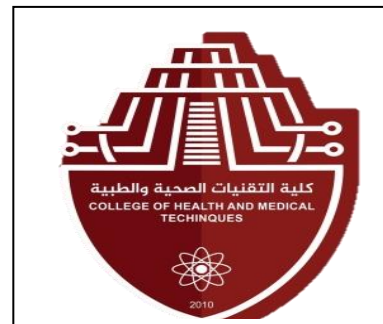ALMUSTAQBAL UNIVERSITY

College of Health and Medical Techniques

Medical Laboratories Techniques Department

Stage   : First year students

Subject : Lecture 7A

Lecturer: Assistant professor Dr. SADIQ . J. BAQIR

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 in acetic acid solution (weak acid), most of the acid remains un dissociated, with only a small fraction dissociated and present as (H_3O^+) in solution.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$
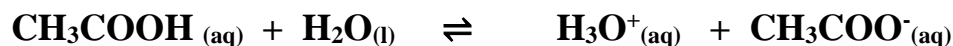
The extent of dissociation is given by the equilibrium constant:

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

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

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 4.93×10^{-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 (Ka=1.4 x 10^{-3}) in the order of increasing their acid strength.

Solution:

We have to convert all to Ka or to pKa which is easier and compare :

Method 1:   (_converting all to pKa_)

$$pK_a = -\log K_a$$

For Chloroacetic acid (ka=1.4 x 10^{-3}) then

$pKa = - \log (1.4 \ x \ 10^{-3}) = 2.85$

Then

Acid	pKa	
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 Ka_)

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

 For acetic acid pK_a= 4.75   then   Ka = $10^{-4.75}$ = 1.77 x 10^{-5}

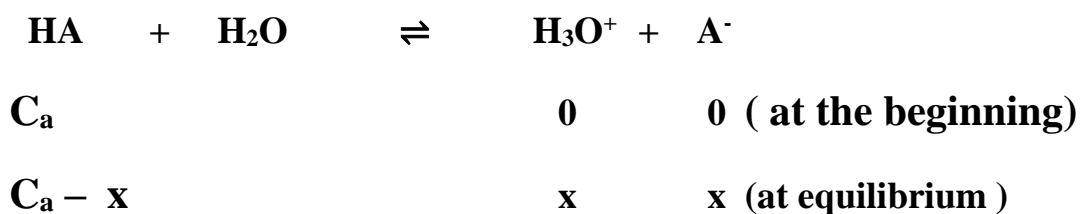For formic acid $pK_a = 3.75$ then $K_a = 10^{-3.75} = 1.77 \times 10^{-4}$

Acid	Ka
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 $[H_3O^+]$ concentration for weak acid $[HA]$:

$$HA \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ \quad + \quad A^-$$

C_a 0   0 (at the beginning)

$C_a - x$ x   x (at equilibrium)

As (**x**) is very small then

$C_a - x \approx C_a = C$

$$Ka = \frac{[X][X]}{C} = \frac{X^2}{C}$$

$x = [H_3O^+]$

$$Ka = \frac{[H_3O^+]^2}{C}$$

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

Example :

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

$$HNO_2 \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ + NO_2^-$$
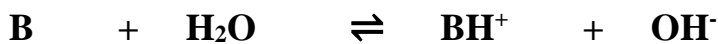
$$[H_3O^+] = \sqrt{Ka\,C}$$

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

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

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

Weak bases

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

$$B \quad + \quad H_2O \quad \rightleftharpoons \quad BH^+ \quad + \quad OH^-$$

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.

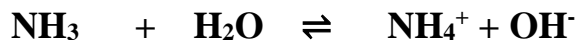| Compound(weak Base)	K_b	pK_b
Acetamide (CH_3CONH_2)	2.5×10^{-13}	12.60 weakest Base
Glycine($C_2H_5NO_2$)	2.24×10^{-12}	11.65
Aniline $C_6H_5NH_2$	7.4×10^{-10}	9.13
Pyridine C_5H_5N	1.7×10^{-9}	8.77
morphine	7.5×10^{-7}	6.12
Codeine($C_{18}H_{21}NO_3$)	1.6×10^{-6}	5.79
Ephedrine($C_{10}H_{15}ON$)	1.3×10^{-4}	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 :

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

C_b 0   0   (at the beginning)

C_b- x   x   x   (at equilibrium)

As (**x**) is very small then

$$C_b - x \approx C_b = C$$

$$Ka = \frac{[X][X]}{C} = \frac{X^2}{C}$$

$$x = [OH^-]$$

$$Ka = \frac{[OH^-]^2}{C}$$

$$[OH^-] = \sqrt{K_b\,C}$$

Example :

Calculate $[H_3O^+]$ concentration of 0.2M aqueous NH_3 solution, $K_b = 1.8 \times 10^{-5}$.

NH_3 + H_2O ⇌ NH_4^+ + OH^-

$[OH^-] = \sqrt{K_b\, C}$

$[OH^-] = \sqrt{1.8x10^{-5} x\, 0.2}$ = $\sqrt{3.6\ x\ 10^{-6}}$

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

$[H_3O^+] = \dfrac{Kw}{[OH-]}$ = $\dfrac{10^{-14}}{1.89\ x10^{-3}}$

$[H_3O^+] = 5.29\ x\ 10^{-12}$

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

Relationship between dissociation constants for conjugate acid-base pair :

NH_3 + H_2O ⇌ NH_4^+ + OH^-

K_b = $\dfrac{[NH4+][OH-]}{[NH3]}$ ----------------- (1)

NH_4^+ + H_2O ⇌ NH_3 + H_3O^+
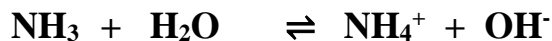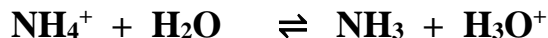
K_a = $\dfrac{[NH3][H3O+]}{[NH4+]}$ ------------- (2)

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

K_b x K_a = $\dfrac{[NH4+][OH-]}{[NH3]}$ x $\dfrac{[NH3][H3O+]}{[NH4+]}$

K_a x K_b = [H_3O^+] [OH^-]

but [H_3O^+] [OH^-] = K_w

Therefore , K_a x K_b= K_w

Exercise :

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

Hint: $CH_3COOH_{(aq)}$ + $H_2O_{(l)}$ ⇌ $H_3O^+{}_{(aq)}$+ $CH_3COO^-{}_{(aq)}$ [w.acid (K_a)]

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COOH_{(aq)} \text{ [conjugate base } (K_b)]$$