ALMUSTAQBAL UNIVERSITY

College of Health and Medical Techniques
Medical Laboratories Techniques Department

Stage : First year students
Subject : General Chemistry 1 - Lecture 6

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

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

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 then comparing:

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	**1.77×10^{-5} (the weakest acid)**
formic acid	**1.77×10^{-4}**
Chloroacetic acid	**1.4×10^{-3} (the strongest acid)**

As the smaller k_a corresponds to a weaker acid. Then

acetic acid is the weakest acid and Chloroacetic acid is the strongest acid.

Exercise *(Homework)* :

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

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

$$\begin{array}{lcccc} HA & + & H_2O & \rightleftharpoons & H_3O^+ & + & A^- \\ C_a & & & & 0 & & 0 \end{array}$$

(at the beginning)

$$\begin{array}{lcc} C_a - x & x & x \end{array}$$

(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= $5.1x10^{-4}$) .

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

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

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

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

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

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	7.5×10^{-7}	6.12
Codeine($C_{18}H_{21}NO_3$)	1.6×10^{-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

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

Example:

Convert $pK_b = 4.75$ to K_b

$K_b = 10^{-4.75} = 1.7\times10^{-5}$

***Exercise (Homework)*: 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 the 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, $K_b= 1.8\times10^{-5}$.

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

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

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

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

As $[H_3O^+][OH^-] = Kw$

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

$[H_3O^+] = 5.\ 29 \times 10^{-12}$

pH = -log (5. 29 x 10 $^{-12}$) = 11.28

or pOH = - log[OH$^-$] = - log(1.89x10^{-3}) = 2.72

As pH + pOH = 14

pH = 14 – 2.72 = 11.28

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 x 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)]

Calculations of $[H_3O^+]$, pH, $[OH^-]$ and pOH for Strong Acids and Bases

A solution is acidic if $[H_3O^+] > [OH^-]$. and is basic if $[H_3O^+] < [OH^-]$.

Strong acids are acids that completely dissociate in water.

Strong acids, such as HNO_3, almost completely dissociated

$$\begin{array}{lllll} HNO_3\,(aq) + & H_2O\,(l) & \rightarrow & H_3O^+(aq) & + \; NO_3^-(aq) \\ 0.1\ M & & & 0.1\ M & \end{array}$$

The hydronium ion $[H_3O^+]$ is the acidic species in solution, and its concentration determines the acidity of the resulting solution

pH of a strong acids:

When a solution of 0.1 M HNO_3 dissolves in water it dissociates completely to its ions (i.e : 0.1M [H_3O^+]) .

$[H_3O^+] = C$ where C is the initial concentration of the strong acid

Example :

Calculate the pH of a 0.1 M solution of HCl.

$$\begin{array}{ll} HCl(aq) + H_2O(l) \rightarrow & H_3O^+(aq) + Cl^-(aq) \\ 0.1\ M & 0.1\ M \end{array}$$

$[H_3O^+]$ = C = The original concentration of the strong acid [HCl] = 0.1 M

pH = - log $[H_3O^+]$ = - log (0.1) = 1

Example:

Calculate the pH of the following strong acid solutions:

(a) $1.3x10^{-3}$ M HCl (b) 1.3×10^{-3} M H_2SO_4, (c) $1.3x10^{-3}$ M H_3PO_4 .

Solution:

a) $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$1.3x10^{-2}$ M $\qquad$ $1.3x10^{-2}$ M

pH = - log [H_3O^+] = - log 1. 3 × 10^{-3} = 2.89

(b) $H_2SO_4 + H_2O \rightarrow 2H_3O^+ + SO_4^{2-}$

$1.3x10^{-3}$ M $\qquad$ $2x1.3x\ 10^{-3}$ M

pH = - log [H_3O^+] = - log 2.6 x 10^{-3} = 2.58

c) $H_3PO_4 + H_2O \rightarrow 3H_3O^+ + PO_4^{3-}$

1.3×10^{-3} M $\qquad$ $3x1.3 \times 10^{-3}$ M = $(3.9\ x\ 10^{-3})$ M

pH = - log [H_3O^+] = - log [3.9×10^{-3}] = 2.41

Example:

Calculate the pOH and pH of the following strong base solutions:

(a) 0.05 M NaOH, (b) 0.05 M $Ca(OH)_2$, (c) 0.05 M $La(OH)_3$.

solution:

a) $NaOH \rightarrow Na^+ + OH^-$

0.05 M 0.05 M

pOH = - log [OH^-] = - log 5× 10^{-2} = 1.3

As pH + pOH = 14

pH = 14 – 1.3 = 12.7

b) $Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^-$

0.05 M 2(0.05) = 0.1 M

pOH = - log [OH^-] = - log 0.1 = 1.0

pH = 14 – 1.0 = 13.0

c) $La(OH)_3 \rightarrow La^{3+} + 3\ OH^-$

0.05 M 3(0.05) = 0.15 M

pOH = - log [OH^-] = - log 0.15 = 0.82

pH = 14 – 0.82 = 13.18

Example:

Calculate the hydrogen ion concentration [H_3O^+] for the solutions with the following pH values: (a) 3.47, (b) 0.20, (c) 8.60 .

solution:

pH = - log [H_3O^+]

log[H_3O^+] = - pH

[H_3O^+] = 10^{-pH}

(a) [H_3O^+] = 10^{-pH} = $10^{-3.47}$ = 3.4 × 10^{-4} M .

(b) [H_3O^+] = 10^{-pH} = $10^{-0.2}$ = 6.3 × 10^{-1} M .

(c) [H_3O^+] = 10^{-pH} = $10^{-8.6}$ = 2.5 × 10^{-9} M .

Example:

Calculate the change in pH for 0.01 M HCl solution on 10 times dilution.

Solution:

$pH = -\log [H_3O^+]$

a. Before dilution (original solution)

$[H_3O^+] = 0.01 = 10^{-2}$ M $pH = -\log (0.01) = 2$

b. After dilution for 10 times

$M_1V_1 = M_2 V_2$

$1 \times 0.01 = 10 \times M_2$

$M_2 = 0.001 = 10^{-3}$ M $pH = -\log(10^{-3}) = 3$

$\Delta pH = 3 - 2 = 1$

Then Changing the concentration for 10 times changes the pH by 1 unit

Exercise:

Calculate the change in pH for 0.1 M HNO_3 solution on dilution of 100 times.

Example :

Calculate the pH of a solution obtained by mixing the following volumes of the two solutions of the strong acid HCl :

a) 100 mL of (pH= 2)

b) 500 mL of (pH= 4) .

solution:

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$[H_3O^+] = 10^{-PH}$

$[H_3O^+]_a = 10^{-2}$ M the concentration of the pH =2 acid

$[H_3O^+]_b = 10^{-4}$ M the concentration of the pH =4 acid

No. of moles of $[H_3O^+]_{total}$ = No. of moles of $[H_3O^+]_a$ + No. of moles of $[H_3O^+]_b$

No. of moles = Molarity (M) x Volume (liter)

$V_a(\text{liter}) = \frac{100\ (mL)}{1000} = 0.1$ L $\qquad V_b(\text{liter}) = \frac{500\ (mL)}{1000} = 0.5$ L

No. of moles of $[H_3O^+]_a = 10^{-2}$ M x 0.1 liter $=10^{-3}$ mole

No. of moles of $[H_3O^+]_b = 10^{-4}$ M x 0.5 liter = 5 x 10^{-5} mole

No. of moles of $[H_3O^+]_{total}$ = 5 x 10^{-5} + 10^{-3} = 1.05 x 10^{-3} moles

Molarity of the resulting solution = $\frac{\text{No.of moles of } [H_3O^+]_{total}}{(V_a+V_b)liter}$

Molarity of the resulting solution = $\frac{1.05 \text{ x}10^{-3}\ mole}{(0.1+0.5)liter}$ = 1.75 x 10^{-3} M

$[H_3O^+]_{total}$ = 1.75 x 10^{-3} M

pH = -log (1.75 x 10^{-3} M) = 2.75

Exercise 1: Calculate the pH of the acidic solution obtained by mixing 100 mL of (pH= 2) of HCl with 400 mL of (pH= 3) of HNO_3.

Exercise 2: Calculate the pH of the basic solution obtained by mixing 200 mL of (pH= 10) of KOH with 300 mL of (pH= 8) of NaOH.

VOLUMETRIC (Titration) CALCULATIONS

In titration (a moles of ACID ≡ b moles of BASE)

Then

$$\frac{M_a V_a}{n_a} = \frac{M_b V_b}{n_b}$$

M_a = molarity of the acid

V_a = volume of the acid

n_a = No. of moles (acid)

M_b = molarity of the base

V_b = volume of the base

n_b = No. of moles (base)

Example 1:

The volume needed of a 0.1 M standard solution of HCl on titration of 100 mL of NaOH solution to the end point is 75.8 mL . Calculate the molar concentration of NaOH solution.

Solution:

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$n_a = 1$ $n_b = 1$ **(stiochiometric mole ratios of acid and base)**

$$\frac{M_a V_a}{n_a} = \frac{M_b V_b}{n_b}$$

$$\frac{75.8 \, x \, 0.10}{1} = \frac{M_b \; x \, 100}{1}$$

$$M_b = \frac{75.8 \, x \, 0.10}{100} = 0.0758 \text{ M}$$

Example 2:

20 mL of H_2SO_4 (98 g/mol) was neutralized with 25mL of 0.1M sodium hydroxide solution. The equation of reaction is

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Calculate:

(i) conc. of acid in M **(ii) acid content of the solution in grams.**

Solution:

$$\frac{M_a\,V_a}{n_a} = \frac{M_b\,V_b}{n_b}$$

$$\frac{M_a x\,20.0}{1} = \frac{0.10\,x\,25}{2}$$

Concentration of H_2SO_4 (M_a) = $\frac{1\,x\,0.10\,x\,25}{2\,x\,20}$ = 0.0625 M

ii) mass of the acid in the solution(g)

mass (g) = Molarity(M) x Volume (L) x Molar mass (g/mol)

mass (g) = 0.0625 x ($\frac{20}{1000}$) L x 98 = 0.1225 g

Example 3:

50 mL portion of HCl solution required 29.71 mL of (0.019M) $Ba(OH)_2$ to reach an end point with bromocresol green indicator , Calculate the molarity of HCl .

Solution:

$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$

1mole 2 mole 1mole

$$\frac{M_a\,V_a}{n_a} = \frac{M_b\,V_b}{n_b}$$

$$\frac{M_{HCl}\,xV_{HCl}}{2} = \frac{M_{Ba(OH)2}\ x\ V_{Ba(OH)2}}{1}$$

$$M_{HCl} = \frac{2[M_{Ba(OH)2}\ x\ V_{Ba(OH)2}\ ]}{V_{HCl}}$$

$$M_{HCl} = \frac{2[0.019x\ 29.71]}{50} = 0.023\ M$$