

ALMUSTAQBAL UNIVERSITY COLLEGE

Biomedical Engineering Department

Stage : Second year students

Subject : Chemistry 1 - Lecture 9

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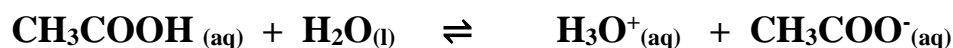


Dissociation equilibria for weak acids and bases (K_a & K_b)

Weak acids

Are acids that dissociate partially in water. So when they are dissolved in water, partial dissociation occurs.

for example acetic acid(weak acid), cannot completely donate all its acidic protons to the solvent (usually water). Instead, most of the acid remains undissociated, with only a small fraction dissociated and present as (H_3O^+) in solution.



The extent of dissociation is given by the equilibrium constant:

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

$$K [H_2O] = K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

K_a is an equilibrium constant and is called acid dissociation constant

The magnitude of K_a provides information about the relative strength of the weak acid,

The smaller k_a corresponding to a weaker acid.

On the opposite, small pk_a values characterize stronger acids

Table : The K_a and pK_a values for a number of common weak acids

Compound (weak acid)	K_a	pK_a
Hydrocyanic acid (HCN)	4.93×10^{-10}	9.31 weakest acid
Acetic acid (CH_3COOH)	1.77×10^{-5}	4.75
Benzoic acid (C_6H_5COOH)	6.46×10^{-5}	4.19
Formic acid ($HCOOH$)	1.77×10^{-4}	3.75
Salicylic acid(HOC_6H_4COOH)	1.05×10^{-3}	2.98
Chloroacetic acid($ClCH_2CO_2H$)	1.4×10^{-3}	2.85 strongest acid

Conversions

1. To convert K_a to pK_a

$$pK_a = -\log K_a$$

Example:

Convert ($K_a = 4.93 \times 10^{-10}$) to pK_a

$$pK_a = -\log 4.93 \times 10^{-10} = 9.31$$

2. To convert pK_a to K_a

$$K_a = 10^{-pK_a}$$

Example:

convert $pK_a = 4.75$ to K_a

$$K_a = 10^{-4.75} = 1.77 \times 10^{-5}$$

Example:

Arrange the following weak acids : acetic acid ($pK_a=4.75$) , formic acid ($pK_a=3.75$), and Chloroacetic acid ($K_a=1.4 \times 10^{-3}$) in the order of increasing their acid strength.

Solution:

We have to convert all to K_a or to pK_a which is easier and compare :

Method 1: (converting all to pK_a)

$$pK_a = -\log K_a$$

For Chloroacetic acid ($K_a=1.4 \times 10^{-3}$) then

$$pK_a = -\log (1.4 \times 10^{-3}) = 2.85$$

Then

<u>Acid</u>	<u>pKa</u>
Chloroacetic acid	2.85 (the strongest acid)
formic acid	3.75
acetic acid	4.75 (the weakest acid)

As small pK_a values characterize stronger acids then Chloroacetic acid is **the strongest acid** and acetic acid is **the weakest acid** .

Method 2: (converting all to K_a)

$$K_a = 10^{-pK_a}$$

For acetic acid $pK_a= 4.75$ then $K_a = 10^{-4.75} = 1.77 \times 10^{-5}$

For formic acid $pK_a= 3.75$ then $K_a = 10^{-3.75} = 1.77 \times 10^{-4}$

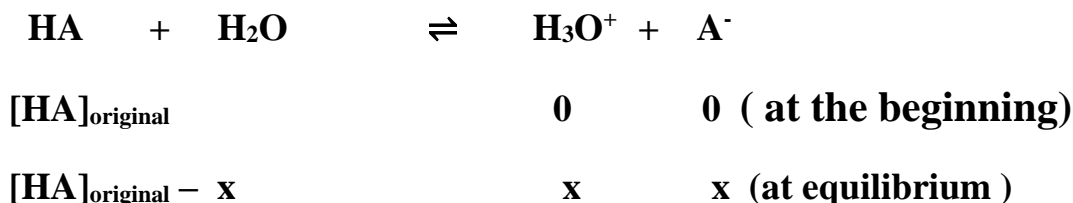
<u>Acid</u>	<u>K_a</u>
acetic acid	1.77×10^{-5} (the weakest acid)
formic acid	1.77×10^{-4}
Chloroacetic acid	1.4×10^{-3} (the strongest acid)

As the smaller k_a corresponding to a weaker acid. Then acetic acid is **the weakest acid** and Chloroacetic acid is **the strongest acid**.

**** Exercise (Home work) :**

Arrange the following weak acids : Oxalic acid ($pK_a=1.23$) , Lactic acid ($pK_a=3.08$) , Citric acid ($K_a=7.41 \times 10^{-4}$) and Ascorbic acid ($K_a=7.94 \times 10^{-5}$) in the order of decreasing their acid strength .

Calculations of [H₃O⁺] concentration for weak acid [HA]:



When dissociation (x) is very small(weak acid), Then:

$$[\text{HA}]_{\text{eq}} = [\text{HA}]_{\text{original}} - x \approx C \quad \text{where } C=[\text{HA}]_{\text{original}}$$

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

Since $[H_3O^+] = [A^-]$ from dissociation equation (stoichiometry)

$$K_a = \frac{[H_3O^+]^2}{[HA]} \quad (\text{by substitution})$$

$$\text{Therefore, } K_a = \frac{[H_3O^+]^2}{C}$$

$$[H_3O^+] = \sqrt{K_a C}$$

Example :

Calculate $[H_3O^+]$ concentration of 0.12 M aqueous solution of Nitrous acid HNO_2 , ($K_a = 5.1 \times 10^{-4}$).



$$K_a = 5.1 \times 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$[H_3O^+] = \sqrt{K_a C}$$

$$[H_3O^+] = \sqrt{5.1 \times 10^{-4} \times 0.12}$$

$$[H_3O^+] = \sqrt{6.12 \times 10^{-5}} = 7.82 \times 10^{-3}$$

$$pH = -\log(7.82 \times 10^{-3}) = 2.11$$

To check the approximation :

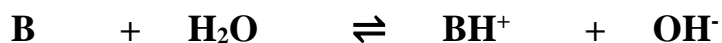
$$\text{Dissociation \%} = \frac{[H_3O^+]}{[HA]} \times 100\%$$

$$** \text{ Dissociation \%} = \frac{7.82 \times 10^{-3}}{0.12} \times 100 = 6.5 \% \quad (\text{i.e.: less than } 10\%)$$

Then approximation is valid .

Weak bases

Are bases that partially dissociate in water and are characterized by base dissociation constant (K_b).



w.base

conjugate acid

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

The magnitude of (K_b) provides information about the relative strength of the weak base,

The smaller K_b corresponding to a weaker base.

On the opposite, small pK_b values characterize stronger base.

Table : The K_b and pK_b values for a number of common weak bases.

Compound(weak Base)	K_b	pK_b
Acetamide (CH_3CONH_2)	2.5×10^{-13}	12.60 weakest Base
Glycine(H_2NCH_2COOH)	2.24×10^{-12}	11.65
Aniline $C_6H_5NH_2$	7.4×10^{-10}	9.13
Pyridine C_5H_5N	1.7×10^{-9}	8.77
morphine	7.5×10^{-7}	6.12
Codeine($C_{18}H_{21}NO_3$)	1.6×10^{-6}	5.79
Ephedrine($C_{10}H_{15}ON$)	1.3×10^{-4}	3.88
Methylamine(CH_3NH_2)	4.38×10^{-4}	3.36
Dimethylamine($(CH_3)_2NH$)	5.4×10^{-4}	3.26 strongest Base

Conversions:

1. To convert K_b to pK_b

$$pK_b = -\log K_b$$

Example:

Convert ($K_b = 2.54 \times 10^{-13}$) to pK_b

$$pK_b = -\log 2.5 \times 10^{-13} = 12.60$$

2. To convert pK_b to K_b

$$K_b = 10^{-pK_b}$$

Example:

Convert $pK_b = 4.75$ to K_b

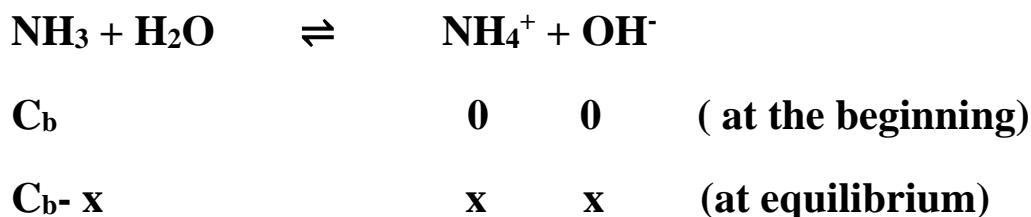
$$K_b = 10^{-4.75} = 1.7 \times 10^{-5}$$

Exercise (Home work) :

Arrange the following weak bases Glycine ($pK_b=11.65$) , Ephedrine ($pK_b=3.88$) , Pyridine($K_b=1.7 \times 10^{-9}$) and Dimethylamine ($K_b=5.4 \times 10^{-4}$) in the order of decreasing their base strength.

Calculations of [OH⁻] concentration for weak bases:

For weak base :



When dissociation(x) is very small (weakbase) then:

$$[\text{NH}_3] = \text{C}_b - x \approx \text{C}_b$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Since $[\text{OH}^-] = [\text{NH}_4^+]$ (from stoichiometry)

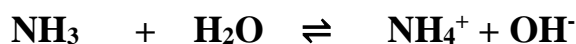
$$\text{Therefore, } K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3]} = \frac{[\text{OH}^-]^2}{C_b}$$

$$K_b = \frac{[\text{OH}^-]^2}{C_b}$$

$$[\text{OH}^-] = \sqrt{K_b C_b}$$

Example :

Calculate $[\text{H}_3\text{O}^+]$ concentration of 0.2M aqueous NH_3 solution, $K_b = 1.8 \times 10^{-5}$.



$$[\text{OH}^-] = \sqrt{K_b C_b}$$

$$[\text{OH}^-] = \sqrt{1.8 \times 10^{-5} \times 0.2} = \sqrt{3.6 \times 10^{-6}}$$

$$[\text{OH}^-] = 1.89 \times 10^{-3}$$

$$\text{Dissociation \%} = \frac{[\text{OH}^-]}{[\text{w.Base}]} \times 100\%$$

$$\text{**Dissociation \%} = \frac{1.89 \times 10^{-3}}{0.2} \times 100\% = 0.95\% \text{ (less than 10\%)}$$

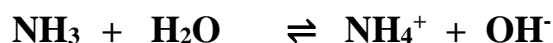
(approximation is valid)

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{1.89 \times 10^{-3}}$$

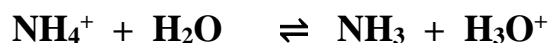
$$[\text{H}_3\text{O}^+] = 5.29 \times 10^{-12}$$

$$\text{pH} = -\log(5.29 \times 10^{-12}) = 11.27$$

Relationship between dissociation constants for conjugate acid-base pair :



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \text{ ----- (1)}$$



$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \text{ ----- (2)}$$

Multiplication of equation (1) with (2) gives :

$$K_b \times K_a = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \times \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$K_a \times K_b = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

$$\text{but } [\text{H}_3\text{O}^+] [\text{OH}^-] = K_w$$

$$\text{Therefore, } K_a \times K_b = K_w$$

Exercise :

prove that for the weak acid CH_3COOH and its conjugate base CH_3COO^- then $(K_a \times K_b = K_w)$.

