Almustaqbal University college

Medical Laboratories Techniques Department

First year students

**Subject :General chemistry 1 - Lecture 7**

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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 their acidic protons to the solvent(usually water). Instead, most of the acid remains undissociated, with only a small fraction present as (H_3O^+) in solution.

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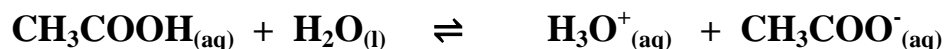
The extent of dissociation is given by the equilibrium constant:

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

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

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, smaller pk_a values characterize stronger acids.

Table : The k_a and pk_a values for a number of common weak acids

Compound	k_a	pk_a
Hydrocyanic acid (HCN)	4.93×10^{-10}	9.31 **weakest acid**
Acetic acid (CH_3COOH)	1.76×10^{-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 x10^{-10}) to pK_a

pK_b = -log 4.93x10^{-10} = 9.31
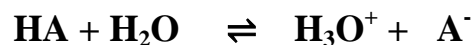
2. to convert pK_a to K_a

$K_a = 10^{-pKa}$

Example: convert pK_a = 4.19 to K_a

$K_a = 10^{-4.19}$ = 6.46 x10^{-5}

Exercise (Home work) : **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.**

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

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

$Ka = \dfrac{[H3O+][A-]}{[HA]}$

As $[H_3O^+] = [A^-]$ from above equation(stiochiometry)

$Ka = \dfrac{[H3O+]^2}{[HA]}$ (by substitution)

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

$[HA]_{eq} = [HA]_{original} - [H_3O^+] \approx C$ where $C = [HA]_{original}$

Then, $K_a = \dfrac{[H3O+]^2}{C}$

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

Example :

Calculate $[H_3O^+]$ concentration of 0.120M aqueous solution of Nitrous acid HNO_2, ($Ka = 5.1 \times 10^{-4}$).

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

$0.12 - x$ $\qquad$ x $\quad$ x $\qquad$ (at equilibrium)

$Ka = 5.1 \times 10^{-4} = \dfrac{[H3O+][NO2-]}{[HNO2]}$

For a very weak acid $[H_3O^+] = [NO_2^-] = x$

$[HNO_2]_{eq.} = 0.120 - [H_3O^+] \approx 0.120$

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

$[H_3O^+] = \sqrt{5.1 \times 10^{-4} \times 0.12} = 7.82 \times 10^{-3}$

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

**relative error% $= \frac{7.82 x\ 10^{-3}}{0.12}$ x 100 = 6.5 % (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). For example the base dissociation constant (k_b) for the conjugate base acetate ion is given by:

$$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$$

$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$ = 5.71 x 10^{-10}

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, smaller pk_b values characterize stronger base.

Table : The k_b and pk_b values for a number of common weak bases.

Compound	k_b	pk_b
Acetamide (CH_3CONH_2)	2.5 x 10^{-13}	12.60 weakest Base
Glycine(H_2NCH_2COOH)	2.24 x 10^{-12}	11.65
Aniline $C_6H_5NH_2$	7.4 x 10^{-10}	9.13
Pyridine C_5H_5N	1.7 x 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($C_{10}H_{15}ON$)	1.32x10-4	3.88
Methylamine(CH_3NH_2)	4.38 x 10^{-4}	3.36
Dimethylamine($CH_3)_2NH$	5.4 x 10^{-4}	3.26 strongest Base

Conversions

1. To convert K_b to pK_b

pK_b = -log K_b

Example:

convert (K_b = 2.5 x10^{-13}) to pK_b

Answer:

pK_b = -log 2.5x10^{-13} = 12.60

2. To convert pK_b to K_b

K_b = 10^{-pKb}

Example:

Convert pK_b = 5.79 to K_b

K_b = $10^{-5.79}$ = 1.62x10^{-6}

Exercise (Home work) : **Arrange the following weak bases Glycine (pK_b=11.65) , Ephedrine(pK_b=3.88), Pyridine(kb=1.7 x 10^{-9}) and Dimethylamine (kb=5.4 x 10^{-4}) in the order of decreasing their base strength.**

For weak base :

$NH_3 + H_2O$ ⇌ $NH_4^+ + OH^-$

C_b 0   0   (at the beginning)

C_b- x   x   x   (at equilibrium)

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

When dissociation is very weak(x is very small): $[NH_3]$ = Cb - x ≈ Cb

Since $[OH^-]$ = $[NH_4^+]$ (from stiochiometry)

Therefore , $\quad K_b = \dfrac{[OH-]^2}{[NH3]} = \dfrac{[OH-]^2}{Cb}$ $\quad$ **(by substitution)**

$$K_b = \dfrac{[OH-]^2}{Cb}$$

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

Example :

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

$NH_3 \quad + \quad H_2O \quad \rightleftharpoons \quad NH_4^+ + OH^- \quad$ (للايضاح)

$0.2 - x \quad\quad\quad\quad\quad\quad x \quad\quad x \quad\quad$ (at equilibrium)

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

For very weak base $[OH^-] = [NH_4^+] = x$

$[NH_3] = 0.2 - [x] = 0.2 \approx C_b$

$[NH_3]_{eq.} = C_b$

$Kb = 1.8 \times 10^{-5} = \dfrac{[OH-]^2}{0.2}$

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

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

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

Relative error % = $\dfrac{1.89 x\, 10^{-3}}{0.2}$ **x 100% = 0.95 % (approximation is valid) للتحقق من صحه التقريب

$[H_3O^+] = \dfrac{Kw}{[OH-]} \quad\quad = \dfrac{10^{-14}}{1.89\, x 10^{-3}}$
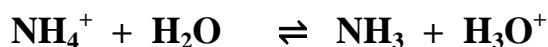
$[H_3O^+] = 5.29 \times 10^{-12}$

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

Relationship between dissociation constants for Base-conjugate acid pair:

e.g : $NH_3 - NH_4^+$

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

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

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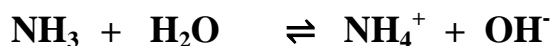
$K_a = \dfrac{[NH3][H3O+]}{[NH4+]}$ ------------(2)

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

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

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

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:

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

$Ka = \dfrac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
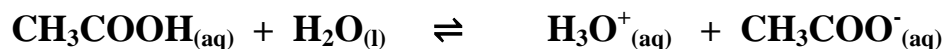
$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$
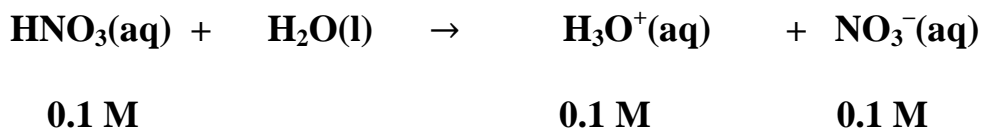
$K_b = \dfrac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$

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

Strong acids:

Are acids that completely dissociate in water. e.g: HNO_3,as astrong acid almost completely gives its protons to the solvent molecules(water):

$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

0.1 M   0.1 M   0.1 M

pH of a strong acid

When a solution of 0.1 M HNO_3 dissolves in water it dissociates completely to give 0.1M [H_3O^+] and 0.1 M [NO_3^-] .

For strong acids HNO_3 Then $[H_3O^+] = C$
where C is the initial concentration of the strong acid

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

Example
Calculate the pH of a 0.1 M solution of HCl.

HCl is a strong acid , It dissociates completely in water to produce 0.1 M of $[H_3O^+$]and 0.1 M of [Cl^-]

$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
0.1 M   0.1 M
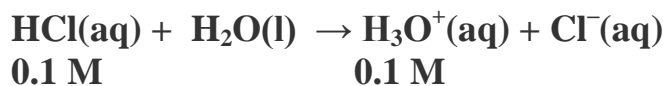
Since the concentration of $[H_3O^+]$ is given as:

$[H_3O^+] = C = [HCl] = 0.1$ M

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

Example:

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

(a) 1.3×10^{-2} M $HClO_4$, (b) 1.3×10^{-3} M HCl, (c) 1.3×10^{-4} M HNO_3 .

Answer:

a) $HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$

   1.3×10^{-2} M 1.3×10^{-2} M

   $pH = - \log [H_3O^+] = - \log 1.3 \times 10^{-2} = 1.89$

   $pOH = 14 - 1.89 = 12.11$

(b) $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

   1.3×10^{-3} M 1.3×10^{-3} M

   $pH = - \log [H_3O^+] = - \log 1.3 \times 10^{-3} = 2.89$

   $pOH = 14 - 2.89 = 11.11$

c) $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$
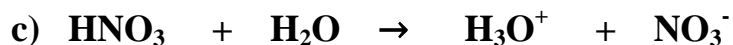
   1.3×10^{-4} M 1.3×10^{-4} M

   $pH = - \log [H_3O^+] = - \log [1.3 \times 10^{-4}] = 3.89$
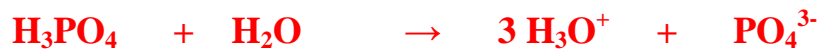
   $pOH = 14 - 3.89 = 10.11$

Excercise:

Calculate the pH of the following strong acid solutions:

(a) 0.1 M HCl   (b) 0.1 M H₂SO₄   (c) 0.1 M H₃PO₄ .

Hint:

HCl   +   H₂O   →   H₃O⁺   +   Cl⁻

H₂SO₄   +   H₂O   →   2H₃O⁺   +   SO₄²⁻

H₃PO₄   +   H₂O   →   3 H₃O⁺   +   PO₄³⁻

Example:

Calculate the hydrogen ion concentration [H₃O⁺] for the solutions with the following pH values: (a) 3.47, (b) 0.20, (c) 8.60 .

Answer:

pH = - log [H₃O⁺]

log[H₃O⁺] = - pH

[H₃O⁺] = 10⁻ᴾᴴ

(a) [H₃O⁺] = 10⁻ᴾᴴ = 10 ⁻ ³·⁴⁷ =   3.4 × 10⁻⁴ M .

(b) [H₃O⁺] = 10⁻ᴾᴴ = 10 ⁻⁰· ² =   0.63 M .

(c) [H₃O⁺] = 10⁻ᴾᴴ = 10⁻⁸·⁶ =   2.5 × 10⁻⁹ M .

pH of a strong Base

Strong bases:

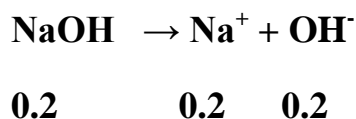Are bases that completely dissociate in water. e.g: NaOH, as astrong base almost completely dissociates to:

$$NaOH(aq) \quad \rightarrow \quad Na^+(aq) \quad + \quad OH^-(aq)$$
$$0.1\ M \qquad\qquad\quad 0.1\ M \qquad\qquad 0.1\ M$$
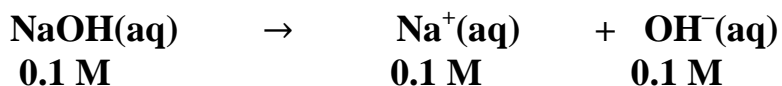
When a solution of 0.1 M NaOH dissolves in water it dissociates completely to give 0.1M [Na^+] and 0.1 M [OH^-] .

For strong bases [OH^-] = C
where C is the initial concentration of the strong base

The hydroxide ion OH⁻ is the basic species in solution, and its concentration [OH⁻] determines the basicity of the resulting solution

Example:

Calculate [H_3O^+] and [OH^-] in 0.2M aqueous solution of NaOH.

$$NaOH \quad \rightarrow Na^+ + OH^-$$

$$0.2 \qquad\quad 0.2 \quad\ 0.2$$

$$2H_2O \quad \rightleftharpoons \quad H_3O^+ + OH^- \qquad (\text{توضيح})$$

$$[\,H_3O^+\,]\,[\,OH^-\,] = Kw$$

$$[\,OH^-\,]_{total} = [OH^-\,]_{NaOH} + [\,OH^-]_{water} \approx [OH^-]_{NaOH} = 0.2$$

$$[\,H_3O^+\,] = \frac{Kw}{[OH^-]} \quad = \quad \frac{1\ x\ 10^{-14}}{0.2} \quad = 5\ x\ 10^{-14}\ M$$

Example:

Calculate the pH and pOH 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.

Answer:

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

   0.05 M   0.05 M

$pOH = - \log [OH^-] = - \log 5 \times 10^{-2} = 1.3$

$pH = 14 - 1.3 = 12.7$

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

   0.05 M   2(0.05) = 0.1 M

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

$pH = 14 - 1.0 = 13.0$

c) $La(OH)_3 \quad \rightarrow \quad La^{3+} + 3 OH^-$
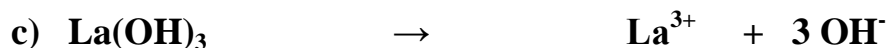
   0.05 M   3(0.05) = 0.15 M

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

$pH = 14 - 0.82 = 13.18$

Example :

Calculate the pH of a solution obtained by mixing 10 mL of the strong acid HCl solution (pH= 3.0) with the same volume of the strong base KOH solution (pH= 12.0) .

Answer:

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

[H_3O^+] for HCl solution = 1.0×10^{-3} M .

[H_3O^+] for KOH solution = 1.0×10^{-12} M .

As [OH^-] = $\frac{K_w}{[H_3O^+]}$ then

[OH^-] for KOH solution = $\frac{1.0x10^{-14}}{1.0x10^{-12}}$ = $1.0x10^{-2}$ M

mmole HCl = Molarity x volume(mL)

mmol HCl = $1.0x10^{-3}$ M x 10 mL = $1.0x10^{-2}$ = 0.01mmol

mmol KOH = $1.0x10^{-2}$ M x 10mL = 0.1 mmol

HCl + KOH → KCl + H_2O

0.01 mmol   0.1 mmol

Excess of KOH = mmole KOH – mmole HCl

Excess of KOH = (0.1 – 0.01)mmol = 0.09 mmole

[OH^-] = $\frac{0.09 \, mmol}{(10+10)mL}$ = $4.5 x10^{-3}$ M

pOH = - log [OH^-] = - log (4.5×10^{-3}) = 2.35

pH = 14 – 2.35 = 11.65

Example:

Calculate the pH and pOH of a solution obtained by mixing 100 mL of each of 0.10 M H_2SO_4 and 0.30 M NaOH .

Answer:

No. mmoles = Molarity x Volume (mL)

mmol H_2SO_4 = 0.10 M x 100 mL = 10 mmol

mmol NaOH = 0.3 M x 100mL   = 30 mmol

H_2SO_4 +   2 NaOH   → Na_2SO_4 + H_2O

1 mole   2 mole

10 mmol   30 mmol

mmol NaOH reacted = 2 (mmoles H_2SO_4) = $2x$ 10 = 20 mmol

Excess of NaOH = mmole NaOH (original) – mmole NaOH(reacted)

mmol NaOH excess = 30 –20 = 10 mmole

Molarity (M) $= \dfrac{mmoles}{V_{mL}} = \dfrac{10}{(100+100)} = \dfrac{10}{200} = 0.05$

∴ [OH⁻] = 0.05 M

pOH = - log [OH⁻] = - log 0.05 = 1.3

pH = 14 – 1.3 = 12.70