CHAPTER II : *Acids and Bases*

1. Definitions of acids and bases

1.1. Acids and bases according to Arrhenius

August Arrhenius first introduced the concept of acids and bases in the 1890s, According to Arrhenius

An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions (H^+) into the solution. This can be represented by the general equation :

$$AH \rightarrow H^+ + A^-$$

Example

$HCl \longrightarrow H^+ + Cl^-$

$CH_3COOH \longrightarrow H^+ + CH_3COO^-$

A **base** is a substance that, when dissolved in water, increases the concentration of hydroxide ions (**OH^-**).

$$BOH \rightarrow B^+ + OH^-$$

Example

$NaOH \longrightarrow Na^+ + OH^-$

$KOH \longrightarrow K^+ + OH^-$

1.2. Acids and bases according to Bronsted-Lowry

A more general definition was proposed by Joanne Bonsted and Thomas Lowry in the 1920s. According to Bronsted-Lowry :

An acid is a chemical species that can donate an H^+ ion, as represented by the equation.

$$AH \rightarrow H^+ + A^-$$

Example

$$NH_4^+ \rightarrow H^+ + NH_3$$

A Base is a chemical species capable of capturing an H^+ ion, which summarizes the equation :

$$B + H^+ \rightarrow BH^+$$

$$AH \rightarrow H^+ + A^-$$

Example

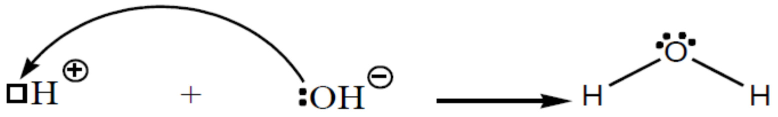
$$CH3COO^- + H^+ \rightarrow CH3COOH$$

$$NH_3 + H^+ \rightarrow NH_4^+$$

1.3. Acids and Bases according to Lewis

An even broader (plus large) definition of acids and bases was proposed by Lewis in the 1920s, and his definitions are as follows :

- An acid is a compound that has a vacancy "Vacant cell": Electron acceptor.
- A base is a compound that has a free electron pair : Electron donor.



Lewis Acid Lewis base

Electron Acceptor Electron Donor

2. Acid/Base Couple in Water

Every acid in solution has a corresponding conjugate base, and vice versa :

$$AH \rightleftharpoons A^- + H^+$$

AH : Acide

A⁻ : Conjugate base

Example

Hydrofluoric acid HF :

$$HF \rightleftharpoons H^+ + F^-$$

The corresponding pair : (Acid/conjugate base) = (HF/F^-)

Ammonia NH_3 (A base) **:**

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

The corresponding pair : (Acid/conjugate base) = (NH_4^+/NH_3)

3. Acid-base reactions

Protons (H^+) do not exist in the free state. For an acid **AH** to be able to give up protons **H^+**, it must have a base **B** capable of fixing them.

First half reaction :

$$AH \rightleftharpoons H^+ + A^- \quad Couple\,(AH/A^-)$$

Second half reaction :

$$B + H^+ \rightleftharpoons BH^+ \quad Couple\,(BH^+/B)$$

acid-base reaction :

$$AH + B \rightleftharpoons BH^+ + A^-$$

Example

First half reaction :

$$HCOOH_{(l)} \rightleftharpoons H^+_{(aq)} + HCOO^-_{(aq)} \quad Couple\,(HCOOH/HCOO^-)$$

Second half reaction :

$$NH_{3(g)} + H^+_{(aq)} \rightleftharpoons NH^+_{4(aq)} \quad Couple\,(NH_4^-/NH_3)$$

acid-base reaction :

$$HCOOH_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + HCOO^-_{(aq)}$$

4. Autodissociation of water

The autodissociation of water is the process by which two water molecules react with each other to produce a hydronium ion (H_3O^+) and a hydroxide ion (OH^-). This reaction is represented by the following equation :

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

or in simplified form:

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

A chemical equilibrium is then established between the water molecules, the hydronium ions and the hydroxide ions, called the water autoprotolysis equilibrium.

The equilibrium constant for this reaction is:

$$K = Ke = [H_3O^+] \times [HO^-]$$

Since no other ions can be present in pure water at 25 °C, the solution's electrical neutrality requires that :

$$[H_3O^+] = [OH^-] = 10^{-7} M$$

So

$$Ke = [H_3O^+] \times [HO^-] = 10^{-14}$$

Ke is called the ionic product of water or autoprotolysis constant of water.

5. The Acid-Base Role of Water

Water can act as an acid or a base, so it has an ampholytic character (two roles).

5.1. As an Acid

With a base B, water plays the role of an acid (Water can donate a proton (H^+) to a base, forming a hydroxide ion (OH^-)).

$$H_2O \rightleftharpoons H^+ + OH^- \quad Couple\,(H_2O/OH^-)$$
$$B + H^+ \rightleftharpoons BH^+ \quad Couple\,(BH^+/B)$$
$$B + H_2O \rightleftharpoons BH^+ + OH^- \quad Réaction\ acido-basique$$

5.2. As an Base

With an acid AH, water plays the role of a base (Water can also accept a proton (H^+) from an acid, forming a hydronium ion (H_3O^+).

$$\begin{array}{lll} AH \rightleftharpoons H^+ + A^- & & Couple\,(AH/A^-) \\ H_2O + H^+ \rightleftharpoons H_3O^+ & & Couple\,(H_3O^+/H_2O) \\ \cdots\cdots\cdots\cdots\cdots\cdots & & \\ AH + H_2O \rightleftharpoons H_3O^+ + A^- & & Réaction\ acido-basique \end{array}$$

6. Strength of acids and bases

6.1. Acid Strength

Consider the dissociation reaction of an acid, AH, in water :

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

$$K_{éq} = \frac{[H_3O^+][A^-]}{[AH]} = Ka$$

With : K_a is the acidity constant of the couple (AH/A^-)

Since the values of Ka are typically small (often negative powers of 10), it is preferred to use the base 10 logarithm of Ka, with the sign changed, a quantity known as pKa :

$$pKa = -log_{10}Ka$$

Note

An acid is considered stronger when its acidity constant K_a is higher (indicating a lower pK_a). Conversely, an acid is weaker when its acidity constant K_a is lower (indicating a higher pK_a).

Example

$$pKa\,(CH_3COOH/CH_3COO^-) = 4.8 < pKa\,(HCN/CN^-) = 9.2$$

So CH_3COOH acid is stronger than HCN acid

6.2. Base Strength

Consider the protonation reaction of a base B in the presence of water

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

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

With : K_b is the basicity constant of the couple (BH^+/B)

$$\Longrightarrow \quad pK_b = -log_{10}K_b$$

Note : A base is considered stronger when its basicity constant K_b is higher (indicating a lower pK_b). Conversely, a base is weaker when its basicity constant K_b is lower (indicating a higher pK_b).

Example

$pK_b\,(CH_3COOH/CH_3COO^-) = 9.2 > pK_b\,(HCN/CN^-) = 4.2$

So the base CN^- is stronger than the base CH_3COO^-

6.3. Relationship between Ka and Kb

Consider the pair (AH/A^-) :

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

$$Ka = \frac{[H_3O^+][A^-]}{[AH]} \cdots\cdots\cdots(1)$$

$$A^- + H_2O \rightleftharpoons AH + OH^-$$

$$K_b = \frac{[OH^-][AH]}{[A^-]} \cdots\cdots\cdots(2)$$

By multiplying equations (1) and (2), we obtain :

$$K_a * K_b = [H_3O^+][OH^-] = K_e = 10^{-14}$$

$$\Longrightarrow \quad pK_a + pK_b = pK_e = 14$$

6.4. The pKa of water pairs

Water can act as both an acid and a base, and it has two relevant pKa values depending on which proton transfer equilibrium is considered.

1. Water acting as an acid : When water donates a proton, it dissociates to form hydroxide ions (OH^-) :

$$H_2O \leftrightarrow H^+ + OH^-$$

The equilibrium constant for this dissociation is :

$$K_e = [H^+][OH^-] = 10^{-14} \rightarrow pK_a \approx 14$$

2. Water acting as a base : When water accepts a proton, it forms the hydronium ion (H_3O^+) :

$$H_2O + H^+ \leftrightarrow H_3O^+$$

For this protonation, the pKa of the hydronium ion is approximately :

$$pK_a \approx -1.7$$

6.5. The pKa Scale

Acid-base pairs can be classified based on their pKa values relative to those of the H_3O^+/H_2O and H_2O/OH^- pairs, allowing us to establish the following scale.

6.5.1. If pKa < 0 :

A pKa below 0 indicates a very strong acid that almost fully dissociates in water to release protons. The general dissociation equation for a **strong acid** in water is :

$$HA + H_2O \rightarrow H_3O^+ + A^- \quad \text{Or} \quad HA \rightarrow H^+ + A^-$$

Example

Hydrochloric Acid (HCl) : $HCl \rightarrow H^+ + Cl^-$ (pKa = -7)

Hydrobromic Acid (HBr) : $HBr \rightarrow H^+ + Br^-$ (pKa = -9)

6.5.2. pKa > 14 :

The base **B** readily accepts protons from water, resulting in nearly complete formation of its conjugate acid, BH^+.

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

Example

Hydrazine (N_2H_4) : $N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$ (pKb ≈ 3.7**)**

6.5.3. 0 < pKa <14 :

The dissociation reaction of AH and the protonation of B are partial in water.

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

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

Example

Formic Acid (HCOOH) : $HCOOH \rightleftharpoons HCOO^- + H^+$ (pKa ≈ **3.75)**

6.6. Ostwald's Dilution Law

Ostwald's dilution law is a fundamental principle in chemistry that deals with the dissociation of weak acids and bases in solution. It describes how the dilution of a solution affects the degree of dissociation of a weak acid or base.

As the concentration of a weak acid (or weak base) decreases, its tendency to dissociate increases, leading to a higher dissociation coefficient α.

Weak acid

Consider the equilibrium of a weak acid HA

	AH	+	H_2O	⇌	A^-	+	H_3O^+
T=0	C_0		ex		0		0
T=eq	$C_0 - \alpha C_0$		ex		αC_0		αC_0

$$K_a = \frac{[A^-][H_3O^+]}{[AH]} = \frac{\propto C_0 \times \propto C_0}{C_0(1-\propto)} = \frac{\propto^2}{(1-\propto)} \rightarrow \frac{K_a}{C_0} = \frac{\propto^2}{(1-\propto)}$$

Case 1 :

If C_0 increase => (Ka/C) decrease => (α^2 / (1-α) decrease => α decrease

Case 2 :

If C_0 decrease => Ka/ C increases => (α^2 / (1-α) increases => α increase.

Weak base

Consider the equilibrium of a weak base

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

Give the dissociation coefficient (α) expressed in terms of Kb ?

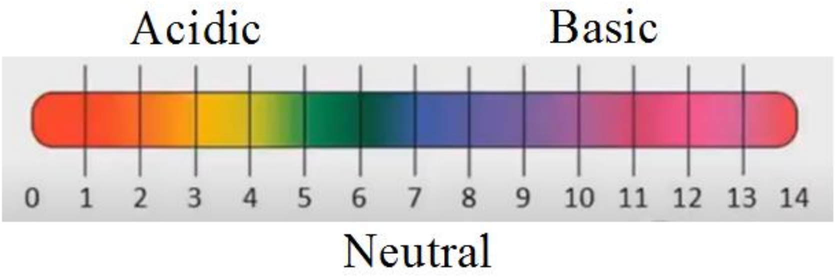
7. pH of Aqueous Solutions

The pH of an aqueous solution is a measure of its acidity or basicity, indicating the concentration of hydrogen ions (H+) present in the solution.

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

The pH scale ranges from 0 to 14, with :

- **pH < 7** : Acidic solutions ($[H_3O^+] > [OH^-]$).
- **pH = 7** : Neutral solutions ($[H_3O^+] = [OH^-]$).
- **pH > 7** : Basic (or alkaline) solutions ($[H_3O^+] < [OH^-]$).



7.1. Case of a Strong acid

If the acid AH is strong, it means it dissociates completely in water, and the equilibrium is fully shifted toward the products.

The reaction can be written as :

	AH	+	H_2O	→	A^-	+	H_3O^+
T=0	C		ex		0		0
T=eq	0		ex		C		C

If [AH] =C → $[AH] = [H_3O^+] = C$

By definition → **$pH = -\log_{10} [H_3O^+]$** → **$pH = -\log_{10} C$**

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

$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

0.1 M 0.1 M

$[H3O^+] = C$ = The original concentration of the strong acid [HCl] = 0.1 M

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

7.2. Case of a Strong base

	B	+	H_2O	→	BH^+	+	OH^-
T=0	C		ex		0		0
T=eq	0		ex		C		C

Bstrog base, if $[B] =C \rightarrow [B] = [OH^-]= C$

and by definition $pOH= -\log [OH^-] \rightarrow pH= 14 – pOH$

$\rightarrow$ **$pH = 14 + \log_{10} [H_3O^+]$**

7.3. Case of weak acid

A weak acid AH with concentration C in water, partially dissociates according to the following reaction :

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

$$K_a = \frac{[A^-][H_3O^+]}{[AH]}$$

1. according to the law of conservation of mass

$C = [AH] + [A^-]$ and $[AH] >> [A^-]$, $[AH] + [A^-] \approx [AH] \rightarrow C= [AH]$

2. according to the electroneutrality law

$\sum$positive charges = $\sum$negative charges $\rightarrow [H_3O^+] = [A^-] + [OH^-]$

The medium is acidic $[H_3O^+] >> [OH^-] \rightarrow [H_3O^+] >> [A^-] \rightarrow K_a = \frac{[A^-][H_3O^+]}{[AH]}$

$\rightarrow K_a.C = [H_3O^+]^2 \rightarrow [H_3O^+] = (K_a.C)^{1/2} \rightarrow -\log_{10} [H_3O^+] = -\log_{10} (K_a.C)^{1/2}$

$= ½ (-\log_{10} K_a -\log C) = ½ (pK_a - \log C)$

$\rightarrow$ **$pH = ½ (pKa - \log_{10} C)$**

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

(a) 0.05 M NaOH,

(b) (b) 0.05 M La(OH)3 .

Solution :

a) NaOH → $Na^+ + OH^-$

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

7.4. Case of weak base

A weak base B with concentration C, in water, partially dissociates according to the following reaction :

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

The base dissociation constant K_B is given by :

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

1. according to the law of conservation of mass

$C = [B] + [BH^+]$ and $[B] >> [BH^+]$, $[B] + [BH^+] \approx [B] \rightarrow C = [B]$

2. according to the electroneutrality law

∑positive charges = ∑negative charges → $[OH^-] = [BH^+] + [H_3O^+]$

The medium is basic $[OH^-] >> [H_3O^+] \rightarrow [H_3O^+] = [BH^+] \rightarrow K_b = \frac{[BH^+][OH^-]}{[B]}$

$\rightarrow K_b.\ C = [OH^-]^2 \rightarrow [OH^-] = (K_b.\ C)^{1/2} \rightarrow -\log_{10}[OH^-] = -\log_{10}(K_b.\ C)^{1/2}$

$= ½ (-\log_{10} K_b - \log_{10} C) = ½ (pK_b - \log_{10} C)$

$\rightarrow$ **$pOH = ½ (pK_b - \log_{10} C)$**

In an aqueous solution at 25°C, we have :

$pH + pOH = 14$ **and** $pK_a + pK_b = 14$

From the equation :

$14 – pH = 1/2(14 − pK_a − \log_{10}C) = 7 −1/2(pK_a + \log_{10}C) \rightarrow pH = 14 - 7 + 1/2(pK_a + \log_{10}C)$

We find :

$\rightarrow$ **$pH = 7 + 1/2 (pK_a + \log_{10}C)$**

7.5. pH of an acid-base pair with different concentrations

Consider the acid-base pair AH/A^-. When we add a highly soluble salt that contains the conjugate base A^- to this pair, we can analyze how this affects the pH.

Weak Acid Dissociation

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

$$K_a = \frac{[A^-][H_3O^+]}{[AH]}$$

When we add a salt MA that dissociates into

$MA \rightarrow M^+ + A^-$

This increases the concentration of the conjugate base A^- and at equilibrium, we have :

[AH] equilibrium, $[H_3O^+]$ formed, the total concentration of A^-
$[A^-]_{\text{total}} = [A^-]_{\text{conjugated from acid}} + [A^-]_{\text{from salt}}$

The concentration of H_3O^+ formed can be expressed using the equilibrium constant :

$$[H_3O^+] = \frac{K_a . [AH]_{equilibrium}}{[A^-]_{total}}$$

The pH can then be calculated using the relationship :

$$pH = pK_a + log_{10}\frac{[A^-]_{total}}{[AH]_{equilibrium}} \rightarrow \boldsymbol{pH = pK_a + log_{10}\frac{[Base]}{[Acid]}}$$

Exo 4

7.6. pH of a mixture of two acid-base pairs of equal concentrations

Consider the Acid-Base Pairs :

1. The weak acid AH/A^- with dissociation constant K_{a1} :

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

$$K_{a1} = \frac{[A^-][H_3O^+]}{[AH]}$$

2. The conjugate acid-base pair BH^+ with dissociation constant K_{a2} :

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

The base dissociation constant K_B is given by :

$$K_{a2} = \frac{[H_3O^+][B]}{[\mathrm{BH}^+]}$$

$$K_{a1}.\ K_{a2} = [H_3O]^2 \times \frac{[A^-]}{[\mathrm{AH}]}\frac{[B]}{[\mathrm{BH}^+]}$$

Let $C_1 = C_2 \rightarrow [AH] + [A^-] = [B] + [BH^+]$

If the dissociation is very weak, we can approximate

$\rightarrow C_1 = [AH]$ and $C_2 = [B] \rightarrow [AH] = [B]$ and $[A^-] = [BH^+]$

$\rightarrow K_{a1}.\ K_{a2} = [H_3O]^+ \rightarrow$ **$pH = 1/2\ (pK_{a1} + pK_{a2})$**

7.7. pH of buffer solutions

A buffer solution is composed of a mixture of a weak acid AH and its conjugate base A−. The equilibrium for this system can be represented as follows :

$AH + H_2O \leftrightharpoons H_3O^+ + A^-$

The acid dissociation constant K_a for the acid-base pair AH/A^- is defined by the equation

$$K_a = \frac{[\mathrm{A}^-][H_3O^+]}{[AH]}$$

$$-\log\ K_a = -log\ (\frac{[\mathrm{A}^-][H_3O^+]}{[AH]})$$

$$-\log\ K_a = -\log([H_3O^+]) - log(\frac{[\mathrm{A}^-]}{[AH]})$$

$$-\log([H_3O^+]) = -\log\ K_a + log(\frac{[\mathrm{A}^-]}{[AH]})$$

$$\rightarrow\ \boldsymbol{pH = pK_a + log_{10}(\frac{[\mathrm{A}^-]}{[AH]})}$$

The buffer zone $\boldsymbol{pK_a - 1 < pH < pK_a + 1}$

8. Color Indicators

A color indicator is typically a weak monoprotic acid with a specific pKapK_apKa, where the form HAHAHA has a distinctly different color from its conjugate base form A−A^-A−.

Examples

1. *Methyl Orange* (Helianthine): Para-Dimethylaminoazobenzene Sulfonic Acid
2. *Bromothymol Blue*
3. *Phenolphthalein*: 2,2-Bis(n-hydroxyphenyl)phthalide

9. Acid-Base Titrations

9.1. Titration of a Strong Acid by a Strong Base

The strong acid and strong base dissociate completely in water.

$AH+B \rightarrow BH^+ + A^-$

The titration curve can be divided into three distinct parts :

Before the equivalence point : Before the equivalence point, Ca·Va is greater than Cb·Vb ($[H_3O^+] > [OH^-]$). The OH^- ions react with an equal number of H_3O^+ ions to form water, leaving in solution a remaining amount of H_3O^+ ions equal to Ca·Va–Cb·Vb.

$$[H_3O^+] = \frac{C_aV_a - C_bV_b}{V_a + V_b} \qquad \boxed{pH = -\log_{10}\left(\frac{C_aV_a - C_bV_b}{V_a + V_b}\right)}$$

At the equivalence point : This corresponds to calculating the pH of a strong acid solution that has been exactly neutralized by a strong base :

Ca·Va = Cb·Vb ($[H_3O^+] = [OH^-]$). At this point, pH=7 at 25°C.

After the equivalence point : After the equivalence point, Ca·Va is less than Cb·Vb ($[OH^-] > [H_3O^+]$). The OH^- ions react with all the H_3O^+ ions to form water, leaving in solution an amount of OH^- ions equal to Cb·Vb–Ca·Va.

$$[OH^-] = \frac{C_bV_b - C_aV_a}{V_a + V_b}$$

$$pOH = -\log_{10}\left(\frac{C_bV_b - C_aV_a}{V_a + V_b}\right)$$

$$\boxed{pH = 14 + \log_{10}\left(\frac{C_bV_b - C_aV_a}{V_a + V_b}\right)}$$

9.2. Titration of a weak Acid by a strong Base

9.3. Titration of a weak acid with a strong base.

9.4. Titration of a strong acid with a weak base.

9.5. Titration of a polyacid with a strong base.