ALMUSTAQBAL UNIVERSITY

College of Health and Medical Techniques

Medical Laboratories Techniques Department

Stage : First year students

Subject : Lecture 7A

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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 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

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

2. To convert pK_a to K_a

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

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 Ka = $10^{-3.75}$ = 1.77 x 10^{-4}

Acid	Ka
acetic acid	1.77 x 10^{-5} (the weakest acid)
formic acid	1.77 x 10^{-4}
Chloroacetic acid	1.4 x 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 (Ka=7.41 x 10^{-4}) and Ascorbic acid (Ka=7.94 x 10^{-5}) in the order of decreasing their acid strength .

Calculations of [H_3O^+] concentration for weak acid [HA]:

HA + H_2O ⇌	H_3O^+ + 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, ($Ka = 5.1x10^{-4}$) .

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

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

$$[H_3O^+] = \sqrt{5.1x10^{-4}\ x\ 0.12}$$

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

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

Weak bases

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

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

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 x 10-7	6.12
Codeine($C_{18}H_{21}NO_3$)	1.6 x 10-6	5.79
Ephedrine($C_{10}H_{15}ON$)	1.3x10-4	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

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

Example:

Convert $pK_b = 4.75$ to K_b

$$K_b = 10^{-4.75} = 1.7x10^{-5}$$

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, $K_b = 1.8x10^{-5}$.

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

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

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

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

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

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

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

Relationship between dissociation constants for conjugate acid-base pair :

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

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

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$K_a = \frac{[NH3][H3O+]}{[NH4+]}$ ---------- (2)

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

$K_b \times K_a = \frac{[NH4+][OH-]}{[NH3]} \times \frac{[NH3][H3O+]}{[NH4+]}$

$K_a \times K_b = [H_3O^+][OH^-]$

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

Therefore , $K_a \times K_b = K_w$

Exercise :

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

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

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