Physical Pharmacy I
Ionic equilibria

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Learning objectives

- Describe the Br¨onsted–Lowry and Lewis electronic theories.
- Identify and define the four classifications of solvents.
- Understand the concepts of acid–base equilibria and the ionization of weak acids and weak bases.
- Calculate dissociation constants K_a and K_b and understand the relationship between K_a and K_b.
- Understand the concepts of pH, pK, and pOH and the relationship between hydrogen ion concentration and pH.
- Calculate pH.
- Define strong acid and strong base.

Introduction

- **Arrhenius** defined an **acid** as a substance that **liberates hydrogen ions** and a **base** as a substance that **supplies hydroxyl ions** on **dissociation**.
- Because of a need for a broader concept, **Brönsted** in Copenhagen and Lowry in London independently proposed parallel theories in 1923.
- The **Brönsted– Lowry** theory, as it has come to be known, is more useful than the Arrhenius theory for the representation of **ionization** in both **aqueous and nonaqueous** systems.

Brönsted–Lowry Theory

- **Acid** is a substance, charged or uncharged, that is capable of **donating a proton**.
- **Base** is a substance, charged or uncharged, that is **capable of accepting a proton** from an acid.
- The relative **strengths** of acids and bases are measured by **the tendencies** of these substances to give up and take on protons.

Brönsted–Lowry Theory

- **Strength of acid and base (acid strength-basic strength)**
  - Ability to give up or accept a proton ?
  - Ability of the solvent to **accept** the proton from the acid
- Classification:
  - Anions: HSO_4^- and CH_3COO^- (base)
  - Cations: NH^{4+} (acid) and H_3O^+ → acid
  - Neutral: HCl (acid) and NH_3 (base)
  - Water can act as either an acid or a base and thus is **amphiprotic** = Amphoteric

Amphoteric → يقدر يكسب H^+ او يعطي H^+

H_2O (Amphoteric)

Brönsted–Lowry Theory

- **Acid–base reactions** occur when an acid reacts with a base to form a new acid and a new base.
- Because the reactions involve a **transfer of a proton**, they are known as **protolytic reactions** or **protolysis**.
- In the reaction between HCl and water, HCl is the acid and water the base:

HCl	+	H_2O	→	H_3O^+	+	Cl^-
$Acid_1$		$Base_2$		$Acid_2$ (conjugate acid)		$Base_1$ (conjugate base)

- Acid1 and Base1 stand for an acid–base pair or conjugate pair, as do $Acid_2$ and $Base_2$
- H^+, is practically nonexistent in aqueous solution, what is normally referred to as the hydrogen ion consists of the hydrated proton, H3O+, known as the **hydronium ion**.
- In an ethanolic solution, the "hydrogen ion" (H^+) is the proton attached to a molecule of solvent, represented as $C_2H_5OH_2^+$

H^+ يكون في Nonaqueous solution

Brönsted–Lowry Theory

neutral متعادل
charge + charge

EXAMPLES OF ACID–BASE REACTIONS

	$Acid_1$		$Base_2$		$Acid_2$		$Base_1$
Neutralization	NH_4^+	+	OH^-	=	H_2O	+	NH_3
Neutralization	H_3O^+	+	OH^-	=	H_2O	+	H_2O
Neutralization	HCl	+	NH_3	=	NH_4^+	+	Cl^-
Hydrolysis	H_2O	+	CH_3COO^-	=	CH_3COOH	+	OH^-
Hydrolysis	NH_4^+	+	H_2O	=	H_3O^+	+	NH_3
Displacement	HCl	+	CH_3COO^-	=	CH_3COOH	+	Cl^-

Lewis Electronic Theory هو التعريف الأشمل

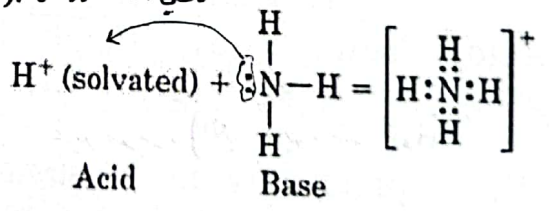
هو اللي عرف الـ NH3 على انها Base

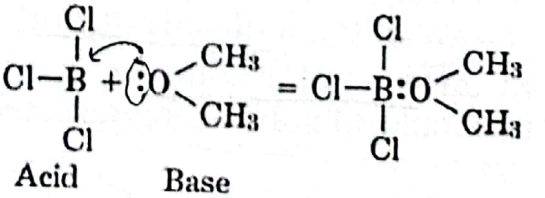
- **Acid** is a molecule or an ion that accepts an electron pair to form a covalent bond.
- **Base** is a substance that provides the **pair of unshared electrons** by which the base coordinates with an acid.

- The Lewis system is probably too broad

المفهوم الأوسع

تعطي الالكترونات لـ acid





BCl_3 $O(CH_3)_2$

ACID–BASE EQUILIBRIA

- Brönsted–Lowry The values of the colligative.

1 $HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$

$Acid_1$ $Base_2$ $Acid_2$ $Base_1$

- The reaction is proceeding to the right and left simultaneously.
- According to the law of mass action, the velocity or rate of the forward reaction, R_f, is proportional to the concentration of the reactants:

$R_f = k_1 \times [HAc]^1 \times [H_2O]^1$ Decrease in the concentration of either the reactants per unit time

$R_r = k_2 \times [H_3O^+]^1 \times [Ac^-]^1$ The reverse reaction expresses the rate, R_r, of re-formation of un-ionized acetic acid.

k_1 and k_2 known as specific reaction rates

at equilibrium $R_r = R_f$

Ionization of Weak Acids

- A balance is attained when the two rates are equal, that is, when **Rf = Rr**
- The concentrations of products and reactants are not necessarily **equal at equilibrium**; the **speeds of the forward and reverse reactions are what are the same**
- $\mathbf{k_1 \times [HAc] \times [H_2O] = k_2 \times [H_3O^+] \times [Ac^-]}$
- $K = \frac{k1}{k2} = \frac{[H3O^+][Ac^-]}{[HAc][H2O]}$ → $Ka = \frac{(H_3O^+)(Ac^-)}{(HAc)} = 55.3 \times k$
- Ka, the ionization constant or the dissociation constant of the acid (acetic acid)
- In dilute solutions of acetic acid, water is in sufficient excess to be regarded as constant at about 55.3 moles/liter

55.3 mol/L

Ionization of Weak Acids

كل ما زاد Ka ح يزيد الـ dissociation لـ acid معناته بكون الـ acid التفكك أقوى

- $K_a = 55.3 K = \frac{[H3O^+][Ac^-]}{[HAc]}$
- **Ka**, the ionization constant or the dissociation constant of the acid (acetic acid) its called **acidity constant**
- $HB + H_2O \rightleftharpoons H_3O^+ + B^-$
- $K_a = \frac{[H3O^+][B^-]}{[HB]}$
-

Ionization of Weak Acids

ratio بنفس الـ

- $HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$

  $(c - x)$ x x
- $K_a = \frac{x^2}{c - x}$ نهمل x لانه كميتها قليلة مقارنة بـ c
- where c is large in comparison with x. The term **c − x** can be replaced by **c** without appreciable error, giving the equation

$$K_a \cong \frac{x^2}{c}$$

$$x^2 = K_a c$$

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

Ionization of Weak Acids

Example

In a liter of a 0.1 M solution, acetic acid was found by conductivity analysis to dissociate into 1.32×10^{-3} g ions ("moles") each of hydrogen and acetate ion at 25°C. What is the acidity or dissociation constant K_a for acetic acid?

- The coof ions is expressed as **moles/liter** and less frequently as molality.ncentration
- A solution containing 1.0078 g of hydrogen ions in 1 liter represents 1 g ion or 1 mole of hydrogen ions.

$$HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$$

$$(c - x) \qquad x \qquad x$$

$C = 0.1\ M$ $\qquad$ $x = 1.32 \times 10^{-3}$

- $K_a = \frac{x^2}{c - x} = \frac{(1.32 \times 10^{-3})^2}{0.1 - 1.32 \times 10^{-3}}$
- X small?
- $K_a = \frac{x^2}{c} = \frac{(1.32 \times 10^{-3})^2}{0.1} = 1.74 \times 10^{-5}$

Ionization of Weak Acids

- K_a means acid into itthat, at equilibrium, **the ratio** of the product of the ionic concentrations to that of the undissociated acid is 1.74×10^{-5}; that is, the dissociation of acetic s ions is small, and acetic acid may be considered **as a weak electrolyte**.

Ionization of Weak Acids

- When a salt formed from a strong acid and a weak base, such as **ammonium chloride**, is dissolved in water, it dissociates completely as follows:
- $NH_4^+Cl^- \xrightarrow{H_2O} NH4^+ + Cl^-$
- NH_4^+ is a cationic acid and its conjugate base is NH_3
- Cl^- is a conjugate base of the strong acid HCl, Cl^- can not react further.
- $\underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{H_3O^+} + \underset{\text{acid}}{NH_3}$

$$K_a = \frac{[H3O^+][NH_3]}{[NH_4^+]}$$

Ionization of Weak Acids

- $BH^+ + H_2O \rightleftharpoons H_3O^+ + B$

$$K_a = \frac{[H_3O^+][B]}{[BH_4^+]}$$

Ionization of Weak Bases

- Nonionized weak bases B, exemplified by NH_3, react with water as follows:
- $B + H_2O \rightleftharpoons OH^- + BH^+$

base acid conjugated base conjugated acid

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

نفس الشيء بالمقام نهمل $[H_2O]$

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

[B] concentration of base

Ionization of Weak bases

Example

The basicity or ionization constant ***Kb*** for morphine base **is** 7.4×10^{-7} at 25°C. What is the hydroxyl ion concentration of a **0.0005 M** aqueous solution of morphine?

concentration of base

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

$[OH^-] = \sqrt{7.4 \times 10^{-7} \times 5.0 \times 10^{-4}}$

$[OH^-] = 1.92 \times 10^{-5}$ mole/liter

Ionization of Weak bases

- Salts of **strong bases** and weak acids, such as sodium acetate, dissociate completely in aqueous solution to given ions:

$$Na^+CH_3COO^- \xrightarrow{H_2O} Na^+ + CH_3COO^-$$

- The sodium ion cannot react with water, because it would form NaOH, which is a strong electrolyte and would dissociate completely into its ions.
- $CH_3COO^- + H2O \rightleftharpoons OH^- + CH_3COOH$
- $K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
- In general, for an anionic base B^-
  - $B^- + H_2O \rightleftharpoons OH^- + HB$
  - $K_b = \frac{[OH^-][HB]}{[B^-]}$

$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$

Ionization of Water

two molecule of water react with each other one act as acid and another one act as base

- The concentration of **hydrogen or hydroxyl ions** in solutions of acids or bases may be expressed as **gram ions/liter** or as moles/liter.
- A solution containing **17.008 g** of hydroxyl ions or 1.008 g of hydrogen ions per liter is said to **contain 1 g ion or 1 mole of hydroxyl or hydrogen ions per liter.**
- Owing to the ionization of water, it is possible to establish a quantitative relationship between the **hydrogen and hydroxyl ion concentrations of any aqueous solution.**
- The concentration of either the **hydrogen or the hydroxyl ion in acidic, neutral, or basic solutions** is usually expressed in terms of the hydrogen ion concentration or, more conveniently, in **pH units.**

Ionization of Water

- A weak electrolyte requires the presence of water or some other polar solvent for ionization. Accordingly, one molecule of water can be thought of as a weak electrolytic solute that reacts with another molecule of water as the solvent.
- This **autoprotolytic** reaction is represented as
- $\mathbf{H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-}$
- $K = \frac{[OH^-][H_3O^+]}{[H_2O]^2}$ → constant
- Because molecular water exists in great excess relative to the concentrations of hydrogen and hydroxyl ions, $[H_2O]^2$ is considered as a constant and is combined with k to give a new constant, $\mathbf{K_w}$, known as the dissociation constant, the **autoprotolysis constant**, or the **ion product of water**.

Ionization of Water

- $K_w = k \times [H_2O]^2$
- The value of the ion product is approximately 1×10^{-14} at 25°C; it depends strongly on temperature (Proportionally)
- $[H3O^+] \times [OH^-] = Kw \cong 1 \times 10^{-14}$ at 25°C
- In pure water, the **hydrogen and hydroxyl ion** concentrations are equal, and each has the value of approximately 1×10^{-7} mole/liter at 25°C.
  $[H3O^+] = [OH^-] \cong 1 \times 10^{-14} \cong 1 \times 10^{-7}$
- The increase in hydrogen ions is offset by a decrease in the hydroxyl ions so that Kw remains constant at about 1×10^{-14} at 25 °C.

Ionization of Water

بالبداية كان تركيز H_3O^+ وتركيز OH^- = 1×10^{-7}

وجود الـ HCl رح يزيد تركيز H_3O^+

Example

A quantity of HCl (1.5×10^{-3} M) is added to water at 25°C to increase the hydrogen ion concentration from 1×10^{-7} to 1.5×10^{-3} mole/liter. What is the new hydroxyl ion concentration?

$$[OH^-] = \frac{1 \times 10^{-14}}{1.5 \times 10^{-3}} = 6.7 \times 10^{-12} \text{ mole/liter}$$

طبيعي رح يقل لأنه زاد تركيز H_3O^+

Relationship Between K_a and K_b

A simple relationship exists between the dissociation constant of a weak acid HB and that of its conjugate base B^-, or between BH^+ and B, when the solvent is amphiprotic.

$$K_a k_b = \frac{[H_3O^+][B^-]}{[HB]} \cdot \frac{[OH^-][HB]}{[B^-]}$$

weak acid with its conjugate base

$$k_a k_b = [H3O^+] \times [OH^-] = k_w$$

$$K_b = \frac{k_w}{k_a}$$

$$K_a = \frac{k_w}{k_b}$$

⇓

Buffer ← يقاوم التغيير بالـ PH

Relationship Between K_a and K_b

Example

Ammonia has a K_b of 1.74×10^{-5} at 25°. Calculate K_a for its conjugate acid, NH_4^+.

$$K_a = \frac{k_w}{k_b} = \frac{1.00 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.75 \times 10^{-10}$$

Strong acids and bases are those that have acidity or basicity constants greater than about 10^{-2}

$Ka/Kb > 10^{-2}$

Ionization of Polyprotic Electrolytes

- Acids that donate a single proton and bases that accept a single proton are called **monoprotic electrolytes**.
- **A polyprotic** (polybasic) acid is one that is capable of donating two or more protons, and a polyprotic base is capable of accepting two or more protons.
- **A diprotic** (dibasic) acid, such as carbonic acid, ionizes in two stages, and a **triprotic** (tribasic) acid, such as phosphoric acid, ionizes in three stages.

Ex: H_2SO_4 → جزئي قوي

جزئي ضعيف ← H_3PO_4

$$H_2SO_4 + H_2O \longrightarrow 2H_3O^+ + SO_4^{-2}$$

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{-2}$$

$$HPO_4^{-2} + H_2O \rightleftharpoons H_3O^+ + PO_4^{-3}$$

Ionization of Polyprotic Electrolytes

- $H_3PO_4 + H_2O = H_3O^+ + H_2PO_4^-$
  (acid 1) (base 1) (conjugate base 1)

$$\frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 = 7.5 \times 10^{-3}$$

- $H_2PO_4^- + H_2O = H_3O^+ + HPO_4^{2-}$
  (acid) (conjugate base)

$$\frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = K_2 = 6.2 \times 10^{-8}$$

- $HPO_4^{2-} + H_2O = H_3O^+ + PO_4^{3-}$
  (acid) (conjugate base)

$$\frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = K_3 = 2.1 \times 10^{-13}$$

Ionization of Polyprotic Electrolytes

- In any polyprotic electrolyte, the **primary protolysis** is greatest, and succeeding stages become less complete at any given acid concentration.
- The **negative charges** on the ion HPO_4^{2-} make it difficult for water to **remove** the proton from the phosphate ion, as reflected in the **small value of K_3**.
- Phosphoric acid is weak in the third stage of ionization, and a solution of this acid contains practically no PO_4^{3-} ions.

Ionization of Polyprotic Electrolytes

- **Each of the species** formed by the ionization of a polyprotic acid can also act as a base. Thus, for the phosphoric acid system,
- $H_2O + PO_4^{3-} \rightleftharpoons HPO_4^{2-} + OH^-$

$$K_{b1} = \frac{[OH^-][HPO_4^{2-}]}{[PO_4^{-3}]} = 4.8 \times 10^{-2}$$

- $HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$

$$K_{b2} = \frac{[OH^-][H_2PO_4^-]}{[HPO_4^{2-}]} = 1.6 \times 10^{-7}$$

- $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$

$$K_{b3} = \frac{[OH^-][H_3PO_4]}{[H_2PO_4^-]} = 1.3 \times 10^{-12}$$

-

Ionization of Polyprotic Electrolytes

- In general, for a polyprotic acid system for which the parent acid is H_nA, there are n + 1 possible species in solution:

$$H_nA + H_{n-j}A^{-j} + \cdots + HA^{-(n-1)} + A^{n-}$$

- J: the number of protons dissociated from the parent acid and goes from 0 to n.
- The total concentration of all species must be equal to C_a

$$H_nA + H_{n-j}A^{-j} + \cdots + HA^{-(n-1)} + A^{n-} = C_a$$

- Each of the species pairs in which j differs by 1 constitutes a conjugate acid–base pair, and in general

$$K_j K_{b(n+1-j)} = K_w$$

- For the phosphoric acid
- $K_1K_{b3} = K_2K_{b2} = K_3K_{b1} = K_w$

Ampholytes

- A species that can function either as an **acid or as a base** is called an **ampholyte** and is said to **be amphoteric in nature.**
- In a polyprotic acid system, **all** the species, with **the exception of HnA and An−**, are **amphoteric.**
- **Amino acids and proteins** are **ampholytes** of particular interest in pharmacy.

$^{+}NH_3CH_2COOH + H_2O \rightleftharpoons {}^{+}NH_3CH_2COO^- + H_3O^+$

$^{+}NH_3CH_2COO^- + H_2O \rightleftharpoons {}^{+}NH_2CH_2COO^- + H_3O^+$

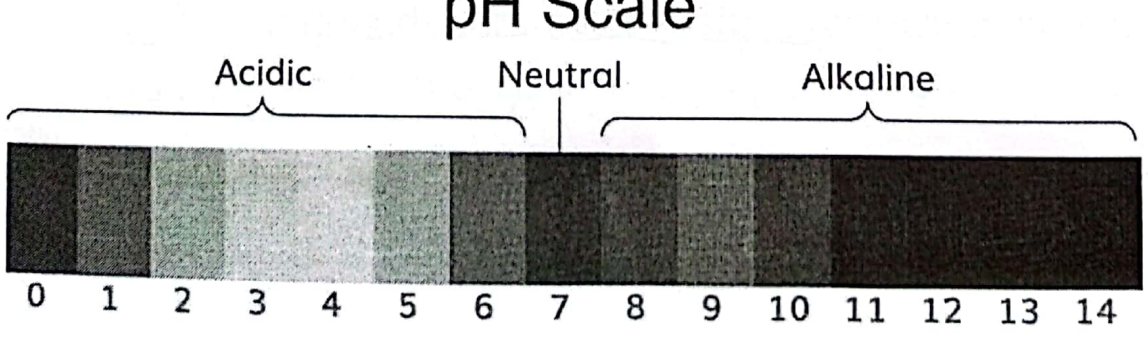
$^{+}NH_3CH_2COO^- + H_2O \rightleftharpoons {}^{+}NH_3CH_2COOH + OH^-$

$^{+}NH_3CH_2COO^-$ (amphoteric called zwitterion, it carries both positive and negative charges)

- The pH at which the zwitterion concentration is a maximum is known as the isoelectric point.

pH

- Sorensen's pH
- It expresses hydrogen ion concentration.
- $pH = \log \frac{1}{[H_3O^+]}$
- $pH = -\log[H_3O^+]$
- The neutral pH at 0◦C is 7.47, and at 100◦C it is 6.15



Example

$[H_3O]^+ = [HCl]$ لأنه حمض قوي فيكون

pH

حتى لو أعطاني تركيز H_3O^+ أقدر أطلعه من HCl

- The hydronium ion concentration of a 0.05 M solution of HCl is 0.05 M. What is the pH of this solution?

$$pH = -\log(5.0 \times 10^{-2}) = 1.30$$

Example

- If the pH of a solution is 4.72, what is the hydronium ion concentration?

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

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

$$4.72 = -\log[H_3O^+]$$

$$[H_3O^+] = 1.91 \times 10^{-5} \text{ mole/liter}$$

∴ $[OH^-]$ لو طلبني

$$[OH^-] = \frac{k_w}{[H_3O^+]}$$

p*K* and pOH

- pOH expresses $-\log[OH^-]$
- pKa is used for $-\log Ka$
- pKb is used for $-\log Kb$
- pK_w is $-\log K_w$
- $pH + pOH = pK_w$ → 14 $\quad pH + pOH = 14$
- $pK_a + pK_b = pK_w$

- pKa and pKb provide a convenient mean to compare the strength of weak acids and bases
  - The **lower** the **pKa** the stronger the acid
  - The lower the **pKb** the stronger the base

Calculation of pH

- According to the Br¨onsted–Lowry theory, every proton donated by an acid must be accepted by a base.
- proton balance equation (PBE) for each system for each system must be accomplished
-

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

عشان اطلع الـ Proton balance equation :

$[H_3O^+] = [Cl^-] + [OH^-]$

① كان نحط كل اشي تكون نتيجة فقد H^+ (غير الـ H_3O^+ الأخطر) = ① كان نحط كل اشي تكون نتيجة إكتساب H^+ ② نضيف OH^- ② نضيف H_3O^+

PBE

A. Always start with the species added to water.
B. On the **left side** of the equation, place **all species** that can form when **protons are consumed** by the starting species.
C. On the **right side** of the equation, place all species that can form when **protons are released** from the starting species.
D. Each species in the PBE should be **multiplied** by the number of **protons lost or gained** when it is formed from the starting species.
E. Add [H3O+] to the **left side** of the equation and **[OH−]** to the **right side** of the equation. These result from the interaction of two molecules of water.

Examples-PBE

- HCl added into water

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

$[H_3O^+] = [OH^-] + [Cl^-]$

- **What is the PBE when Na_2HPO_4 is added to water?**

- $Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{2-}$

$[H_3O^+] + [H_2PO_4^-] + 2[H_3PO_4] = [OH^-] + [PO_4^{3-}]$

Examples-PBE

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$

- **What is the PBE when H_3PO_4 is added to water?**
- The species $H_2PO_4^-$ forms with the release of one proton.
- The species HPO_4^{2-} forms with the release of two protons.
- The species PO_4^{3-} forms with the release of three protons.

$$[H_3O^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

Examples-PBE

- **What is the PBE when sodium acetate is added to water?**
  - The salt dissociates into one Na+ and one CH_3COO^- ion. The
  - CH_3COO^- is considered to be the starting species.
  - The CH_3COOH can form when CH_3COO^- consumes one proton. Thus,
- **$[H_3O+] + [CH_3COOH] = [OH^-]$**

Uses of the PBE

- The **PBE** allows the **pH** of any solution to be calculated readily,
  as follows:
  - Obtain the PBE for the solution in question.
  - Express the concentration of all species as a function of equilibrium constants and [H3O+] using equations
  - Solve the resulting expression for [H3O+] using any assumptions that appear valid for the system.
  - Check all assumptions.
  - If all assumptions prove valid, convert [H3O+] to pH.

➢ If the solution contains a base, it is sometimes more convenient to solve the expression for [OH−], **then convert this to pOH, and finally to pH by use of equation**

$pH = 14 - pOH$

Strong acids and bases

- $HCl \rightarrow [H3O^+] + [Cl^-]$ ----------conc. of Cl^- = conc. Of HCl
- PBE: $[H3O^+] = [OH^-] + [Cl^-]$
- Ka× Kb=Kw
- $[H_3O^+] = \frac{Kw}{[H_3O^+]} + C_a$ → HCl is a strong acid → $[Cl^-] = [HCl]$ (يكون)

concentration of acid HCl

- $[H_3O^+]^2 = Kw + [H_3O+]\ Ca$ → بعد ما عوضنا كل الاطراف بـ $[H_3O^+]$
- $[H_3O^+]^2 - [H_3O+]\ Ca - Kw = 0$ $(ax^2+bx+c=0)$

ترتيب ← صيغة معادلة تربيعية

$$X = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$ ← ناخذ بس (+)

$$[H_3O^+] = \frac{Ca+\sqrt{Ca^2-4Kw}}{2}$$

b = -Ca
a = 1
c = -kw

strong acid N

Strong acids and bases

- When the concentration of acid is 1×10^{-6} M or greater, $[Cl^-]$ becomes much greater than $[OH^-]$ in equation and Ca^2 becomes much greater than 4Kw in equation).
- Thus, both equations simplify to

$Ca^2 > 4Kw$ (اذا كان Ca اعلى من 1×10^{-6} معناتة اكبر بكثير)

$[H_3O^+] \cong C_a$ (لما يكون مربع تركيز الحمض اكبر من Kw نهمل $[OH^-]$)

- A similar treatment for a solution of a strong base such as NaOH gives

- $[OH^-] = \frac{Cb+\sqrt{Cb^2-4Kw}}{2}$ → اذا ما كان $Ca > 1\times10^{-6}$ نعمل على هذا القانون
- $[OH^-] \cong C_b$ → concentration base N → $Cb > 1\times10^{-6}$ M

Conjugate Acid–Base Pairs

- **pH of solutions composed of weak acids, weak bases, or a mixture of a conjugate acid– base pair.**
- a solution made by dissolving both a **weak acid, HB**, and a salt of its conjugate **base, B–**, in water.
  - Acid-base equilibrium

$$HB + H_2O \rightleftharpoons H_3O^+ + B^-$$
$$B^- + H_2O \rightleftharpoons OH^- + HB$$
$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

- **PBE**

$$[H3O^+] + [HB] = [OH^-] + [B^-]$$

تكون نتيجة كسب بروتون

تكون نتيجة فقد بروتون

Conjugate Acid–Base Pairs

The concentrations of the acid and the conjugate base can be expressed as:

$$[HB]=\frac{[H_3O^+]Cb}{[H_3O^+]+Ka} \quad [B^-]$$

$$[B^-]=\frac{Ka\ Ca}{[H_3O^+]+Ka}$$

حفظا #

$$[H_3O^+]=Ka\frac{(Ca-[H_3O^+]+[OH^-])}{(Cb+[H_3O^+]-[OH^-])}$$

Solutions contain only weak acids

① $C_b = 0$ (اذا ما كان في base)

② $[H_3O^+] >>> [OH^-]$ (اكبر بكثير — كل اشي الا علاقة بال base اصغره)

$$[H_3O^+] = Ka \frac{(Ca - [H_3O^+] + [OH^-])}{(Cb + [H_3O^+] - [OH^-])}$$

$[H_3O^+]^2 - Ka[H_3O^+] - Ka\,Ca = 0$

$$[H_3O^+] = \frac{-Ka + \sqrt{Ka^2 - 4Ka\,Ca}}{2}$$

In many instances, C_a ([HA]) **is much greater** than $[H_3O+]$, and equation simplifies to: ③

$$[H_3O^+] = \sqrt{KaCa}$$

weak acid لأنه بينما هاد تفكك كثير

اذا كان weak acid وحقق ٣ شروط ① + ② + ③

Solutions contain only weak acids

Example:

Calculate the pH of a 0.01 M solution of salicylic acid, which has a Ka= 1.06×10^{-3} at 25°C.

$[H_3O^+] = \sqrt{KaCa}$ ← اطبق هاد اول شي

✓ ① weak acid ✓ لأنه $Ka < 10^{-2}$

✓ ② base ما في $C_b = 0$ ✓

$[H_3O^+] = \sqrt{1.06 \times 10^{-3} \times 0.01}$ (صحيح لانه احد العاملين الطويل × ③ Ca not much greater than $[H_3O^+]$ صار اكبر بكثير)

$= 3.26 \times 10^{-3}$ M so $C_a >>> [H_3O+]$ is **not valid** غير صحيح

$Ca = 10^{-2}$

$[H_3O^+] = 3.26 \times 10^{-3}$

$$[H_3O^+] = \frac{-1.06 \times 10^{-3} + \sqrt{(1.06 \times 10^{-3})^2 - 4 1.06 \times 10^{-3} \times 0.01}}{2}$$

$= 2.77 \times 10^{-3}$ M

$pH = -\log(2.77 \times 10{-}3) = 2.56$

يعني بالبداية احل على القانون الصغير واذا ما تطبق الشرط الثالث ارجع احل على القانون الكبير

Solutions contain only weak acids

Example:

Calculate the pH of a 1-g/100 mL solution of **ephedrine sulfate**. The molecular weight of the salt is 428.5, and K_b for ephedrine base is 2.3×10^{-5}.

$(BH^+)_2SO_4 \rightarrow 2BH^+ + SO_4^{-2}$

$$\text{Ca (cationic acid)} = 2\,(1)/428.5/0.1 = 4.67 \times 10^{-2}\ \text{M}$$

$$K_a = k_w/k_b = 1 \times 10^{-14} / 2.3 \times 10^{-5} = 4.35 \times 10^{-10}$$

$$[H_3O^+] = \sqrt{KaCa}$$

$$[H_3O^+] = \sqrt{4.35 \times 10^{-10} \times 4.67 \times 10^{-2}}$$

$$= 4.51 \times 10^{-6}\ \text{M} \quad \text{is } Ca >>> [H_3O^+]$$

$$\text{pH} = -\text{Log } 4.51 \times 10^{-6} = 5.35$$

Solutions contain only weak bases

$$[H_3O^+] = Ka\,\frac{(Ca - [H_3O^+] + [OH^-])}{(Cb + [H_3O^+] - [OH^-])}$$

① $Ca = 0$

② $[OH^-] >>>> [H_3O^+]$

$$[H_3O^+] = \frac{Ka\,[OH^-]}{Cb - [OH^-]} = \frac{Ka\,Kw}{[H_3O^+]Cb - Kw}$$

$$C_b[H_3O^+]^2 - KwKa[H3O^+] - K_aK_w = 0$$

$$[H_3O^+] = \frac{K_w + \sqrt{K_w^2 - 4K_wK_acb}}{2C_b}$$

③ If K_a is much greater than $[H_3O^+]$, which is generally true for solutions of weak bases,

$$[H_3O^+] = \sqrt{\frac{Ka\ kw}{Cb}}$$

Solutions contain only weak bases

وقانون الحميز

$$[OH^-] = \frac{-K_b \pm \sqrt{K_b^2 - 4K_b C_b}}{2}$$

ناخذ (+) بس

لأنه weak base وعاطيها تفكك كثير

(3) If C_b is much greater than $[OH^-]$, which generally obtains for solutions of weak bases,

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

نفس الشي اذا كان Cb اكبر بكثير (بـ ١٠٠ مرة او اكثر) من $[OH^-]$

بالامتحان استعمل القانون الصغير

اذا ماكان اكبر ترجع لقانون الحميز (بيبين ما طبق الشرط)

Solutions contain only weak bases

Example:

Cb

What is the pH of a 0.0033 M solution of cocaine base, which has a basicity constant of 2.6×10^{-6}? → weak base لأنه اقل من 10^{-2}

Kb

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

$$[OH^-] = \sqrt{2.6 \times 10^{-6} \times 0.0033}$$

$$= 9.26 \times 10^{-5}\ M$$

Cb اعلى بكثير → مباشرة الحل صح جائز لقانون الحميز

$$POH = -\text{Log}\ 9.26 \times 10^{-5} = 4.03$$

$$pH = 14 - POH = 14 - 4.03 = 9.97$$

أو نطلع $[H_3O^+]$ ومنه نحسب PH

$PH = -\text{Log}[H_3O^+]$

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

Solutions contain only weak bases

Example:

Calculate the pH of a 0.165 M solution of sodium sulfathiazole. The acidity constant for sulfathiazole is 7.6×10^{-8}

$$NaB \rightarrow Na^+ + B^-$$

$$[H_3O^+] = \sqrt{\frac{Ka\ kw}{Cb}}$$

$$[H_3O^+] = \sqrt{\frac{7.6 \times 10^{-8} \times 1 \times 10^{-14}}{0.165}}$$

$$= 6.79 \times 10^{-11} \qquad Ca >> [H_3O^+]$$

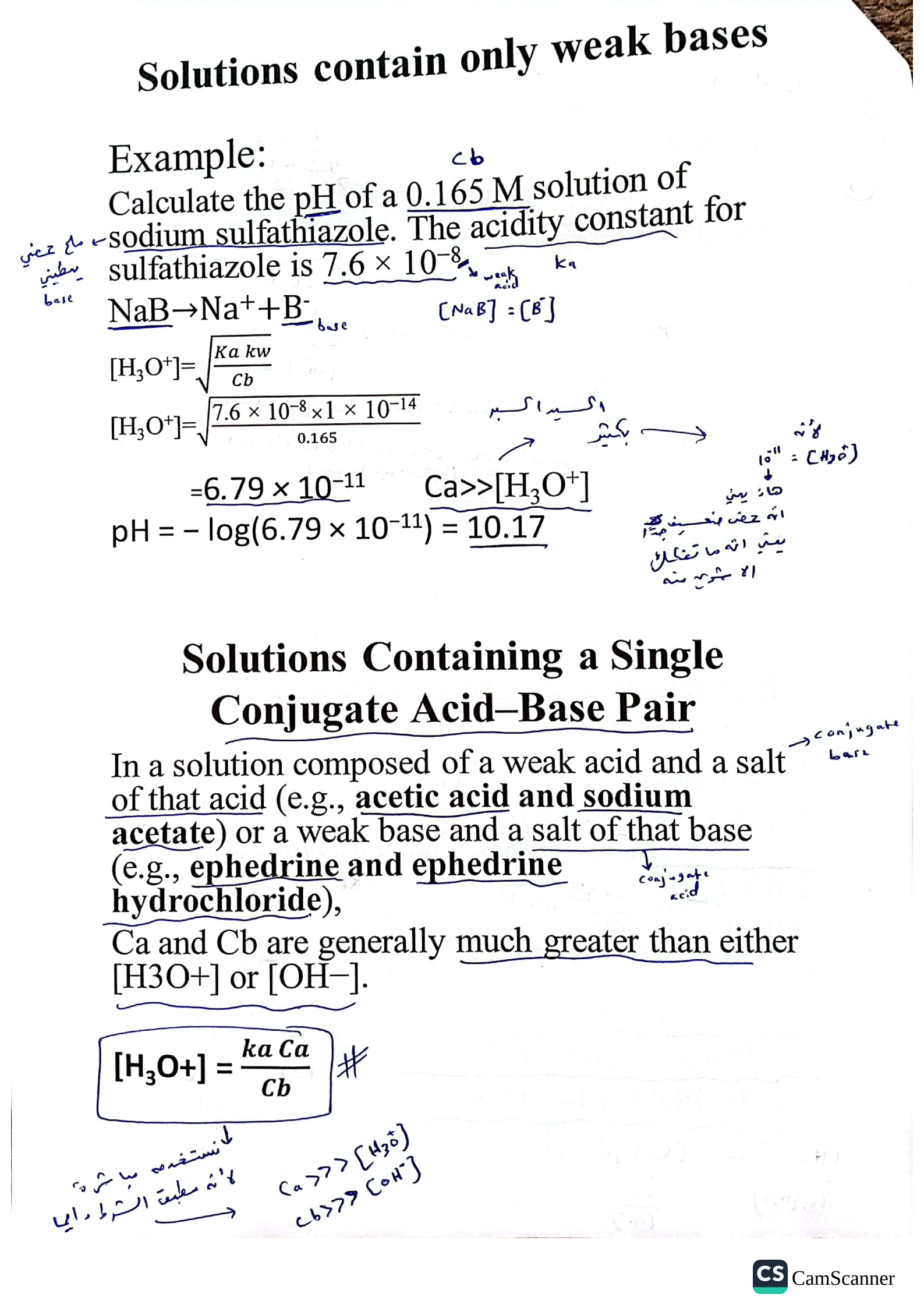
$$pH = -\log(6.79 \times 10^{-11}) = 10.17$$

Solutions Containing a Single Conjugate Acid–Base Pair

In a solution composed of a weak acid and a salt of that acid (e.g., **acetic acid and sodium acetate**) or a weak base and a salt of that base (e.g., **ephedrine and ephedrine hydrochloride**),

Ca and Cb are generally much greater than either [H3O+] or [OH−].

$$[H_3O+] = \frac{ka\ Ca}{Cb} \quad \#$$



Solutions Containing a Single Conjugate Acid–Base Pair

Example:

What is the pH of a solution containing acetic acid **0.3 M** and sodium **acetate 0.05 M**? (Ka= **1.75 × 10^{-5}**)

weak acid

weak acid

conjugated base

$[H_3O+] = (ka\ Ca)/Cb = (1.75 \times 10^{-5} \times 0.3)/0.05 = 1.05 \times 10^{-4}\ M$

$pH = -\log(1.05 \times 10^{-4}) = 3.98$

Solutions Containing a Single Conjugate Acid–Base Pair

Example:

What is the pH of a solution containing ephedrine 0.1 M and ephedrine hydrochloride 0.01 M? Ephedrine has a basicity constant of 2.3×10^{-5}

weak base

conjugated acid

Kb

weak base

① $Ka = \frac{Kw}{Kb} = \frac{1 \times 10^{-14}}{2.3 \times 10^{-5}} = 4.34 \times 10^{-10}$ #

Answer:10.36

② $[H_3O^+] = \frac{Ka \cdot Ca}{Cb} = \frac{4.34 \times 10^{-10} \times 0.01}{0.1} = 4.34 \times 10^{-11}\ M$ #

③ $PH = -Log[H_3O^+] = -Log(4.34 \times 10^{-11}) = 10.36$ #