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CHAPTER II :

ACID-BASE REACTIONS

1-Definitions

1-1-ARHENIUS definition

- ✓ An acid is a substance that can release H^+ ions:

$$HCl \text{----------}> H^+ + Cl^-.$$

- ✓ Une base est une substance pouvant libérer des ions OH^-:

$$NaOH \text{---------}> Na^+ + OH^-$$

This theory doesn't explain why **NH_3** in water is basic when it contains no **OH** group. It is therefore generalized by **BRONSTED.**

1-2-BRONSTED definition

Among the various theories of acids and bases, the one proposed by **BRONSTED** in **1923** is still the most widely used.

An acid: is a chemical species, ion or molecule, capable of releasing (giving up) an H^+ proton. An acid therefore necessarily contains the hydrogen element, but not every hydrogenated compound is an acid:

$$AH \text{---------}> A^- + H^+$$

A base: is a chemical species, ion or molecule, which can accept (bind) an H^+ proton:

$$A^- + H^+ \text{-------------}> AH$$

Or;

$$B + H^+ \text{--------------}> BH^+.$$

It should be noted that compounds such as NaOH, KOH, ... , in water dissociate to give OH^- ions, which are bases since they can bind a proton:

$$OH^- + H^+ \text{-------------}> H_2O$$

1-3- Conjugated acid-base pairs

Let's consider the following reaction,

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

The species A- and the protons formed can recombine to give AH; so A- is a base.

The set of two associated species in the same equilibrium constitutes an **acid/base couple**. The acid and base of the same couple are said to be **Conjugated**.

The conjugated acid-base pair is **HA/A^-.**

1-3-1 Amphoteric compounds or ampholytes.

These are compounds which, depending on the nature of the medium, can donate or capture an H+ proton, and therefore behave like acids or bases.

Example:

H_2O is the acid in the H_2O/OH^- couple. $H_2O \Longleftrightarrow OH^- + H^+$

H_2O is the base in the H_3O^+/H_2O couple. $H_3O^+ \Longleftrightarrow H_2O + H$

An acid-base reaction involves 2 acid/base pairs. This reaction involves the transfer of H+ ions between the acid of one pair and the base of the other.

$$A_1 + B_2 \Longleftrightarrow B_1 + A_2.$$

1-3-2 Strength of acids and bases

There are two types of acids and bases, depending on their dissociation:

a-Strong acids and strong bases

These are strong electrolytes: the dissociation reaction is total.

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

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

b-Weak acids and bases

These are weak electrolytes. The dissociation equilibrium is clearly in favor of the reverse reaction.

$$HCN + H_2O \Longleftrightarrow H_3O^+ + CN^- \qquad \text{HCN : weak acid}$$

$$F^- + H_2O \Longleftrightarrow HF + OH^- \qquad F^- : \text{weak base}$$

1-3-2 Acidity and basicity constants.

HA is a weak acid.

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

Using the law of mass action, we can write:

$$Kc = [H_3O^+]\,[A^-] / [HA]\,[H_2O]$$

Where $$[H_2O]\,Kc = [H_3O^+]\,[A^-] / [HA]$$

We have then, $$Ka = [H_3O^+]\,[A^-] / [HA]$$

$$\mathbf{Ka = [H_3O^+]\,[base] / [acid]}$$

Ka is the acidity constant of the acid **HA**

Ka constants vary, depending on the nature of the acids in the calculations, so we replace Ka by pKa with,

$$\mathbf{pKa = -\log Ka.}$$

Note that, a solution is more acidic => Ka is larger and its pKa is smaller.

Note:

Strong acids are totally dissociated in solution, and therefore have no K_a. On the other hand, the strength of bases can be defined on the basis of the equilibrium established in aqueous solutions. The corresponding equilibrium constant would be a basicity constant K_b.

For example, for the pair AH/A- :

$$A^- + H_2O \Longleftrightarrow HA + OH^-$$

$$K_b = [OH^-]\,[HA] / [A^-]$$

$$\mathbf{K_b = [OH^-]\,[acid] / [base]}$$

But we can see that, for a conjugated acid and base, K_a and K_b are related:

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

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

This product is called **the ionic product of Ke water**, and its value depends solely on temperature.

$$Ke = [H_3O^+][OH^-] = 10^{-14} \quad \text{at } 25°C$$

With,

$$pke = -\log ke = 14$$

This relationship is general and applies to any aqueous solution, whatever the origin of the H_3O^+ and OH^- ions and whatever the other species present in solution. In all cases, we have :

$$Ka \times K_b = 10^{-14}$$

and,

$$pKa + pK_b = 14.$$

It's not necessary to establish a basicity scale for bases.

But it's only necessary to know the K_a constants of conjugated acids.

Example:

Let's take the two acid/base pairs:

HF/F^- ($pKa1 = 3,2$) and CH_3COOH/CH_3COO^- ($pKa2 = 4.8$).

$pK_{b1} = 14 - 3,2 = 10,8$ and $pK_{b2} = 14 - 4.8 = 9,2$

- $pK_{a1} < pK_{a2}$, So HF acid is stronger than CH_3COOH

- $pK_{b2} < pK_{b1}$, So the $CH3COO^-$ base is stronger than F^-.

We conclude that:

1-**K_a** increases **pk_a** decreases therefore the acidity strength increases.

2-**K_b** increases **pk_b** decreases so the strength of basicity increases.

3- The stronger the acid, the weaker its conjugate base.

-Ka and pKa of common acid/base pairs in aqueous solution at 25°C

Acid	HF	HNO_2	HCOOH	CH_3OOH	H_2S	HClO	HCN	$CH_3NH_3^+$
Base conj	F^-	NO_2^-	$HCOO^-$	CH_3OO^-	HS^-	ClO^-	CN^-	CH_3NH_2
pKa	3,2	3,02	3,8	4,7	7.04	7,5	9,2	10,6
ka	$10^{-3.2}$	$10^{-3.02}$	$10^{-3.8}$	$10^{-4.7}$	$10^{-7.04}$	$10^{-7.5}$	$10^{-9.2}$	$10^{-10.6}$

1-3-4 Dissociation coefficient of a weak acid :

Consider the ionization equilibrium of the acid AH. The composition of the system is expressed as a function of the ionization coefficient α (dissociation rate or dissociated or ionized fraction) of this acid, without taking into account the dissociation equilibrium of water:

$$\boldsymbol{\alpha = n_{eq} / n_0}$$

Number of moles dissociated at equilibrium divided by Number of moles initially dissolved

$$0<\boldsymbol{\alpha}<\mathbf{1}$$

-For a strong electrolyte, $\boldsymbol{\alpha}$ is close to 1.

-For a weak electrolyte, $\boldsymbol{\alpha}$ is less than 1.

For a weak acid HA, [HA]i = C , we have the equilibrium :

	$HA + H_2O$ <=====>	A^-	+	H_3O^+
t=0	C	0		0
Teq	$C(1-\alpha)$	αC		αC

$$\mathbf{Ka = [H_3O^+]\,[A^-] / [HA] \implies Ka = \alpha C \times \alpha C / C(1-\alpha)}$$

Case 1: **If,** C: increases => (**Ka/C**) decreases

Therefore, (α^2 / **(1-**α) decreases => α : decreases

Case2: **If,** C: decreases => (**Ka/C**) increases

Therefore, (α^2 / **(1-**α) increases => α : increases

Dilution increases electrolyte dissociation. At infinite dilution ($C_0 \rightarrow 0$), the ionization coefficient α increases and tends towards a limiting value α limit. This is OSTWALD's law or the law of dilution.

2- pH of aqueous solutions

Measuring the pH of an aqueous solution classifies it as acidic or basic.

By definition :

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

- Neutral solution $[H_3O^+] = [OH^-] \rightarrow [H_3O^+]^2 = 10^{-14}$, $[H_3O^+] = 10^{-7}$mol/L and pH = 7
- acid Solution $[H_3O^+] > [OH^-]$ ===> pH < 7
- base Solution $[H_3O^+] < [OH^-]$ ===> pH > 7

2.1. Case of a strong acid

Case of an aqueous solution of a fully ionized strong acid of molar concentration C_a.

- **Chemical reactions taking the form of :**

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

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

- **Chemical species present in solution :**

H_2O ; A^- ; H_3O^+ ; OH^- (AH est totalement ionisé donc [AH] =0)

- **Relationship between concentrations :**

Law of mass action: $Ke = [H_3O^+] [HO^-]$

Material conservation: $[A^-] = C$

Electrical neutrality: $[OH^-] + [A^-] = [H_3O^+]$

We obtain the equation:

$$[H_3O^+]^2 - C[H_3O^+] - Ke = 0$$

In some cases (solutions with average concentrations), an approximation can be adopted to obtain a simple expression for the pH of the solution.

- **Approximation :**

1- The solution is slightly diluted: $C > 10^{-6.5}$ M:

The quantity of H_3O^+ ions released by the acid is significant compared to that resulting from the dissociation of water. The latter is equal to the concentration of OH^- ions,

This gives; $[OH^-] << [H_3O^+]$

The solution is said to be sufficiently acidic, and the water dissociation equilibrium is neglected.

- **Calculations**

$$[A^-] = [H_3O^+] = C \implies \mathbf{pH = -log\ C}$$

2- The solution is highly diluted: $C < 10^{-6.5}$ M:

The quantity of H_3O^+ ions released by the water is not negligible compared with that resulting from the ionization of the acid AH. No approximation is made.

The 2nd degree equation must be solved:

$$[H_3O^+]^2 - C[H_3O^+] - K_e = 0$$

$$[H_3O^+] = (c + 4k_e)^{1/2} / 2$$

$$\mathbf{pH = -log\ [H_3O^+] = -log\ (c + 4k_e)^{1/2} / 2}$$

Example:

1-Calculate the pH of a decimolar nitric acid solution at 25°C.

2-Calculate the pH of a 10^{-8} M nitric acid solution at 25°C.

Solution :

1-For C= 0,1 M ; then $C > 10^{-6.5}$ M ,So pH = -log C ==> **pH=1**

2- For C = 10^{-8} M ; then $C < 10^{-6.5}$ M .So the auto ionization of water cannot be neglected, as the quantity of H_3O^+ ions supplied by this reaction is no longer negligible.

The expression for the concentration of H_3O^+ ions is :

$$[H_3O^+] = (c + 4k_e)^{1/2} / 2$$

And the pH is: $pH = -\log [H_3O^+] = -\log (c + 4k_e)^{1/2} / 2$

NA : $pH = -\log [H_3O^+] = -\log (10^{-8} + 4 \times 10^{-14})^{1/2} / 2$

pH= 6.68

2-2 Case of a weak acid :

Consider a weak acid with a concentration of C_a

- Chemical reactions that take place:

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

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

- Chemical species present in solution:

$$AH ; A^- ; H_2O ; H_3O^+ ; OH^-$$

- Relationship between concentrations :

Law of mass action (**L. M .A**) : $K_e = [H_3O^+] [HO^-]$ ………. 1

$K_a = [H_3O^+] [A^-] / [AH]$ …….. 2

Material conservation (**M .C**): $[AH] + [A^-] = C$ …………..3

Electric neutrality (**E .N**): $[OH^-] + [A^-] = [H_3O^+]$ ………..4

According to equations 3 and 4 we have:

$[A^-] = [H_3O^+]-[OH^-]$ ==> $[A^-] = [H_3O^+]- (K_e / [H_3O^+])$

$[AH] = C - [A^-]$

$$\Longrightarrow \quad K_a = [H_3O^+]^2 - k_e \,/\, C - ([H_3O^+] - (K_e / [H_3O^+]))$$

$$\Longrightarrow \quad \mathbf{[H_3O^+]^3 + Ka \times [H_3O^+]^2 - (Ka \times Ca + Ke) \times [H_3O^+] - KaKe = 0}$$

The result is an equation that is not easy to solve, hence the need for approximations.

- **Approximations:**

Approximation 1 :

The medium can be sufficiently acidic to neglect water autoprotolysis:

$$[OH^-] \ll [H_3O^+]$$

Approximation 2 :

Case where the acid is weakly ionized: $[A^-] \ll [AH]$, to be able to make this approximation, we need to check that:

$$\mathbf{K_a/c \leq 10^{-2} M^{-1}}$$

So if we apply these approximations we get:

$$[A-] = [H_3O^+] - [OH^-] \quad \Longrightarrow \quad [A^-] \approx [H_3O^+]$$

$$[AH] = C - [A^-] \quad \Longrightarrow \quad [AH] \approx C$$

So if we replace the acidity constant in the expression, we get :

$$Ka = [H_3O^+]^2/c$$

$$[H_3O^+] = (k_a \times c)^{1/2}$$

So; $pH = -\log [H_3O^+] \Longrightarrow \quad pH = -\log (k_a \times c)^{1/2}$

$$pH = -1/2 (\log k_a + \log c) \Longrightarrow \mathbf{pH = 1/2 (pk_a - \log c)}$$

Case where the acid is not weakly ionized:

$$\mathbf{K_a/c > 10^{-2} M^{-1}}$$

Approximation 2 is no longer legitimate. And we have:

$[A-] \approx [H_3O^+]$ is still valid as the medium is assumed to be sufficiently acidic

$$[AH] = C - [A-] \quad \Longrightarrow [AH] = C - [H_3O^+]$$

Then:

$$Ka = [H_3O^+]^2/(c-[H_3O^+])$$

Either, $$\mathbf{[H_3O^+]^2 + [H_3O^+] - Ka \times C = 0}$$

Resolution of this equation gives us the expression for the concentration of $[H_3O^+]$ ions.

$$[H_3O^+] = -k_a + (k^2_a + 4k_aC)^{1/2} / 2$$

$$\mathbf{pH = -log[H_3O^+] = -log(\,-k_a + (k^2_a + 4k_aC)^{1/2} / 2)\ ;}\quad \text{Si}\quad \mathbf{K_a/C > 10^{-2}M^{-1}}$$

Example :

-Calculate the pH of an aqueous hydrofluoric acid solution of concentration:

1- C = 10^{-1}M

2- C = 10^{-3}M

We have at 25°C, pKa (HF/F^-) = 3,2 , pKe = 14.

Solution

-For C=10^{-1} M.

1- Chemical reactions that take place:

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

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

2- Chemical species in solution :

$$HF\ ;\ F^-\ ;\ H_2O\ ;\ H_3O^+\ ;\ OH^-$$

3- Relationship between concentrations :

L .M.A: $$Ke = [H_3O^+][OH^-]$$

$$Ka = [H_3O^+][F^-]/[HF]$$

M .C : $$C = [F^-]+[HF]$$

E .N : $$[H_3O^+] = [F^-] + [OH^-]$$

Approximation 1 : the medium is sufficiently acidic, so : $[F^-] \ll [H_3O^+]$.

Approximation 2 : We calculate the ratio: ka/C

NA : $k_a/C = 10^{-3.2}/10^{-1} = 10^{-2.2}$

When ; $ka/C = 10^{-2.2}$ => $ka/C \leq 10^{-2}\ M^{-1}$

So the expression for pH is :

$$\mathbf{pH = 1/2(\,pk_a - \log C) \Rightarrow pH = 2.1}$$

-For C = 10^{-3} M.

We calculate the ratio : ka/c

$$Ka/c = 10^{-3.2}/10^{-3} = 10^{-0.2}$$

$$Ka/c = 10^{-0.2} > 10^{-2} M^{-1}$$

So the expression for pH is :

$$\mathbf{pH = -\log(\,-k_a + (k_a^2 + 4k_aC)^{1/2}/\,2)}$$

NA : => $\mathbf{pH = -\log(10^{-3.2} + ((10^{-6.4} + 4x10^{-6.2})^{1/2}/2)}$ => **pH =….**

Example 2 : (homework)

We Consider a weak acid solution of initial concentration C0, and Ka. Without making any approximations, establish the equation in $[H_3O^+]$, the solution of which would express the pH of the solution as a function of C_0 , Ka and Ke.

2-3 Case of weak base

1/ $B + H_2O \rightarrow BH^+ + OH^-$

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

2/

L. M. A: $Ke = [H_3O^+]\,[OH^-]$ …..1

M .C: $C = [BH^+] = [B]$

E.N : $[H_3O^+] + [BH^+] = [OH^-]$

1…………..$Ke/\,[OH^-] = [H_3O^+]$ $Ke/\,[OH^-] + c = [OH^-]$

⇨ $[OH^-]^2 - c\,[OH^-] - Ke = 0$

The auto ionization of water is also neglected if the base concentration is not very low ($C > 10^{-6.5}$ M).

We have ;

$$pOH + pH = 14 \text{ , et } pOH = -\log C$$

So, $$pH = 14 - pOH \Rightarrow \mathbf{pH = 14 + \log C}$$

If the base concentration is very low ($C < 10^{-6.5}$ M), we need to take into account the self-ionization of the water: we need to solve the 2nd degree equation:

$$[OH^-]^2 - c\,[OH^-] - Ke = 0$$

$$[OH^-] = [(c + (c^2+4ke)^{1/2})/2]$$

$$\mathbf{pH = 14 - pOH = 14 + \log [(c + (c^2+4ke)^{1/2})/2]}$$

$$\mathbf{pH = 14 + \log [(c + (c^2+4ke)^{1/2})/2]}$$

Example :

The NaOH solution has a concentration of $C = 10^{-8}$ mol.l-1, the concentration of OH^- ions is 1.051×10^{-7} M the pH of the solution is pH = 14 – p OH = 7.02

2-4 Case of weak bases.

Consider, B: is a weak base with initial concentration $[B]_0 = C$.

$$B + H_2O \Longleftrightarrow BH^+ + OH^- \qquad [B]o = C$$

$$2H_2O \Longleftrightarrow H_3O^+ + OH^-$$

Law of mass action:

$$K_b = [OH^-][BH^+] / [B]$$

Elecroneutrality: $[BH+] = [OH^-]$ the medium is basic, so we neglect the H3O+ ions coming from the water.

M .C : $$C = [BH^+] + [B] \text{ ;}$$

-IF: $\mathbf{K_b/C > 10^{-2}}$ (the base is strongly dissociated) so the concentration of $[BH^+]$ cannot be neglected in front of [B].

M. C: $[B] = C - [BH^+] \Rightarrow [B] = C - [OH^-]$

$\Rightarrow$ $K_b = [OH^-]^2 / C - [OH^-]$

$\Rightarrow$ $[OH^-]^2 + K_b[OH^-] - K_bC = 0$

Resolution of this equation gives us the expression for the concentration of $[OH^-]$ ions:

$$[OH^-] = -k_b + (k^2_b + 4k_bC)^{1/2} / 2$$

$$pOH = -\log(-k_b + (k^2_b + 4k_bC)^{1/2} / 2)$$

$$pH = 14 + \log(k_b + (k^2_b + 4k_bC)^{1/2} / 2)$$

$$\mathbf{pH = 14 + \log(k_b + (k^2_b + 4k_bC)^{1/2} / 2).}$$

-If : $\mathbf{K_b/C \leq 10^{-2}}$ (the base is weakly dissociated), then the concentration of [BH+] can be neglected in front of [B].

M .C: $C = [B] + [BH^+] \Rightarrow [B] = C$

$\Rightarrow$ $K_b = [OH^-]^2 / C$

$$C \times K_b = [OH^-]^2 \Rightarrow [OH^-] = (C \times K_b)^{1/2}$$

$$-\log [OH^-] = -\log(C \times K_b)^{1/2}$$

$$pOH = -\log(C \times K_b)^{1/2} \Rightarrow pOH = 1/2(-\log C - \log K_b)$$

$$pOH = ½ (pK_b - \log C)$$

$$\mathbf{pH = 14 - ½\, pK_b + ½ \log C}$$

3-Buffering solutions.

3-1 Definition of BS.

A buffer solution is a mixture of a weak acid HA and its weak conjugate base A- in equal or similar proportions.

3-2 Buffer properties.

A buffer solution is characterized by a constant pH. It is used to fix the pH of a reaction medium.

3-2 Preparation of the BS.

-By mixing adjacent concentrations of a weak acid (CH_3COOH) and a salt of its conjugate base (CH_3COONa).

-By mixing adjacent concentrations of a weak base (NH_3) and a salt of its conjugate acid (NH_4Cl).

3-3 Calculating the pH of BS

Species HA and A^- are in equilibrium:

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

$$K_a = [H_3O^+]\,[A^-] / [AH]$$

So, the expression of $[H_3O^+]$ is:

$$[H_3O^+] = K_a\,[AH] / [A^-]$$

$$-\log [H_3O^+] = -\log(K_a\,[AH] / [A^-])$$

$$pH = -\log K_a - \log([AH] / [A^-])$$

$$pH = pK_a + \log([A^-]/[AH])$$

Witch ;

$$\mathbf{pH = pK_a + \log([Base]/[Acid])}$$

If ; $[Base] = [Acid]$ **=>** $\mathbf{pH = pK_a}$

4- Acid-base titrations.

Homework n 1: Titration of a strong acid with a strong base.

Homework n 2: Titration of a weak acid with a strong base.