Dissociation or Ionization of Acids in Water

- $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
- The first equation shows H_2O, which pulls the H_+ from the acid.
  or We can write
  $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
- **Dissociation in Strong Acid:**
  $HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)$
  or We can write
  $HA(aq) \rightarrow H^+(aq) + A^-(aq)$
  A strong acid almost fully dissociates.
- Note: The yield sign drawn in the right side only to show the almost complete ionization of strong acids
- Common Strong acids are: H_2SO_4, HNO_3, $HClO_4$, HCl, HBr, HI
- In general organic acids are weak.
- Thumb Rule for oxyacids: No. of Oxygen – No. of Hydrogen ≥ 2, than the acid is strong.

Acid Dissociation Constant for a Weak Monoprotic Acid:

- $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
- Applying Law of Chemical Equilibrium:
- $Ka = \dfrac{[H_3O^+][A^-]}{[HA]}$ or $Ka = \dfrac{[H^+][A^-]}{[HA]}$
- Thumb Rule: For a weak acid $\rightarrow$ Ka is small. & for strong acids $\rightarrow$ Ka is high (cannot be calculated accurately.
- Calculation of H_3O^+ Ion & Degree of Ionisation(α):
- $Ka = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{(C\alpha)(C\alpha)}{C(1-\alpha)}$
- $Ka = C\alpha^2$ ……. For weak electrolyte $1- \alpha = 1$
- Therefor $\alpha = \sqrt{(K_a)/C}$
- Concentration of $(H_3O^+) = C\alpha$
- Relation between Ionization constant of a Acid and its conjugate base:
  $Ka \times Kb = Kw$
- **Dissociation or Ionization of Bases:**
- $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$
  or
  $BOH \rightarrow B^+(aq) + OH^-(aq)$
- $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
- A strong base almost fully dissociates. The equilibrium shifts to the right.

- Note: The yield may be drawn to point only to the right to show the almost complete ionization of strong bases.
- Examples: Hydroxides of Group I and Larger Metals of Group II.
- $Mg(OH)_2$ and $Ca(OH)_2$ are slightly soluble but whatever small amount dissolves, almost completely ionizes.
- Base Dissociation Constant for a Weak Base:
- $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

    OR
- $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$
- Applying Law of Chemical Equilibrium:
- $K_b = \dfrac{[BH^+][OH^-]}{[B]}$ or $K_b = \dfrac{[B^+][OH^-]}{[BOH]}$
- Thumb Rule:
- For a weak base $\rightarrow K_b$ is small.
- For strong bases $\rightarrow K_b$ is high(cannot be calculated accurately)

Calculation of OH⁻ Ion & Degree of Ionisation(α):

- $K_b = \dfrac{[B^+][OH^-]}{[BOH]} = \dfrac{(C\alpha)(C\alpha)}{C(1-\alpha)}$
- $K_b = C\alpha^2$ .... For weak base $1-\alpha = 1$
- Therefor $\alpha = \sqrt{(K_b)} / C$
- Concentration of $(OH^-) = C\alpha$
- Relation between Ionization constant of a base and its conjugate acid:
    Kb X Ka = Kw
- **Polyprotic Acids**: An acid that can furnish more than one proton are called polyprotic acids.
- A polyprotic acid dissociates in a stepwise manner, one proton at a time.
- Each dissociation of a proton, gives its own Ka value.
- The conjugate base in the first step is the acid in the second step.
- They are also known as polybasic acids.
- Examples: H_2PO_4, H_3PO_4
- Triprotic:
- $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_{a1} = 7.5 \times 10^{-3}$
- $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_{a2} = 6.2 \times 10^{-8}$
- $HPO4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_{a3} = 4.8 \times 10^{-13}$
- $K_{a1} > K_{a2} > K_{a3}$
- Each acid involved in dissociation steps is successively weaker. **The reason for this is that it is more difficult to remove a proton from a negative ion due to electrostatic force.**
- Similarly polyhydroxy or polyacidic bases ionize in steps and have the corresponding dissociation constant k_{b1}, k_{b2} etc.
- Eg: $Ba(OH)_2$, $Al(OH)_3$

Common Ion Effect on Ionization of Weak Acids & Bases

- When a compound containing an ion in common with an already dissolved substance is added to a solution at equilibrium, the equilibrium shifts to the left. This phenomenon is known as the **common ion effect.**
- The degree of ionization of a weak base or weak acid is suppressed by common ion effect.
- Common ion is an ion that is common to two or more components in a mixture of an ionic solution.
- Common ion effect is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances.
- The effect of common ion on ionization of Weak Base is as follows
- CH_3COOH (aq) $\rightleftharpoons$ CH_3COO^-(aq) + H^+(aq)
  CH_3COONa(aq) $\rightarrow$ CH_3COO^-(aq) + Na^+(aq)
                      Common Ion
- CH_3COONa dissociates completely and produces high concentration of CH_3COO^-.
- The high concentration of CH_3COO^- will disturb the equilibrium of the dissociation of ethanoic acid, CH_3COOH.
- Equilibrium of acid shifts backward direction according to Le-Chatlier Principle, thus less CH_3COOH dissociates.
- The effect of common ion on ionization of Weak Base is as follows
- NH_4OH (aq) $\rightleftharpoons$ NH_4^+ (aq) +OH^-(aq)
  NH_4Cl (aq) $\rightarrow$ NH_4^+ (aq) +Cl^-(aq)
                      Common Ion
- Ionization of ammonium hydroxide is suppressed by addition of ammonium chloride or sodium hydroxide.

Self Ionization of Water

- When water molecules ionized, transferring a proton from one water molecule to another producing a hydroxonium and hydroxide ion.
- $2H_2O$ (l) $\rightleftharpoons$ H_3O^+ (aq) + OH^- (aq)
- H_2O (l) $\rightleftharpoons$ H^+ (aq) + OH^- (aq)
- The equilibrium constant expression can be written as follows:
  $$K_a = \frac{[H^+][OH^-]}{[H_2O]}$$
- K_a is the ionization constant for water at 25°C.
- Ka X $[H_2O]$ = $[H^+]$ $[OH^-]$ :: Since Concentration of water is very high=55.5 M, therefore $[H_2O]$ may be taken as constant
- K_w = $[H^+]$ $[OH^-]$
- **K_w is called the Ionic product of water.**
- For pure water, at 25°C,
- $[H+]$ = $[OH-]$ = 1×10^{-7} M
- Kw = $[H+]$ $[OH-]$ = $(1 \times 10^{-7})(1 \times 10^{-7})$
- Therefore Kw = 1×10^{-14} M^2
- **Ionization constant of water Ka = Kw / 55.5 = 1.8×10^{-16}**

- Note: Temperature ↑, Kw ↑ because the dissociation of water is an endothermic process.
- We define an aqueous solution as being neutral when the [H+] = [OH-].
- We define an aqueous solution as being acidic when [H+] > [OH-].
- We define an aqueous solution as being basic when [H+] < [OH-].
- However, **in each case Kw = 1 x 10^{-14} M^2 at 298K**