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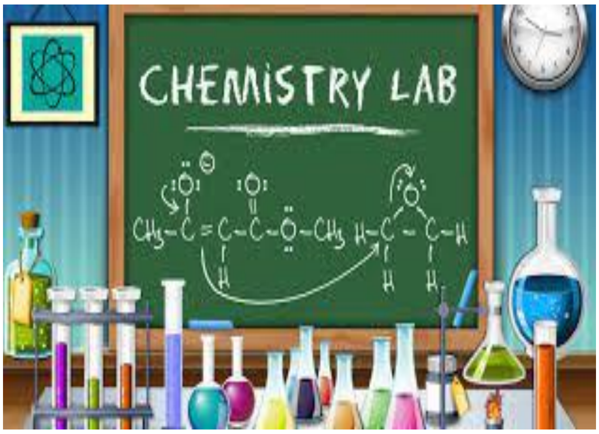
# Chemistry of Solutions *Lessons*



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# INTRODUCTION

**This handout has been specifically prepared for second-year students in Process Engineering under the LMD system.**

**We hope it will contribute, even in a small way, to clarifying some topics in solution chemistry for this group. The handout consists of five chapters, each containing a lecture along with solved examples for better understanding. It serves as a guide to help students grasp complex concepts and solve scientific problems they may encounter.**

**Our goal is to provide an effective educational tool that enables university students to acquire valuable scientific knowledge that they can rely on in their field of study.**

**We hope this modest effort will be a useful addition to the academic library and that it will be well-received by students, especially those in technical sciences. We also welcome any feedback or suggestions from readers, with our sincere thanks and appreciation.**

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# CHAPTER I:

# BACKGROUND AND GENERAL INFORMATION

*This chapter provides fundamental definitions and general information related to chemical solutions. It begins with key definitions, followed by an exploration of solutions and the concentration of species within them. The concept of volumic mass is introduced, highlighting its significance in determining solution properties. Density, an essential parameter for comparing substances, is also discussed. Finally, different ways of expressing the composition of a solution, such as percentage and fraction, are covered. These foundational concepts are crucial for understanding solution behavior in various scientific.*

## 1-Definitions

### 1-1-Solution

A solution can be defined as a homogeneous mixture in which the constituents are divided and dispersed within each other at the molecular level. A solution always consists of :

-a solvent (majority constituent),

-one or more solutes.

Liquid solutions (called aqueous solutions when the solvent is water).

Solutes can be :

-a gas: ($CO_2$ , $O_2$, $N_2$, etc.)

-a liquid: HCl, $H_2SO_4$, ……

-a solid: NaCl, KCl, KOH, NaOH, ……

### 1-2-Concentration of a species in solution:

A distinction is made between:

#### 1-2-1 Molar concentration, Cn :

The molar concentration of a chemical species in solution $C_A$ is the quantity of this species present in one liter of solution.

$$C_A = n_A/V_{sol} \quad (mol/l)$$

**Where:** $n_A$ is the quantity of A in solution and $V_{sol}$ is the volume of the solution.

**- Preparation of aqueous solutions**

**Case1: From a solid :**

A volume V of a solution containing species X, of molar mass M(x), at concentration [X]= $C_X$, is to be prepared. We need to determine the mass m(x) of species X to be weighed.

Therefore ;

$$\Rightarrow \; n(x) = m(x) / M(x)$$

$$C_x = n_x/V_{sol} \Rightarrow Cx = m(x)/M(x) * V_{sol}$$

**Example:**

Calculate the mass of NaOH needed to prepare 50 mL of a 0.01M solution.

M(NaOH) = 40 g/mol.

**Solution:**

We have:

$$\Rightarrow \; n(NaOH) = m(NaOH) / M\ NaOH)$$

$$C_{NaOH} = n_{NaOH} / V_{sol} \Rightarrow C_{NaOH} = m(NaOH) / M(NaOH) * V_{sol}$$

$$m(NaOH) = M(NaOH) \times C(NaOH) \times V_{sol}$$

$$AN: \; m(NaOH) = 40 \times 50 \times 10^{-3} \times 0{,}01$$

$$\mathbf{m(NaOH) = 2 \times 10^{-2} g} = 0.02 g$$

**Case2: dissolving a gas**

V(G) the volume of gas to be dissolved, V the volume of the solution, Vm the molar volume of the gases under the conditions of the experiment, n(G) the quantity of gas and [G] the molar concentration of the gas in the solution.

We have :

$$n_{gaz} = V_{gaz} / Vm \quad (Vm=22.4 \text{ litre})$$

$$C_{gaz} = n_{gaz} / (V\,sol * Vm)$$

$$C_{gaz} = n_{gaz} / (V\,sol * 22.4)$$

**Example:**

We dissolve 20 cm$^3$ $NH_3$ gas in 500 ml of water.

-Calculate the $NH_3$ concentration ?

**Solution:**

From the previous expression we can write:

We have:

$$n_{NH3} = V_{NH3} / Vm$$

$$C_{NH3} = n_{NH3} / (V\,sol * Vm)$$

$$C_{NH3} = n_{NH3} / (V\,sol * 22.4)$$

NA : $$C_{NH3} = 20*10^{-3} / (500*10^{-3} * 22.4)$$

$$\mathbf{C_{NH3} = 1.78 * 10^{-3}\ mol/l}$$

**Case3: From a liquid compound**

A volume $V_0$ of the stock solution of concentration $C_0$ is taken and diluted with distilled water to obtain a dilute solution of volume $V_1$ and desired concentration $C_1$.

**Determining the volume $V_0$ to be withdrawn**

The quantity of solute in volume $V_0$ is:

$$n(X) = C_0 * V_0$$

This quantity of matter remains in the solution after dilution. This reflects the conservation of matter:

$$n(X) = C_1 * V_1$$

And the dilution relation is :

$$C_0 * V_0 = C_1 * V_1$$

Therefore ; ;

$$V_0 = (C_1 * V_1) / C_0$$

During dilution, the dilution factor is the ratio of the concentration of the mother solution (initial) to that of the solution obtained (final):

$$F = C_{initial} / C_{final}$$

Or ;

$$F = C_0 / C_1$$

**Example:**

Take a volume V0 = 20 mL of an aqueous copper II sulfate solution of concentration $C_0 = 5\times10^{-2}$ mol/L. This volume is introduced into a 0.5L volumetric flask, and then made up to the mark with distilled water.

A-What is the concentration of the solution obtained?

B-Calculate the dilution factor F.

**Solution :**

A- The concentration of the resulting solution $C_1$:

We know that the concentration of solution $C_1$ and that of the stock solution $C_0$ are linked by the dilution relationship

$$C_0 * V_0 = C_1 * V_1$$

Where $V_0$ and $V_1$ denote the initial and final volumes of solution, respectively.

$$\mathbf{C_1 = (C_0 * V_0) / V_1}$$

**NA :** $C_1 = (0.05 * 0.02) / 0.5$

$$\mathbf{C_1 = 2 * 10^{-3}\ mol/l}$$

B- Calculation of the dilution factor F:

Recall that ;

$$\mathbf{F = C_0 / C_1}$$

$$\mathbf{F = 5*10^{-2} / 2*10^{-3}}$$

$$\mathbf{F = 25}$$

**1-2-2 Mass concentration, Cmass :**

This is the ratio of the mass of compound **X** contained in a certain volume of solution divided by that volume of solution. Mass is expressed in **g** and volume is often expressed in **L**.

$$\mathbf{C_{mass} = m(x) / v(sol)}$$

**Example :**

We dissolve 5 g of copper sulfate (**$CuSO_4$**) in 400 mL of water. What is the mass concentration of copper sulfate?

We have: m(CuSO4) = 5g, V= 400 mL

**Solution :**

$$C_{mass} = m(CuSO4) / v(sol)$$

AN : $C_{mass} = 5 / (400 * 10^{-3})$

$$\mathbf{C_{mass} = 12.5\ g/L}$$

**1-2-3-Molar concentration (molality) ,Cm :**

This corresponds to the quantity of compound **X** per 1 kg of solvent.

$$C_m = n(CuSO4) / m(solvent)(kg)$$

**1-2-4-Normal concentration (Normality) ,$C_N$ :**

The normality (or normal concentration) of a solution is the number of gram equivalents of solute contained in one liter of solution.

**The unit of normality is the gram equivalent per liter**, represented by the symbol $C_N$ :

$$C_N = néq / V\ (sol)$$

Normality is related to molarity by the equation :

$$C_N = Z * Cn$$

**-How to determine the Z parameter:**

*In the case of an acid: **Z** is the number of $H^+$ protons.

* In the case of a base: **Z** is the number of $OH^-$ ions.

*In the case of a salt: **Z** is the number of cations * their charge.

*In the case of a redox reaction: **Z** is the number of electrons exchanged.

**Example :**

| **Compound** | **HCl** | **$H_2SO_4$** | **$H_3PO_4$** | **NaOH** | **NaCL** | **$Na_2CO_3$** |
|---|---|---|---|---|---|---|
| **Parameter Z** | **Z=1** | **Z=2** | **Z=3** | **Z=1** | **Z=1** | **Z=2** |

**3- Volumic mass**

The volumic mass of a solution is defined by the ratio of the mass of solution **m** (sol) to the total volume **V** (sol).

$$\rho(\textbf{solution}) = \mathbf{m}(\text{ solution }) / \mathbf{v}\ (\text{solution })$$

**4- Density**

**-For a liquid :**

Density is the ratio of solution density to water density.

$$\mathbf{d(solution)} = \rho\ (\text{ solution }) / \rho\ (\text{water })$$

**-For a gas :**

Density is the ratio of gas Volumic mass to air density.

$$\mathbf{d(gas)} = \rho\ (\text{ gas}) / \rho\ (\text{air })$$

When , $\mathbf{d(gas)} = \mathbf{M}\ (\text{gas})/29$

**5-Percentage or Fraction**

**5-1-Percentage or mass fraction, w(%) :**

The mass percentage or mass fraction of a solute $\mathbf{w_x(\%)}$ in solution is the quotient of the mass of this solute **m(X)** dissolved in one liter of solution by the mass of one liter of solution **m(sol).**

$$w_x(\%) = (\mathbf{m}(\mathbf{X}) / \mathbf{m}\ (\mathbf{sol})) * 100$$

**Example :**

An ammonia solution with density 0.910 and concentration C=12.8 mol/L $NH_3$. Calculate the mass fraction of water and $NH_3$. The density of the solution is 0.910.

Knowing that: $\rho$ (water) = 1 g/cm$^3$.

**Solution :**

$$\mathbf{d}\ (\text{solution}) = \mathbf{0.910} = \rho\ (\text{solution}) / \rho\ (\text{water})$$

We have : $1cm^3 = 1\ ml = 10^{-3}L$

Wherefore,

$$\rho\ (\text{water}) = 1\ g/cm^3 \Rightarrow \rho\ (\text{water}) = 1000\ g/l.$$

Then ,

$$\mathbf{0.910} = \rho\ (\text{solution})\ \mathbf{/1000}$$

$$\Rightarrow \rho\ (\text{solution}) = \mathbf{910\ g/L}$$

If we consider one liter of solution (V(sol) = 1L) it weighs 910 g of solution that's to say: m (sol)=910g

in addition, 1L of solution -----------> $n(NH_3)$=12,8 mol de $NH_3$

wherefore ; $m(NH_3) = n(NH3) \times M(NH_3) = 12{,}8 \times 17 = 217{,}6$ g

=> $m(H_2O) = 910 - m(NH_3) = 692{,}4$ g.

Then ;

$$w_{NH3}(\%) = (\mathbf{m}(NH_3) / \mathbf{m}\ (\mathbf{sol})) * 100$$

$$w_{NH3}(\%) = (217.6 / 910 * 100$$

$$w_{NH3}(\%) = 24\%$$

And ;

$$w_{H20}(\%) = (\mathbf{m}(H_2O) / \mathbf{m}\ (\mathbf{sol})) * 100$$

$$w_{H20}(\%) = 692.4 / 910.6 * 100$$

$$w_{H20}(\%) = 76\%$$

**5-2 Percentage or molar fraction (X) :**

The molar fraction of the solute is the ratio of the number of moles of solute n(x) to the total number of moles of solution n (T), where n (T) = n(solvent)+n(solute).

$$X(x) = n(x) / n_{(T)}$$

and ; $\Sigma Xi = 1$

**Example :**

Calculate the molar fraction of glycine in an aqueous solution of molality 14 mol/kg.

From the expression for molality, we can say that 1 kg of solvent ($H_2O$) contains 14 mol of glycine (**$C_2H_5NO_2$**).

that's to say:

$$n(glycine) = 14 \text{ mol}$$

whit, $m(H_2O)= 1kg=1000g$

First, we calculate the amount of water contained in one kilogram:

$$n\ (H_2O) = m(H_2O) / M\ (H_2O) = 1000g\ /18$$

$$n\ (H_2O) = 55.55 \text{ mol}$$

Wherefore, $n\ (totale) = n(glycine) + n\ (H_2O)$

NA : $n\ (totale) = 14+55.55$

$$n\ (totale) = 69.55 \text{ mol}$$

Molar fraction of glycine :

$$X(glycine)= n(glycine)\ /\ n_{(T)}$$

$$\Rightarrow \quad X(glycine)= 14\ /\ 69.55$$

$$\Rightarrow \quad X(glycine)= 0.2$$

Molar fraction of water:

$$X(glycine) + X(H_2O) =1$$

$$\Rightarrow \quad X(H_2O) =1- X(glycine)$$

$$\Rightarrow \quad X(H_2O) =1 -0.2$$

$$\Rightarrow \quad X(H_2O) = 0.8$$

# CHAPTER II :

# ACID-BASE REACTIONS

*This chapter explores different definitions of acids and bases, including the Arrhenius and Brønsted-Lowry concepts, and introduces conjugate acid-base pairs. It also delves into the determination of pH in aqueous solutions, the role of buffer solutions in maintaining pH stability, and the principles of acid-base titrations. Understanding these concepts is essential for analyzing chemical equilibrium, reaction mechanisms, and practical applications in laboratory.*

## 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.

$$HCl + H_2O \text{-------->} H_3O+ + Cl^-$$

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

**b-Weak acids and bases**

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

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

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

**1-3-2 Acidity and basicity constants.**

HA is a weak acid.

$$HA+ H_2O \quad <\text{=========}> \quad H_3O^+ + A^-$$

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.

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

With,

$$\mathbf{pke = -log\ ke = 14}$$

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,

$$\mathbf{pKa + pK_b = 14.}$$

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 $\alpha$ (dissociation rate or dissociated or ionized fraction) of this acid, without taking into account the dissociation equilibrium of water:

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

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

$$0<\alpha<1$$

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

-For a weak electrolyte, $\alpha$ 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 | $C(1-\alpha)$ | $\alpha C$ | | $\alpha C$ |

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

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

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

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

**Therefore,** ($\alpha^2$ / (1-$\alpha$)) increases => $\alpha$ : increases

Dilution increases electrolyte dissociation. At infinite dilution ($C_0 \rightarrow 0$), the ionization coefficient $\alpha$ increases and tends towards a limiting value $\alpha$ 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:

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

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

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

==> $\mathbf{[H_3O^+]^3 + Ka×[H_3O^+]^2 – (Ka×Ca + Ke)×[H_3O^+] – KaKe = 0}$

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:

$$[OH^-] << [H_3O^+]$$

**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:

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

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

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

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

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

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

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.

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

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

**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 :

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

*-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 :

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

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 ;

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

So, $pH=14- pOH$ => $\mathbf{pH = 14+ logC}$

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 $1.051\times10^{-7}$ 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 :** $C = [BH^+] + [B]$ ;

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

=> $K_b = [OH^-]^2 / C - [OH^-]$

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

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

=> $K_b = [OH^-]^2/ C$

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

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

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

$$pOH = ½ (pK_b - \log C )$$

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

**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.

# CHAPTER III:

## REDOX REACTIONS

*This chapter introduces key concepts such as oxidants, reductants, oxidation, and reduction. It covers oxidation numbers, which help in identifying redox processes, and explores redox potentials using the Nernst equation. Additionally, the chapter discusses methods for writing balanced redox reactions and examines electrochemical cells, with a focus on the Daniell cell as a fundamental example.*

### 1-General information.

### 1-1-Oxidant, reductant, oxidation, reduction.

- ✓ **An oxidant** is a compound capable of capturing electrons.

**Example :**

$Cu^{2+} + 2e^- \rightarrow Cu$ **$Cu^{2+}$** undergoes a reduction

- ✓ **An reductant** is a compound capable of yielding electrons.

**Example :**

$Cu \rightarrow Cu^{2+} + 2e^-$ **Cu** undergoes oxidation

**Oxidant** = e- acceptor , **Reducer** = e- donor

**Oxidation** = loss of e- , **Reduction** = gain of e-

Oxidation and reduction are reversible reactions:

oxidant + ne- <===> reducer

The species Ox is Red forms a redox couple: **Ox/Red**

**Example: Ox/Red pair**

| | |
|---|---|
| $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | $Fe^{3+}/Fe^{2+}$ |
| $Fe^{2+} + 2e^- \rightleftharpoons Fe$ | $Fe^{2+}/Fe$ |
| $Cu^{2+} + 2e^- \rightleftharpoons Cu$ | $Cu^{2+}/Cu$ |

### 1-2-Redox reaction

This involves two redox couples, as it consists in transferring electrons from the reducing agent of one couple to the oxidizing agent of the other:

$$Ox_1 + Red_2 <==> Red_1 + Ox_2$$

To equilibrate this reaction :

$$(Ox_1 + n1e^- <==> Red1) \times n_2 : \text{half-reaction 1}$$

$$(Red_2 <==> Ox2 + n2e^- ) \times n_1 : \text{half-reaction 2}$$

Global reaction (1+2) :

$$n_2Ox_1 + n_2n_1e^- + n_1 Red_2 <==> n_2Red_1 + n_1Ox_2 + n_1n_2e^-$$

**Example:** $Fe^{+3}/Fe^{+2}$, $Sn^{+4}/Sn^{+2}$

$$(Fe^{+3}+1é <===> Fe^{+2})x2 \text{ (reduction)}$$

$$(Sn^{+2} <===> Sn^{+4}+2é)x1 \text{(oxidation)}$$

Global reaction:

$$2Fe^{+3}+Sn^{+2} <===> Sn^{+4}+ 2Fe^{+2}$$

**2-Oxidation number (degree of oxidation)**

**2-1-Definition.**

The oxidation number (O.N.) of an atom represents the apparent elementary charge assigned to it according to certain conventional rules:

**a-**The oxidation number of the atoms of an element in the Free State is zero.

**Example :** Fe : O.N = 0 ; Cu : O. N = 0.

**b-**The oxidation number of an atom in the monoatomic ion state is equal to the charge of the ion.

**Example :**

| Element | $Sn^{2+}$ | $Fe^{3+}$ | $Sn^{4+}$ | $Fe^{2+}$ |
|---|---|---|---|---|
| | | | | |

| **O.N** | **2** | **3** | **4** | **2** |
|---|---|---|---|---|

**c-** When electrons are shared in covalent bonds between two atoms of different natures, they are allocated to the more electronegative atom.

**Example :**

| | **H-H** | **Cl-Cl** | **CO** | **$H_2S$** | **2H-Cl** |
|---|---|---|---|---|---|
| **O.N** | 0 0 | 0 0 | +2 -2 | +1 -2 | +1 -1 |

**d-** The algebraic sum of the oxidation numbers of the atoms in a (neutral) molecule is zero.

**Example :** $NH_3$ : ΣO.N = O.N (N) + 3 ×O.N (H) = 0

When ; O . N (N) = -3 à partir de (O .N (H) = +1)

**e-** For a polyatomic ion, the sum of the O .N of the atoms in the ion is equal to the total charge of the ion.

**Exemple:**

$CO_3^{2-}$ Σ O.N = -2 => O .N (C)+3× O .N (O)= -2 => O .N (C)=+4

$SO_4^{2-}$ Σ O.N = -2 => O .N (S)+4× O .N (O)= -2 => O .N (S)=+6

$PO_4^{3-}$ Σ O.N = -3 => O .N (P) +4× O .N (O)= -3 => O .N (P)=+5

**2-2-Oxidation number of some elements.**

-Fluorine: the most electronegative element: O .N = -1.

-Oxygen: the 2nd most electronegative element: O .N = -2, Sauf: $OF_2$ because F is more electronegative than O so O .N (O)=+2.

**-Alkali metals:** highly electropositive : O .N = +1, $Li^+$, $Na^+$, $K^+$,...

**-Alkaline earth metals:** electropositive : O .N = +2, $Mg^{2+}$, $Ba^{2+}$, $Ca^{2+}$, ...

**-Hydrogen:** electropositive element : O .N = +1.

**3-Redox potentials: Nernst equation**

**3-1-Normal (standard) potential**

The oxidising or reducing power of a chemical species is characterized by its redox potential E°. E° is measured under normal conditions of temperature and pressure (P = 1 atm, T = 25°C). It is given as **E° (Ox/red).**

By convention: E° ($H^+/H_2$) = 0 V.

All **E°** values are then referenced to **E° ($H^+/H_2$)**.

**Example :**

| **Redox pair** | **$Fe^{2+}/Fe$** | **$MnO_4^-/Mn^{2+}$** | **$Fe^{3+}/Fe^{2+}$** | **$Zn^{2+}/Zn$** | **$Cu^{2+}/Cu$** |
|---|---|---|---|---|---|
| **E° (V/ENH)** | - 0,44 | 1,51 | 0,77 | -0,76 | 0,34 |

**3-2-Nernst equation :**

The oxidising or reducing power of a species depends not only on E° but also on the concentrations in solution.

$$a\ Ox + n\acute{e} \Leftrightarrow b\ red$$

So ; $E_{ox/red} = E°_{ox/red} + RT/nF\ \ln([ox]^a/[red]^b)$ : Nernst equation

**n:** number of electrons involved at 25°C.

We can write:

$$E_{ox/red} = E°_{ox/red} + 0,06/n\ \log([ox]^a/[red]^b)$$

**Example :**

1) **$Fe^{2+}/Fe$ :** $Fe^{2+} + 2\acute{e} \Longleftrightarrow Fe$

$$E_{Fe^{2+}/Fe} = E°_{Fe^{2+}/Fe} + 0,06/2\ \log([Fe^{2+}]/[Fe])\ ;\quad [Fe]=1$$

⇨ $E_{Fe^{2+}/Fe} = E°_{Fe2+/Fe} + 0/03\ log\ [Fe^{2+}]$

**2) $MnO_4^-/Mn^{2+}$**

$$MnO_4^- + 8H^+ + 5é <===> Mn^{2+} + 4H_2O$$

$$E_{MnO4^-/Mn^{2+}} = E°_{MnO4^-/Mn^{2+}} + 0,06/5\ log\ ([MnO_4^-][H^+]^8 / [Mn^{2+}])$$

## 4-Writing redox reactions

-Let the redox couples be :

$$E°_{Fe^{3+}/Fe^{2+}} = 0,77 \text{ V/ENH and } E°_{MnO4^-/Mn^{2+}} = 1,51 \text{ V/ENH}$$

We note that: $E°_{MnO4^-/Mn^{2+}} > E°_{Fe^{3+}/Fe^{2+}}$

Possible half-reactions are:

$$(Fe^{+3}+1é <===>Fe^{+2})x5 \quad \text{(oxidation)}$$

$$(MnO_4^- + 8H^+ + 5é <===> Mn^{2+} + 4H_2O)x1 \quad \text{(reduction)}$$

Global reaction:

$$MnO_4^- + 8H^+ + 5Fe^{+3} <===> Mn^{2+} +5\ Fe^{+2}+4H_2O$$

### 4-1- Calculation of the equilibrium constant

Let the two redox couples $(Ce^{4+}/Ce^{3+})$ et $(Fe^{3+}/Fe^{2+})$:

$$E°(Ce^{4+}/Ce^{3+})=1,44 \text{ V /ENH et } E°(Fe^{3+}/Fe^{2+}) = 0,77 \text{ V/ENH}$$

We see that : $E°(Ce^{4+}/Ce^{3+}) > E°(Fe^{3+}/Fe^{2+})$

Possible half-reactions are :

$$Fe^{2+} <==> Fe^{3+}+1é \text{ (oxidation)…..1}$$

$$Ce^{4+}+1é <==> Ce^{3+} \text{ (reduction)……2}$$

Global reaction :

$$Ce^{4+}+Fe^{2+} <==> Fe^{3+}+ Ce^{3+}$$

Nersnt equations for the two redox couples :

- eq 1 : $E_{Fe^{+3}/Fe^{2+}} = E°_{Fe^{+3}/Fe^{2+}} + 0,06 \log([Fe^{3+}]/[Fe^{+2}])$
- eq 2 : $E_{Ce4+/Ce3+} = E°_{Ce4+/Ce3+} + 0,06 \log([Ce^{4+}]/[Ce^{3+}])$

When the reaction is complete **;**

$$\Delta E = 0 \implies E_{Ce4+/Ce3+} - E_{Fe^{+3}/Fe^{2+}} = 0$$

So ,

$$E°_{Fe^{+3}/Fe^{2+}} + 0,06 \log([Fe^{3+}]/[Fe^{+2}]) = E°_{Ce4+/Ce3+} + 0,06 \log([Ce^{4+}]/[Ce^{3+}])$$

$$\implies E°_{Ce4+/Ce3+} - E°_{Fe^{+3}/Fe^{2+}} = 0.06 \log k_c$$

$$\implies k_c = 10^{\Delta E°/0.06}$$

**NA :** $k_c = 1.47 \times 10^{11}$

**Kc** is very large, so the reaction is complete in direction (1).

**4-2-Redox dosage**

Oxidation-reduction reactions are often used to carry out assays. One of the solutions contains an oxidant and the other a reductant.

At equivalence the relation is : $N_{ox} \times V_{ox} = N_{red} \times V_{red}$

**Example 1 :**

**-Determination of a solution of $MnO_4^-$ by a solution of $Fe^{2+}$ ions in an acid medium.**

**Dosage reactions:**

$$(Fe^{+3} + 1é \Longleftrightarrow Fe^{+2}) x5 \text{ (oxidation)}$$

$$(MnO_4^- + 8H^+ + 5é \Longleftrightarrow Mn^{2+} + 4H_2O) x1 \text{(reduction)}$$

**Global reaction:** $MnO_4^- + 8H^+ + 5Fe^{+3} \Longleftrightarrow Mn^{2+} + 5 Fe^{+2} + 4H_2O$

**At equivalence point:**

$$N_{MnO4-} \times V_{MnO4-} = N_{Fe+2} \times V_{Fe+2} \ldots\ldots\ldots 1$$

Normality : $N = Z \times C_n$

$C_n$ : concentration in mol/l. , Z: number of electrons exchanged.

For : $MnO_4^-$ ==> Z = 5 donc ; $\mathbf{N}_{MnO4-} = \mathbf{5\ C}_{MnO4-}$

For : $Fe^{+2}$ ==> Z = 1 donc ; $\mathbf{N}_{Fe+2} = \mathbf{C}_{Fe+2}$

$$1 \iff 5C_{MnO4-} \times \mathbf{V}_{MnO4-} = \mathbf{C}_{Fe+2} \times \mathbf{V}_{Fe+2}$$

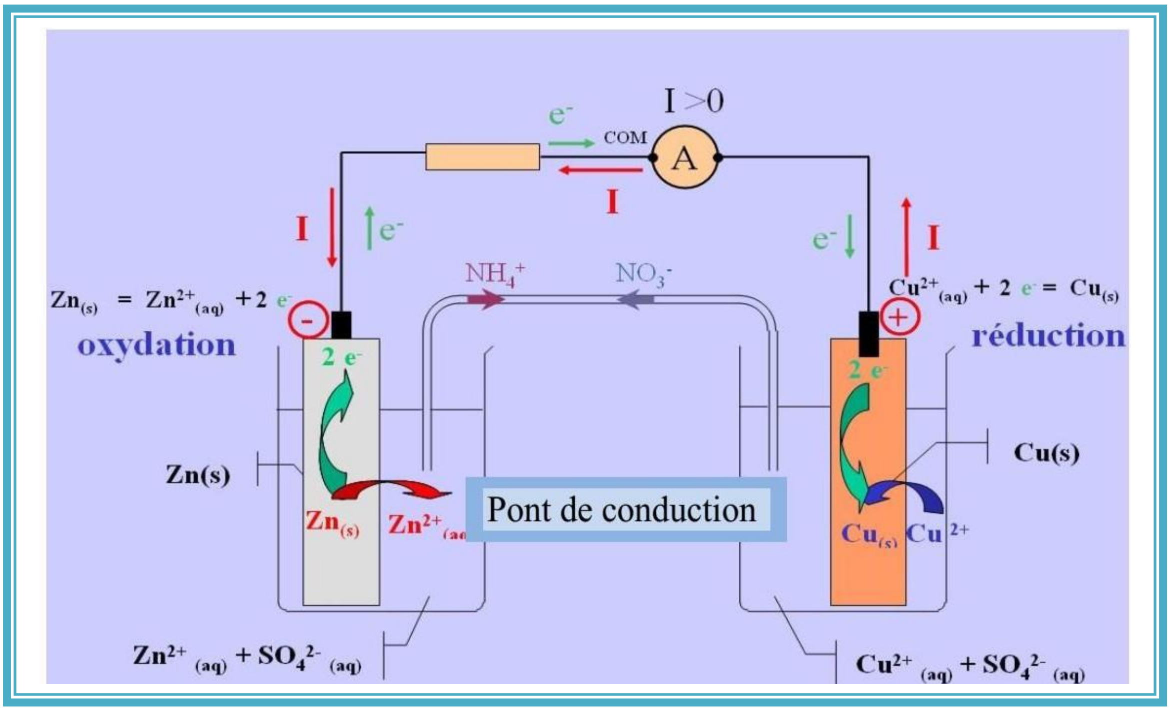
$$\Longrightarrow \mathbf{C}_{Fe+2} = 5C_{MnO4-} \times \mathbf{V}_{MnO4-} / \mathbf{V}_{Fe+2}$$

## 5-Electrochemical batteries - DANIELL battery.

### 5-1-Description

When redox reactions are spontaneous, it is possible to transfer electrons from the reducing agent to the oxidising agent via an external electrical circuit.

This is illustrated by the principle of the **DANIELL cell:**




**The Daniell cell has two compartments:**

**A left-hand compartment:** containing a zinc strip immersed in a zinc(II) sulphate solution;

**A right compartment:** which contains a copper plate immersed in a copper(II) sulphate solution.

The two plates are linked by an electric wire that allows electrons to circulate. The two solutions are linked by a salt bridge (conductive bridge or junction) which allows ions to circulate.

**We observe:**

-the gradual dissolution of the zinc layer;

-the deposition of copper on the copper plate.

Copper strip: Cathode (Reduction) : $Cu^{2+} + 2e^- \Longleftrightarrow Cu$ (Reduction)

Zinc strip: Anode (Oxidation) : $Zn \Longleftrightarrow Zn^{2+} + 2e^-$ (Oxidation)

Global reaction: $Cu^{2+} + Zn \Longleftrightarrow Zn^{2+} + Cu$

The electrons therefore flow from the zinc plate to the copper plate.

The direction of the current is opposite to the direction of the electrons: Direction of the current from the copper plate (+ pole) to the zinc plate (- pole).

The sulphate ions flow from the right-hand compartment (excess $SO_4^{2-}$ ) to the left-hand compartment (lack of $SO_4^{2-}$).

Representation of the **DANIELL** battery : **(-) Zn /Zn²⁺(aq) // Cu²⁺(aq) / Cu (+)**

**5-2- Calculating the e.m.f. of the battery**

Potential of the cathode:

$$E_c = E_{Cu^{2+}/Cu} = E°_{Cu^{2+}/Cu} + 0{,}03\ \log([Cu^{2+}] / [Cu])\ ;\quad [Cu]=1$$

Potential of the anode:

$$E_a = E_{Zn^{2+}/Zn} = E°_{Zn^{2+}/Zn} + 0{,}03\ \log([Zn^{2+}] / [Zn])\ ;\quad [Zn]=1$$

At equilibrium $\Delta E = 0$ ; So ;

$$\textbf{e.m.f} = 0 \Longrightarrow \textbf{e.m.f} = E_c - E_a = 0$$

$$E_{Cu^{2+}/Cu} - E°_{Zn^{2+}/Zn} = 0{,}03\ \log [Cu^{2+}]/ [Zn^{2+}]$$

$$E°_{Cu^{2+}/Cu} - E°_{Zn^{2+}/Zn} = 0{,}03\ \log 1/K_c \Longrightarrow K_c = 10^{\Delta E°/0.03}\text{; (Kc : Equilibrium constant)}$$

# CHAPTER IV :

# DISSOLUTION-PRECIPITATION REACTIONS

*This chapter explores the concept of solubility, the principles behind precipitation reactions, and the solubility product constant (Ksp), which quantifies the equilibrium between dissolved and undissolved species. Additionally, it examines various factors influencing solubility, such as temperature, common ion effect, and pH. Understanding these processes is essential for applications in analytical chemistry.*

## 1-Solubility

The solubility **S** of a solid compound is the maximum number of moles of this solid that can dissolve in one liter of solvent at a given temperature.

**Example :**

- NaCl: S ≈ 6 mole/L, NaCl is a very water-soluble compound.

- AgCl: S ≈ 10-5 mole/L. AgCl is a compound with very low solubility in water.

When the concentration of a compound AB is greater than the solubility value, the solution is said to be saturated with AB and precipitation occurs.

## 2-Precipitation reaction.

When two solutions containing the two ions ($Ba^{2+}$ and $SO^{-2}_4$) of a poorly soluble compound $BaSO_4$ are mixed separately, the latter precipitates during mixing (provided that saturation with $BaSO_4$ is reached).

| | | | | |
|---|---|---|---|---|
| $BaCl_2$ Solution<br>$BaCl_2 \text{---}> Ba^{+2}+2Cl^-$ | + | $NaSO_4$ Solution<br>$NaSO_4 \text{---}> Na^+ + SO^{-2}_4$ | = | $BaSO_4$ Precipitate<br>$Ba^{+2} + SO^{-2}_4 \text{---}> BaSO_4$ |

## 3-Solubility product.

### 3-1-Definition

When a compound ($BaSO_4$) precipitates during a precipitation reaction, traces of its ions ($Ba^{2+}$(aq) and $SO_4^{2-}$(aq)) always remain in solution, even if the solubility is very low.

An equilibrium is therefore established between the solid formed ($BaSO_4$) and the ions remaining in solution ($Ba^{2+}$(aq) and $SO_4^{2-}$(aq)): heterogeneous equilibrium:

$$BaSO_4(s) \Longleftrightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$$

**L.A.M:** $K_C = [Ba^{2+}][SO_4^{2-}]/[BaSO_4]$ ; $[BaSO_4]=1$

$$K_C = K_s = [Ba^{2+}][SO_4^{2-}] \ \ mol^2.l^{-2}$$

**Ks** is the solubility product of **$BaSO_4$.**

We also define **pKs = -log Ks**, which is a characteristic of **$BaSO_4$**.
The more soluble the compound, the greater Ks, the smaller the **pKs.**

To compare two compounds, it is more accurate to compare their solubility.
For a solid of general formula , **AxBy**:

$$\mathbf{A_xB_y \Longleftrightarrow xA^{+y} + yB^{-x}}$$

$$\mathbf{xS \qquad yS}$$

$$\boldsymbol{K_s = [A^{y+}]^x[B^{x-}]^y}$$

$$\Rightarrow \quad \boldsymbol{K_s = (XS)^x(yS)^y}$$

$$\mathbf{S = (k_s / X^xY^y)^{1/x+y}}$$

**Example :**

| | | |
|---|---|---|
| $CaCO_3 \Longleftrightarrow Ca^{2+} + CO_3^{2-}$ | $K_s = [Ca^{2+}][CO_3^{2-}]$ <br> $= S \times S = S^2$ | $S = (K_s)^{1/2}$ |
| $BaF_2 \Longleftrightarrow Ba^{2+} + 2F^-$ | $K_s = [Ba^{2+}][F^-]^2$ <br> $= S \times (2S)^2 = 4S^3$ | $S = (K_s/4)^{1/3}$ |

| | | |
|---|---|---|
| $Ca_3(PO_4)_2$ <==> $3Ca^{2+}$ + $2PO_4^{3-}$ | $K_s = (3S)^3(2S)^2 = 108\ S^5$ | $S = (K_s/108)^{1/5}$ |

### 3-2-Precipitation conditions :

$A^+ + B^-$ <==> AB  $Ks = [A+]_{eq}\ [B^-]_{eq}$ at equilibrium

If we mix **[A+]** and **[B⁻]** we find three cases:

**$[A+]\ [B^-] < K_s$** : case of under-saturation: no precipitation of **AB**.

**$[A+]\ [B^-] = K_s$** : saturation, so precipitation of **AB**

**$[A+]\ [B^-] > K_s$** : saturation, so precipitation of **AB** with return to equilibrium conditions

**Exercice :** A mixture containing :

-50 ml of $BaCl_2 = 10^{-5}$M

- 50 ml of$NaSO_4 = 2.10^{-2}$M

-100 ml of $AgNO_3 = 10^{-5}$M

total volume = 200 ml

Is there any precipitation of $BaSO_4$ and **AgCl** during mixing?

Given that at 25°C : $K_s(BaSO_4) = 1,1\times10^{-10}$ et $K_s(AgCl) = 1,6\times10^{-10}$.

**Solution :**

$[Ba^{2+}] = 2,5\times10^{-6}$ M and $[SO_4^{2-}] = 5\times10^{-3}$ M

-$[Ba^{2+}][SO_4\ ] = 1,25\times10^{-8}\ mol^2.l^{-2} > 1,1\times10^{-10}\ mol^2.l^{-2}$

-So there is a precipitation of **$BaSO_4$** with a return to equilibrium conditions:

$[Ba^{2+}]\ [SO_4^{-2}\ ] = 1,1\times10^{-10}\ mol^2.l^{-2}$ .

-$[Cl^-] = 5\times10^{-6}$ M et $[Ag+] = 5\times10^{-6}$ M

- $[Ag+][Cl^-] = 2,5\times10^{-11}\ mol^2l^{-2} < 1,6\times10^{-10}\ mol^2.l^{-2}$ - Therefore, no precipitation of AgCl.

**4-Factors influencing solubility.**

**4-1-Influence of temperature.**

$$AxBy \underset{2}{\overset{1}{<=>}} xA^{y+} + yB^{x-} \qquad \Delta Hr\ ° = \text{enthalpy of dissolution.}$$

**Direction 1 --> : dissolution**

**Direction 2 <-- : precipitation**

According to the vanthoff equation; $(d\ln Ks)/dT = \Delta H°r(dissolution) / RT^2$

Note that;

**-If $\Delta H > 0$ :**

- Temperature increases: system evolves in the direction of the **endothermic reaction direction (1): dissolution ↑: Ks ↑ (solubility ↑).**

**-If $\Delta H < 0$ :**

-the temperature decreases: evolution of the system in the direction of the **exothermic reaction direction (2): dissolution↓ Ks ↓ (solubility ↓)**

**Example :**

$$MgF_2 <==> Mg^{2+} + 2F^- \qquad \Delta H < 0 \text{ (exothermic)}$$

The reaction is exothermic in direction 2, if we increase the temperature, the reaction will move towards direction 1, so we obtain an endothermic system => **the solubility decreases.**

**4-2-Effect of common ions :**

We are looking for the solubility of (AB) in a strong electrolyte solution (AC). Let

A+: common ion.

$$AB <==> A^+ + B^- \quad ; \quad AC ==> A^+ + C^-$$

$$S+[A^+] \quad S$$

$$Ks = [A+][B-]$$

So; $\mathbf{Ks} = (\mathbf{S} + [\mathbf{AC}]) \mathbf{x} \mathbf{S}$

If the solubility is negligible compared to the concentration of **AC**, we can write that :

$$\mathbf{K_s} = \mathbf{S} \times [\mathbf{AC}]$$

So ; $\mathbf{S} = \mathbf{K_s} / [\mathbf{AC}]$

**4-3- Influence of pH.**

**Example 1 :**

$$Fe(OH)_3 \Longleftrightarrow Fe^{+3} + 3OH^- \ ; \ K_s = [Fe^{+3}][OH^-]^3$$

$$K_e = [OH^-][H_3O^+] \Longrightarrow [OH^-] = K_e / [H_3O^+]$$

$$K_s = [Fe^{+3}] \ (K_e / [H_3O^+])^3$$

Or; $S = [Fe^{+3}] \Longrightarrow Ks = S \times (K_e / [H_3O^+])^3$

$$S = K_s \times ([H_3O^+] / K_e)^3$$

- If $[H_3O^+]$ : increases ==> **pH:** decreases ==> **S:** increases.

- If $[H_3O^+]$ : decreases ==> **pH:** increases ==> **S:** decreases.

# CHAPTER V :

# COMPLEXATION REACTIONS

*Complexation reactions involve the formation of coordination compounds where a central metal ion binds to surrounding ligands. These reactions are defined by key concepts such as coordination number and molecular geometry, which determine the structure of the resulting complex. The nomenclature of complexes follows standardized rules to describe their composition and charge. The formation of complexes is governed by a global stability constant, which quantifies the strength of metal-ligand interactions.*

## 1-Definitions

A complex is a polyatomic **MLn** structure consisting of a central atom or cation **M** surrounded by n molecules or ions **L** called ligands or coordinates. The complex may or may not be charged.

The central atom or ion is often a transition (d-block) element: $Cu^{2+}$, Fe, $Fe^{2+}$, $Fe^{3+}$, Co, $Co^{2+}$, Ni, $Ni^{2+}$... but $Ca^{2+}$ , $Mg^{2+}$ and $Ag^{+}$ ions can also form complexes.

The central metal cation is positively charged (it has electron vacancies) and acts as an attractor for ligands.

Ligands are molecules or ions with at least one non-bonding doublet (Lewis bases): $Cl^-$, $CN^-$, $HO^-$, $H_2O$, $NH_3$…

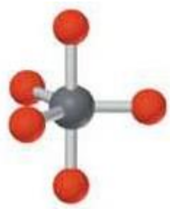
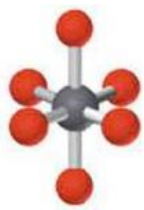
**- n:** Coordination number: number of bonds around the central atom.

-A ligand that can bind only once is monodentate.

-A ligand that can bind several times is polydentate.

## 2-Coordinance and geometry

Three main factors influence the coordination of a complex: the size of the central atom, steric interactions and electronic interactions.

| | | |
|---|---|---|
| Weak coordinations (1, 2 or 3) are rare.<br><br>**2 coordinates** have a **linear** geometry,<br><br>**3 coordinates** have a **trigonal planar** geometry. | <br> | |
| **Coordinence 4**<br><br>This is a very common coordination. Ligands can be organized in a **tetrahedral** or **square plane.** | **tetrahedral**<br> | **square plane**<br> |
| **Coordinence 5**<br><br>5 coordination complexes can be **square-based pyramid** or **trigonal bipyramid.** | **Trigonal bipyramid**<br> | **square based pyramid**<br> |
| **Coordinence 6**<br><br>Most coordination compounds are hexacoordinated. The structure adopted is generally an **octahedron**, more or less regular.<br><br>Sometimes a triangular prism is formed. |  | |

**3-complex nomenclature :**

The rules below are proposed by IUPAC (International Union of Pure and Applied Chemistry).3-1-Atome central.

**Formulas:**

the central atom is indicated first **M**, then, in order, the negative (**La**), neutral (**Ln**) and positive (**Lc**) ligands; the formula is bracketed [**M**(**La**)(**Ln**)(**Lc**)]charge.

**Names:** the central atom is named last; ligands appear in negative, neutral and positive order, or in alphabetical order.

-The oxidation number of the central atom is indicated by a Roman numeral to emphasize its formal character: Fe(II) or FeII.

-When the complex is anionic, the name of the central atom is suffixed with **-ate**:

**3-2-Name of ligands :**

- Anions: these are given the suffix "o":

| | | | | | |
|---|---|---|---|---|---|
| $H^-$ | hydruro | $OH^-$ | hydroxo | $OCN^-$ | cynato |
| $O^{2-}$ | Oxo | $S^{2-}$ | Thio | $SCN^-$ | thiocyanato |
| $I^-$ | Iodo | $HS^-$ | mercapto | $PO_4^{3-}$ | phosphato |
| $Br^-$ | Bromo | $CO_3^{2-}$ | carbonato | $NO^{3-}$ | nitrato |
| $Cl^-$ | Chloro | $C_2O_4^{2-}$ | oxalato | $NO^{2-}$ | nitrito |
| $F^-$ | Fluoro | $O_2^{2-}$ | peroxo | $SO_4^{2-}$ | sulfato |
| $CN^-$ | Cyano | $HO^{2-}$ | hydrogénoperoxo | $CH_3O^-$ | méthoxo |
| $S_2O_3^{2-}$ | thiosulfato | $SO_3^{2-}$ | sulfito | $CH_3S^-$ | méthylthio |

-Molecules, cations: name unchanged. Exceptions :

$H_2O$: aqua; $NH_3$: ammine; CO: carbonyl; NO: nitrosyl.

-The number of ligands is indicated by the prefixes di-, tri-, tetra-, penta-, hexa-, etc.

The total charge of the complex, also known as the EWING-BASSET number.

This is the load carried by the entire structure. It is noted after the end bracket, like the charge of a single ion or a complex ion.

**Example :**

-$[Al(H_2O)_6]^{3+}$ : ion hexaaquaaluminium (III)

-$[Cu(NH_3)_4]^{2+}$ : ion tétraamminecuivre (II)

-$[Fe(CN)_6]^{4-}$ : ion hexacyanoferrate (II)

-$[CuCl_4]^{2-}$ : ion tétrachlorocuprate (II)

-$[Fe(CO)_5]$ : pentacarbonylefer ((NO(Fe) = 0, Les complexes neutres)

-$[CoCl(NH_3)_5]Cl_2$ : chlorure de chloropentaaminecobalt (III)

-$[CoCl_3(NH_3)_3]$ : trichlorotriaminecobalt (III)

-$[Cr(SCN)_4(NH_3)_2]^-$ : ion tétrathiocyanatodiamminechromate (III)

-$[CrCl_2(H_2O)_4]^+$ : ion dichlorotétraaquachrome (III)

**4-Complex formation equilibrium**

Given the complex $[Ag(NH_3)_2]^+$, its equilibrium of formation is written :

$$Ag^+ + 2NH_3 \rightleftarrows [Ag(NH_3)_2]^+$$

So;

$$K_f = [Ag(NH_3)_2]^+ / [Ag^+][NH_3]^2$$

**$K_f$** is called the overall formation constant or stability constant; it is denoted **β** or **$K_f$**. It characterizes the equilibrium of complex formation. The greater the **$K_f$**, the more stable the complex.

We can also define the complex dissociation constant **$K_d$** :

$$\mathbf{K_d = 1/k_f}$$

==> $\mathbf{K_d = 1/k_f} = [Ag^+][NH_3]^2 / [Ag(NH_3)_2]^+$

We also find that: $pK_d = -logK_d = logK_f$; These constants depend only on temperature. We note that the complex is more stable, the greater the **$K_f$** and the smaller the **$K_d$.**

**Example :**

| | | |
|---|---|---|
| $Fe^{2+} + 6CN^- \rightleftarrows [Fe(CN)_6]^{4-}$ | $K_f = 10^{24}$ | $K_d = 10^{-24}$ |
| $Ag^+ + 2NH_3 \rightleftarrows [Ag(NH_3)_2]^+$ | $K_f = 10^{7,1}$ | $K_d = 10^{-7,1}$ |

$[Fe(CN)_6]^{4-}$ is more stable than $[Ag(NH_3)_2]^+$ because $K_f [Fe(CN)_6]^{4-} > K_f [Ag(NH_3)_2]^+$

**5-Competitive complexations : reaction prediction**

When there is competition between two metals for a ligand (or between two ligands for a metal), the complexation equilibrium constant depends on the formation constants of the complexes involved. The equilibrium is shifted towards the formation of the most stable complex, i.e. the one with the highest formation constant.

**Example :**

**1-** Thiocyanate ions $SCN^-$ are added to a solution of $Fe^{3+}$ and $Cu^{2+}$ ions. What complex is formed?

**2-** To a solution of $Fe^{3+}$ ions (orange in color), we add thiocyanate ions $SCN^-$ and then oxalate ions $C_2O_4^{2-}$.

The solution changes color from orange to blood red, then to pale green. What happened?

Given at 25°C:

(1) $Cu^{2+} + SCN^- \rightleftharpoons Cu(SCN)^+$ $\quad K_f(1) = 10^{1,7}$

(2) $Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+}$ $\quad K_f(2) = 10^3$

(3) $Fe^{3+} + C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)]^+$ $\quad K_f(3) = 10^{9,4}$

1- Both complex-forming reactions take place, but since

**$K_f$ (2) > $K_f$(1)**, the **$[Fe(SCN)]^{2+}$** complex is more stable than the **$[Cu(SCN)]^{+}$** complex. Cu(SCN)]+ complex.

To compare their relative stability, we calculate the equilibrium constant between the two complexes:

$$Cu(SCN)^{+} + Fe^{3+} \rightleftharpoons Cu^{2+} + Fe(SCN)^{2+} \qquad K_c = K_f\,(2)/\,K_f\,(1)$$

$K_c = 10^{3-1,7} = 10^{1,3} = 20 > 1$, so the $Fe(SCN)^{2+}$ complex is in the majority, but the reaction between the two complexes is not complete.

When $SCN^{-}$ ions are added to the $Fe^{3+}$ solution, the blood-red complex $[Fe(SCN)]^{2+}$ is formed in an almost complete reaction($K_f$ (2)=$10^3$).

2- When $C_2O_4^{2-}$ ions are added, the equilibrium between the two complexes is established since $K_f$ (3) > $K_f$(2)

$$[Fe(SCN)]^{2+} + C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)]^{+} + Fe^{3+} \qquad K' = K_f\,(3)/\,K_f(2)$$

$K' = 10^{9,4-3} = 10^{6,4} >>1$

The blood red complex $[Fe(SCN)]^{2+}$ is destroyed and the pale green complex $[Fe(C_2O_4)]^{+}$ is formed, in a total reaction ($K' >>1$).

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