EQUILIBRIUM

IONIZATION OF ACIDS AND BASES

PROPERTIES OF WATER Amphoteric (Amphiprotic) Acid/Base Nature

Water - an acid as well as base according to Bronsted - Lowry theory but according to Lewis concept it can only be taken as base only.

In pure water $[H^+] = [OH^-]$ so it is neutral.

Molar Concentration / Molarity of Water

Molarity = No. of moles/litre = $\frac{1000g/litre}{18 g/mole}$

= 55.55 mole/litre = 55.55 M (density = 1 g/cc)

Ionic Product of Water

According to Arrhenius concept

 $H_20 \longrightarrow H^+ + 0H^-$ so, ionic product of water,

 $k_W = [H^+][OH^-] = 10^{-14} \text{ at } 25^\circ \text{ (exp.)}$

Dissociation of water is endothermic, so on increasing temperature ${\rm K}_{eq}$ increases.

K_w increases with increase in temperature.

Ionic product of water is always a constant whatever has been dissolved in water since it's an equilibrium constant so will be dependent only on temperature.

• Degree of Dissociation of Water

H₂0
$$\longrightarrow$$
 H⁺ + OH⁻ $\Rightarrow \alpha = \frac{\text{no.of moles dissociated}}{\text{Total no.of moles initially taken}}$
$$= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7} \%$$

Absolute Dissociation Constant of Water

H₂0 \longrightarrow H⁺ + OH⁻ K_a = K_b = $\frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$ So, pK_a = pK_b = $-\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$

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Acidity and pH Scale

Acidic strength means the tendency of an acid to give H_30^+ or H^+ ions in water.

So greater then tendency to give H^+ , more will be the acidic strength of the substance. Basic strength means the tendency of a base to give OH^- ions in water.

So greater the tendency to give OH⁻ ions, more will be basic strength of the substance. The concentration of H⁺ ions is written in a simplified form introduced by Sorenson known as pH scale. pH is defined as negative logarithm of activity of H⁺ ions. activity (a) = $\gamma \cdot \frac{C}{C_0}$

 $C \rightarrow$ unitless, $C_0 \rightarrow$ standard concentration



 \therefore pH = - log (where is the activity of H⁺ ions)



Activity of H^+ ions is the concentration of free H^+ ions or H_3O^+ ions in a solution. The pH scale was marked from 0 to 14 with central point at 7 at 25 °C taking water as solvent. If the temperature and the solvent are changed, the pH range of the scale will also change.

For example,

0 - 14	at 25 °C ($K_W = 10^{-14}$)	Neutral point, $pH = 7$
0 - 13	at 80 °C ($K_w = 10^{-13}$)	Neutral point, pH = 6.5

pH can also be negative or > 14

pH Calculation of Different Types of Solutions

(a) Strong acid Solution

(i) If concentration is greater than 10^{-6} M.

In this case H^+ ions coming from water can be neglected,

so $[H^+]$ = normality of strong acid solution

(ii) If concentration is less than 10^{-6} M

In this case H^+ ions coming from water cannot be neglected.

So $[H^+]$ = normality of strong acid + H^+ ions coming from water in presence of this strong acid

- (b) Strong Base Solution: Calculate the $[OH^-]$ which will be equal to normality of the strong base solution and then use $K_W = [H^+] \times [OH^-] = 10^{-14}$, to calculate $[H^+]$
- (c) **pH of Mxture of Two Strong Acids :** If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2 , then

Number of H^+ ions from I-solution = N_1V_1

Number of H^+ ions from II-solution = N_2V_2

If final normality is N and final volume is V, then

$$NV = N_1V_1 + N_2V_2$$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[H^+] = N = \frac{N_1 \ V_1 + N_2 \ V_2}{V_1 + V_2}$$

Chemistry

(d) pH of Mixture of Two Strong Bases

similar to above calculation

$$[OH^{-}] = N = \frac{N_1 \ V_1 + N_2 \ V_2}{V_1 + V_2} \quad [H^{+}] = \frac{10^{-14}}{[OH^{-}]}$$

(e) pH of Mixture of a Strong Acid and a Strong Base

Acid Base neutralisation reaction will take place.

The solution will be acidic or basic depending on which component has been taken in excess.

If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution of normality N_2 , then

Number of H^+ ions from I-solution = N_1V_1

Number of OH^- ions from II-solution = N_2V_2



(f) pH of a Weak Acid (Monoprotic) Solution

Weak acid does not dissociated 100 % therefore we have to calculate the percentage dissociation using K_a dissociation constant of the acid.

We have to use Ostwald's Dilution law (as have been derived earlier)

$$HA \longrightarrow H^{+} + A^{-}$$

$$t = 0 \qquad C \qquad 0 \qquad 0$$

$$t_{eq} \qquad C(1 - \alpha) \qquad C\alpha \qquad X\alpha$$

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]} = \frac{Ca^{2}}{1 - \alpha}$$

If
$$\alpha << 1 \Rightarrow (1 - \alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \text{ (is valid if } \alpha < 0.1 \text{ or } 10\%)$$

 $[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \text{ So } pH = \frac{1}{2}(pK_a - \log C) \text{ valid only if } \alpha <<< 1$
on increasing the dilution $\Rightarrow C\downarrow = \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

(g) pH of a Mixture of Weak Acid (Monoprotic) and a Strong Acid Solution

Weak acid and Strong acid both will contribute H^+ ion.

For the first approximation we can neglect the H⁺ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.

To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

If
$$[SA] = C_1$$
 and $[WA] = C_2$, then $[H^+]$ from $SA = C_1$

the weak acid will dissociate as follows.

$$HA \longrightarrow H^{+} + A^{-}$$

$$C_{2} \qquad 0 \qquad 0$$

$$C_{2}(1-\alpha) \quad C_{2}\alpha + C_{1} \quad C_{2}\alpha$$

$$K_{a} = \frac{(C_{2}\alpha + C_{1})C_{2}\alpha}{C_{2}(1-\alpha)} \quad (\alpha <<<1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

$$K_a = (C_2 \alpha + C_1) \alpha$$

Total H^+ ion concentration = $C_1 + C_2 \alpha$

If the total $[H^+]$ from the acid is more than 10^{-6} M, then contribution from the water can be neglected, if not then we have to take $[H^+]$ from the water also.

Relative Strength of Weak Acids and Bases

The relative strength of weak acids and bases are generally determined by their dissociation constants K_a and K_b respectively. For weak acid, i.e. CH₃COOH

$$\begin{array}{rcl} \mathrm{CH}_{3}\mathrm{COOH} &\longrightarrow & \mathrm{CH}_{3}\mathrm{COO^{-}} &+ & \mathrm{H}^{+} \\ \mathrm{C} & & 0 & & 0 \\ \mathrm{C}(1-\alpha) & & \mathrm{C}\alpha & & \mathrm{C}\alpha \\ \mathrm{K}_{a} &= \frac{\mathrm{C}\alpha \cdot \mathrm{C}\alpha}{\mathrm{C}(1-\alpha)} &= \frac{\mathrm{C}\alpha^{2}}{(1-\alpha)} \Rightarrow & \mathrm{K}_{a} &= \mathrm{C}\alpha^{2} & (\mathrm{if} \; \alpha << 1) \end{array}$$

Similarly, for weak base, i.e., NH4OH

$$\begin{array}{rcl} \mathrm{NH}_{4}\mathrm{OH} & \longrightarrow & \mathrm{NH}_{4}^{+} + & \mathrm{OH} \\ \mathrm{C} & & 0 & & 0 \\ \mathrm{C}(1-\alpha) & & \mathrm{C}\alpha & & \mathrm{C}\alpha \\ \mathrm{K}_{b} = \mathrm{C}\alpha^{2} \end{array}$$

 K_a and K_b are just the equilibrium constants and hence depends only on temperature. Greater the value of dissociation constant of the acid (K_a), more is the strength of the acid and similarly greater the value of dissociation constant of the base, more is the strength of the base. For two acids of different concentrations.

Similarly for bases, $\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{\text{K}_{a_1} \cdot \text{c}_1}{\text{K}_{a_2} \cdot \text{c}_2}}$

The modern method is to convert K_a as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit p K_a . Thus, if K_a for acid is equal to 10^{-4} , p $K_a = 4$. So higher p K_a value means lower acid strength,

that is, $pK_a = -\log K_a$

Also, $pK_b = -\log K_b$

Total [H⁺] in a mixture of two weak Acids.

$$[\mathbf{H}^{+}] = \sqrt{\mathbf{K}_{\mathbf{a}_{1}}\mathbf{c}_{1} + \mathbf{K}_{\mathbf{a}_{2}}\mathbf{c}_{2}}$$

Similarly for two weak bases

$$[OH^{-}] = \sqrt{K_{b_1}c_1 + K_{b_2}c_2}$$

(h) pH of a Mixture of Two Weak Acid (Both Monoprotic) Solution

Both acids will dissociate partially.

Chemistry

Let the acid are ${\rm HA}_1$ & ${\rm HA}_2$ and their final concentrations are ${\rm C}_1$ & ${\rm C}_2$ respectively, then

$$HA_{1} \longrightarrow H^{+} + A_{1}^{-} HA_{2} \longrightarrow H^{+} + A_{2}^{-}$$

$$t = 0 \quad C_{1} \qquad 0 \qquad 0 \qquad C_{2} \qquad 0 \qquad 0$$

$$At \text{ eq.} \quad C_{1}(1-\alpha_{1}) \quad C_{1}\alpha_{1} + C_{2}\alpha_{2} \quad C_{1}\alpha_{1} \quad C_{2}(1-\alpha_{2}) \quad C_{2}\alpha_{2} + C_{1}\alpha_{1} \quad C_{2}\alpha_{2}$$

$$K_{a_{1}} = \frac{C_{1}\alpha_{1}(C_{1}\alpha_{1} + C_{2}\alpha_{2})}{C_{1}(1-\alpha_{1})} \qquad K_{a_{2}} = \frac{(C_{2}\alpha_{2} + C_{1}\alpha_{1})C_{2}\alpha_{2}}{C_{2}(1-\alpha_{2})}$$

(Since α_1, α_2 both are small in comparison to unity)

$$= (C_{1}\alpha_{1} + C_{2}\alpha_{2})\alpha_{1} \quad ; = (C_{1}\alpha_{1} + C_{2}\alpha_{2})\alpha_{2} \quad \Rightarrow \frac{K_{a_{1}}}{K_{a_{2}}} = \frac{\alpha_{1}}{\alpha_{2}}$$
$$[H^{+}] = C_{1}\alpha_{1} + C_{2}\alpha_{2} = \frac{C_{1} K_{a_{1}}}{\sqrt{C_{1} K_{a_{1}} + C_{2} K_{a_{2}}}} + \frac{C_{2} K_{a_{2}}}{\sqrt{C_{1} K_{a_{1}} + C_{2} K_{a_{2}}}}$$
$$\Rightarrow [H^{+}] = \sqrt{C_{1} K_{a_{1}} + C_{2} K_{a_{2}}}$$

If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

So,
$$[H^+] = C_1 \alpha_1 + C_2 \alpha_2 \approx C_1 \alpha_1$$

ISOHYDRIC SOLUTIONS

- (i) Solutions of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solutions, there occurs no change in the degree of dissociation of either of the electrolyte.
- (ii) Let the isohydric solution is made by HA_1 and HA_2 acids, then $[H^+]$ of both acids should be equal i.e.

$$\sqrt{K_{a_1}C_1} = \sqrt{K_{a_2}C_2}$$
 or $\frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$

(i) pH of a Solution of a Polyprotic Weak Acid

Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid (H_2A) in water whose concentration is c M.

In an aqueous solution, following equilibria exist.

If

α_1 = degree of ionization of H ₂ A in	K_{a_1} = first ionisation constant of H_2A
presence of HA ⁻	
α_2 = degree of ionisation of HA ⁻ in	K_{a_2} = second ionisation constant of
presence of H ₂ A	H ₂ A
$H_2A + H_2O HA^- + H_3O^+$	$HA^{-} + H_2O A^{2-} + H_3O^{+}$
at eq. C – x x – y	x + y
at eq. x – y y	x + y
$(K_{eq})_1 [H_20] = \frac{[H_30^+][HA^-]}{[H_2 A]} = K_{a_1}$	$(K_{eq})_2 [H_20] = \frac{[H_30^+][A^{2^-}]}{[HA^-]} = K_{a_2}$
$\therefore \mathbf{K}_{a_1} = \frac{(x-y)(x+y)}{(\mathbf{C}-x)}$	$K_{a_2} = \frac{(y)(x+y)}{(x-y)}$

Approximation

For diprotic acids, << and y would be even smaller than x.

$$\therefore \qquad \qquad y < < < x \Rightarrow x - y \ x \ and \ x + y \ x$$

Thus, equation (i) can be reduced to $K_{a_1} = \frac{x^2}{C-x}$, $K_{a_2} = y$

This is expression similar to the expression for a weak monoprotic acid.

Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^+]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} << K_{a_1}$

(j) pH of a Mixture of a Polyprotic Weak Acid and a Strong Acid

pH can be calculated by taking the concentration of strong acid only (for first approximation)For precise calculation we should take only the first dissociation constant of the weak polyprotic acid. (As can be predicted from the equations we have presented so far for different cases.)All these steps can be followed for the calculation of pOH for weak base and their mixtures (we just have to replace Ka with Kb)

pH of a Mixture of a Weak Acid/Weak Base with Weak/Strong Base/Acid Respectively.

For this type of mixtures there can be two cases in general,

(i) if the acids and bases are mixed in equal amounts (equivalents)

(ii) if the acids and bases are mixed in different amounts (equivalents)

First case will lead to phenomenon of Salt hydrolysis and second case will lead to formation of Buffer Solution.

Relation Between K_a and K_b for Conjugate Acid Base Pair

For conjugate-acid base pairs, the acid dissociation constant K_a and base ionization constant K_b are related by the following equations :

 K_a . $K_b = K_W$ where Kw is the autoionization constant

 $pK_a + pK_b = 14 \text{ at } 25^{\circ}C$

Weak acids, generically abbreviated as HA, donate H^+ (or proton) to water to form the conjugate base A^- and H_3O^+ :

$$HA(aq) + H_2O(I) H_3O^+(aq) + A^-(aq)$$

acid base acid base

Similarly, a base (abbreviated as B) will accept a proton in water to form the conjugate acid, HB^+ , and OH^- :

base acid acid base

For a weak acid or base, the equilibrium constant for the ionization reaction quantities the relative amount of each species. In this article, we will discuss the relationship between the equilibrium constants K_a and K_b for a conjugate acid-base pair.

Let's look more closely at the dissociation reaction for a monoprotic weak acid HA :

$$HA(aq) + H_2O(I) H_3O^+(aq) + A^-(aq)$$

The products of this reversible reaction are A⁻, the conjugate base of HA, and H_3O^+ . We can write the following expressing for the equilibrium constant K_a :

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Finding Kb for A- Reacting as a Base

Since A⁻ is a base, we can also write the reversible reaction for A⁻ acting as a base by accepting a proton from water :

$$A^{-}(aq) + H_2O(l) HA(aq) + OH^{-}(aq)$$

The products of this reaction are HA and OH^- . We can write out the equilibrium constant K_b for the reaction where A^- acts as a base :

$$\mathrm{K}_{b} = \frac{\mathrm{[HA][OH^{-}]}}{\mathrm{[A^{-}]}}$$

Even though this almost looks like the reverse of HA acting as an acid, they are actually very different reactions. When HA acts as an acid, one of the products is H_3O^+ . When the conjugate base A⁻ acts as a base, one of the products is OH⁻.

Relationship between Ka and Kb for conjugate acid-base pair

If we multiply K_a for HA with the K_b of its conjugate base A⁻, that gives :

$$K_{a} \cdot K_{b} = \left(\frac{[H_{3}O^{+}][A^{-}]}{[HA]}\right) \left(\frac{[HA][OH^{-}]}{[A^{-}]}\right)$$
$$= [H3O^{+}] [OH^{-}]$$
$$= K_{W}$$

where K_W is the water dissociation constant. This relationship is very useful for reading K_a and K_b for a conjugate acid-base pair. We can also use the value of K_W at 25°C to derive other handy equations.

$$K_a \cdot K_b = K_w$$

= 1.0 × 10⁻¹⁴ at 25°C (Eq. 1)

If we take the negative \log_{10} of both sides of the Eq. 1, we get:

$$pK_a + pK_b = 14 \text{ at } 25^{\circ}C$$
 (Eq. 2)

We can use these equations to determine K_b (or pK_b) of a weak base given K_a of the conjugate acid. We can also calculate the K_a (or Pk_a) of a weak acid given K_b of the conjugate base.

An important thing to remember is that these equations only work for conjugate acidbase pairs.

SALTS

- (i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.
- (ii) Salts may taste salty, bitter, astringent or sweet or tasteless.
- (iii) Solution of salts may be acidic, basic or neutral.
- (iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis.
- (v) The salts are generally crystalline solids.

Classification of Salts

The salts may be classified into four categories.

• Simple Salts

The salts formed by the neutralisation process between acid and base. These are of three types.

(i) Normal Salt

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

Ex. NaCl, NaNO₃, K₂SO₄, Ca₃(PO₄)₂, Na₃BO₃, Na₂HPO₃, NaH₂PO₂ etc.

(ii) Acid Salts

- (i) Salts formed by incomplete neutralisation of polybasic acids. Such salts contain one or more replaceable H atom.
- **Ex.** NaHCO₃, NaHSO₄, NaH₂PO₄, Na₂HPO₄ 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)₂ Cl, 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. FeSO₄ (NH₄)₂SO₄. 6H₂O (Ferrous ammonium sulphate), K₂SO₄ Al₂ (SO₄)₃.
24H₂O (Alum) and other alums.

- (ii) Above salts are stable in solid state only.
- (iii) When dissolved in water, it furnishes all the ions present in the simple salt from which it has been constituted.
- (iv) The solution of double salt shows the properties of the simple salts from which it has been constituted.

Complex Salts

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

Ex.
$$K_4Fe(CN)_6$$
, $Co(NH_3)_6$ SO₄ etc.

(ii)
$$\underbrace{\operatorname{FeSO}_4 + 6\mathrm{KCN}}_{\text{simple salt}} \longrightarrow \underset{\text{complex salt}}{\operatorname{K}_4 \operatorname{Fe}(\mathrm{CN})_6 + \operatorname{K}_2 \operatorname{SO}_4}$$

(iii)
$$CoSO_4 + 6NH_3 \longrightarrow Co(NH_3)_6SO_4$$

Simple Molecular complex

salt compound salt

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

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

$$K_4 Fe(CN)_6 \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

complex ion

(vi) The properties of the solution are different from the properties of the substance from which it has been constituted.

Mixed Salts

- (i) The salt which furnishes more than one cation or more than one anion when dissolved in water is called mixed salt.
- **Ex.** CaOCl₂, NaKSO₄, NaNH₄HPO₄ etc.

 $\begin{bmatrix} Ca \swarrow OCl \\ Cl \end{bmatrix} \begin{bmatrix} Na \searrow SO_4 \\ K \end{pmatrix} \begin{bmatrix} Na & \\ NH_4 & PO_4 \\ H \end{bmatrix}$

Hydrolysis of Salt

Salt Hydrolysis

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

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

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

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

Here H_20 is a solvent (in excess) so active mass of H_20 is 1.

Types of Salt Hydrolysis

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

Ex.	CaSO ₄ , NH ₄ Cl, (NH ₄) ₂ SO ₄ , Ca(NO ₃) ₂ , ZnCl ₂ , CuCl ₂ , CaCl ₂		
	$\rm NH_4Cl + H_2O \longrightarrow$	$NH_4OH + HCl$	
	$\mathrm{NH_4}^+ + \mathrm{Cl}^- + \mathrm{H_2O} \longrightarrow$	$NH_4OH + H^+ + Cl^-$	
	$\mathrm{NH_4}^+ + \mathrm{H_2O} \longrightarrow$	$NH_4OH + H^+$	

 In this type of salt hydrolysis, cation reacts with H₂O, 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

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Now

i.e.

$$\begin{split} & K_{h} = \frac{[NH_{4}OH][H^{+}]}{[NH_{4}^{+}]} &(1) \\ & \text{For weak Base} & NH_{4}OH \longrightarrow & NH_{4}^{+} + OH^{-} \\ & K_{b} = \frac{\left[\frac{[NH_{4}^{+}]}{[NH_{4}OH]} \right]}{[NH_{4}OH]} &(2) \\ & \text{For water} & H_{2}O \longrightarrow & H^{+} + OH^{-} \\ & K_{w} = [OH^{-}][H^{+}] &(3) \\ & \text{Now multiplying Eq. (1) & (2) = Eq. (3)} \\ & \frac{[NH_{4}OH][H^{+}]}{[NH_{4}^{+}]} \times \frac{[NH_{4}^{2}][OH^{-}]}{[NH_{4}OH]} = [H^{+}][OH^{-}] \\ & \text{i.e.} & K_{h} \times K_{b} = K_{w} \\ & K_{h} \leq \frac{K_{w}}{K_{b}} \\ & \text{(b) Degree of hydrolysis - Represented by h} \\ & NH_{4}^{+} + H_{2}O \longrightarrow & NH_{4}OH + H^{+} \\ & C & 0 & 0 \\ & (Initial concentration at equilibrium) \\ & C - x & x & x \\ & nx = a\alpha \\ & 1x = Ch \\ & x = Ch \\ & C - Ch & Ch & Ch \\ & K_{h} = \frac{[NH_{4}OH][H^{+}]}{[NH_{4}^{+}]} = \frac{Ch \times Ch}{C-Ch} \\ & = \frac{C^{2}h^{2}}{C(1-h)} = \frac{Ch^{2}}{(1-h)} \\ & \text{Since} & h < < < 1 \\ & \text{then} & (1-h) \approx 1 \\ & \therefore & K_{h} = Ch^{2} \\ & h^{2} = \frac{K_{h}}{C} \Rightarrow h = \sqrt{\frac{K_{h}}{C}} \\ \end{aligned}$$

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$$K_{h} = \frac{K_{w}}{K_{b}} \implies h = \sqrt{\frac{\frac{K_{w}}{K_{b}}}{c}} \implies h = \sqrt{\frac{K_{w}}{K_{b} \times c}}$$

(c) pH of the solution:

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

On taking - log on both sides

$$-\log \qquad [H^+] = -\log \sqrt{\frac{K_W \times C}{K_b}} \Rightarrow pH = -\log \left(\frac{K_W \times C}{K_b}\right)^{1/2}$$

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

$$pH = -\frac{1}{2} \log K_W - \frac{1}{2} \log C - \frac{1}{2} \left(-\log K_b\right)$$

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

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

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

Ex. KCN, NaCN, K₂CO₃, BaCO₃, K₃PO₄ NaCN + H₂O \longrightarrow NaOH + HCN Na⁺ + CN⁻ + H₂O \longrightarrow Na⁺ + OH⁻ + HCN CN⁻ + H₂O \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

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

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$$\begin{split} & K_{h} = \frac{[HCN][OH^{-}]}{[CN^{-}]} &(1) \end{split}$$
 For weak acid $HCN \longrightarrow CN^{-} + H^{+}$
 $& K_{a} = \frac{[CN^{-}][H^{+}]}{[HCN]} &(2) \end{split}$ For water $H_{2}O \longrightarrow H^{+} + OH^{-}$
 $& K_{W} = [OH^{-}][H^{+}] &(3)$
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:
 $CN^{-} + H_{2}O HCN + OH^{-}$
 $C 0 0 0$ Initial concentration at equilibrium
 $C - x \quad x \quad x$
 $& nx = a\alpha$
 $& 1x = Ch$
 $& x = Ch$
 $& x = Ch$
 $& C - Ch & Ch & Ch$
 $& K_{h} = \frac{[HCN][OH^{-}]}{[CN^{-}]} = \frac{C^{2}h^{2}}{C(1-h)}$
 $& K_{h} = \frac{Ch^{2}}{(1-h)}$
Since $h < < < 1$
Therefore $(1 - h) \approx 1$
 $\therefore \qquad K_{h} = Ch^{2}$

Chemistry

$$h^{2} = \frac{K_{h}}{C} \Rightarrow h = \sqrt{\frac{K_{h}}{C}}$$
$$h = \sqrt{\frac{K_{w}}{K_{a} \times C}}$$

(c) pH of the solution

 \because

...

$$[OH^{-}] = Ch$$
$$[OH^{-}] = C \times \sqrt{\frac{K_{w}}{K_{a} \times C}}$$
$$[OH^{-}] = \sqrt{\frac{K_{w} \times C}{K_{a}}}$$
$$K_{w} = [OH^{-}] [H^{+}]$$
$$[H^{+}] = \frac{K_{w}}{[OH^{-}]}$$
$$[H^{+}] = \frac{K_{w}}{\sqrt{\frac{K_{w} \times C}{K_{a}}}}$$
$$[H^{+}] = \sqrt{\frac{K_{w} \times K_{a}}{C}}$$

On taking – log on both sides

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

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

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

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

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

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

3. Hydrolysis of (WA - WB) Type Salt

Ex.

NH₄CN, CaCO₃, (NH₄)₂ CO₃, ZnHPO₃ NH₄CN + H₂O \longrightarrow NH₄OH + HCN NH₄⁺ + CN⁻ + H₂O \longrightarrow NH₄OH + HCN

Chemistry

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 , $K_a \& K_b$

$$NH_4^+ + CN^- + H_2O \longrightarrow NH_4OH + HCN$$
$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} \qquad \dots (1)$$

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

$$K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{4}OH]} \qquad \dots (2)$$

For weak acid HCN \longrightarrow H⁺ + CN⁻

$$K_{a} = \frac{[H^{+}][CN^{-}]}{[HCN]} \qquad \dots (3)$$

For water $H_2 O \longrightarrow H^+ + OH^-$

 $K_{W} = [OH^{-}][H^{+}]$ (4)

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

$$\frac{[\mathrm{NH}_{4}\mathrm{OH}][\mathrm{HCN}]}{[\mathrm{NH}_{4}^{+}][\mathrm{CN}^{-}]} \times \frac{[\mathrm{NH}_{4}^{+}][\mathrm{OH}^{-}]}{[\mathrm{NH}_{4}\mathrm{OH}]} \times \frac{[\mathrm{H}^{+}][\mathrm{CN}^{-}]}{[\mathrm{HCN}]} = [\mathrm{H}^{+}] [\mathrm{OH}^{-}]$$

$$K_{\mathrm{h}} \times K_{\mathrm{b}} \times K_{\mathrm{a}} = K_{\mathrm{W}}$$

$$K_{\mathrm{h}} = \frac{K_{\mathrm{w}}}{K_{\mathrm{a}} \times K_{\mathrm{b}}}$$

(2) Degree of Hydrolysis -

$$NH_{4}^{+} + CN^{-} + H_{2}O \longrightarrow NH_{4}OH + HCN$$

$$C \qquad C \qquad 0 \qquad 0 \text{ Initial concentration}$$

$$C - x \qquad C - x \qquad x \qquad x \qquad \text{at equilibrium}$$

$$nx = a\alpha$$

$$x = Ch$$

$$C - Ch \qquad C - Ch \qquad Ch \qquad Ch$$

$$K_{h} = \frac{[NH_{4}OH][HCN]}{[NH_{4}^{+}][CN^{-}]} = \frac{Ch \times Ch}{(C - Ch)(C - Ch)} = \frac{C^{2}h^{2}}{C(1 - h) \times C(1 - h)} = \frac{h^{2}}{(1 - h)^{2}}$$

$$h < < < 1$$

Since

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...

0r

Then $(1 - h) \approx 1$ $K_h = h^2$ $h^2 = \frac{\kappa_W}{\kappa_a \times \kappa_b}$ $h = \sqrt{\frac{K_W}{K_a \times K_b}}$ (5)

(b) pH of the solution

From eq. (3)

 $K_{a} = \frac{[H^{+}][CN^{-}]}{[HCN]}$ $[\mathrm{H^+}] = \frac{\mathrm{K_a \times [\mathrm{HCN}]}}{[\mathrm{CN^-}]}$ $[H^+] = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$

Since

$$h <<<< 1$$

(1 - h) ≈ 1

$$[H^+] = K_a \times h$$

 $[H^+] = K_a \times h$ [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

$$-\log [H^{+}] = -\log(\frac{K_{W} \times K_{a}}{K_{b}})^{1/2}$$

$$pH = -\frac{1}{2} [\log (K_{W} \times K_{a}) - \log K_{b}]$$

$$pH = -\frac{1}{2} [\log K_{W} + \log K_{a} - \log K_{b}]$$

$$pH = -\frac{1}{2} [\log K_{W}] - \frac{1}{2} [\log K_{a}] - \frac{1}{2} [-\log K_{b}]$$

$$pH = +\frac{1}{2} pK_{W} + \frac{1}{2} pK_{a} - \frac{1}{2} pK_{b}$$

$$pH = 7 + \frac{1}{2} pK_{a} - \frac{1}{2} pK_{b}$$

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Chemistry

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

Ex. NaCl, BaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, KClO<sub>4</sub> etc.

NaCl + H<sub>2</sub>O \rightarrow NaOH + HCl

Na<sup>+</sup> + Cl<sup>-</sup> + H<sub>2</sub>O\rightarrow Na<sup>+</sup> + OH<sup>-</sup> + H<sup>+</sup> + Cl<sup>-</sup>

H<sub>2</sub>O\rightarrow H<sup>+</sup> + OH<sup>-</sup> (It is not salt hydrolysis)

(1) Hydrolysis of salt of [SA – SB] is not possible
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- (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 will take place in steps (just like dissociation of weak acids). Out of different steps generally first step hydrolysis dominants mainly because of two reasons The hydrolysis constant of second and further steps is generally negligible in comparison to first step hydrolysis constant.

The second and further step hydrolysis will be suppressed in presence of ions produced due to first step hydrolysis.

For a polyprotic acid (H₂S, H₃PO₄, H₂CO₃, H₂C₂O₄) we already know that the dissociation always takes place in steps, so for example for H₃PO₄

$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$	$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$	(1)
$\mathrm{H_2PO_4}^- \rightarrow \mathrm{H^+} + \mathrm{HPO_4}^{-2}$	$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^{-}]}$	(2)
$\mathrm{HPO_4}^{2-} \rightarrow \mathrm{H^+} + \mathrm{PO_4}^{-3}$	$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$	(3)

For all acids we always have $K_{a1} >> K_{a2} >> K_{a3}$

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.

Chemistry

Now for the hydrolysis of polyvalent ions of salts (like K_3PO_4 , $Na_2C_2O_4$, $ZnSO_4$, FeCl₃, (NH₄)₂C₂O₄ or ions like PO_4^{3-} , $C_2O_4^{2-}$, Zn^{2+} , Fe^{3+} etc).

Consider the hydrolysis in step

$$PO_{4}^{3-} + H_{2}O^{-} \rightarrow HPO_{4}^{2-} + OH^{-}$$

$$C \qquad 0 \qquad 0$$

$$C(1-h) \qquad Ch \qquad Ch$$

$$K_{h_{1}} = \frac{[OH^{-}][HPO_{4}^{2-}]}{[PO_{4}^{3-}]} \qquad \dots (4)$$

$$HPO_{4}^{2-} + H_{2}O^{-} \rightarrow H_{2}PO_{4}^{-} + OH^{-} \qquad K_{h2} = \frac{[OH^{-}][H_{2}PO_{4}^{-}]}{[HPO_{4}^{2-}]} \qquad \dots (5)$$

$$H_{2}PO_{4}^{-} + H_{2}O^{-} \rightarrow H_{3}PO_{4} + OH^{-} \qquad K_{h3} = \frac{[OH^{-}][H_{3}PO_{4}]}{[H_{2}PO_{4}^{-}]} \qquad \dots (6)$$

$$H_{2}O^{-} \rightarrow H^{+} + OH^{-} \qquad K_{W} = [H^{+}] [OH^{-}] \qquad \dots (7)$$

From above equations we get.

$$K_{a1} \times K_{h3} = K_W$$
$$K_{a2} \times K_{h2} = K_W$$
$$K_{a3} \times K_{h1} = K_W$$

Genarally pH is calculated only using the first step hydrolysis

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

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

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

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

So

Hydrolysis of Amphiprotic Anion (Cation is not Hydrolyzed)

NaHCO₃, 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)

Chemistry

- (ii) HCO₃⁻ + H₂O→ H₂CO₃ + OH⁻ (base) pH(HCO₃⁻) = $(\frac{pK_{a_1}+pK_{a_2}}{2})$
- (b) Similarly, for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions.

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

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