Class: XI Chemistry
Chapter 7: EQUILIBRIUM
Module 5 of 6

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Contents

This module contains:

- ***Ionisation of Acids and Bases***
- ***Dissociation Constants of Acids and Bases***
- ***Common Ion effect***
- ***Self Ionisation of Water& Ionic Product***

Ionisation of Acids and Bases

Ionisation of Acids in Water

Dissociation:

$$HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

or We can write

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The first equation shows H_2O*, which pulls the* H^+ *from the acid.*

Ionisation of Acid in Water

Dissociation in Strong Acid:

$HA(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + A^-(aq)$

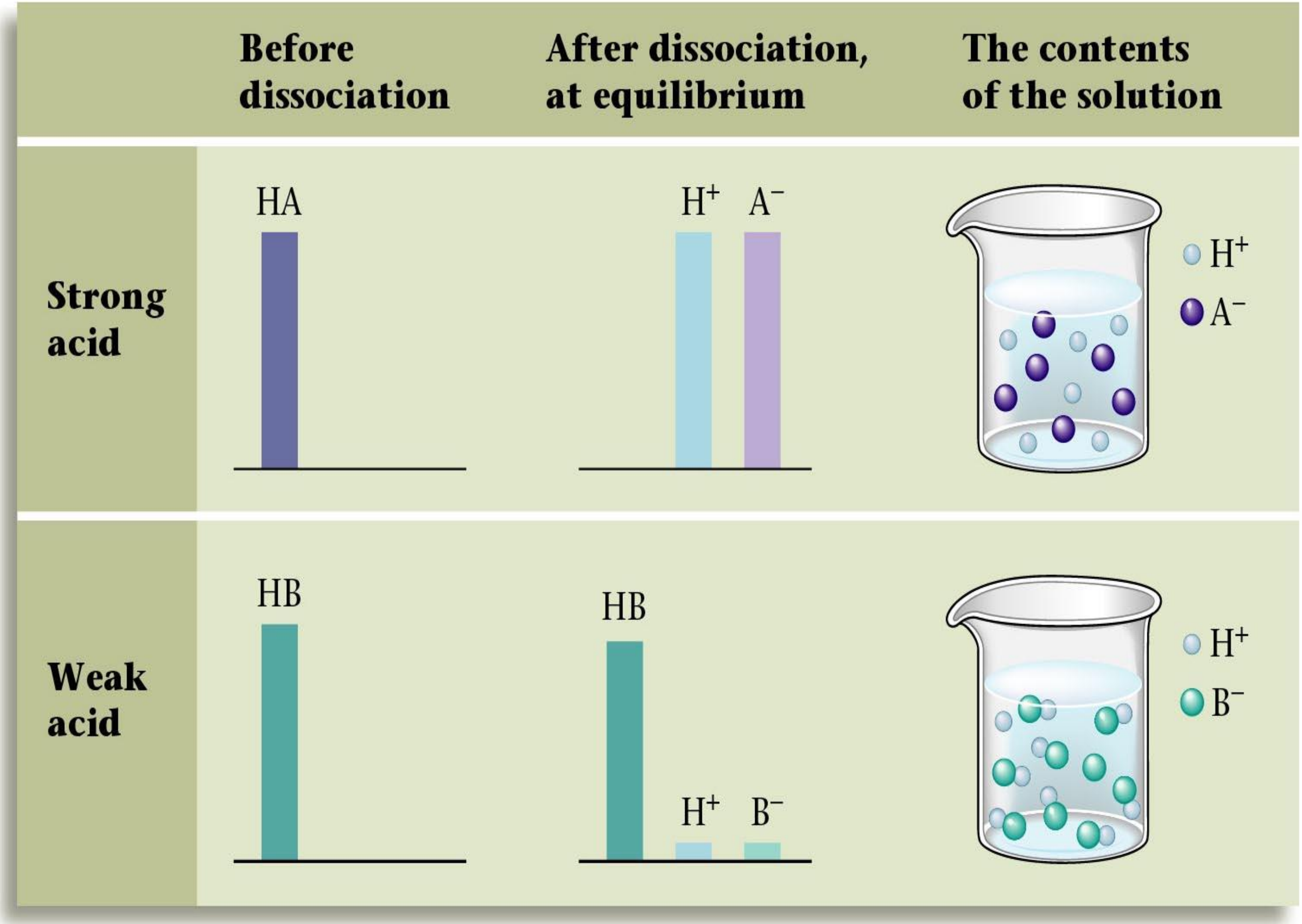
or We can write

$HA(aq) \rightarrow H^+(aq) + A^-(aq)$

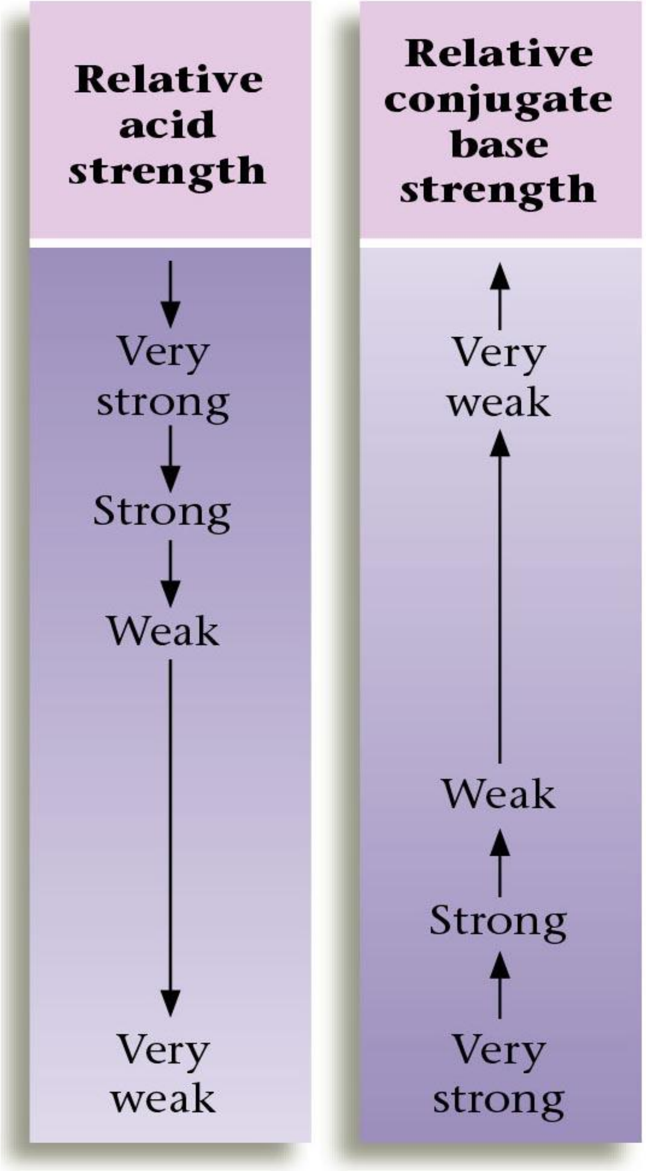
A ***strong acid*** *almost fully dissociates.*

Note: The yield sign drawn in the right side only to show the almost complete ionization of strong acids.

Ionisation of Acid in Water



Ionisation of Acid in Water



Common Strong Acids

- H_2SO_4
- HNO_3
- $HClO_4$
- HCl,
- HBr,
- HI (Remember: HF is weak)

In general organic acids are weak.

Thumb Rule for oxyacids:

No. of Oxygen – No. of Hydrogen ≥ 2, than the acid is strong.

(Example: H_3PO_4 is weak whereas H_2SO_4 is strong)

Dissociation Constant of Weak Acid

Acid Dissociation Constant for a Weak Monoprotic Acid:

$HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Applying Law of Chemical Equilibrium:

$$Ka = \frac{[H_3O^+]\,[A^-]}{[HA]} \qquad \text{or} \qquad Ka = \frac{[H^+]\,[A^-]}{[HA]}$$

Thumb Rule:

For a weak acid →Ka is small.

For strong acids → Ka is large .cannot be calculated accurately.

Calculation of H_3O^+ Ion & Degree of Ionisation

- ***Calculation of H_3O^+ Ion & Degree of Ionisation(α):***

$$Ka = \frac{[H^+]\,[A^-]}{[HA]} = \frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)}$$

$Ka = C\alpha^2$……. For weak electrolyte $1-\alpha = 1$

Therefor $\alpha = \sqrt{}\,(Ka) / C$

Concentration of (H_3O^+) = $C\alpha$

Ionisation of Bases

- **Dissociation:**

$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$

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.

Dissociation Constant of Acid and Bases

Base Dissociation Constant for a Weak Base:

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Or

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

Applying Law of Chemical Equilibrium:

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]} \quad \text{or} \quad K_b = \frac{[B^+]\,[OH^-]}{[BOH]}$$

Thumb Rule:

For a weak base →K_b is small.

For strong bases → K_b is large cannot be calculated accurately

Calculation of OH^- Ion & Degree of Ionisation

Calculation of OH^- Ion & Degree of Ionisation(α):

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]} = \frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)}$$

$K_b = C\alpha^2$……. For weak base 1- α = 1

Therefor $\alpha = \sqrt{(K_b)} / C$

Concentration of (OH^-) = $C\alpha$

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_2SO_4, H_3PO_4

Polyprotic Acids and Bases

Triprotic:

$$H_3PO_4 = H^+ + H_2PO_4^- \; ; K_{a1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^- = H^+ + HPO_4^{2-} \; ; K_{a2} = 6.2 \times 10^{-8}$$

$$HPO4^{2-} = H^+ + PO_4^{3-} \; ; K_{a3} = 4.8 \times 10^{-13}$$

$K_{a1} > K_{a2} > K_{a3}$

- Each acid involved in dissociation steps is successively weaker.

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

Common Ion effect

- 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.***

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.

Common Ion effect

- The effect of common ion on ionization of Weak Base is as follows
- : $CH_3COOH\ (aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

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

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**.

Common Ion effect

- The **effect of common ion** on **ionization of Weak Base** is as follows

$$NH_4OH\,(aq) \rightleftharpoons NH_4^+\,(aq) + OH^-(aq)$$

$$NH_4Cl\,(aq) \longrightarrow \underbrace{NH_4^+\,(aq)}_{\text{Common Ion}} + Cl^-(aq)$$

- Ionization of ammonium hydroxide is suppressed by addition of ammonium chloride or sodium hydroxide.

Self Ionisation of Water

Self Ionisation of Water

- *In **pure water** (no solute) water molecules behave as both an **acid** and **base!!***

It is called amphoteric meaning it will act as either an acid or a base depending on the situation.

e.g. $H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$

*This is called the **self-ionization** (auto-ionizaion) of water. Although the equilibrium lies far to the **left** it is very important to take into consideration, especially for **living systems**.*

Self Ionisation of Water

The **auto-ionization** of water is described by the equation:

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

- This **equilibrium** lies very much to the **left** i.e. mostly water.

- For **pure water** $[OH^-] = [H^+]$

Ionic Product

Ionic Product

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.

$$Ka \times [H_2O] = [H^+]\,[OH^-]$$

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

K_w is called the <u>Ionic product</u> of water.

Ionic Product

- For pure water, at 25°C,

$$[H^+] = [OH^-] = 1 \times 10^{-7}\ M$$

$$\begin{aligned} K_w &= [H^+]\ [OH^-] \\ &= (1 \times 10^{-7})\ (1 \times 10^{-7}) \end{aligned}$$

$$\therefore\ K_w = 1 \times 10^{-14}\ M^2$$

Ionizaztion of water $K_a = K_w / 55.5 = 1.8 \times 10^{-16}$

Note:

Temperature ↑, K_w ↑ because the dissociation of water is an endothermic process .

Ionic Product

- 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 $Kw = 1 \times 10^{-14}\ M^2$

$$pKw = -\,Log\ Kw = 14$$

Relation between Ionization constant of a base and its conjugate acid:

$Kb \times Ka = Kw$

Similarly,For an acid and its conjugate base:

$Ka \times Kb = Kw$

Module 5 of 6 Ends…