_4 \leftrightharpoons 2Ag + CrO_4^{2-}$
$\quad\quad\quad$ x $\quad\quad\quad$ x $\quad$ x
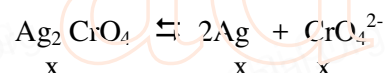
$\quad$ x is the solubility of Ag_2CrO_4 in 0.1M K_2CrO_4

$\quad\quad K_2Cr_2O_7 \leftrightharpoons$ $\quad 2K^+ + CrO_4^{2-}$
$\quad\quad$ 0.1M $\quad\quad\quad\quad$ 0.2 M $\quad$ 0.1 M
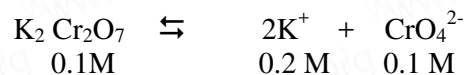
$\quad\quad\quad [Ag^+]$ = 2x

$\quad\quad\quad [CrO_4^{2-}]$ = $(x + 0.1)$ $\approx$ 0.1 $\quad\quad$ X << 0.1

$\quad\quad Ksp$ = $[Ag^+]^2 [CrO_4^{2-}]$

$\quad\quad 1.1 \times 10^{-12}$ = $(2x)^2 (0.1)$

$\quad\quad\quad 1.1 \times 10^{-12}$ = $0.4 x^2$

X^2 = $\dfrac{1.1 \times 10^{-12}}{0.4}$

X = $\sqrt{\dfrac{1.1 \times 10^{-12}}{}}$

$\sqrt{}$ 0.4

$X = \sqrt{2.57 \times 10^{-12}}$

$\therefore X = 1.65 \times 10^{-6}$ M

26. Will a precipitate be formed when 0.150 L of 0.1M $Pb_2(NO_3)$ and 0.100L of 0.2 M NaCl are mixed? K_{sp} $(PbCl_2)=1.2 \times 10^{-5}$. sp 2

When two are more solution are mixed, the resulting concentrations are different from the original.

Total volume = 0.250L

$Pb(NO_3) \rightleftharpoons Pb^{2+} + 2NO_3$

0.1 M   0.1 M   0.2 M

Number of moles

Pb^{2+} = molarity × Volume of the solution in lit

= 0.1 × 0.15

$[Pb^{+2}]_{mix} = \dfrac{0.1 \ \times \ 0.15}{0.25} = 0.06$ M

NaCl Na +Cl

No.of moles Cl = 0.2 0.1

$[Cl^-]_{mix} \ \dfrac{0.2 \ 0.1}{0.25} = 0.08$ M

Precipitation of $PbCl_2(s)$ occurs if

$[Pb^{2+}] [Cl^-] > K_{sp}$

$[Pb^{2+}] [Cl^-] = (0.06) (0.08)$

$= 3.84 \times 10^{-4}$

Since ionic product $[Pb^{2+}][Cl^-] > K_{sp}$,

$PbCl_2$ is precipitated.

27. Ksp of $Al(OH)_3$ is 1×10^{-15} M. At what pH does 1.0×10^{-3} M Al^{3+} precipitate on the addition of buffer of $NH_4 Cl$ and $NH_4 OH$ solution?

$Al(OH) \rightleftharpoons Al (aq)+3OH (aq)$

$K = [Al^{3+}] [OH^-]^3$

$Al(OH)_3$ precipitates when

$[Al^{3+}][OH^-]^3 > K_{sp}$

$(1 \times 10^{-3})[OH^-]^3 > 1 \times 10^{-15}$

$[OH^-]^3 > 1 \times 10^{-12} M$

$[OH^-]^3 > 1 \times 10^{-4}$

$[OH^-] = 1 \times 10^{-4} M$

$POH = -\log[OH^-] = -\log(1 \times 10^{-4}) = 4$

$\therefore pH = 14 - 4 = 10$

Thus, $Al(OH)_3$ precipitates at a pH of 10

Additional questions:

1. Fine the pH of a buffer solution containing 0.20 mole per litre sodium acetate and 0.18 mole per litre acetic acid. Ka for acetic acid is 1.8×10^{-5}.

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

Given that $K_a = 1.8 \times 10^{-5}$

$pK_a = -\log(1.8 \times 10^{-5}) = 5 - \log 1.8$

$\qquad\qquad\qquad = 5 - 0.26$

$\qquad\qquad\qquad = 4.74$

$\therefore pH = 4.74 + \log\dfrac{0.20}{0.18}$

$\qquad = 4.74 + \log 10/9$

$\qquad = 4.74 + \log 10 - \log 9$

$\qquad = 4.74 + 1 - 0.95$

$\qquad = 5.74 - 0.95$

$\qquad = 4.79$

29. What is buffer action?

Buffer solution resists drastic changes in its pH upon addition of a small quantities of acids (or) bases, and this ability is called buffer action.

30. What are the types of buffer solutions? Give examples.

1. Acidic buffer solution : a solution containing a weak acid and its salt.

Example : solution containing acetic acid and sodium acetate

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2. Basic buffer solution : a solution containing a weak base and its salt.

Example : Solution containing NH_4OH and $NH Cl$

31. Define Buffer capacity and buffer index

The buffering ability of a solution can be measured in terms of buffer capacity. Vanslyke introduced a quantity called buffer index, β, as a quantitative measure of the buffer capacity. It is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(pH)}$$

Here,

dB = number of gram equivalents of acid / base added to one litre of buffer solution.

d(pH) = The change in the pH after the addition of acid / base.

32. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong base and weak acid.

Let us consider the reactions between sodium hydroxide and acetic acid to give sodium acetate and water.

$NaOH (aq) + CH_3COOH(aq) \leftrightharpoons CH_3COONa(aq) + H_2O(l)$
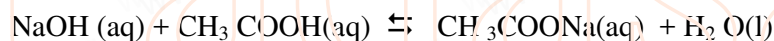
In aqueous solution, CH_3COONa 3 is completely dissociated as below

$CH_3COONa (aq) \rightarrow CH_3COO^- (aq) + Na^+ (aq)$

CH_3COO^- is a conjugate base of the weak acid $CH COOH$ 3 and it has a tendency to react with H^+ from water to produce unionised acid .

There is no such tendency for Na+ to react with OH^- .

$CH_3COO (aq) + H_2O(l) \leftrightharpoons CH_3COOH (aq) + OH^- (aq)$ and therefore [OH-]>[H+] , in such cases, the solution is basic due to hydrolysis and the pH is greater than 7.

Let us find a relation between the equilibrium constant for the hydrolysis reaction (hydrolysis constant) and the dissociation constant of the acid.

$$K_h = \frac{[CH COOH][OH]}{[CH_3COO][H_2O]}$$

$$K_h = \frac{[CH_3COOH][OH^-]}{} \quad ....(1)$$

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$[CH_3 COO^-]$
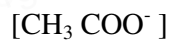
$$CH_3 COOH \leftrightarrows H^+ + CH_3 COO^-$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3 COOH]} \quad ....(2)$$

(1) x (2)

$$K_h . K_a = [H^+][OH^-]$$

we know that $[H^+][OH^-] = K_w$

$$K_h . K_b = K_w$$

K_h value in terms of degree of hydrolysis (h) and the concentration of salt (C) for the equilibrium can be obtained as in the case of ostwald's dilution law. $K = h^2 C$. and

i.e $[OH^-] = \sqrt{K_h . C}$

pH of salt solution in terms of K_a and the concentration of the electrolyte.

$$pH + pOH = 14$$

$$pH = 14 - pOH = 14 - \{-\log [OH^-]\}$$

$$= 14 + \log [OH^-]$$

$$pH = 14 + \log (K_h C)^{1/2}$$

$$pH = 14 + \log \left[\frac{K_w C}{K_a}\right]^{1/2}$$

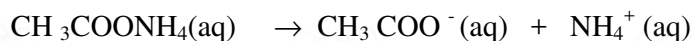$$pH = 14 + (\ \tfrac{1}{2} \log K_w + \tfrac{1}{2} \log C - \tfrac{1}{2} \log K_a\ )$$

we know $K_w = 10^{-14}$ and $1/2\ K_w = 10^{-14} = -7$ and $\log K_a = P^{Ka}$
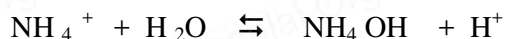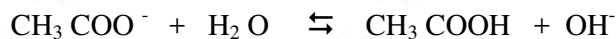
$$P^H = 14 - 7 + 1/2\ \log C - 1/2\ P^{Ka}$$

$$P^H = 7 + 1/2\ \log C - 1/2\ P^{Ka}$$

33.   Hydrolysis of Salt of weak acid and weak base.

Let us consider the hydrolysis of ammonium acetate.

$$CH_3COONH_4(aq) \rightarrow CH_3COO^-(aq) + NH_4^+(aq)$$

In this case, both the cation (NH_4^+) and anion (CH_3COO^-) have the tendency to react with water

$$CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \leftrightarrows NH_4OH + H^+$$

The nature of the solution depends on the strength of acid (or) base i.e, if $K_a > K_b$; then the solution is acidic and pH < 7, if $K_a < K_b$; then the solution is basic and pH < 7,   if $K_a = K_b$ then the solution is neutral.

The relation between the dissociation constant (K_a, K_b) and the hydrolysis constant K_h is given by the following expression.

$$K_a . K_b . K_h = K_w$$

pH of the solution

pH of the solution can be calculated using the following expression,

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

34. Derive Henderson -- Hasselbalch equation

We have already learnt that the concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution i.e.,

$$[H_3O^+] = K_a \frac{[acid]_{eq}}{[base]_{aq}} \quad ------ (1)$$

✓ The weak acid is dissociated only to a small extent, due to common ion effect, the dissociation is further suppressed and hence the equilibrium concentration of the acid is nearly equal to the initial concentration of the unionised acid.

✓ Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of the added salt.

$$[H_3O^+] = K_a \frac{[acid]}{[salt]} \quad -------- (2)$$

Here [acid] and [salt] represent the initial concentration of the acid and salt, respectively used to prepare the buffer solution

Taking logarithm on both sides of the equation

$$- \log [H_3O^+] = \log K_a + \log \frac{[acid]}{[salt]} \quad \text{------- (3)}$$

reverse the sign on both sides

$$- \log [H_3O^+] = - \log K_a - \log \frac{[acid]}{[salt]} \quad \text{------- (4)}$$

We know that

$$pH = \log [H_3O^+] \quad \text{and} \quad pK_a = \log K_a$$

$$\Rightarrow pH = pK_a - \log \frac{[acid]}{[salt]} \quad \text{-------------- (5)}$$

$$\Rightarrow pH = pK_a - \log \frac{[acid]}{[salt]} \quad \text{------- (6)}$$

Similarly for a basic buffer, $\quad pOH = pK_b + \log \frac{[salt]}{[base]} \quad \text{------- (7)}$

35. Explain the determination of solubility product from molar solubility

Solubility can be calculated from the molar solubility i.e., the maximum number of moles

of solute that can be dissolved in one litre of the solution.

For a solute $X_m Y_n$,

$$X_m Y_n (s) \leftrightarrows mX^n (aq) + nY^m (aq)$$
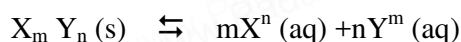
From the above stoichiometrically balanced equation we have come to know that 1 mole of X $_mY_n$ (s) dissociated to furnish 'm' moles of and 'n' moles of Y^{m-} if 's' is molar solubility of $X_m Y_n$, then

$\therefore [X^{n+}] = ms$ and $[Y^{m-}] = ns$

$K_{sp} = [X^{n+}]^m [Y^{m-}]^n$

$K_{sp} = (ms)^m (ns)^n$

$K_{sp} = (m)^m (n)^n (s)^{m+n}$

36. Drive the Relation between pH and pOH

A relation between pH and pOH can be established using their following definitions

$$pH = - \log_{10} [H_3O^+] \quad \text{.......(1)}$$

$$pOH = - \log 10 [OH^-] \quad \text{........(2)}$$

Adding equation (1) and (2)

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$pH + pOH = -\log_{10}[H_3O^+] - \log_{10}[OH^-]$

$= -(\log_{10}[H_3O^+] + \log_{10}[OH^-])$

$pH + pOH = -\log_{10}[H_3O^+][OH^-]$ $(\log a + \log b = \log ab)$

We know that $[H_3O^+][OH^-] = K_w$

$\Rightarrow pH + pOH = \log_{10} K_w$

$\Rightarrow pH + pOH = pK_w$.........(3) $(pK_w = -\log_{10} K_w)$

at 25^oC, the ionic product of water, $K_w = 1 \times 10^{-14}$

$P^K_w = -\log_{10} 10^{-14} = {}^{14}\log_{10} 10$

$\qquad\qquad\qquad = 14$

$\therefore$ At 25^oC, $p^H + p^{OH} = 14$

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