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UNIT - 8. IONIC EQUILIBRIUM

1. What are Lewis acids and bases? Give two examples for each.

A Lewis acid is a species that accepts an electron pair while a base is a species that donates an electron pair. We call such species as Lewis acids and bases. BF₃, AlCl₃.

A Lewis acid is a positive ion (or) an electron deficient molecule and a Lewis base is an anion (or) neutral molecule with at least one lone pair of electrons NH₃, H₂O.

2. Discuss the Lowry – 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 a base is a substance that has a tendency to accept a proton from another substance. In other words, an acid is a proton donor and a base is a proton acceptor.

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

   i)     \( \text{HS} \ (aq) + \text{HF} \rightleftharpoons \text{F} \ (aq) + \text{H}_2\text{S} \ (aq) \)

   \[ \text{acid} \text{1} \ \text{base} \text{2} \ \text{acid} \text{2} \ \text{base} \text{1} \]

   ii)   \( \text{HPO}_4 \text{2-} + \text{SO}_3 \text{2-} \rightleftharpoons \text{PO}_4 \text{3-} + \text{HSO}_3 \)

   \[ \text{acid} \text{1} \ \text{base} \text{2} \ \text{acid} \text{2} \ \text{base} \text{1} \]

   iii)  \( \text{NH}_4 \text{+} + \text{CO}_3 \text{2-} \rightleftharpoons \text{NH}_3 + \text{HCO}_3 \)

   \[ \text{acid} \text{1} \ \text{base} \text{2} \ \text{acid} \text{2} \ \text{base} \text{1} \]


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

   \[ \text{Acid} + \text{Base} \rightleftharpoons \text{Acid} + \text{Base} \]

   \[ \text{HClO}_4 \rightleftharpoons \text{H}^+ + \text{ClO}_4^- \]

5. When aqueous ammonia is added to CuSO₄ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, \([\text{Cu(H}_2\text{O})_2 \text{]}_2 \text{ + 4NH}_3 \ (aq) [\text{Cu(NH}_3)_4 \text{]}_2 \text{ (aq)} \]

   (a) among H₂O and NH₃ Which is stronger Lewis base.

   \( \sqrt{\text{H}_2\text{O}} \text{ has two nonbonding electron pairs and is, therefore, a stronger Lewis base than NH}_3 \text{ which only has one.} \)

   \( \sqrt{\text{H}_2\text{O}} \text{ is a stronger Lewis base because the extra hydrogen in NH}_3 \text{ shields the lone pair of the central nitrogen atom. H}_2\text{O should be a stronger Lewis base because oxygen is more electronegative than nitrogen.} \)
6. The concentration of hydroxide ion in a water sample is found to be 
2.5 x 10^-6 M. Identify the nature of the solution.

\[ \text{pOH} = - \log [\text{OH}^-] \]
\[ \text{pOH} = - [ \log 2.5 \times 10^{-6} ] \]
\[ \text{pOH} = - [ \log 2.5 - 6 \log 10 ] \]
\[ \text{pOH} = [- \log 2.5 + 6 ] \]
\[ = [6 - \log 2.5 ] \]
\[ = [6 - 0.3979 ] \]
\[ \text{pOH} = 5.6 \]
\[ \text{pH} = 14 - 5.6 = 8.4 \quad \text{It is basic in nature} \]

7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas 
25°C to get a solution with [H₂O] = 4 \times 10^{-5} M Is the solution neutral (or) acidic (or) 
basic.

\[ \text{HCl} \quad \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{H}_3\text{O}^+ \quad + \quad \text{Cl}^- \]
\[ [\text{H}_3\text{O}^+] = 10^{-7} \quad \text{(from water)} \quad + \quad [\text{H}_3\text{O}^+] \quad \text{(from acid)} = 4 \times 10^{-5} \]
\[ \text{pH} = - \log [\text{H}_3\text{O}^+] = 4 \times 10^{-5} \]
\[ \text{pH} = - [ \log 4 \times 10^{-5} ] \]
\[ \text{pH} = [- \log 4 - 5 \log 10 ] \]
\[ \text{pH} = [- \log 4 + 5 ] \]
\[ = [5 - \log 4 ] \]
\[ = [4 - 0.6020 ] \]
\[ \text{pH} = 3.398 \]

The solution is acidic

8. Calculate the pH of 0.04 M HNO₃ Solution.

Concentration of HNO₃ = 0.04M
\[ [\text{H}_3\text{O}^+] = 0.04 \text{ mol} / \text{dm}^3 \]
pH = -log [H\text{O}^-] \\
= - log (0.04) \\
= - log (4 \times 10^{-2}) \\
= 2 - log 4 \\
= 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 \(X_m Y_n\)

\[
\text{H}_2\text{O} \\
X_m Y_n (s) \rightleftharpoons m \text{X} (aq) + n \text{Y} (aq)
\]

The equilibrium constant for the above is

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

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 coefficient 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 another water molecule.
- This is known as auto ionisation of water and it is represented as below.

\[
\text{H}_2\text{O}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^{-}
\]

One water molecule acts as an acid while the another water molecule acts as a base.
Let us analyse why this happens. Acetic acid is a weak acid. It is not completely dissociated

\[
\text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-
\]

However, the added salt, sodium acetate, completely dissociates to produce Na$^+$ and

\[
\text{CH}_3\text{COO}^-
\]
CH₃ COONa(aq) → Na (aq)+ CH₃ COO (aq)

Hence, the overall concentration of CH₃COO⁻ is increased, and the acid dissociation equilibrium is disturbed. the equilibrium will shift towards the left. In other words, the dissociation of CH₃ 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 (Kₐ) 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.

α = total number of moles
     Number of moles dissociated

We shall derive an expression for ostwald’s law by considering a weak acid, i.e. acetic acid (CH₃ COOH) . The dissociation of acetic acid can be represented as

CH₃ COOH ⇌ H⁺ + CH₃ COO⁻

The dissociation constant of acetic acid is,

\[ K_a = \frac{[H^+][CH_3 COO^-]}{[CH_3 COOH]} \quad \text{(1)} \]

<table>
<thead>
<tr>
<th></th>
<th>CH₃ COOH</th>
<th>H⁺</th>
<th>CH₃ COO⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial No. of moles</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Degree of dissociation of CH₃ COOH</td>
<td>α</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>No. of moles at equilibrium</td>
<td>1-α</td>
<td>α</td>
<td>α</td>
</tr>
<tr>
<td>Equilibrium concentration</td>
<td>(1-α)C</td>
<td>αC</td>
<td>αC</td>
</tr>
</tbody>
</table>

Substituting the equilibrium concentration in equation (1)

\[ K_a = \frac{(αC)(αC)}{(1-α)C} \]
\[ k = \frac{C}{1 - \alpha} \]  

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

\[ K_a = \alpha^2 C \]

\[ \Rightarrow \alpha^2 = \frac{K_a}{C} \]

\[ \alpha^2 = \frac{K_a}{\sqrt{C}} \]  

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

**13. Define pH**

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

\[ \text{pH} = - \log [H_3O^+] \]

**14. Calculate the pH of 1.5 \times 10^{-3} \text{M solution of } \text{Ba} (\text{OH})_2**

\[ \text{Ba(OH)}_2 \ L_{\text{Ba}^2+} + 2\text{OH}^- \]

\[ 1.5 \times 10^{-3} \text{M} \]

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

\[ [\text{pH} + \text{pOH} = 14] \]

\[ \text{pH} = 14 - \text{pOH} \]

\[ \text{pH} = 14 - (- \log [\text{OH}^-]) \]

\[ = 14 + \log [\text{OH}^-] \]

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

\[ = 14 + 3 + \log 10^{-3} \]

\[ = 14 + 0.4771 - 3 \]

\[ = 11 + 0.4771 \]

\[ \text{pH} = 11.48 \]
15. 50ml of 0.05M HNO$_3$ is added to 50ml of 0.025M KOH. Calculate the pH of the resultant solution.

Number of moles of HNO$_3$ = $0.05 \times 50 \times 10^{-3}$ = $2.5 \times 10^{-3}$

Number of moles of KOH = $0.025 \times 50 \times 10^{-3}$ = $1.25 \times 10^{-3}$

Concentration of HNO$_3$ after mixing = Number of moles of HNO$_3$ after mixing

After mixing, total volume = 100 ml = $100 \times 10^{-3}$ L

$$[H^+] = \frac{2.5 \times 10^{-3} - 1.5 \times 10^{-3}}{100 \times 10^{-3}} = 1.25 \times 10^{-1} \text{ moles L}^{-1}$$

pH = -log[$[H^+]$] = 2 - 0.0969 = 1.9031

16. The $K_a$ value for HCN is $10^{-9}$. What is the pH of 0.4M HCN solution?

Given

$K = 10^{-9}$

C = 0.4M

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

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

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

$= 2 \times 10^{-5}$

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

= 5 - 0.3010 = 4.699

17. Calculate the extent of hydrolysis and the pH of 0.1 M ammonium acetate. Given that $K_a = K_b = 1.8 \times 10^{-5}$
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\[
\begin{align*}
\nu = \sqrt{K_b} &= \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-7} \times 1.8 \times 10^{-5}}} \\
\nu = \sqrt{K_b} &= \sqrt{\frac{1}{1.8} \times 10^{-14}} = \sqrt{0.5555 \times 10^{-4}} \\
\end{align*}
\]

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

Given that \( K_a = K_b = 1.8 \times 10^{-5} \)

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, NH\(_4\) OH, to produce a salt, NH\(_4\) Cl, and water

\[
\begin{align*}
\text{HCl (aq) + NH}_4 \text{OH (aq) } &\rightarrow \text{NH}_4 \text{Cl (aq) + H}_2 \text{O (l)} \\
\text{NH}_4 \text{Cl (aq) } &\rightarrow \text{NH}_4^+ + \text{Cl}^-(aq)
\end{align*}
\]

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\(_4\)OH shown below.

\[
\text{NH}_4^+ (aq) + \text{H}_2 \text{O(l) } \Leftrightarrow \text{NH}_4 \text{OH (aq) } + \text{H}^+ (aq)
\]

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.

\[
K_h = \frac{[\text{NH}_4 \text{OH}][H^+]}{[\text{NH}_4^+][\text{H}_2 \text{O}]}
\]

\[
K_h = \frac{[\text{NH}_4 \text{OH}][H^+]}{[\text{NH}_4^+]} \quad (1)
\]

\[
\text{NH}_4 \text{OH (aq) } \Leftrightarrow \text{NH}_4^+ (aq) + \text{OH}^- (aq)
\]

\[
[\text{NH}_4^+][\text{OH}^-]
\]
K_h = ........................ (2)

\[ \text{[NH}_4\text{OH]} \]

\[ K_h \cdot K_b = [H^+] [OH^-] \]

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

we can establish a relationship between the K_h and K_b as

\[ K_h \cdot K_b = K_w \]

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.

\[ K_h = h^2 C \quad \text{and} \quad [H^+] = \sqrt{K_h \cdot C} \]

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

\[ p^H = - \log [H^+] \]

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

\[ = - 1/2 \log K_w - 1/2 \log C + 1/2 \log K_b \]

\[ p^H = 7 - 1/2 \log K_w - 1/2 \log C \]

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

Given that \(K_{sp} = 1 \times 10^{-12}\)

\[
\text{Ag}_2\text{CrO}_4 (s) \rightleftharpoons 2\text{Ag}^+ (aq) + \text{CrO}_4^{2-}
\]

\[
\text{AgNO}_3 (s) \rightleftharpoons \text{Ag}^+ (aq) + \text{NO}_3^- (aq)
\]

\[
[\text{Ag}^+] = 2s + 0.01 \\
0.01 \gg 2s \\
[\text{Ag}^+] = 0.01
\]
Ksp = \([Ag^+]^2 \cdot [CrO_4^{2-}]\)

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

1 x 10\(^{-12}\)

(s) = \----------------- = 1 x 10\(^{-8}\) M

20. Write the expression for the solubility product of Ca\(_3\) (PO\(_4\))\(_2\)

\[
Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}
\]

\[
K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]
\]

\[
K_{sp} = (3s)(2s) = 27s \cdot 4s = 108s^6
\]

21. A saturated solution, prepared by dissolving 2 CaF\(_2\) (s) in water, has

\[
[Ca^{2+}] = 3.3 \times 10^{-4} \text{ M}
\]

What is the Ksp of CaF\(_2\)?

\[
CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)
\]

\[
[F^-] = 2[Ca^{2+}] = 2 \times 3.3 \times 10^{-4} \text{ M} = 6.6 \times 10^{-4} \text{ M}
\]

\[
K_{sp} = [Ca^{2+}] [F^-]^2 = (3.3 \times 10^{-4})(6.6 \times 10^{-4})^2 = 1.44 \times 10^{-10}
\]

22. Ksp of AgCl is 1.8 x 10\(^{-10}\). Calculate molar solubility in 1 M AgNO\(_3\)

AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)

x = solubility of AgCl in 1M AgNO\(_3\)

\[
AgNO_3(aq) \rightleftharpoons Ag^+(aq) + NO_3^-(aq)
\]

\[
1M \quad 1M
\]

\[
[Ag^+] = x + 1 = +1 \quad x << 1
\]

\[
[Cl^-] = x
\]

\[
K_{sp} = [Ag^+] [Cl^-]
\]
23. A particular saturated solution of silver chromate $\text{Ag}_2\text{CrO}_4$ has $[\text{Ag}^+] = 5 \times 10^{-5}$ and $[\text{CrO}_4^{2-}] = 4.4 \times 10^{-4}$ M. What is the value of $K_{sp}$ for $\text{Ag}_2\text{CrO}_4$?

$$K_{sp} = [\text{Ag}^+] [\text{CrO}_4^{2-}]$$

$$= (5 \times 10^{-5})^2 (4.4 \times 10^{-4})$$

$$= 1.1 \times 10^{-12}$$

24. Write the expression for the solubility product of $\text{Hg}_2\text{Cl}_2$.

$$\text{Hg}_2\text{Cl}_2 (s) \rightleftharpoons \text{Hg}^+ + 2\text{Cl}^-$$

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

$$= (s)(2s)^2$$

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

25. $K_{sp}$ of $\text{Ag}_2\text{CrO}_4$ is $1.1 \times 10^{-12}$. What is solubility of $\text{Ag}_2\text{CrO}_4$ in $0.1\text{M} \text{K}_2\text{CrO}_4$?

$$\text{Ag}_2\text{CrO}_4 (s) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$$

$x$ is the solubility of $\text{Ag}_2\text{CrO}_4$ in $0.1\text{M} \text{K}_2\text{CrO}_4$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$= (2x)(x + 0.1) = 0.1$$

$x << 0.1$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

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

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

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

$$x = \sqrt{\frac{1.1 \times 10^{-12}}{0.4}}$$

$$X = \sqrt{\frac{1.1 \times 10^{-12}}{0.4}}$$
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\[ X = \sqrt{2.57 \times 10^{-12}} \]

\[ \therefore X = 1.65 \times 10^{-6} \text{ M} \]

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? \(K_{sp} (\text{PbCl}_2) = 1.2 \times 10^{-5}\).

When two or more solutions 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

\[
Pb^{2+} = \text{molarity} \times \text{Volume of the solution in lit} = 0.1 \times 0.15 
\]

\[
0.1 \times 0.15 
\]

\[
[Pb^{2+}]_{\text{Mix}} = \frac{\text{Number of moles}}{\text{Total volume}} = 0.06 \text{ M} 
\]

NaCl  \(Na + Cl^-\)

\[
\text{No.of moles Cl} = 0.2 \times 0.1 
\]

\[
[Cl^-]_{\text{Mix}} = \frac{\text{Number of moles}}{\text{Total volume}} = 0.08 \text{ M} 
\]

Precipitation of \(\text{PbCl}_2(s)\) occurs if

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

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

\[
= 3.84 \times 10^{-4} 
\]

Since ionic product \([\text{Pb}^{2+}][\text{Cl}^-] > K_{sp}\), \(\text{PbCl}_2\) is precipitated.

27. \(K_{sp}\) of \(\text{Al(OH)}_3\) is \(1 \times 10^{-15}\) M. At what pH does \(1.0 \times 10^{-3}\) M \(\text{Al}^{3+}\) precipitate on the addition of buffer of \(\text{NH}_4\text{Cl}\) and \(\text{NH}_4\text{OH}\) solution?

\[
\text{Al(OH)} \rightleftharpoons \text{Al (aq)} + 3\text{OH (aq)} 
\]

\[
K = [\text{Al}^{3+}] \times [\text{OH}^-]^3 
\]
Al(OH)$_3$ precipitates when

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

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

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

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

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

$\therefore \text{pH} = 14 - 4 = 10$

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

Additional questions:

1. Find the pH of a buffer solution containing 0.20 mole per litre sodium acetate and 0.18 mole per litre acetic acid. $K_a$ for acetic acid is $1.8 \times 10^{-5}$.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

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

$$\text{pK}_a = -\log (1.8 \times 10^{-5}) = 5 - \log 1.8$$

$$= 5 - 0.26$$

$$= 4.74$$

$$0.20$$

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

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

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

$$= 4.74 + 1 - 0.95$$

$$= 5.74 - 0.95$$

$$= 4.79$$

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

Example: Solution containing NH₄ OH 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,

\[dB = \frac{\text{number of gram equivalents of acid / base added to one litre of buffer solution.}}{d(pH)} = \frac{\text{The change in the pH after the addition of acid / base.}}{\text{The change in the pH after the addition of acid / base.}}
\]

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

\[\text{NaOH} (aq) + \text{CH}_3\text{COOH} (aq) \rightleftharpoons \text{CH}_3\text{COONa} (aq) + \text{H}_2\text{O} (l)\]

In aqueous solution, CH₃ COONa 3 is completely dissociated as below

\[\text{CH}_3\text{COONa} (aq) \rightarrow \text{CH}_3\text{COO}^- (aq) + \text{Na}^+ (aq)\]

CH₃ COO⁻ 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⁻.

\[\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{CH}_3\text{COOH} (aq) + \text{OH}^- (aq)\]

and therefore \( [\text{OH}^-] > [\text{H}^+] \), 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.

\[
K_h = \frac{[\text{CH COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}_2\text{O}]}
\]

\[
K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}_2\text{O}]} \quad \text{.........(1)}
\]
\[ \text{[CH}_3\text{COO}^-] \]

\[ \text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^- \]

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

(1) x (2)

\[ K_h \cdot K_a = [\text{H}^+][\text{OH}^-] \]

we know that \([\text{H}^+][\text{OH}^-] = K_w\)

\[ K_h \cdot K_b = K_w \]

\(K_h\) 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. \(K = h^2 \cdot C\) and i.e \([\text{OH}^-] = \sqrt{K_h \cdot C}\)

**pH of salt solution in terms of \(K_a\) and the concentration of the electrolyte.**

\[ \text{pH} + \text{pOH} = 14 \]

\[ \text{pH} = 14 - \text{pOH} = 14 - \left\{-\log [\text{OH}^-]\right\} \]

\[ = 14 + \log [\text{OH}^-] \]

\[ \text{pH} = 14 + \log (K_h \cdot C)^{1/2} \]

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

\[ \text{pH} = 14 + \left(\frac{1}{2} \log K_w + \frac{1}{2} \log C - \frac{1}{2} \log K_a\right) \]

we know \(K_w = 10^{-14}\) and \(1/2 \cdot K_w = 10^{-14} = -7\) and \(\log K_a = P \cdot K_a\)

\[ \text{pH} = 14 - 7 + \frac{1}{2} \log C - \frac{1}{2} \cdot P \cdot K_a \]

\[ \text{pH} = 7 + \frac{1}{2} \log C - \frac{1}{2} \cdot P \cdot K_a \]
33. Hydrolysis of Salt of weak acid and weak base.

Let us consider the hydrolysis of ammonium acetate.

\[ \text{CH}_3\text{COONH}_4(\text{aq}) \rightarrow \text{CH}_3\text{COO}^- (\text{aq}) + \text{NH}_4^+ (\text{aq}) \]

In this case, both the cation \((\text{NH}_4^+)\) and anion \((\text{CH}_3\text{COO}^-)\) have the tendency to react with water.

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \]
\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+ \]

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.

\[ K_a \cdot K_b \cdot K_h = K_w \]

**pH of the solution**

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

\[ \text{pH} = 7 + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b \]

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.,

\[ [\text{H}_3\text{O}^+] = \frac{[\text{acid}]_{\text{eq}}}{[\text{base}]_{\text{eq}}} \quad \text{(1)} \]

✓ 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.

\[ [\text{H}_3\text{O}^+] = \frac{[\text{acid}]}{[\text{salt}]} \quad \text{(2)} \]

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

\[- \log [\text{H}_3\text{O}^+] = \log [\text{acid}] \]

reverse the sign on both sides

\[- \log [\text{H}_3\text{O}^+] = - \log K_a + \log [\text{salt}] \]

We know that

\[\text{pH} = \log [\text{H}_3\text{O}^+] \quad \text{and} \quad pK_a = \log K_a\]

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

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

Similarly for a basic buffer,

\[\text{pOH} = pK_b + \log [\text{base}] \quad \text{(7)}\]

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 \(X_m Y_n\),

\[X_m Y_n (s) \rightleftharpoons mX^n (aq) + nY^m (aq)\]

From the above stoichiometrically balanced equation we have come to know that 1 mole of \(X_m Y_n (s)\) dissociated to furnish ‘m’ moles of and ‘n’ moles of \(Y^m\) if ‘s’ is molar solubility of \(X_m Y_n\), then

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

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

\[K_{sp} = (ms)^m (ns)^n\]

\[K_{sp} = (m)^m (n)^n (s)^{m+n}\]

36. Drive the Relation between pH and pOH

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

\[\text{pH} = - \log_{10} [\text{H}_3\text{O}^+] \quad \text{....(1)}\]

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

Adding equation (1) and (2)
pH + pOH = -log$_{10}$[H$_3$O$^+$] - log$_{10}$[OH$^-$]
= - (log$_{10}$[H$_3$O$^+$] + log$_{10}$[OH$^-$])

We know that [H$_3$O$^+$][OH$^-$]=Kw
⇒ pH + pOH = log$_{10}$ K$_w$
⇒ pH + pOH = pK$_w$........(3)  ( pK$_w$ = - log$_{10}$ K$_w$)

at 25°C, the ionic product of water, K$_w$ = 1 x 10$^{-14}$

pK$_w$ = - log$_{10}$ 10$^{-14}$ = 14 log$_{10}$ 10

= 14

∴ At 25°C,  p$^H$ + p$^OH$ = 14