

CHAPTER II:

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CHAPTER II :
ACID-BASE REACTIONS

1-Definitions**1-1-ARRHENIUS definition**

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



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

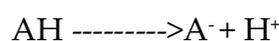


This theory doesn't explain why NH₃ in water is basic when it contains no OH group. It is therefore generalized by **BRONSTED**.

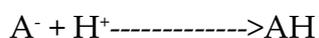
1-2-BRONSTED definition

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:



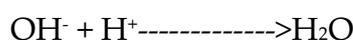
A base: is a chemical species, ion or molecule, which can accept (bind) an H⁺ proton:



Or;

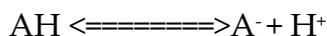


It should be noted that compounds such as NaOH, KOH, ... , in water dissociate to give OH⁻ ions, which are bases since they can bind a proton:



1-3- Conjugated acid-base pairs

Let's consider the following reaction,



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.

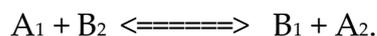
These are compounds which, depending on the nature of the medium, can donate or capture an H⁺ proton, and therefore behave like acids or bases.

Example:

H₂O is the acid in the H₂O/OH⁻ couple. $\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$

H₂O is the base in the H₃O⁺/H₂O couple. $\text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{O} + \text{H}^+$

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.

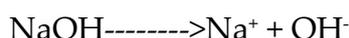


1-3-2 Strength of acids and bases

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

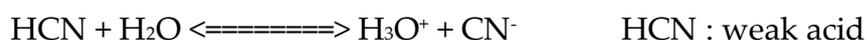
a-Strong acids and strong bases

These are strong electrolytes: the dissociation reaction is total.



b-Weak acids and bases

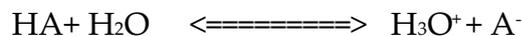
These are weak electrolytes. The dissociation equilibrium is clearly in favor of the reverse reaction.





1-3-2 Acidity and basicity constants.

HA is a weak acid.



Using the law of mass action, we can write:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Where $[H_2O] K_c = \frac{[H_3O^+][A^-]}{[HA]}$

We have then, $K_a = \frac{[H_3O^+][A^-]}{[HA]}$

$$K_a = \frac{[H_3O^+][\text{base}]}{[\text{acid}]}$$

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

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

$$pK_a = -\log K_a.$$

Note that, a solution is more acidic => K_a is larger and its pK_a 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⁻ :



$$K_b = \frac{[OH^-][HA]}{[A^-]}$$

$$K_b = \frac{[OH^-][\text{acid}]}{[\text{base}]}$$

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 K_e water**, and its value depends solely on temperature.

$$K_e = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \quad \text{at } 25^\circ\text{C}$$

With,

$$pK_e = -\log K_e = 14$$

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 :

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

and,

$$pK_a + pK_b = 14.$$

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^- ($pK_{a1} = 3,2$) and $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ ($pK_{a2} = 4.8$).

$pK_{b1} = 14 - 3,2 = 10,8$ 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 CH_3COO^- 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.

-K_a and pK_a of common acid/base pairs in aqueous solution at 25°C

Acid	HF	HNO ₂	HCOOH	CH ₃ OOH	H ₂ S	HClO	HCN	CH ₃ NH ₃ ⁺
Base conj	F ⁻	NO ₂ ⁻	HCOO ⁻	CH ₃ OO ⁻	HS ⁻	ClO ⁻	CN ⁻	CH ₃ NH 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:

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

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

$$0 < \alpha < 1$$

-For a strong electrolyte, α is close to 1.

-For a weak electrolyte, α is less than 1.

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



$$K_a = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}] \implies K_a = \alpha C \times \alpha C / C(1-\alpha)$$

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

Therefore, ($\alpha^2 / (1-\alpha)$) decreases => α : decreases

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

Therefore, ($\alpha^2 / (1-\alpha)$) 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 :

$$\text{pH} = -\log [H_3O^+]$$

❖ Neutral solution $[H_3O^+] = [OH^-] \rightarrow [H_3O^+]^2 = 10^{-14}$, $[H_3O^+] = 10^{-7} \text{ mol/L}$ and $\text{pH} = 7$

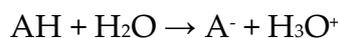
❖ acid Solution $[H_3O^+] > [OH^-] \implies \text{pH} < 7$

❖ base Solution $[H_3O^+] < [OH^-] \implies \text{pH} > 7$

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 :**



➤ **Chemical species present in solution :**



➤ **Relationship between concentrations :**

Law of mass action: $K_e = [H_3O^+] [OH^-]$

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

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

We obtain the equation:

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

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

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

➤ **Calculations**

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

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:

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

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

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

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 $C = 0,1 \text{ M}$; then $C > 10^{-6.5} \text{ M}$,So $\text{pH} = -\log C \implies \text{pH}=1$

2- For $C = 10^{-8} \text{ M}$; then $C < 10^{-6.5} \text{ M}$.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 :

$$[\text{H}_3\text{O}^+] = (c + 4k_e)^{1/2} / 2$$

And the pH is: $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (c + 4k_e)^{1/2} / 2$

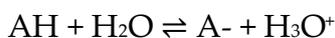
NA : $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (10^{-8} + 4 \times 10^{-14})^{1/2} / 2$

$$\text{pH} = 6.68$$

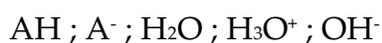
2-2 Case of a weak acid :

Consider a weak acid with a concentration of C_a

- Chemical reactions that take place:



- Chemical species present in solution:



- Relationship between concentrations :

Law of mass action (L . M .A) : $K_e = [\text{H}_3\text{O}^+] [\text{OH}^-] \dots\dots\dots 1$

$K_a = [\text{H}_3\text{O}^+] [\text{A}^-] / [\text{AH}] \dots\dots\dots 2$

Material conservation (M .C): $[\text{AH}] + [\text{A}^-] = C \dots\dots\dots 3$

Electric neutrality (E .N): $[\text{OH}^-] + [\text{A}^-] = [\text{H}_3\text{O}^+] \dots\dots\dots 4$

According to equations 3 and 4 we have:

$$[\text{A}^-] = [\text{H}_3\text{O}^+] - [\text{OH}^-] \implies [\text{A}^-] = [\text{H}_3\text{O}^+] - (K_e / [\text{H}_3\text{O}^+])$$

$$[\text{AH}] = C - [\text{A}^-]$$

$$\implies K_a = \frac{[\text{H}_3\text{O}^+]^2 - k_e / C - ([\text{H}_3\text{O}^+] - (K_e / [\text{H}_3\text{O}^+]))}{[\text{H}_3\text{O}^+]}$$

$$\implies [\text{H}_3\text{O}^+]^3 + K_a[\text{H}_3\text{O}^+]^2 - (K_a C + K_e)[\text{H}_3\text{O}^+] - K_e = 0$$

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:

$$[\text{OH}^-] \ll [\text{H}_3\text{O}^+]$$

Approximation 2 :

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

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

So if we apply these approximations we get:

$$[\text{A}^-] = [\text{H}_3\text{O}^+] - [\text{OH}^-] \implies [\text{A}^-] \approx [\text{H}_3\text{O}^+]$$

$$[\text{AH}] = C - [\text{A}^-] \implies [\text{AH}] \approx C$$

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

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{c}$$

$$[\text{H}_3\text{O}^+] = (k_a \times c)^{1/2}$$

So; $\text{pH} = -\log [\text{H}_3\text{O}^+] \implies \text{pH} = -\log (k_a \times c)^{1/2}$

$$\text{pH} = -1/2 (\log k_a + \log c) \implies \text{pH} = 1/2 (\text{p}k_a - \log c)$$

Case where the acid is not weakly ionized:

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

Approximation 2 is no longer legitimate. And we have:

$[\text{A}^-] \approx [\text{H}_3\text{O}^+]$ is still valid as the medium is assumed to be sufficiently acidic

$$[\text{AH}] = C - [\text{A}^-] \implies [\text{AH}] = C - [\text{H}_3\text{O}^+]$$

Then:

$$K_a = [\text{H}_3\text{O}^+]^2 / (c - [\text{H}_3\text{O}^+])$$

Either,

$$[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+] - K_a \times C = 0$$

Resolution of this equation gives us the expression for the concentration of $[\text{H}_3\text{O}^+]$ ions.

$$[\text{H}_3\text{O}^+] = \frac{-K_a + (K_a^2 + 4K_a C)^{1/2}}{2}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{-K_a + (K_a^2 + 4K_a C)^{1/2}}{2}\right); \text{ Si } K_a/C > 10^{-2} \text{M}^{-1}$$

Example :

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

1- $C = 10^{-1} \text{M}$

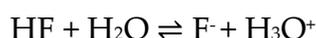
2- $C = 10^{-3} \text{M}$

We have at 25°C, $\text{p}K_a (\text{HF}/\text{F}^-) = 3,2$, $\text{p}K_e = 14$.

Solution

-For $C=10^{-1} \text{M}$.

1- Chemical reactions that take place:



2- Chemical species in solution :



3- Relationship between concentrations :

L .M.A: $K_e = [\text{H}_3\text{O}^+] [\text{OH}^-]$

$$K_a = \frac{[\text{H}_3\text{O}^+] [\text{F}^-]}{[\text{HF}]}$$

M .C : $C = [\text{F}^-] + [\text{HF}]$

E .N : $[\text{H}_3\text{O}^+] = [\text{F}^-] + [\text{OH}^-]$

Approximation 1 : the medium is sufficiently acidic, so : $[\text{F}^-] \ll [\text{H}_3\text{O}^+]$.

Approximation 2 : We calculate the ratio: k_a/C

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

$$\text{When ;} \quad k_a/C = 10^{-2.2} \Rightarrow k_a/C \leq 10^{-2} \text{ M}^{-1}$$

So the expression for pH is :

$$\text{pH} = 1/2(\text{pk}_a - \log C) \Rightarrow \text{pH} = 2.1$$

-For $C = 10^{-3} \text{ M}$.

We calculate the ratio : k_a/c

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

$$K_a/c = 10^{-0.2} > 10^{-2} \text{ M}^{-1}$$

So the expression for pH is :

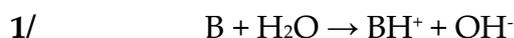
$$\text{pH} = -\log(-k_a + (k_a^2 + 4k_a C)^{1/2} / 2)$$

$$\text{NA :} \quad \Rightarrow \text{pH} = -\log(10^{-3.2} + ((10^{-6.4} + 4 \times 10^{-6.2})^{1/2} / 2)) \Rightarrow \text{pH} = \dots$$

Example 2 : (homework)

We Consider a weak acid solution of initial concentration C_0 , and K_a . Without making any approximations, establish the equation in $[\text{H}_3\text{O}^+]$, the solution of which would express the pH of the solution as a function of C_0 , K_a and K_e .

2-3 Case of weak base



2/

$$\text{L. M. A:} \quad K_e = [\text{H}_3\text{O}^+] [\text{OH}^-] \dots\dots 1$$

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

$$\text{E.N :} \quad [\text{H}_3\text{O}^+] + [\text{BH}^+] = [\text{OH}^-]$$

$$1 \dots\dots\dots K_e / [\text{OH}^-] = [\text{H}_3\text{O}^+] \quad K_e / [\text{OH}^-] + c = [\text{OH}^-]$$

$$\Leftrightarrow [\text{OH}^-]^2 - c [\text{OH}^-] - K_e = 0$$

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:

$$[OH^-]^2 - c [OH^-] - K_e = 0$$

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

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

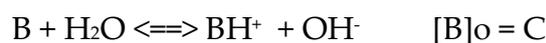
$$\mathbf{pH = 14 + \log [(c + (c^2 + 4K_e)^{1/2})/2]}$$

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 $pH = 14 - pOH = 7.02$

2-4 Case of weak bases.

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



Law of mass action:

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

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

M.C :

$$C = [BH^+] + [B] ;$$

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

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

$$\Rightarrow \quad K_b = [\text{OH}^-]^2 / \text{C} - [\text{OH}^-]$$

$$\Rightarrow \quad [\text{OH}^-]^2 + K_b[\text{OH}^-] - K_b\text{C} = 0$$

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

$$[\text{OH}^-] = \frac{-K_b + (K_b^2 + 4K_b\text{C})^{1/2}}{2}$$

$$\text{pOH} = -\log\left(\frac{-K_b + (K_b^2 + 4K_b\text{C})^{1/2}}{2}\right)$$

$$\text{pH} = 14 + \log\left(\frac{K_b + (K_b^2 + 4K_b\text{C})^{1/2}}{2}\right)$$

$$\text{pH} = 14 + \log(K_b + (K_b^2 + 4K_b\text{C})^{1/2} / 2).$$

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

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

$$\Rightarrow \quad K_b = [\text{OH}^-]^2 / \text{C}$$

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

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

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

$$\text{pOH} = 1/2 (\text{p}K_b - \log\text{C})$$

$$\text{pH} = 14 - 1/2 \text{p}K_b + 1/2 \log\text{C}$$

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.

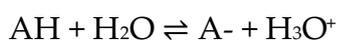
3-2 Preparation of the BS.

-By mixing adjacent concentrations of a weak acid (CH₃COOH) and a salt of its conjugate base (CH₃COONa).

-By mixing adjacent concentrations of a weak base (NH₃) and a salt of its conjugate acid (NH₄Cl).

3-3 Calculating the pH of BS

Species HA and A⁻ are in equilibrium:



$$K_a = [\text{H}_3\text{O}^+] [\text{A}^-] / [\text{AH}]$$

So, the expression of [H₃O⁺] is:

$$[\text{H}_3\text{O}^+] = K_a [\text{AH}] / [\text{A}^-]$$

$$-\log [\text{H}_3\text{O}^+] = -\log(K_a [\text{AH}] / [\text{A}^-])$$

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

$$\text{pH} = \text{p}K_a + \log ([\text{A}^-] / [\text{AH}])$$

Witch ;

$$\text{pH} = \text{p}K_a + \log ([\text{Base}] / [\text{Acid}])$$

If ;

$$[\text{Base}] = [\text{Acid}] \Rightarrow \text{pH} = \text{p}K_a$$

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.