SALT HYDROLYSIS

Salts

(i) Salts are ionic compounds that result from the combination of a cation from a base and an anion from an acid.

(ii) The taste of salts can vary, with possibilities including salty, bitter, astringent, sweet, or even tasteless.

(iii) Solutions containing salts can exhibit acidity, basicity, or neutrality.

(iv) Fused salts and their aqueous solutions are conductive and can undergo electrolysis.

(v) Salts are typically found in the form of crystalline solids.

Classification of Salts

The salts may be classified into four categories.

Simple Salts

The compounds resulting from the neutralization reaction between an acid and a base fall into three categories.

(i) Normal Salt

The salt formed by the loss of all possible protons (replaceable H^+ ions)

Ex. $NaCl$, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_3BO_3, Na_2HPO_3, NaH_2PO_2 etc.

(ii) Acid Salts

(i) Salts formed by incomplete neutralisation of polybasic acids. Such salts contain one or more replaceable H atom.

Ex. $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4 etc.

(these are salts containing amphiprotic ions)

(ii) Above salts when neutralized by base form normal salts.

(iii) Basic Salts

(i) Salts formed by in complete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.

Ex. $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

(ii) Above salts when neutralized by acids form normal salts.

Double Salts

(i) The addition compounds formed by the combination of two simple salts are termed as double salts.

Ex. $FeSO_4(NH_4)_2SO_4.6H_2O$ (Ferrous ammonium sulphate), $K_2SO_4Al_2(SO_4)_3.$

$24H_2O$ (Alum) and other alums.

(ii) These salts exhibit stability solely in their solid state.

(iii) Upon dissolution in water, they release all the ions that constitute the corresponding simple salt.

(iv) Solutions of double salts demonstrate the characteristics of the basic salts from which they are derived.

Complex Salts

(i) These are formed by combination of simple salts or molecular compounds.

Ex. $K_4Fe(CN)_6$, $Co(NH_3)_6SO_4$ etc.

(ii) $\underbrace{FeSO_4 + 6KCN}_{\text{simple salt}} \longrightarrow K_4Fe(CN)_6 + K_2SO_4$ complex salet

(iii) $\underset{\text{Simple salt}}{CoSO_4} + \underset{\text{Molecular compound}}{6NH_3} \longrightarrow \underset{\text{complex salt}}{Co(NH_3)_6SO_4}$

(iv) These are stable in solid states as well as in solutions.

(v) On dissolving in water, if furnishes a complex ion.

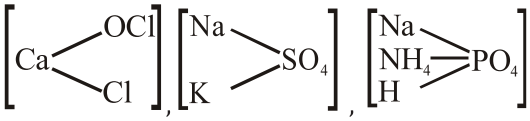
$$K_4Fe(CN)_6 \longrightarrow 4K^+ + \underset{\text{complex ion}}{[Fe(CN)_6]^{4-}}$$

(vi) The characteristics of the solution vary from those of the original substance from which it is derived.

Mixed Salts

A mixed salt is defined as a type of salt that yields multiple cations or anions when dissolved in water.

Ex. $CaOCl_2$, $NaKSO_4$, $NaNH_4HPO_4$ etc.



Hydrolysis of Salt

Salt hydrolysis is defined as the process in which water reacts with salt to form acid & base.

$$\text{Water} + \text{Salt} \longrightarrow \text{Acid} + \text{Base}$$
$$\Delta H = +\text{ve}$$

It is always an endothermic process because it is reverse of acid – base neutralization reaction which is always exothermic.

Hydrolysis constant $K_h = \frac{[\text{Acid}][\text{Base}]}{[\text{Salt}]}$

Here H_2O is a solvent (in excess) so active mass of H_2O is 1.

Hydrolysis of Salt and their pH

Types of Salt Hydrolysis

(1) Hydrolysis of Strong Acid - Weak Base [SA - WB] Type Salt:

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$

$$NH_4Cl + H_2O \longrightarrow NH_4OH + HCl$$
$$NH_4^+ + Cl^- + H_2O \longrightarrow NH_4OH + H^+ + Cl^-$$
$$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$$

(1) In this type of salt hydrolysis, cation reacts with H_2O, therefore called as cationic hydrolysis.

(2) Solution is acidic in nature (SA WB) as $[H^+]$ is increased.

(3) pH of the solution is less than 7.

(a) Relation between K_h, K_W & K_b

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

Hydrolysis constant K_h

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad \text{..... (1)}$$

For weak Base $NH_4OH \longrightarrow NH_4^+ + OH^-$

$$K_b = \frac{[OH_4^+][H^-]}{[NH_4OH]} \qquad \text{..... (2)}$$

For water $H_2O \longrightarrow H^+ + OH^-$

$$K_W = [OH^-]\,[H^+] \qquad \text{..... (3)}$$

Now multiplying Eq. (1) & (2) = Eq. (3)

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} = [H^+]\,[OH^-]$$

i.e. $K_h \times K_b = K_W$

$$K_h = \frac{K_w}{K_b}$$

(b) Degree of hydrolysis – Represented by h

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

C 0 0

(Initial concentration at equilibrium)

C – x x x

nx = aα

1x = Ch

x = Ch

C – Ch Ch Ch

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{Ch \times Ch}{C - Ch}$$

$$= \frac{C^2h^2}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

Since $h <<<< 1$

then $(1 - h) \approx 1$

$\therefore$ $K_h = Ch^2$

$$H^2 = \frac{K_h}{C}$$

$\Rightarrow$ $h = \sqrt{\frac{K_h}{C}}$

$\therefore$ $K_h = \frac{K_w}{K_b}$

$\Rightarrow$ $h = \sqrt{\frac{\frac{K_w}{K_b}}{C}}$

$\Rightarrow$ $h = \sqrt{\frac{K_w}{K_b \times C}}$

(c) pH of the solution:

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

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

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

On taking – log on both sides

– log $$[H^+] = -\log\sqrt{\frac{K_w \times C}{K_b}}$$

$\Rightarrow$ $$pH = -\log \left(\frac{K_w \times C}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}[\log K_w + \log C - \log K_b]$$

$$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log C - \frac{1}{2}(-\log K_b)$$

$$pH = \frac{1}{2}pK_w - \frac{1}{2}\log\ C - \frac{1}{2}pK_b$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log\ C$$

(2) Hydrolysis of [WA – SB] Type Salt:

Ex. KCN, NaCN, K_2CO_3, $BaCO_3$, K_3PO_4

$$NaCN + H_2O \longrightarrow NaOH + HCN$$

$$Na^+ + CN^- + H_2O \longrightarrow Na^+ + OH^- + HCN$$

$$CN^- + H_2O \longrightarrow HCN + OH^-$$

(1) In this type of salt hydrolysis anion reacts with water therefore called as anionic hydrolysis.

(2) Solution is basic in nature as $[OH^-]$ increases.

(3) pH of the solution is greater than 7.

(a) Relation between K_h, K_w, K_a

$$CN^- + H_2O \longrightarrow HCN + OH^-$$

$$K_h = \frac{[HCN+OH^-]}{CN^-} \qquad \text{..... (1)}$$

For weak acid $$HCN \longrightarrow CN^- + H^+$$

$$K_a = \frac{[CN^- + OH^+]}{[HCN]} \qquad \text{..... (2)}$$

For water $$H_2O \longrightarrow H^+ + OH^-$$

$$K_w = [OH^-][H^+] \qquad \text{..... (3)}$$

eq. (1) × eq. (2) = eq. (3)

$$\frac{[HCN][OH^-]}{[CN^-]} \times \frac{[CN^-][H^+]}{[HCN]} = [H^+][OH^-]$$

$$K_h \times K_a = K_w$$

$$K_h = \frac{K_w}{K_a}$$

(b) Degree of hydrolysis:

$CN^{-} + H_2O \quad HCN \quad + \quad OH^{-}$

$C \qquad 0 \qquad 0$ Initial concentration at equilibrium

$C - x \qquad x \qquad x$

$nx = a\alpha$

$1x = Ch$

$x = Ch$

$C - Ch \qquad Ch \qquad Ch$

$$K_h = \frac{[HCN][OH^{-}]}{[CN^{-}]} = \frac{Ch \times Ch}{C - Ch} = \frac{C^2h^2}{C(1-h)}$$

$$K_h = \frac{Ch^2}{(1-h)}$$

Since $h <<<< 1$

Therefore $(1 - h) \approx 1$

$\therefore$ $K_h = Ch^2$

$$h^2 = \frac{K_h}{C}$$

$\Rightarrow$ $h = \sqrt{\frac{K_h}{C}}$

$$h = \sqrt{\frac{K_w}{K_a \times C}}$$

(c) pH of the solution

$$[OH^{-}] = Ch$$

$$[OH^{-}] = C \times \sqrt{\frac{K_w}{K_a \times C}}$$

$$[OH^{-}] = \sqrt{\frac{K_w \times C}{K_a}}$$

$\because$ $K_w = [OH^{-}]\,[H^{+}]$

$\therefore$ $[H^{+}] = \frac{K_w}{[OH^{-}]}$

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

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

On taking – log on both sides

$$-\log\,[H^{+}] = -\log\sqrt{\frac{K_w \times K_a}{C}}$$

$$pH = -\log\left(\frac{K_w \times K_a}{C}\right)^{1/2}$$

$$pH = -\frac{1}{2}\,[\log K_w + \log K_a - \log C\,]$$

$$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a - \frac{1}{2}\log C$$

$$pH = \frac{1}{2}\,pK_w + \frac{1}{2}\,pK_a + \frac{1}{2}\log C$$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

3. Hydrolysis of (WA - WB) Type Salt:

Ex. NH_4CN, $CaCO_3$, $(NH_4)_2CO_3$, $ZnHPO_3$

$$NH_4CN + H_2O \longrightarrow NH_4OH + HCN$$

$$NH_4^+ + CN^- + H_2O \longrightarrow NH_4OH + HCN$$

(1) Solution is almost neutral but it may be acidic or basic depending upon the nature of acid & base & pH of the solution is near to 7.

(a) Relation between K_h, K_w, K_a & K_b

$$NH_4^+ + CN^- + H_2O \longrightarrow NH_4OH + HCN$$

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} \quad \text{..... (1)}$$

For weak base $NH_4OH \longrightarrow NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \text{..... (2)}$$

For weak acid $HCN \longrightarrow H^+ + CN^-$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \quad \text{..... (3)}$$

For water $H_2O \longrightarrow H^+ + OH^-$

$$K_w = [OH^-][H^+] \quad \text{..... (4)}$$

Multiply Eq. (1) × Eq. (2) × Eq. (3) = Eq. (4)

$$\frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} \times \frac{[H^+][CN^-]}{[HCN]} = [H^+][OH^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$K_h = \frac{K_w}{K_a \times K_b}$$

(2) Degree of Hydrolysis

$$NH_4^+ + CN^- + H_2O \longrightarrow NH_4OH + HCN$$

$C \quad C \quad 0 \quad 0$ Initial concentration

$C - x \quad C - x \quad x \quad x$ at equilibrium

$nx = a\alpha$

$x = Ch$

$C - Ch \quad C - Ch \quad Ch \quad Ch$

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} = \frac{Ch \times Ch}{(C-Ch)(C-Ch)} = \frac{C^2h^2}{C(1-h)\times C(1-h)} = \frac{h^2}{(1-h)^2}$$

Since $h <<<< 1$

Then $(1 - h) \approx 1$

∴ $K_h = h^2$

Or $h^2 = \frac{K_W}{K_a \times K_b}$

$$h = \sqrt{\frac{K_W}{K_a \times K_b}} \quad \text{..... (5)}$$

(b) pH of the solution

From eq. (3)

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$[H^+] = \frac{K_a \times [HCN]}{[CN^-]}$$

$$[H^+] = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$$

Since $h <<<< 1$

$(1 - h) \approx 1$

$[H^+] = K_a \times h$ [Now put the value of h from eq. (5)]

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}}$$

On taking – log on both sides

$$-\log [H^+] = -\log\left(\frac{K_w \times K_a}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}[\log (K_w \times K_a) - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log K_b]$$

$$pH = -\frac{1}{2}[\log K_w] - \frac{1}{2}[\log K_a] - \frac{1}{2}[-\log K_b]$$

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

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

(4) Hydrolysis of [SA – SB] Type Salt –

Ex. NaCl, $BaCl_2$, Na_2SO_4, $KClO_4$ etc.

$NaCl + H_2O \rightarrow NaOH + HCl$

$Na^+ + Cl^- + H_2O \rightarrow Na^+ + OH^- + H^+ + Cl^-$

$H_2O \rightarrow H^+ + OH^-$ (It is not salt hydrolysis)

(1) Hydrolysis of salt of [SA – SB] is not possible

(2) Solution is neutral in nature (pH = pOH = 7)

(3) pH of the solution is 7

Hydrolysis of Polyvalent Anions or Cations

The hydrolysis of these species occurs gradually, much like the dissociation of weak acids. In most cases, the initial step of hydrolysis prevails for two primary reasons. First, the hydrolysis constant for the second and subsequent steps is typically significantly smaller in comparison to the constant for the first step of hydrolysis. Second, the presence of ions resulting from the initial step of hydrolysis tends to inhibit the hydrolysis of the second and subsequent steps.

For a polyprotic acid (H_2S, H_3PO_4, H_2CO_3, $H_2C_2O_4$) we already know that the dissociation always takes place in steps, so for example for H_3PO_4

$$H_3PO_4 \rightarrow H^+ + H_2PO_4^- \quad K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \quad \text{..... (1)}$$

$$H_2PO_4^- \rightarrow H^+ + HPO_4^{-2} \quad K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \quad \text{..... (2)}$$

$$HPO_4^{2-} \rightarrow H^+ + PO_4^{-3} \quad K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \quad \text{..... (3)}$$

For all acids we always have $Ka_1 >> Ka_2 >> Ka_3$

pH of the solution can be calculated from Ist step only because $[H^+]$ from IInd & IIIrd step can be neglected as

(a) $K_{a1} >> K_{a2} >> K_{a3}$

(b) $[H^+]$ from Ist dissociation will suppress the dissociation of IInd & IIIrd step.

Now for the hydrolysis of polyvalent ions of salts (like K_3PO_4, $Na_2C_2O_4$, $ZnSO_4$, $FeCl_3$, $(NH_4)_2C_2O_4$ or ions like PO_4^{3-}, $C_2O_4^{2-}$, Zn^{2+}, Fe^{3+} etc).

Consider the hydrolysis in step

$$\begin{array}{llll} PO_4^{3-} + H_2O & ^{-}\rightarrow & HPO_4^{2-} + & OH^- \\ C & & 0 & 0 \\ C(1-h) & & Ch & Ch \end{array}$$

$$K_{h_1} = \frac{[OH^-][HPO_4^{2-}]}{[PO_4^{3-}]} \quad \text{..... (4)}$$

$$HPO_4^{2-} + H_2O ^{-}\rightarrow H_2PO_4^- + OH^- \quad K_{h2} = \frac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]} \quad \text{..... (5)}$$

$$H_2PO_4^- + H_2O ^{-}\rightarrow H_3PO_4 + OH^- \quad K_{h3} = \frac{[OH^-][H_3PO_4]}{[H_2PO_4^-]} \quad \text{..... (6)}$$

$$H_2O ^{-}\rightarrow H^+ + OH^- \quad K_W = [H^+][OH^-] \quad \text{..... (7)}$$

From above equations we get.

$$K_{a1} \times K_{h3} = K_W$$

$$K_{a2} \times K_{h2} = K_W$$

$$K_{a3} \times K_{h1} = K_W$$

Generally, pH is calculated only using the first step hydrolysis

$$K_{h1} = \frac{ChCh}{C(1-h)} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h_1}}{C}}$$

$\Rightarrow$ $[OH^-] = Ch = \sqrt{K_{h_1} \times C}$

$\Rightarrow$ $[H^+] = \dfrac{K_W}{[OH^-]} = K_W \sqrt{\dfrac{K_{a_3}}{K_W C}} = \sqrt{\dfrac{k_W \times K_{a_3}}{C}}$

So, $pH = [pK_W + \frac{1}{2} + \log C]$

Hydrolysis of Amphiprotic Anion (Cation is not Hydrolyzed)

$NaHCO_3$, NaHS, etc., can undergo ionisation to from H^+ ion and can undergo hydrolysis to from OH^-

(Na^+ ion is not hydrolyzed)

(a) (i) $HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$ (acid)

(ii) $HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$ (base)

$$pH\ (HCO_3^-) = \left(\frac{pK_{a_1}+pK_{a_2}}{2}\right)$$

(b) Similarly, for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions.

$$pH_{(H_2PO_4^-)} = \left(\frac{pK_{a_1}+pK_{a_2}}{2}\right) \quad \text{and} \quad pH_{(HPO_4^{2-})} = \left(\frac{pK_{a_2}+pK_{a_3}}{2}\right)$$

Cation is Also Hydrolyzed

(i) Salts like NH_4HCO_3, NH_4HS in which HCO_3^- and HS^- are amphiprotic respectively but NH_4^+ will also hydrolyzed.

(ii) Equilibria in such solutions will be:

(Hydrolysis of anion)

$$HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$$

(Hydrolysis of cation)

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

so, $$[H^+] = \sqrt{K_{a_1}\left(\frac{K_w}{K_b} - K_{a_2}\right)}$$