Biophysical Chemistry
Acid & Bases
Lecture-4

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Acid Dissociation Constant

Acid Dissociation Constant (K_a)

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

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

Where, K_a is the acid dissociation constant. In dilute solution we can assume that the concentration of liquid water remains essentially constant when an acid is dissolved.

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Acid Strength

The strength of an acid is defined by the equilibrium position of its dissociation (ionization) reaction:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Strong Acid:

- Its equilibrium position lies far to the right. (HNO_3)
- Yields a weak conjugate base. (NO_3^-)
- Common strong acids are H_2SO_4, HCl, HNO_3, $HClO_4$

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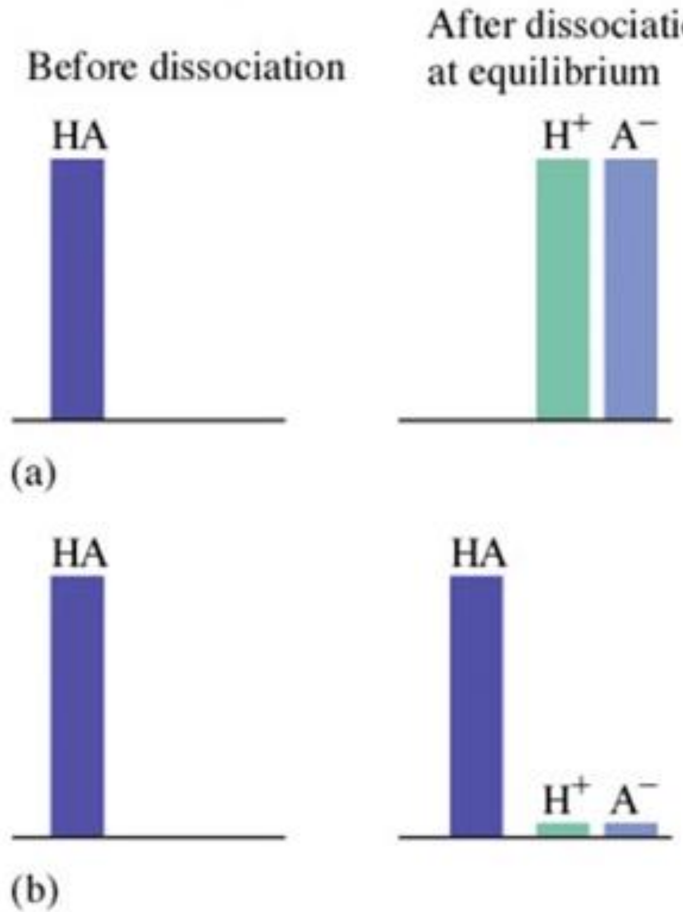

Figure 14.4 Graphic Representation of the Behavior of Acids of Different Strengths in Aqueous Solution

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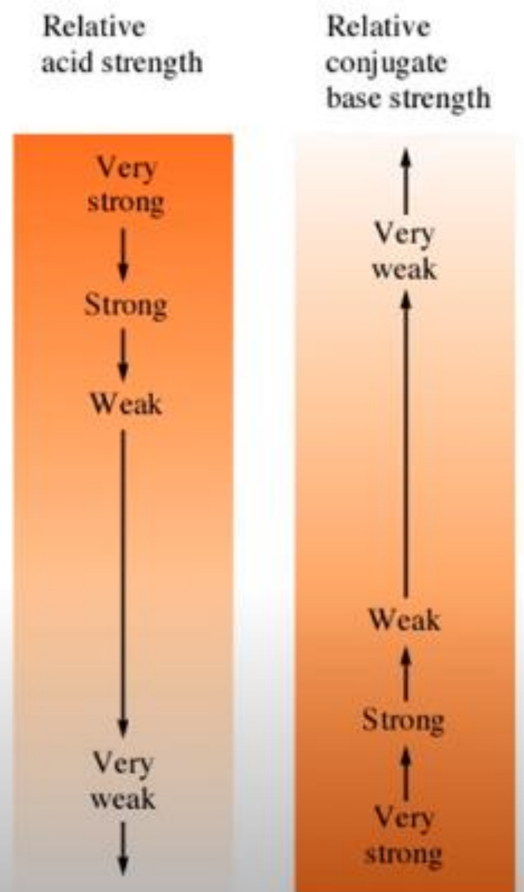

Figure 14.5 Acid Strength Versus Conjugate Base Strength

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RELATIVE STRENGTH OF ACIDS

The strength of an acid depends on its ability to transfer its proton (H^+) to a base to form its conjugate base. When a monoprotic acid (HA) dissolves in water, it transfers its proton to water (a Bronsted base) to form hydronium ion (H_3O^+) and a conjugate base.

$$HA + H_2O \rightleftharpoons H_3O^+ + \underset{\text{conjugate base}}{A^-} \qquad ...(1)$$

For simplifying our discussion, we take

$$H_3O^+ = H^+$$

Thus we can write the equilibrium reaction (1) as

$$HA + H_2O \rightleftharpoons H^+ + A^- \qquad ...(2)$$

This equation represents the dissociation of the acid HA into H^+ ion and A^- ion.

Applying the Law of Mass action to the acid dissociation equilibrium, we can write

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad ...(3)$$

where K_a is called the **acid dissociation constant.** In dilute solution of the acid (HA) we note that the concentration of liquid water remains essentially constant. Therefore, the terms included in the equilibrium expression (3).

The strength of an acid is defined as the concentration of H^+ ions in its aqueous solution at a given temperature.

From the equilibrium (3), it is evident that the concentration of H^+ ions, $[H^+]$, depends on the value of K_a. **Therefore, the value of K_a for a particular acid is a measure of its acid strength or acidity.**

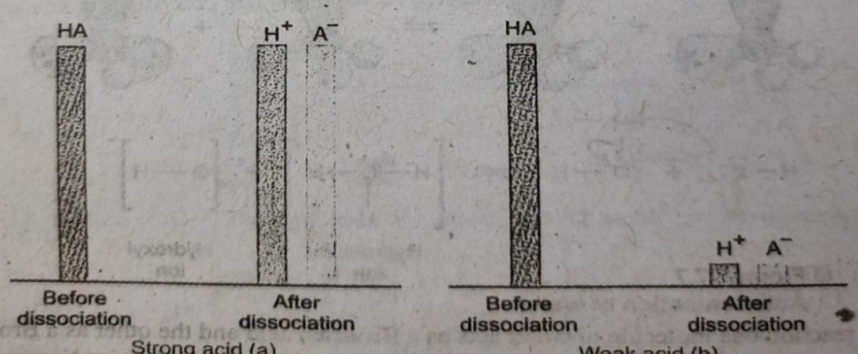

Figure 27.8
Graphical extent of concentrations of H^+ and A^- in aqueous solution compared to original concentration of HA for : (*a*) a strong acid; and (*b*) a weak acid.

Relative Strength of Acids

Ethanoic acid is a weak acid that dissociates according to the following:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

What is the acid dissociation constant for this acid?

acid dissociation constant, K_a

- the equilibrium constant for the reaction of an acid with water
- quantitative measurement of the strength of an acid

↑ K_a ↑ acid strength

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

concentration

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

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

concentration

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

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
$HOCl$	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

↑ Increasing acid strength

Calculation of Relative Strength of Weak acids from Ka

Calculation of relative strength of weak acids from Ka

The weak acid is represented as HA and initial concentration of HA is c moles per litre (moles/L).
α is the degree of dissociation

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

	HA		H^+	A^-
Initial conc.	c		0	0
at equilibrium	$c - c\alpha$		$c\alpha$	$c\alpha$

Applying the Law of mass action to the acid dissociation equilibrium, we can write

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{— (i)}$$

where Ka is called the acid dissociation constant.

we can write,

$$[H^+] = c\alpha$$
$$[A^-] = c\alpha$$
$$[HA] = c - c\alpha$$
$$= c(1-\alpha)$$

From equation (i) we can write

$$K_a = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)}$$
$$= \frac{c\alpha^2}{(1-\alpha)} \quad \text{— (ii)}$$

As the degree of dissociation for a weak acid very small, we can take $1-\alpha \simeq 1$.

Therefore from equation (ii) we get

$$K_a = c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}}$$

For two different acids, 1 and 2.

Let the degree of dissociation be α_1 and α_2; and the dissociation constants k_1 and k_2. The

for acid I $\quad k_1 = c\alpha_1^2$ —— (iii)

for acid 2 $\quad k_2 = c\alpha_2^2$ —— (iv)

Dividing equation (iii) by (iv), we get

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{k_1}{k_2}}$$

Since $[H^+]$ is a measure of acid strength and it depends on the degree of dissociation α, we can write.

$$\frac{\text{strength of acid 1}}{\text{strength of acid 2}} = \sqrt{\frac{k_1}{k_2}}$$

Relative strength of bases

$$BOH_{(aq)} \longrightarrow B^{+}_{(aq)} + OH^{-}_{(aq)}$$

Strong Base

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^{+}_{(aq)} + OH^{-}_{(aq)}$$

Weak Base

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b - base dissociation constant

Larger K_b : strong base : more product : more OH^-.

Acid-base Dissociation

- For any acid, describe it's reaction in water:
  - $H_xA + H_2O \rightarrow x\ H^+ + A^- + H_2O$
  - Describe this as an equilibrium expression, K (often denotes K_A or K_B for acids or bases…)

$$K = \frac{[A][H^+]^x}{[H_xA]}$$

- Strength of an acid or base is then related to the dissociation constant → Big K, strong acid/base!
- pK = -log K → as before, lower pK=stronger acid/base!