The title (العنوان):

Chemistry of solutions

APA Citation (توثيق APA):

Djemam, Nihed (2025). Chemistry of solutions.[polycopie pédagogique]. ENSH.

ALGERIAN REPUBLIC DEMOCRATIC AND POPULAR
MINISTRY OF HIGHER EDUCATION AND ASCIETIFIC RESEARCH
NATIONAL HIGHER SCHOOL OF HYDRAULICS

Teaching handout

Chemistry of solutions

Course designed for students of 2nd CPST

Prepared by: PhD. DJEMAM Nihed

Academic year : 2024/2025

The course on analytical chemistry or solution chemistry is designed to provide students with a deep understanding of the fundamental concepts of chemistry, particularly those essential for explaining chemical phenomena in living organisms and in chemical systems in general. Below is a summary of the key points and objectives of the course.

- ➢ **Course Objectives**
- ✓ Fundamental Concepts:

  - Understand and apply the concepts of concentration, dilution, and dissolution.

  - Deduce the rate of a chemical reaction.

  - Master the concepts related to acids and bases in solution, including calculating the pH for different types of aqueous solutions.

  - Understand the role and functioning of buffer solutions.

- ✓ Chemical Reactions:

  - Study oxidation-reduction reactions: balance equations, predict the direction of reactions, and calculate redox potentials.

  - Analyze precipitation and complexation reactions: calculate the solubility product, formation constants, and dissociation constants of complexes, and understand the factors influencing their stability.

- ✓ Practical Applications:

  - Interpret titrations (acid-base, redox, complexometric, and precipitation).

  - Apply this knowledge to concrete problems, particularly in the field of hydraulics and other scientific specialties.

- ➢ **Course Structure**

The course is divided into five chapters:

1. General Concepts on Solutions: Concentration, dilution, dissolution.
2. Acid-Base Reactions: pH, buffer solutions, acid-base titrations.
3. Oxidation-Reduction Reactions: Redox potential, redox equilibria.
4. Precipitation Reactions: Solubility product, precipitation equilibria.
5. Complexation Reactions: Formation and dissociation constants, stability of complexes.

Each chapter is structured to facilitate progressive and logical learning, with practical exercises to illustrate the theoretical concepts.

- ➢ **Prerequisites**

To successfully follow this course, students must master:

- The notions of dissolution, dilution, and molar concentration.
- Basic mathematical skills (equations, exponential functions, logarithms).

➢ Learning Outcomes

By the end of the course, students will be able to:

- ✓ Manipulate basic concepts: dilution, dissolution, precipitation.
- ✓ Calculate the pH of complex solutions and understand the behavior of acids and bases.
- ✓ Determine the redox potential of a solution at equilibrium.
- ✓ Predict and interpret complexation, precipitation, and dissolution reactions.
- ✓ Interpret chemical titrations (acid-base, redox, complexometric, and precipitation).

➢ Pedagogical Approach

The course is designed to promote structured learning and the development of formal thinking. Each chapter is organized hierarchically, with practical exercises to reinforce the understanding of concepts. The goal is for students to integrate these notions into their mental framework, enabling them to apply them in various contexts.

In summary, this course in analytical chemistry is a comprehensive introduction to the key concepts of solution chemistry, with an emphasis on practical applications and problem-solving. It is essential for students wishing to pursue studies in science and engineering.

TABLE OF CONTENTS

Chapter I: General informations about the solutions

Chapter II: Acid-base Reactions

Chapter III: Redox Reactions

Chapter IV: Precipitation Reactions

Chapter V: Complexation Reactions

CHAPTER I : GENERAL INFORMATIONS ABOUT THE SOLUTIONS

I INTRODUCTION

A solution is a homogeneous liquid mixture (consisting of a single phase) in which one of the constituents (the solvent) is in excess compared to the other constituents of the mixture (the solutes).

In the case of an aqueous solution, water plays the role of solvent. The H2O molecule is polar, it therefore has a significant dissolving power against to ionic compounds and polar compounds.

II DEFINITIONS

When a compound goes into solution in water, it can remain in molecular form like sucrose $C_{11}H_{22}O_{11}$, and the dissolution will be written:

$$C_{11}H_{22}O_{11\,(Solid)} \xrightarrow{H_2O} C_{11}H_{22}O_{11\,(Dissolved)}$$

A molecular dissolution

Either dissociate into ions like sodium chloride NaCl; the dissolution will be written:

$$NaCl_{\,(solid\ )} \xrightarrow{H_2O} Na^{+}_{aq} + Cl^{-}_{aq}$$

An ionic dossilution

II.1 Electrolytes :

An electrolyte is a chemical substance which, in aqueous solution, dissociates into ions and therefore allows the conduction of electric current. The ions formed are solvated, that is to say surrounded by solvent molecules (H_2O).

The solution is electrically neutral: $\sum_i z_i [i] = 0$ *Zi is the charge carried by the ion i*
[i] its molar concentration in the solution.

***Example :* Dissolution of solid $CaCl_2$ in water**

$$CaCl_2 \rightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

We have : $2\,[Ca^{2+}] - [Cl^{-}] = 0$

II.2 Ionic balance

As with all chemical reactions, a dissolution reaction has a reaction constant K.

When K is very high, dissolution can be considered as a total reaction. Chemical species whose dissolution in water is almost complete are called **strong electrolytes**.

The latter can be either ionic solids at ordinary temperature such as sodium chloride NaCl, gases such as hydrogen chloride HCl or even liquids such as nitric acid HNO_3:

$$NaCl_{(solide)} \xrightarrow{H_2O} Na^+_{aq} + Cl^-_{aq} \qquad K_1$$

$$HCl_{(gaz)} \xrightarrow{H_2O} H^+_{aq} + Cl^-_{aq} \qquad K_2$$

$$HNO_{3\,(liquid)} \xrightarrow{H_2O} H^+_{aq} + NO_3{}^-_{aq} \qquad K_3$$

Example of strong electrolytes

When the constant K associated with the dissolution reaction is small compared to 1, ionic dissociation occurs at a low rate of progress and the dissolved species is a **weak electrolyte.**

$$\underline{AgCl}_{(solid\ )} \xleftrightarrow{H_2O} Ag^+_{aq} + Cl^-_{aq} \qquad K_4$$

$$CH_3COOH_{(liquid\ )} \xleftrightarrow{H_2O} H^+_{aq} + CH_3COO^-_{aq} \qquad K_5$$

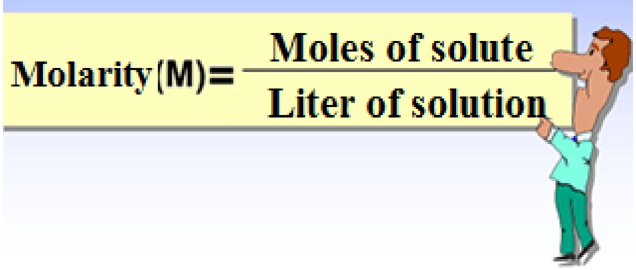
Example of weak electrolytes

III. DIFFERENT EXPRESSIONS OF THE CONCENTRATION

The different chemical species present in the solution are characterized by their concentrations.

III.1 The molar concentration (molarity)

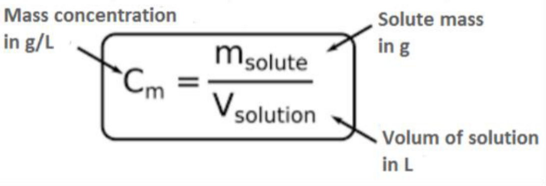
It is the quantity of material of X contained in one liter of the solution. It is expressed in mol/L and symbolized by M.



$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liter of solution}}$$

III.2 The mass concentration

It is the ratio of the mass of compound X contained in a certain volume of solution divided by this volume of solution. It is expressed in g/l.



$$C_m = \frac{m_{solute}}{V_{solution}}$$

III.3 The mass fraction

It is the mass of compound X (in g) over the mass of solution (in g).

$$\boxed{P(X) = \frac{masse\ of\ solute}{masse\ of\ solution} = \frac{m(X)}{m}}$$

III.4 The mass percentage

It is the mass fraction multiplied by 100.

$$\% = \frac{\text{masse of solute}}{\text{masse of solution}} \text{ x } 100$$

III.5 The molar fraction

It is the number of moles of solute i over the total number of moles

$$x_i = \frac{n_i \ (\text{in } mol)}{\sum_i n_i \ (\text{in } mol)}$$

III.6 The molality

The molality corresponds to the quantity of solute contained in 1000 g of solvent.
The molality is expressed in moles per Kilogram (Symbol: mole/Kg). Molality is noted m, not to be confused with the abbreviation of mass: m.

$$\text{Molality} = \frac{\left[\dfrac{\text{mass of solute}}{\text{molar mass of solute}}\right]}{\text{kilograms of solvent}} = \text{mol}/\text{Kg}$$

III.7 The normality

Normality is the number of gram equivalents of solute per volume of solution.

$$N = \frac{\text{Number of gram equivalent of solute}}{\text{Volum of solution (L)}}$$

In an acid-base reaction: the gram equivalent is the quantity in grams of this substance which can capture or release one mole of H^+, OH^- during the reaction considered.

Examples : HCl, H_3PO_4, NaOH
HCl can release one mole of H+ per mole. Therefore, its normality is equal to its molarity. A M/10 solution of HCl has a normality of 1/10 (or N/10).
Generally speaking, for a monoacid (or a monobase) we have:
Normality (N)=Molarity (M)
For a polyacid (p times acid) or a polybase: **N=p * M**, where p is the number of equivalents.

In a Redox reaction: the gram equivalent is the quantity in grams of this substance which can capture or release one mole of e-during the reaction considered**.**

The gram equivalent varies with the reaction: $\mathbf{1Eq.g} = \frac{\mathbf{Mm}}{\mathbf{p}}\ \mathbf{(g)}$; $\mathbf{1Eq.g} = \frac{\mathbf{1}}{\mathbf{p}}\ \mathbf{(mole)}$

For an acid: p = number of H+ released

For a base: p = number of H+ captured

For an oxidant: p = number of e- captured

For a reducer: p = number of e- released

For a salt: p = charge of the ions participating in the reaction

NB : p can also be mentioned under the name Z.

Calculation examples: Calculate p in the different possible reactions

HF, H_3PO_4, KOH, $Ca(OH)_2$, $KAl(SO_4)_2$

IV CONCEPT OF CHEMICAL ACTIVITY, ACTIVITY COEFFICIENT AND IONIC FORCE

IV.1 Chemical activity of a species in solution

In a real solution, chemical species (ions, molecules, etc.) interact with each other:

- Solute-solvent interactions.
- Solute-solute interactions.

These interactions will make the solute less available for a chemical reaction.

In an ideal solution the solute molecules are not subject to any interaction. Which means that the concentration provided in solute is really the concentration available for a chemical reaction.

To reflect this deviation from an ideal solution, we then introduced the notion of activity ***a***, which is a corrective quantity which takes into account the interactions between the different constituents of a solution.

The activity for the chemical species "i" is denoted "a_i" and is written: $\boxed{a_i = \gamma_i \,.C_i}$

a_i : The activity of constituent i

γ_i : the activity coefficient of i **$0 \leq \gamma i \leq 1$** si **$\gamma i = 1$** the solution is ideal

C_i : The concentration of i

IV.2 Calculation of the activity coefficient and ionic strength

This law takes into account the charge carried by each ion as well as its concentration provided in solution. The Debye-Hückel theory allows the calculation of the activity coefficient relating to an ionic species. Electrolytes are always made up of anions and cations.

$$\log(\gamma_i) = \frac{-0{,}5\, z_i^2 \sqrt{I}}{1+\sqrt{I}} \quad \textbf{with} \quad I = \frac{1}{2}\sum z_i^2\, C_i \qquad \text{if } 10^{-2} < I < 0{,}1 \text{ M}$$

$$\log(\gamma_i) = -0{,}5\, z_i^2 \sqrt{I} \qquad \text{if } I \leq 10^{-2}\text{M}$$

I : ionic strength of the solution (in mol.L^{-1}*) ;* z_i *: charge of the ion considered ; Ci concentration of the ion considered (in mol.*L^{-1}*)*

The ionic force does not depend on the nature of the ionic species in solution but on their electric charge, Z and their concentrations, C. It is expressed in mol/L, in mol/Kg or without units.

V PREPARATION OF A SOLUTION

V.1 BY DISSOLUTION OF A SOLID COMPOUND

Either to prepare a volume V of a solution containing the species X, of molar mass M, at the concentration [X].

The masse of species X to weigh **m = [X].M.V**

V.2 By DISSOLUTION OF A GASEOUS COMPOUND

Let VG be the volume of gas to dissolve, V the volume of the solution, the molar volume VM of the gases under the conditions of the experiment and [G] the molar concentration of the gas in the solution

We have **: [G] = VG / (VM. V)**

V.3 BY DILUTION OF A SOLUTION OF KNOWN CONCENTRATION

Dilution is the act of reducing the value of the concentration of a constituent X of a solution by adding to this solution either a certain volume of pure solvent, or a certain quantity of another solution less concentrated in X.

1st case: We take a volume V_0 *of the stock solution of concentration* C_0 *which we dilute with distilled water to obtain a diluted solution of volume* ***Vf*** *and concentration* C_f*.*

The quantity of solute material in the volume V_0 is found in the solution after dilution. This reflects the conservation of matter $V_0=C_f.V_f$

2nd case: To a volume V_1 *of a solution of concentration* C_1 *we add* V_2 *of another solution of concentration* C_2*. The new concentration will be obtained by adding the quantities of materials of X and dividing by the total volume:*

$$C_f = (C_1V_1 + C_2V_2)/(V_1+V_2)$$

VI AQUEOUS ELECTROLYTE SOLUTIONS

Solutions that give rise to partial or total ionic dissociation in a solvent constitute electrolytes. We distinguish:

- **Strong electrolytes**: Only A+ and B- exist after dissociation from AB. $AB \longrightarrow A^+ + B^-$
- **Weak electrolytes**: Ionic dissociation is partial and can be expressed as a function of the dissociation coefficient

$$AB \Leftrightarrow A^+ + B^-$$

$$\alpha = \frac{\text{number of ionized moles}}{\text{number of moles in solution}}$$

The degree of ionization is between 0 and 1.

$0 < \alpha < 1$ (weak electrolyte)

$\alpha = 0$ means there is no ionization

$\alpha = 1$ means that the ionization is complete (strong electrolyte)

The degree of ionization can also be expressed in percentage terms.

$$\begin{array}{lcccc} & AB & \Leftrightarrow & A^+ \; + & B^- \\ t = 0 & C_0 & & 0 & 0 \\ teq & C_0(1-\alpha) & & C_0\,\alpha & C_0\,\alpha \end{array} \qquad K = \frac{\alpha^2 C_o^{\,2}}{(1-\alpha)\,C_o} = \frac{\alpha^2 C_o}{(1-\alpha)}$$

The equilibrium constant is written:

We see that if C_0 increases then α decreases and vice versa.

The more the solution is diluted, the more the electrolyte dissociates and can behave like a strong electrolyte if the dilution is very thorough.

VII CHEMICAL KINETICS

VII.1 Definition

Chemical kinetics is the science that deals with how chemical reactions proceed (mechanism) and their rate over time. The reaction rate (speed) is the variation in the concentration of a reactant or product as a function of time.

VII.2 Calculation of instantaneous rate (speed)

Given the total general reaction:

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

Its speed is generally expressed in relation to a reactant or a product.

The speed of a reaction is always a positive quantity:

If we measure the speed of disappearance of a reactant, the speed is assigned the sign (-), whereas if we measure the speed of formation of a product the speed is preceded by the sign (+).

The reaction rate is then defined as a rate of variation of concentration with respect to time:

$$\boxed{V_A = -\frac{d[A]}{dt}, \qquad V_B = -\frac{d[B]}{dt}, \qquad V_C = +\frac{d[C]}{dt}, \qquad V_D = +\frac{d[D]}{dt}}$$

It is obvious that these speeds are different (when a moles of A disappear, b moles of B disappear).

The overall reaction speed is written:

$$\boxed{V = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}}$$

Example : Decomposition reaction of H_2O_2 **$2H_2O_2 (aq) \rightarrow 2H_2O(l) + O_2(g)$**

VII.3 Calculation of average speed

The average speed of the reaction expresses the variation in the concentration during a fairly large time interval Δt.

$$v = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example :

We have the following reaction: **$A + 2B \longrightarrow 2C + D$**

At t=0 [D]= 0,3675 M

At t= 3mn25s [D]= 0,4931 M

a) What is the average speed expressed as a function of reagent D in mol/L.mn?

What is the rate of formation of C, expressed in moles per liter per sec.

Answer :

- ***(a) 0,0367 mole/L.mn***
- ***(b) $1,22.10^{-3}$ mole per liter per sec***

VII.4 comparison between average speed and instantaneous speed

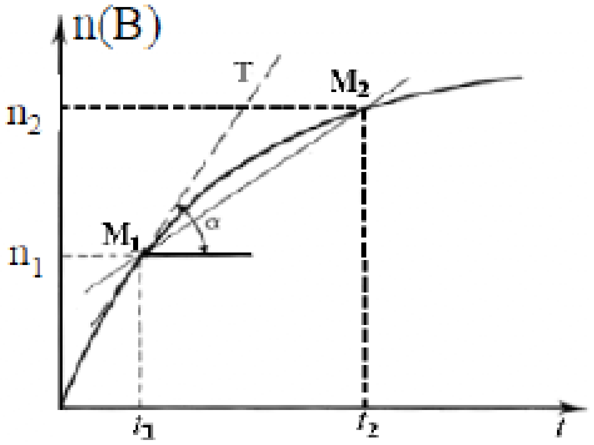
In reality the speed v of the reaction is important at the start (V > Vav) and decreases gradually.

At the end we have: V < Vav

It is therefore more precise to use a very short period dt, which therefore amounts to measuring the instantaneous speed.

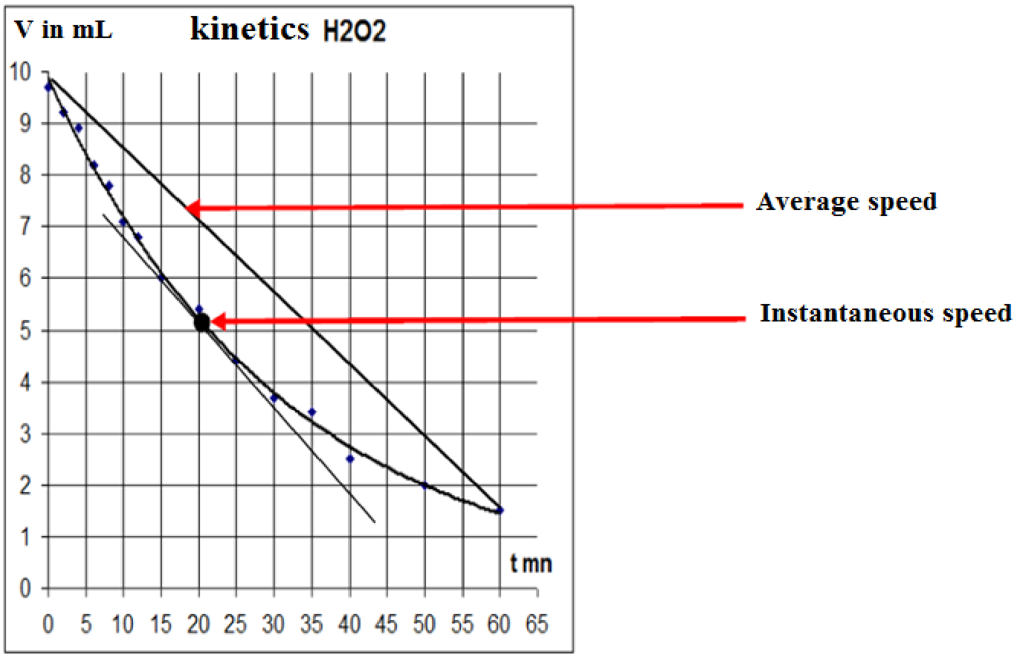
To do this, we plot the concentration as a function of time. The speed at time corresponds to the slope of the tangent at that point on the curve.

We follow the evolution at T=Cte, in a closed system of volume V, of the formation of product B over time: **n(B) =*f*(t)**



$$v_{av} = \frac{n_2 - n_1}{t_2 - t_1} = \text{slope of the tangent}$$

Example : Decomposition of H_2O_2



VII.5 Kinetic factors

The main factors influencing speed are:

a. The concentration (ou pression partielle) of reagents :

Disproportionation (dismutaion) of thiosulfate ions in acidic environment; If we increase the concentration of the thiosulfate **$S_2O_3^{2-}$** the speed of appearance of the precipitate increases (the sulfur increases): appearance of a yellowish white precipitate of sulfur.

$$S_2O_3^{2-} + 2\,H^+ \longrightarrow S + SO_2 + H_2O$$

b. Temperature of the environment :

The oxidation of water by permanganate, the speed of the reaction increases by increasing the temperature (shock, meeting of the reagents, agitation).

Low temperature slow reaction (refrigerator).

c. Presence of substances other than the reagent (The catalyst):

A chemical species accelerates the reaction without intervening in the reaction balance.

$$H_2O_2 \xrightarrow[\text{FeC13,CuC12}]{} H_2O + \tfrac{1}{2}\,O_2$$

d. Contact between the reagents

The speed of the reaction depends on the possibility of contact between the reactants; thus the vigorous mixing of two **immiscible** reagents will accelerate their reaction.

e. The light

Certain reactions only occur with appreciable speed in the presence of light; this is the case for certain radical reactions in organic chemistry.

VII.6 Speed law and reaction order

Experience shows, in many cases, that the rate of a reaction is proportional to the concentration of each of the reactants; raised to a suitable power.

So the speed of the reaction: $a\,A + b\,B \longrightarrow$ products

Can frequently be put in the form: $\mathbf{V = k\,[A]^{\alpha} \times [B]^{\beta}}$ ...... ***(I)***

[A], [B] : molar concentrations of the reactants at the time the speed is measured
k : rate constant it depends on the reaction considered and the temperature. The unit of k varies with the order of reaction.
α and **β** : are the partial orders of the reaction with respect to the reactants.
(α +β) overall order of the reaction.

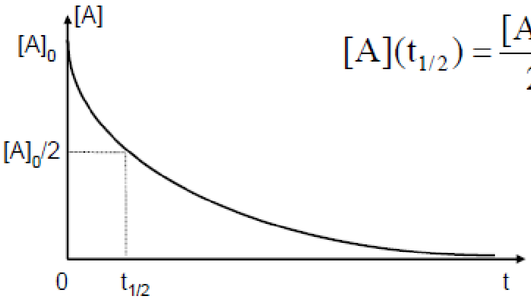
- There is no relationship between α and β and the stoichiometric coefficients of the reaction
- When the relation (I) is verified, we say that the reaction follows Van't Hoff's law and admits an order.
- When the relation (I) is not verified, we say that the reaction is without order.

Remark :

- The partial orders α, β, ... can be integers or fractions. They can also be zero, which means that the concentration of the corresponding reagent does not affect the reaction rate. They are not predictable and their value can only be determined by experience.
- The order of a reaction is purely experimental notion. It is determined experimentally, either by graphic representation or by calculating the rate constant k.

Complement :

We call half-reaction time $t_{1/2}$ the length of time needed to consume half of the limiting reagent initially present.



$$[A](t_{1/2}) = \frac{[A]_0}{2}$$

Example :

Let the following reactions be :

$NO_2 + CO \rightarrow NO + CO_2$ v = k $[NO]^2$

$NO + H_2 \rightarrow \frac{1}{2} N_2 + H_2O$ v = k $[NO_2]^2.[H_2]$

$4\ O_2 + 2PH_3 \rightarrow P_2O_5 + 3\ H_2O$ v = k $[PH_3]^{3/2}.[O_2]^{1/2}$

Give partial and global orders for the different reactions.

VII.7 Concentration versus time: integrated rate law

Case of a zero-order reaction: integrated rate law (α=0)

Let the reaction of type: A $\longrightarrow$ products

$$V = -\frac{d[A]}{dt} = k\ [A]^0 \Rightarrow k.dt = -d[A] by\ integration\ we\ will\ have: \Rightarrow -kt = [A] - [A_0] \Rightarrow [A] = -kt + [A_0]$$

At t=0: [A]= $[A_0]$ So : $\boxed{[A] = [A_0] - kt}$

- If we draw [A]=*f*(t) we obtain a descending line, its slope is = -k and the Y-intercept is = **$[A_0]$.**

- The rate constant **k=**$\frac{[A_0]-[A]}{t}$ is expressed in (mole/L.S).

- Calculation of half-reaction time (or half-life) :

At $t_{1/2}$, [A]= $\frac{[A_0]}{2} \Rightarrow \boxed{t_{1/2} = \frac{[A_0]}{2k}}$

a) Case of a reaction of order 1 :

Let the reaction be : A $\longrightarrow$ C + D

$$V = -\frac{d[A]}{dt} = k\ [A]^1 \Rightarrow \frac{d[A]}{[A]} = -k.dt\ \ by\ integration\ we\ will\ have:$$

$$\Rightarrow ln[A]/[A_0] = -kt \Rightarrow ln[A] - ln[A_0] = -kt$$

At t=0: [A]= $[A_0]$ So : $\boxed{ln[A] = ln[A_0] - kt}$

- If we draw ln[A]=f(t) we obtain a descending line, its slope is = -k and the Y-intercept is = $\boldsymbol{ln}[\boldsymbol{A_0}]$

- If we draw [A]=*f*(t) we obtain a descending curve.

- The rate constant **k=**$\frac{(ln[A_0]/[A])}{t}$ is expressed in (S^{-1}).

- Calculation of half-reaction time (or half-life) :

At $t_{1/2}$, [A]= $\frac{[A_0]}{2} \Rightarrow \boxed{t_{1/2} = \frac{ln2}{k}}$

b) Case of a reaction of order 2 :

Let be the reaction : $A \longrightarrow C + D$

$$V = -\frac{d[A]}{dt} = k\,[A]^2 \Rightarrow -\frac{d[A]}{[A]^2} = k.dt \;\; by\ integration\ we\ will\ have$$

$$\Rightarrow 1/[A] - 1/[A_0] = kt$$

At t=0: [A]= [A$_0$] So : $\boxed{1/[A] = 1/[A_0] + kt}$

- If we draw 1/[A]=f(t) we obtain an ascending line, its slope is = k and the Y-intercept is = $\mathbf{1/[A_0]}$
- The rate constant k=$\frac{(1/[A]-1/[A_0])}{t}$ is expressed in (L.mole^{-1}.S^{-1}).
- Calculation of half-reaction time (or half-life)

At t$_{1/2}$,[A]= $\frac{[A_0]}{2} \Rightarrow \boxed{t_{1/2} = \frac{1}{k[A_0]}}$

We "see that for a reaction of order 1, t1/2 2 is independent of the initial concentration".

On the other hand, for reactions of order zero and 2, t$_{1/2}$ depends on the initial concentration.

Summary table:

Order	Rate law	Integrated rate law	Graph of a line	k	Unit of k	Half-life
0	**V=k**	**$[A]_t=[A_0]-kt$**	**[A] function of t**	**-slope**	**mol/L.S**	**$[A_0]/2k$**
1	**V=k[A]**	$\boldsymbol{ln[A] = ln[A_0] - kt}$	**Ln[A] function of t**	**-slope**	**S^{-1}**	**Ln2/k**
2	**$V=k[A]^2$**	$\boldsymbol{1/[A] = 1/[A_0] + kt}$	**1/A function of t**	**slope**	**L/mol.S**	**$1/k[A_0]$**

VII.8 Determining the overall order of a reaction

Case of one reactant

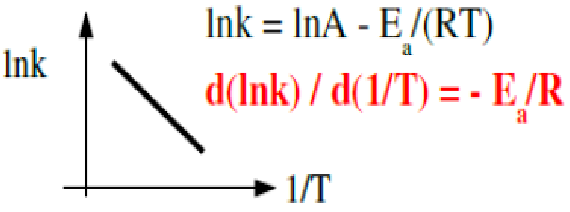
Let the reaction be: : $A \longrightarrow C + D$ **$V=k[A]^m$**

- If [A] = *f*(t) or ln[A] = *f*(t) or 1/[A] = *f*(t) is a line, then the overall order of the reaction is respectively 0, 1 or 2.

- Draw [A] = *f*(t) ⟹ determine v for different t (by drawing the tangent to the curve, at point t).
- $v = k[A]^m \Longrightarrow \boxed{\mathbf{lnv = lnk + mln[A]}}$
- Draw **lnv = *f* (ln[A])** ⟹ is a line where the **slope = m** and the Y-intercept is **= lnk**

VII.9 Influence of the temperature : Arrhenius law

Temperature has a very significant effect on the rate constant k.
From experimental data, Arrhenius established the following equation:
$\mathbf{dlnk/ dT = Ea/RT^2} \Longrightarrow \boxed{\mathbf{k = Ae -Ea/RT}}$



K= rate constant
A = Pre-exponential Arrhenius factor It has the same unit as k (Integration constant).
Ea = Arrhenius activation energy. It has the same unit as RT.
R= Ideal gas constant.
T= Temperature.

a)- Determination of Ea graphically :

We draw **ln K** in function of **1/T** and we determine the slope of the line: **-EA/R** and the Y-intercept= **Ln A**.

b)- Determination of Ea without a graph :

Let be k_1 the rate constant at T_1
$\mathbf{\ln k_1 = lnA - Ea/RT_1}$

And K_2 the rate constant at T_2
$\mathbf{\ln k_2 = lnA-Ea/RT_2}$

$\mathbf{\ln k_2/k_1 = \ln V_2/V_1 = Ea/R(1/T_1 - 1/T_2)}$

VII APPLICATION EXERCICES

- **Exercise 01 :**

187.6 g of chromium sulfate $Cr_2(SO_4)_3$ are dissolved in water, then the solution is adjusted to one liter. The density of this solution is 1.172. Calculate for this solution:

1. Molar concentration
2. Molality
3. The mole fraction of each constituent
4. The mass percentage of this solution
5. Normality

Data : Cr : 52 ; S : 32 ; O :16

- **Exercise 02:**

SP commercial hydrochloric acid (strictly pure) comes with the following indications:

d=1.19, HCl%= 38%, M_{HCl}= 36.5g

How to prepare a 0.1N solution of this acid?

- **Exercise 03:**

Calculate the activity of $H_2PO_4^-$ and HPO_4^{2-} ions in an aqueous solution containing: KH_2PO_4 and Na_2HPO_4 having a concentration of 10^{-2}mol/L.

- **Exercise 04:**

The decomposition reaction of N_2O_5 is written:

$$N_2O_5\,(g) \longrightarrow 2\,NO_2(g) + \tfrac{1}{2}\,O_2(g)$$

We carry out a series of experiments at 25°C, where we measure the initial speed v_O of the reaction depending on the initial concentration of $[N_2O_5]_o$.

Experience N°	1	2
$[N_2O_5]_o$ (mol/l)	0.01	0.02
V_o ($mol.l^{-1}.mn^{-1}$)	0.018	0.036

1) Determine the initial order of the reaction
2) Calculate the rate constant k.

- **Exercise 05:**

When heated, acetaldehyde decomposes into methane and carbon monoxide in a second-order reaction, represented by the following equation:

$CH_3CHO\,(g) \rightarrow CH_4\,(g) + CO\,(g)$

A kinetic study of the reaction is carried out and the results obtained are mentioned in the table below:

1. Establish the rate law for the reaction studied
2. Calculate the rate constant of this reaction.
3. Calculate the half-life time of this reaction.
4. What will be the CO concentration obtained after 120 s of reaction?

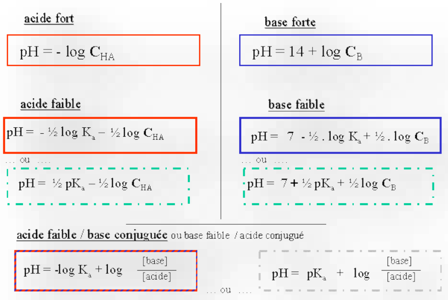
Time (s)	$[CH_3CHO]$ (mol/L)
0	1,000
40	0,637

A rule of thumb in kinetics states that, for many reactions, an increase of 10°C roughly doubles the speed. What must be the activation energy of a reaction if we find that its speed effectively doubles between 25°C and 35°C?

CHAPTER II : ACID-BASE REACTIONS

I INTRODUCTION

Acid-base balances are part of the larger problem of chemical balances. The acid-base phenomenon is important, for example in the human body where complex systems control blood acidity. Acids and bases are also important in industry: the large quantity of sulfuric acid produced each year makes it possible, for example, to produce fertilizers or polymers.



acide fort

$pH = -\log C_{HA}$

base forte

$pH = 14 + \log C_B$

acide faible

$pH = -\frac{1}{2}\log K_a - \frac{1}{2}\log C_{HA}$

… ou ….

$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C_{HA}$

base faible

$pH = 7 - \frac{1}{2}.\log K_a + \frac{1}{2}.\log C_B$

… ou ….

$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C_B$

acide faible / base conjuguée ou base faible / acide conjugué

$pH = -\log K_a + \log \frac{[base]}{[acide]}$ … ou …. $pH = pK_a + \log \frac{[base]}{[acide]}$

II DEFINITIONS

II.1 Acids and bases

a. According to Arrhénius theory:

- An acid is every body that can release H^+ ions in solution.
- A base is every body that can release OH^- ions in solution.

b. According to Brönsted – Lowry theory :

- An acid is every body that donates a protons H^+
- A base is every body that accepts a proton H^+

c. According to Lewis theory :

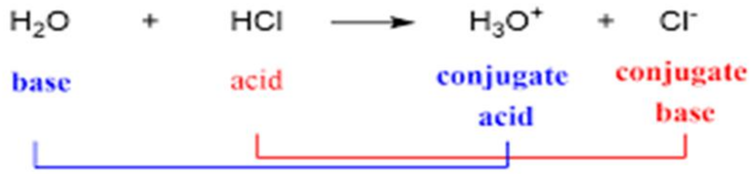
- An acid is every body that accepts an electron pair.
- A base is every body that donates an electron pair.

It is the definition of Brönsted that will be adopted in the following study.

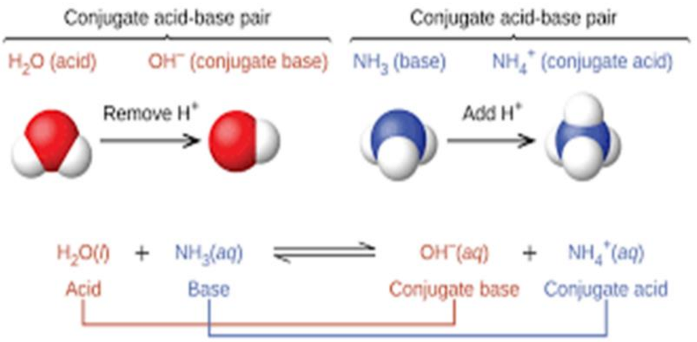
II.2 Acid-Base reaction

An acid-base reaction is an H^+ ion exchange reaction between an H^+ donor (acid) and an H^+ acceptor (base). The acid AH and the base A^- are conjugated. The set of two species associated in the same equilibrium is an **acid/base** pair.

Conjugate Acid and Conjugate Base

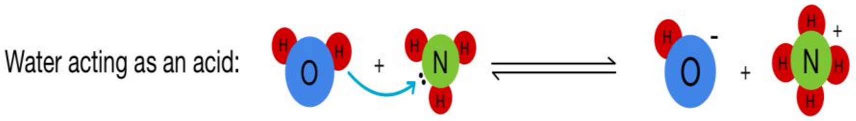


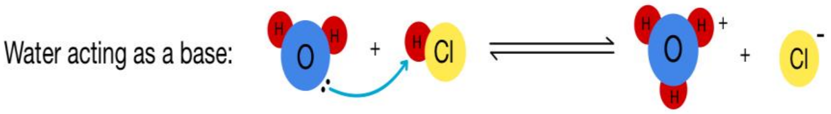
*In acid-base reactions, the **acid** is converted into its **conjugate base**, and the **base** is converted into its **conjugate acid**.*



II.3 Amphoterics

Some compounds have both a releasable H in the H^+ form and one or more non-binding doublets. They can thus participate in two couples, being the acid of one and the base of the other. They are amphoteric or ampholytic. (Example of water)

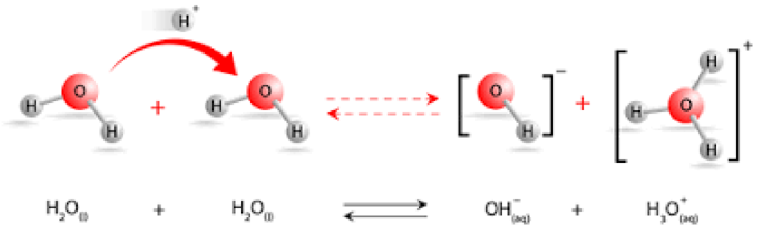




III IONIC BALANCE OF WATER (AUTOPROTOLYSIS OF WATER)

It is the reaction between two molecules of water according to the equilibrium:

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



$$K_a = \frac{[H3O+][OH-]}{[H2O]} = 1.8 \,.\, 10^{-16} \text{ at } 25°C$$

This balance is governed by the constant: **$K_w = [H_3O^+].[OH^-]$** called ionic product of water.
This relation is always applied, whatever the origin of the ions H_3O^+ and OH^-.
The value of K_w only depend on the temperature, it is equal to *10^{-14}* at *25°C*.

$[H_2O] = 1000/18 = 55.5$ mol/l => $[H_3O^+].[OH^-] = 55.5 \times Ka = 55.5 \times 1.8\ 10\text{-}^{-16} = 10^{-14}$ mol^2/L^2

$[H_3O^+].[OH^-] = K_w = 10^{-14}$ => pH + pOH = pK_w = 14 at 25°c

In pure water: $[H_3O^+] = [OH^-] = 10^{-7}$mol/l so the environment is neutral.

Remark :

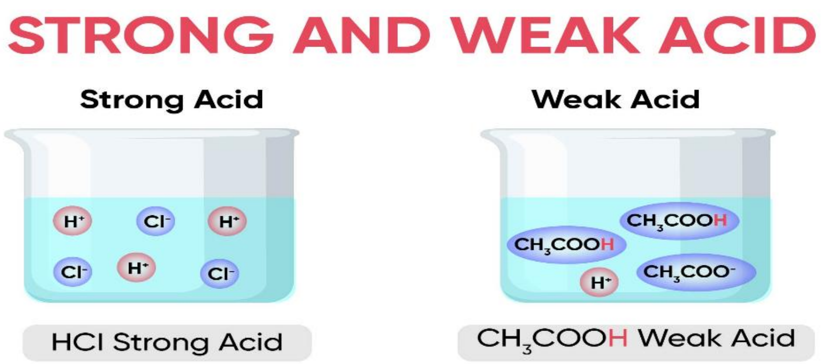
- If we add H_3O^+ ions, the self-ionization balance of water shifts to the left. Therefore OH^- decreases.
- Let $[OH^-] < 10^{-7}$; it results that $[H_3O^+] > 10^{-7}$ Then the environment is **acidic**.
- If we add OH^- ions the self-ionization balance of water shifts to the left. Therefore H_3O^+ decreases.
- Let $[H_3O^+] < 10^{-7}$; it results that $[OH^-] > 10^{-7}$. So the environment is **basic**.

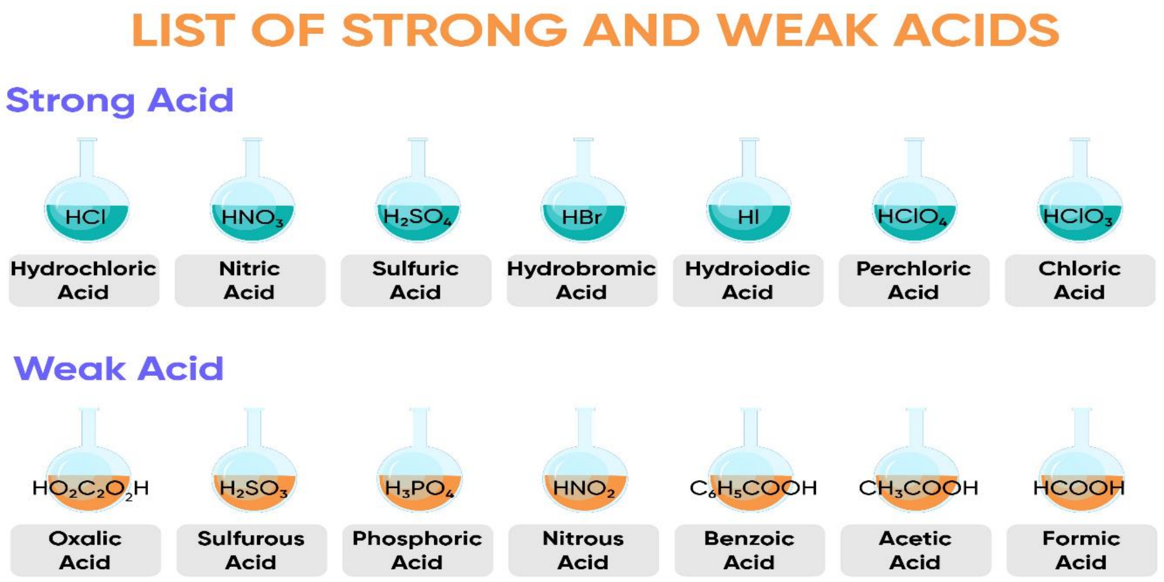
IV STRENGTH OF ACIDS AND BASES

IV. 1 Strength of acids

A strong acid is an acid which is completely ionized in an aqueous solution. Hydrogen chloride (HCl) ionizes completely into hydrogen ions and chloride ions in water.

A weak acid is an acid that ionizes only slightly in an aqueous solution. Acetic acid (found in vinegar) is a very common weak acid.





The equilibrium constant for dissociation of the acid AH, called “Acidity constant Ka” is written:

$$\boxed{K_a = [H_3O^+].[A^-] / [AH]}$$

The H^+ concentration is very low and cannot be measured. It would therefore be necessary to measure the strength of the acid in relation to a base (P/P to a reference couple), i.e. determine the relative strength of this acid.
Consider two acid-base couples: $\mathbf{A_1H/A_1^-}$ **et** $\mathbf{A_2H/A_2^-}$

$$\mathbf{A_1H + A_2^- \Leftrightarrow A_2H + A_1^-}$$

We measure the strength of the acid $\mathbf{A_1H}$ by the constant $\boldsymbol{Ka} = \frac{[A2H]\,[A1-]}{[A1H]\,[A2-]}$

- If **K >1** the equilibrium is shifted to the right ⟹ the acid A_1H is **stronger** than A_2H and the base A_2^- is **stronger** than A_1^-
- If **K < 1** the equilibrium is shifted to the left ⟹ the acid A_1H is **weaker** than A_2H and the base A_2^- is **weaker** than A_1^-
- **It should be noted that the stronger an acid, the weaker its conjugate base and vice versa.**

To be able to compare the strengths of different acids, it is necessary to measure their tendency to give up a proton to the same base (e.x. water). $\mathbf{AH + H_2O \Leftrightarrow A^- + H_3O^+}$

The acidity constant is the dissociation constant of AH in water: $K_a = \frac{[H_3O^+][A^-]}{[AH]}$

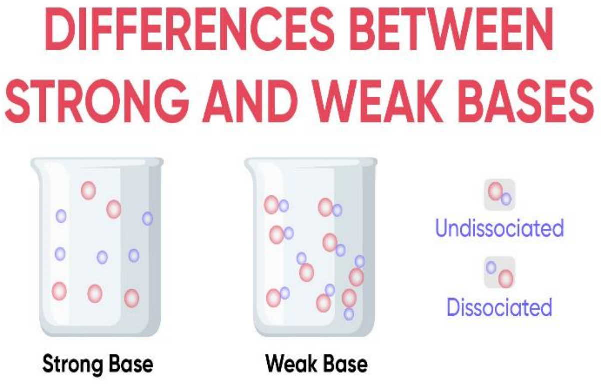
Ka is measurable and can be considered as the strength of acid in water.

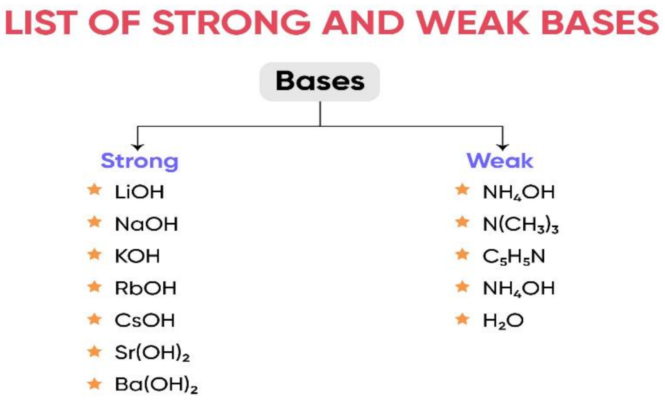
Ka is generally very low which leads to using **pKa = -log Ka**.

The lower the pKa value, the greater the Ka, the stronger the acid.

IV.2 Strength of bases

The issue is similar with bases: a strong base is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a weak base.





IV.2.1 Relative strength of a weak base in water

Bases are also classified by their degree of dissociation in water

Example : B + H2O ⟺ BH⁺+ OH⁻ $K_b = \frac{[BH+]\,[OH-]}{[B]}$

B et BH⁺ coexist and we can establish a relationship between Kb, B, Ka et BH⁺

$BH^+ + H_2O \Leftrightarrow B + H_3O^+$ $K_{a,BH+} = \frac{[B]\,[H3O+]}{[BH+]}$

We find : $\boxed{pK_b = 14 - pK_a}$

IV.3 Relative strength of a strong acid and a strong base in water

$HBr + H_20 \longrightarrow H_3O^+ + Br^-$

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

HBr and HNO_3 are both strong acids, their strength can't be measured by their constant of acidity $Ka,_{HBr}$ and $Ka,_{HNO3}$. The two acids were transformed in H_3O^+.

Likewise, NaOH and KOH are strong bases and therefore completely dissociated in water. Their strength cannot be measured by $Kb,_{NaOH}$ and $Kb,_{KOH}$. They turned into OH^-. We are talking about the phenomenon of leveling.

Discussion of the leveling phenomenon

A strong acid (or base) is completely dissociated in water and transformed into **H_3O^+**(or **OH^-**), ions, there cannot be an acid in water stronger than the **H_3O^+** ion and it cannot be in the basic water stronger than the **OH^-** ion. This finding is called **solvent leveling**.

- **The strongest acid that exists in water is H_3O^+. All strong acids are transformed into H_3O^+ .**
- **The strongest base in water is OH^-. All strong bases are transformed into OH^- .**

In water, the strengths of acids and bases are limited and we can only measure the forces where $0 \leq PKa \leq 14$.

How can this be remedied?

To be able to compare the relative strengths of strong acids (or strong bases) it is necessary to choose other reference pairs ⟹ choose other solvents.

Example : The dissociation of strong acids in pure acetic acid

$HCl + CH_3COOH \Leftrightarrow Cl^- + CH_3COOH_2^+$

The reaction is balanced so we can calculate $Ka,_{HCL}$
In pure acetic acid, the strong acids (H_2SO_4, HBr, HNO_3, …) are partially dissociated and we can therefore compare their strengths : **$Ka,_{HClO4} > Ka,_{HBr} > Ka,_{H2SO4} > Ka,_{HCl}$.**

IV.4 Strength of a polyacid

Polyacids are capable of releasing several protons. Each dissociation equilibrium corresponds to an acidity constant.

Example 1: H_2CO_3

$H_2CO_3 + H_2O \Leftrightarrow HCO_3^- + H_3O^+$ **$Ka_1 = 4.5\ 10^{-7}$**

$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$ **$Ka_2 = 5.7\ 10^{-11}$**

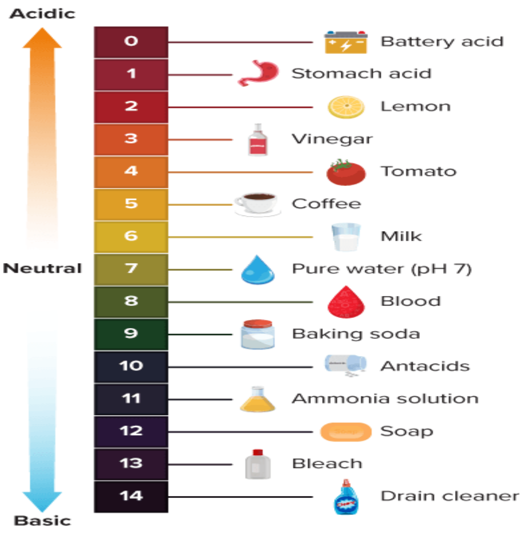
Example 2 : H_3PO_4 :

$H_3PO_4 + H_2O \Leftrightarrow H_2PO_4^-$ **$Ka_1 = 7.5\ 10^{-3}$**

$H_2PO_4^- + H_2O \Leftrightarrow HPO_4^{2-}$ **$Ka_2 = 6.2\ 10^{-8}$**

$HPO_4^{2-} + H_2O \Leftrightarrow PO_4^{3-}$ **$Ka_3 = 5\ 10^{-13}$**

V CONCEPT OF PH



pH is a unitless quantity between 0 and 14. An index that allows you to measure the acidity or basicity of a solution.

For a given environment, the pH depends on the concentration of hydronium ions H_3O^+. It is given by the following relation: $pH = -\log [H_3O^+]$

$[H_3O^+]$: Total molar concentration total of hydronium ions (mol/L)

An acidic environment therefore contains more hydronium ions H_3O^+, while a basic medium contains more hydroxide ions OH^-.

Similarly, we can define the pOH of a basic solution: $pOH= -\log [OH^-]$

Since: $[H_3O^+].[OH^-]=10^{-14}\ mol^2 /l^2$

=> $\log [H_3O^+] + \log [OH^-] = -14$ => $\boxed{pH + pOH = 14}$

It's important to know: Law of conservation of matter

The total mass of products that appear during a chemical reaction is equal to the total mass of products that disappear.

V.1 pH and predominance diagram

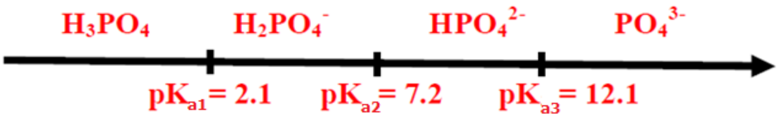
Any Acid/Base couple is characterized by its constant of acidity

We can define : **$pH= pKa + \log [A^-] / [AH]$**

- If pH = pKa ⟹ [A-] = [AH]

- If pH > pKa ⟹ [A-] > [AH] ⟹ the base is predominanting
- If pH < pKa ⟹ [A-] < [AH] ⟹ the acid is predominanting

Example : Predominance diagram H_3PO_4 ($pKa_1 = 2.1$; $pKa_2 = 7.2$; $pKa_3 = 12.1$)

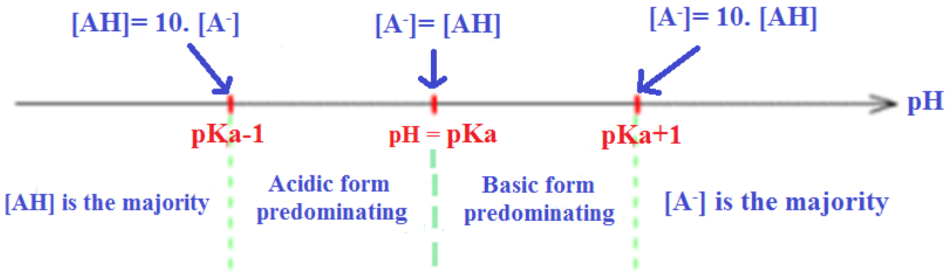


In general it is assumed that a species is more dominant than another if it is ten times more important.

We say that [AH] is dominant if $[AH] \geqslant 10.[A^-] \Longrightarrow [A^-]/[AH] \leqslant 10\text{-}1 \Longrightarrow \text{Log } [A^-]/[AH] \leqslant -1$
$\Longrightarrow$ **pH $\leqslant$ pKa** -1

Likewise we say that $[A^-]$ is dominant if $[A^-] \geqslant 10.[AH] \Longrightarrow [A^-]/[AH] \geqslant 10 \Longrightarrow \text{Log } [A^-]/[AH] \geqslant 1$
$\Longrightarrow$ **pH $\geqslant$ pKa** +1

It can be concluded that $[A^-]$ et [AH] only coexist appreciably in the interval **[pKa -1, pKa +1].**



V.2 pH of a strong acid

a) Case of a string monoacid

Consider a strong acid AH of concentration C.

$AH + H_2O \longrightarrow A^- + H_3O^+$ AH is completely dissociated $\Longrightarrow [A^-] = C$

The equation for the electroneutrality of the solution is written:

$[H_3O^+] = [A^-] + [OH^-]$ (I)

The dissociation of water gives us: **$H_2O + H_2O \Longleftrightarrow H_3O^+ + OH^-$**

At the equilibrium: **$Kw = [H_3O^+]\,[OH^-] = 10^{-14}$**

What happens if we add a strong acid to water?

If we add AH the equilibrium moves to the left (**Lechatelier principle**)
So **$[H_3O^+]_{water} < 10^{-7}$** we can therefore neglect $[H_3O^+]_{water}$
The new equilibrium gives us : **$Kw = [H_3O^+]_{tot}.\,[OH^-]_{water}$**

The addition of an acid to water reverses the dissociation of water so as to maintain Kw.

So **$[OH^-]_{water} < 10^{-7}$** we can neglet it in front of **$[A^-]$.**
The equation (**I**) is written : **$[H_3O^+] = [A^-]$**   **=>**   **$[H_3O^+] = C$**   **so**   **pH = - log C**

In the case of a strong acid, of not very low concentration, the dissociation of water is neglected.

Example 1 : Consider a strong acid AH of a $C = 10^{-2}$ M

The concentration C is not very low, so we can neglect $[H_3O^+]_{water}$

pH = - log C = 2

Let's calculate $[OH^-]_{water} = Ke/[H_3O^+]_{tot} = Ke/C = 10^{-14}/10^{-2} = 10^{-12}$ M $\Longrightarrow$ $\mathbf{[OH-]_{water} = 10^{-12}\ M}$

Or, $\mathbf{[OH-]_{eau} = [H_3O+]_{eau} = 10^{-12}\ M}$

So we can neglect $[H_3O^+]$ coming from the dissociation of water.

Example 2 :

Calculate the pH of an HCl solution with a concentration $C = 10^{-7}$ M

The equation for the electroneutrality of the solution is written:

$[H_3O^+] = [A^-] + [OH^-] \Longrightarrow [H_3O^+] = [Cl^-] + [OH^-]$ (I)

At the equilibrium: $Kw = [H_3O^+]\,[OH^-] = 10^{-14} \Longrightarrow [OH^-] = Ke / [H_3O^+]$

(I) $\Longleftrightarrow [H_3O^+] = [Cl^-] + Ke / [H_3O^+] = [Cl^-] + 10^{-14}/[H_3O^+]$

(I) $\Longleftrightarrow [H_3O^+]^2 - C.\,[H_3O^+] - 10^{-14} = 0$

$$\Longrightarrow [H_3O^+] = \frac{C + (C^2 + 4.\,10^{-14})^{1/2}}{2}$$

From what value of C can we neglect the dissociation of water?

We neglect the dissociation of water if $[AH] \geq 2.10^{-6}$ M

b) Case of a strong diacid

Consider a diacid H_2A of a molar concentration C.

$\mathbf{H_2A + 2H_2O \longrightarrow A_2^{2-} + 2\,H_3O^+}$

We are in the presence of a strong diacid, we can therefore neglect the dissociation of water

$\mathbf{[H_3O^+] = 2C \Longrightarrow}$ $\boxed{\mathbf{PH = - Log\ 2C}}$

V.3 pH of a strong base

a) Case of a strong monobase

Let B be a strong base of a concentration C.

$\mathbf{B + H_2O \longrightarrow BH^+ + OH^-}$ B is completely dissociated

$\mathbf{pOH = - log[OH^-]_{tot}}$

$\mathbf{[OH^-]_{tot} = [OH^-]_B + [OH^-]_{water}}$

In the presence of a strong base, water retrogrades$\Longrightarrow$ $\mathbf{[OH-]_{water} < 10^{-7}}$ so we can neglect $[OH-]_{water}$

$\mathbf{pOH = - log[OH^-]_B \Longrightarrow pOH = - log\ C}$ $\Longrightarrow$ $\boxed{\mathbf{pH = 14 + log\ C}}$

In the case of a strong base, of not too low concentration, we neglect the dissociation of water

b) Case of a strong dibase

Consider a strong base such as Na_2O with molar concentration C:

$Na_2O \longrightarrow 2\ Na^+ + O^{2-}$

$O^{2-} + H_2O \longrightarrow 2\ OH^-$ $[OH^-] = 2C$ and $[H_3O^+] = Kw / [OH^-]$

=> $[H_3O^+] = 10^{-14} / 2C$ so $\boxed{PH = 14 + Log\ 2\ C}$

V.4 pH of a weak acid

Consider a weak acid AH of molar concentration C.

- **Dissociation of AH**

$AH + H_2O \longrightarrow A^- + H_3O^+$ with $Ka = [A^-]\,[H_3O^+] / [AH]$ **(I)**

- **Dissociation of water**

$H_2O + H_2O \longrightarrow H_3O^+ + OH^-$ with $Kw = [OH^-]\,[H_3O^+]$ **(II)**

- **Conservation of matter (C.M.) :**

$[AH] + [A-] = C$ **(III)**

Where : $[AH] = C - [A-]$

- Electroneutrality of the solution (E.N.S.) :

$[A^-] + [OH^-] = [H_3O^+]$ **(IV)**

Where: $[A^-] = [H_3O^+] - [OH^-] \Longrightarrow$ $\mathbf{[A^-] = [H_3O^+] - Kw/ [H_3O^+]}$

According to **(III)** $[AH] = C - [A-] \Longrightarrow$ $\mathbf{[AH] = C - ([H_3O^+] - Kw/ [H_3O^+])}$

By replacing [A-] and [AH] in equation **(I)** we obtain a 3rd degree equation:

$$\boxed{[H_3O^+]^3 - Ka.[H_3O^+]^2 - (Ka.C + Kw)\,[H_3O^+] + Ka.\,Kw = 0} \qquad \textbf{(V)}$$

We can simplify equation (**V**) by making approximations:

<u>1st approximation :</u>

We neglect the dissociation of water. This approximation is verified if **pH ≤ 6.5**

We can therefore write : $\mathbf{[A-] = [H_3O^+]}$

<u>2nd approximation :</u>

We suppose that AH is weakly dissociated. This approximation is verified if **pH ≤ pKa - 1**

We can therefore write : **[AH] = C**

By replacing in (I) we will have: $Ka = [H_3O^+]^2/C$

$\Longrightarrow \boxed{pH = ½\ pKa - ½\ log\ C}$ with **pH ≤ 6.5** and **pH ≤ pKa – 1**

V.5 pH of a weak base

Consider a weak acid B of molar concentration C

(Same reasoning as for a weak acid)

$B + H_2O \longrightarrow BH^+ + OH^-$ $$K_b = \frac{[BH+]\,[OH-]}{[B]}$$

If we neglect **$[OH^-]_{water}$** and admit that the base B is weakly dissociated, the pH expression of the weak base is written:

pOH = ½ pkb – ½ LogC

With: pOH = 14 – pH ⟹ pH = 14 – pOH

$\boxed{\textbf{pH = 14 – ½ pkb + ½ Log C}}$ with: **pH ≥7.5** and **pOH ≤ pKb -1** (ou pH ≥ pKa + 1)

VI. HYDROLYSIS OF A SALT

VI.1 Definition

Hydrolysis is the reaction of an ionic compound with water.

Salts from strong acids and strong bases do not undergo hydrolysis(Ex : NaBr, $CaSO_4$, KNO_3,…)

On the other hand, undergo hydrolysis all the salts produced by:

- Of a strong acid and a weak base (ex : NH_4Cl)
- Of a weak acid and a strong base (ex : HCOONa)
- Of a weak acid and a weak base (ex : CH_3COONH_4)

VI.2 Case of a salt resulting from a strong acid and a strong base

$HCl + NaOH \longrightarrow NaCl + H_2O$

Strong acid + Strong base $\longrightarrow$ Salt + Water

In aqueous solution, there is a total dissociation of the salt: **NaCl** (s) $\longrightarrow$ **Na^+**(aq) + **Cl^-**(aq)

Cl^-: conjugated base (very weak) of the strong acid (HCl), it does not participate in any chemical equilibrium.
Na^+: the conjugated acid of the base NaOH, is very weak (inerte), he has no responsiveness.
Na^+ and Cl^- therefore do not hydrolyze $[H_3O^+] = [OH^-] = 10^{-7}$ mol/l (dissociation of water).

⇒ $\boxed{\textbf{pH (NaCl) = 7 the environment is neutral at 25°C}}$

VI.3 Case of a salt resulting from a strong acid and a weak base

$HCl + NH_3 \longrightarrow NH_4Cl$

In aqueous solution, there is total dissolution of the salt: $NH_4Cl \longrightarrow NH_4^+ + Cl^-$

Cl^-: does not participate in any chemical equilibrium, it does not hydrolyze. But **NH_4^+** hydrolyzes.

$NH_4^+ + H_2O \Leftrightarrow NH_3 + H_30^+$ (I)

so $[H_3O^+] > 10^{-7}$ mol/l $\Longrightarrow$ pH < 7 $\Longrightarrow$ The saline solution is **acidic**

Calculating the pH of the solution :

According to the equation (I) we have a weak acid so : pH = ½ pKa – ½ Log C
Ka : constant of acidity of NH_4^+ and C=[NH_4^+]
In general we give $K_{b,\ NH3}$ but we know that pKa + pKb = 14 $\Longrightarrow$ pKa = 14 - pKb

pH = ½ (14 – pKb) – ½ Log C $\Longrightarrow$ $\boxed{\textbf{pH = 7 - ½ pKb - ½ Log C}}$

VI.4 Case of a salt resulting from a weak acid and a strong base

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$CH_3COONa + H_2O \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$

Na^+ does not hydrolyze, however CH_3COO^- hydrolyzes:
$CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH^-$ (II)
So OH- > 10^{-7} mol/l $\Longrightarrow$ pH > 7 $\Longrightarrow$ the saline solution is **basic**.

Calculation the pH of the solution :

According to the equation **(II)** we have a weak base so : **pH = 14 - ½ pKb + ½ Log C**
Kb : basicity constant of CH_3COO^- and C = [CH_3COO^-]
Knowing that pKb = 14 – pKa, w'll have:

$\boxed{\textbf{pH = 7 + ½ pKa + ½ Log C}}$

VI.5 case of a salt resulting from a weak acid and a weak base

$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$

$CH_3COONH_4 + H_2O \longrightarrow CH_3COO^-_{(aq)} + NH_4^+{}_{(aq)}$

The two ions hydrolyze:
$NH_4^+ + H_2O \Leftrightarrow NH_3 + H_30^+$

$CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH$

Will the saline solution be acidic, basic or neutral?

If Ka, NH_4^+ > Kb, CH_3COO^- ⇒ the saline solution is **acidic.**

If Ka, NH_4^+ < Kb, CH_3COO^- ⇒ the saline solution will be **basic.**

If Ka, NH_4^+ = Kb, CH_3COO^- ⇒ the saline solution will be **neutral.**

Calculating the pH of the solution :

Consider a saline solution of concentration C in **CH_3COONH_4**

Conservation of matter:

C = $[NH_4^+] + [NH_3] = [CH_3COO^-] + [CH_3COOH]$ **(I)**

Electroneutrality of the solution :

$[CH_3COO^-] + [OH^-] = [NH_4^+] + [H_30^+]$ **(II)**

We neglect the participation of water

The predominant reaction will be :

$CH_3COO^- + NH_4^+ \Leftrightarrow CH_3COOH + NH_3$ (transfer of H^+ between NH_4^+ and CH_3COO^-)

to C C 0 0

teq C – x C – x x x

where: **$[CH_3COO^-] = [NH_4^+]$ (II)**

The equation **(I)** is written: **$[NH_3] = [CH_3COOH]$**

Let's write the hydrolysis reaction of NH_4^+ and CH_3COO^- :

$NH_4^+ + H_2O \Leftrightarrow NH_3 + H_30^+$ $$Ka_{NH4+} = \frac{[NH3]\,[H3O+]}{[NH4+]}$$

$CH_3COO^- + H_2O \Leftrightarrow CH_3COOH + OH^-$ $$Kb_{CH3COO-} = \frac{[CH3COOH]\,[OH-]}{[CH3COO-]}$$

We can deduce: $$Ka/Kb = \frac{[NH3]\,[H3O+]\,[CH3COO-]}{[NH4+]\,[CH3COOH]\,[OH-]}$$

$\Rightarrow Ka/Kb = [H_3O^+]/[OH^-]$ $\Rightarrow Ka/Kb = [H_3O^+]^2/10^{-14}$

$$\Rightarrow \boxed{pH = 7 + ½\ pKa,\ NH_4^+ – ½\ pKb,\ CH_3COO^-} \quad \textbf{(III)}$$

If we replace pKb, $_{CH3COO-}$ by pKa, $_{CH3COOH}$, w'll have:

$$\Rightarrow \boxed{pH = \frac{pKa,NH4+ + pKa, CH3COOH}{2}}$$

VI. BUFFER SOLUTIONS

VII.1 Definition od a buffer solution

A buffer solution is a solution whose pH varies little when small quantities of acids or bases are added. Likewise, the pH is very stable despite the effects of dilution.

VII.2 Preparing a buffer solution

We prepare a buffer solution, by mixing :

- A weak acid and its salt from a strong base (Ex. CH_3COOH/CH_3COONa).

- A weak base and its salt from a strong acid (Ex. NH_3/NH_4Cl).
- Two salts of a weak polyacid and a strong base (Ex. NaH_2PO_4/Na_2HPO_4).

VII.3 Calculating the pH of a buffer solution

A buffer solution has a well-defined pH. The OH^- and the H_3O^+ ions introduced in the solution are neutralized in order to maintain the pH of this buffer mixture.

Example : consider the buffer mixture **: AH/A^-**

If we introduce H_3O^+ $\longrightarrow$ $\mathbf{A^- + H_3O^+ \Leftrightarrow AH + H_2O}$
If we introduce OH^- $\longrightarrow$ $\mathbf{AH + OH^- \Leftrightarrow A^- + H_2O}$

a)- Calculating the pH of a buffer solution : Weak acid and its salt from a strong base (AH/A^-) :

Consider Ca the concentration of AH
Let be Cs the concentration of the salt (Ex. CH_3COOH/CH_3COONa)

$\mathbf{AH + H_2O \Leftrightarrow A^- + H_3O^+}$ $\quad Ka = \frac{[A-]\,[H3O+]}{[AH]} \quad \Rightarrow [H_3O+] = \frac{Ka\,[AH]}{[A-]}$

pH = pKa – Log $[AH]/[A^-]$ $\Rightarrow$ $\boxed{\mathbf{pH = pKa - Log\ Ca/Cs}}$ (equation of Henderson-Hasselbach)

If Ca = Cs $\Rightarrow$ **pH = pKa**

b)- Calculating the pH of a buffer solution : weak base and its salt from strong acid (B/BH^+) :

Consider C_b the concentration of B

Let be C_s the concentration of salt BHA (Ex. NH_3/NH_4Cl)

$\mathbf{B + H_2O \Leftrightarrow BH^+ + OH^-}$ $\quad Kb = \frac{[BH+][OH-]}{[B]} \quad \Rightarrow \quad [OH^-] = \frac{Kb\,[B]}{[BH+]}$

pOH = pKb – Log $[B]/[BH^+]$ $\Rightarrow$ $\boxed{\mathbf{pH = 14 - pKb + Log\ Cb/Cs}}$

if Cb = Cs $\Rightarrow$ **pH = 14 - pKb**

VII.4 buffer power and activity zone

- The buffering power is the ability of this solution to resist the change in pH when an acid or a base is added.
- This capacity is measured by the quantity of H_3O^+ or OH^- ions that the solution can absorb without the variation in pH being significant.
- In general, a buffer solution is effective if: **pKa -1 ≤ pH ≤ pKa +1**

  - If pH ≤ pKa the solution buffers better **OH^-** than H_3O^+

  - If pH ≥ pKa the solution buffers better **H_3O^+** than OH^-

Choice of a buffer solution

- The couple AH/A- must have a pH : pKa -1 ≤ pH ≤ pKa +1
- The buffer power depends on the concentrations Ca et Cs :

- The higher Ca et Cs the greater the buffering power.
- The power is maximum if Ca = Cs

Example 1 :

Une buffer solution contains **0.24M** of NH_3 and **0.2M** of NH_4Cl.

a) Calculate the pH of this solution.

b) What happens to the pH if we add **5.10^{-3} mole** of NaOH to **0.5L** of this solution

c) What happens to the pH if we add **5.10^{-2} mole** of NaOH to **0.5L** of this solution

d) What happens to the pH if we add **5.10^{-3} mole** of NaOH to **0.5L** of pure water

$pKb_{,NH_3} = 4.75$.

Example 2 :

We give the following acid-base couples:

Couple acid-base	**$HCOOH/HCOO^-$**	**CH_3COOH/CH_3COO-**	**$H_2C_2O_4/HC_2O_4$**	**HF/F^-**
pKa	3,75	4,8	1,2	3,17

Which of these pairs best corresponds to buffering a solution at pH=3. Justify your answer.

VI. NEUTRALIZATION CURVES OF AN ACID BY A BASE OR OF A BASE BY AN ACID

Acid-base assays are extremely common in chemistry. Two techniques are used:

- pH metric dosage
- Volumetric dosing with colored indicator

- Colored indicators are used to determine the end of the reaction during a titration.
- These are acid-base couples whose acidic form **AH** is clearly distinct in color from the basic form **A^-** . This acid-base couple has a well-defined pKa.
- The color of the colored indicator varies within a narrow pH range, called: **turning zone**. It is located in a pH zone ranging from **pKa – 1** to **pKa + 1**.

The change in color of an indicator must occur when the equivalent point of a dosage is reached. Colored indicators are compounds capable of coloring a solution even in trace amounts.

The table below gives some examples showing that the turning zones of the indicators are very varied :

Colored indicator	Acid color	Turning zone	Basic color
Helianthin	Red	3.1-4.4	Yellow
Bromocresol green	Yellow	3.8-5.4	Blue
Bromothymol blue	Yellow	6.0-7.6	Blue
Cresol red	Yellow	7.2-8.8	Red
Phenolphthalein	Colorless	8.2-10.0	Pink
Alizarin red	purpule	10.0-12.0	Yellow
Indigo carmin	Blue	11.6-14.0	Yellow

• VIII.1 Neutralization of a strong acid by a strong base

$AH + H_2O \longrightarrow A^- + H_3O^+$ AH completely dissociated

$BOH + H_2O \longrightarrow B^+ + OH^-$ BOH completely dissociated

A^- et B+ are indifferent, neutralization sums up to the reaction :

$OH^- + H_3O^+ \Leftrightarrow 2\ H_2O$ At the equivalence point: **pH = 7**

The curve of Neutralization is obtained by drawing the pH of the solution as a function of the volume of the base added.

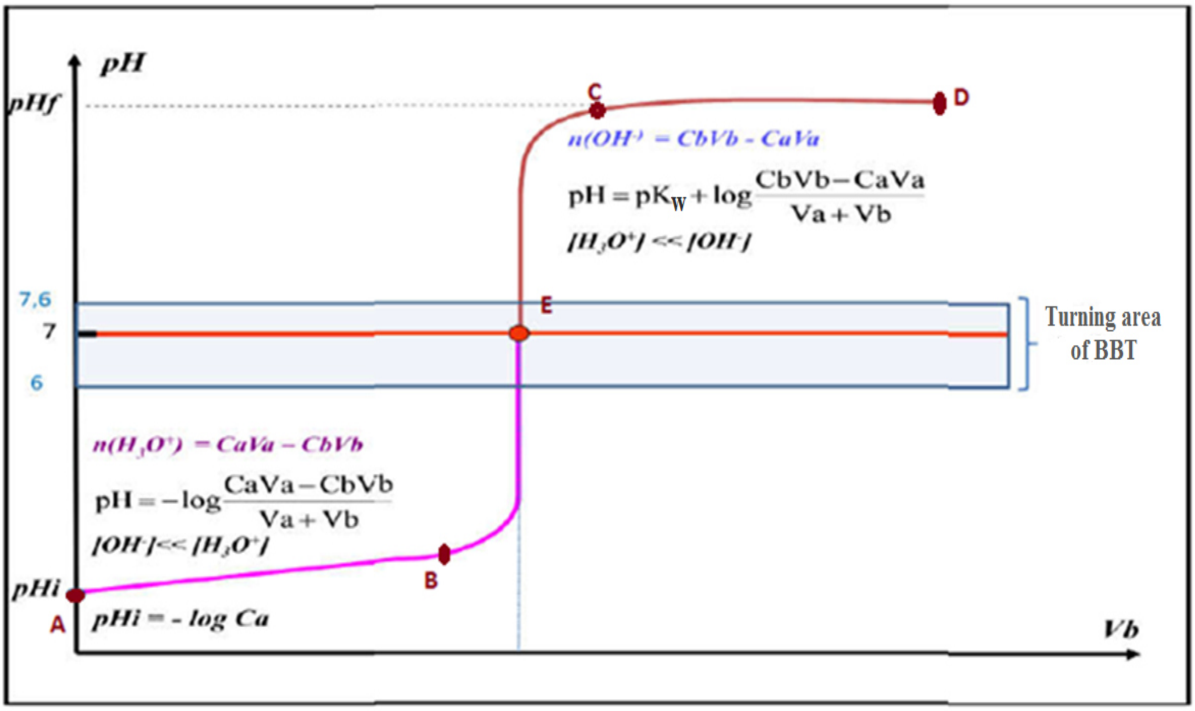
Example : Titration of HCl by NaOH

Strong acid (HCl) : V_a = 10mL of a concentration $C_a = 10^{-1}$ mol/L

Strong base (NaOH) : V_b mL at a concentration $C_b = 10^{-1}$ mol/L

Resulting reaction of dosage:

$HCl + NaOH \rightarrow (Cl^-, Na^+) + H_2O$ Or $H_3O + OH \rightarrow 2H_20$



The neutralization curve can be summarized on the following points :

- **Point A** : we have a solution of a strong acid ⟹ $\boxed{pH = -\log[H_3O^+] = -\log Ca}$; **$Ca=[HCl]_0$**

- **Between point A and B** : the pH varies a little. This zone corresponds to $0<V_{NaOH}<Ve$

- **Point B** : situated before the equivalence point, where : **pH= - log Ca'**

$$\boxed{pH = -\log\frac{CaVa - CbVb}{Va + Vb}}$$

- **Point E (equivalent point) :** is located in an area where there is a jump in pH.

$V_e=V_{NaOH}$ and $n_{HCl} = n_{NaOH}$. The saline solution is **neutral** : $\boxed{pH=7}$

- **Point C :** is situated after the equivalent point, we are in the presence of an excess of strong base. $V_{NaOH}>V_e$ and **$pH=14+\log[OH^-]= 14 +\log C_{b'}$**

$$\boxed{pH = 14 + \log\frac{CbVb - CaVa}{Va + Vb}}$$

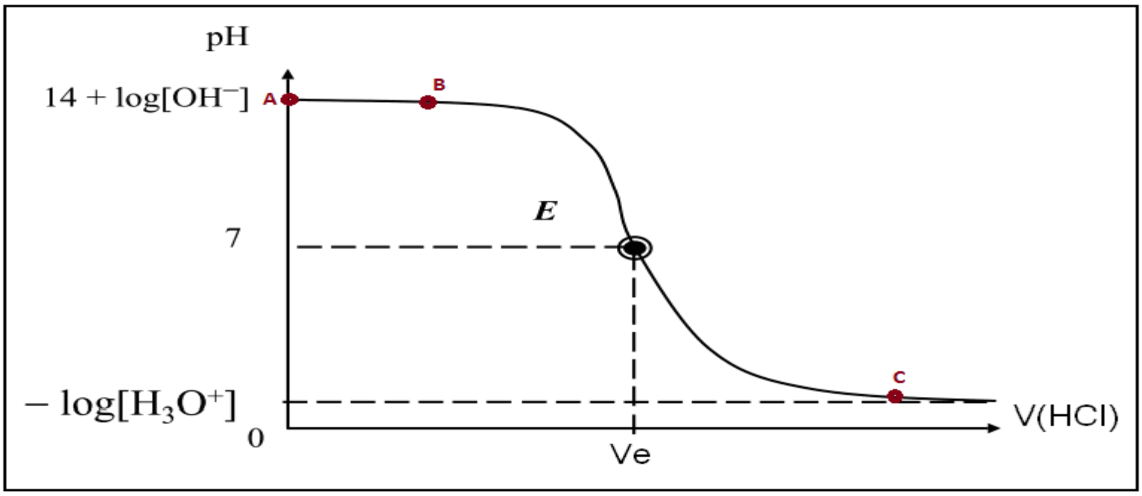
Choice of the indicator: near the equivalence point the variation in pH is very rapid, therefore any indicator varying between *pH = 3* and *pH = 11* will be ideal.

VIII.2 Neutralization of a strong base by a strong acid

When titrating a strong base with a strong acid, we find the previous curve but reversed and the same colored indicators are used.

Example : Titration of NaOH by HCl

Very similar calculations make it possible to determine the pH during the dosage. We obtain the graph:



- **Point A** : we are in the presence of a strong base ⟹ $\boxed{pH = 14 + \log Cb ;\ Cb = [NaOH]_0}$

- **Point** B : situated before the equivalent point, where : **pH= 14 + log Cb'**

$$\boxed{pH = 14 + \log \frac{\mathbf{CbVb - CaVa}}{\mathbf{Va + Vb}}}$$

- **Point E (equivalent point) :** Ve=VHCl and nNaOH = nHCl. The saline solution is **neutral** : pH=7

- **Point C** : is situated after the equivalent point, we are in the presence of an excess of a strong acid.

$V_{HCl}>V_e$ and **pH= -log Ca'**

$$\boxed{pH = -\log \frac{\mathbf{CbVb - CaVa}}{\mathbf{Va + Vb}}}$$

- **VIII.3 Neutralisation of a weak acid by a strong base**

Example : Titration of de CH_3COOH by NaOH

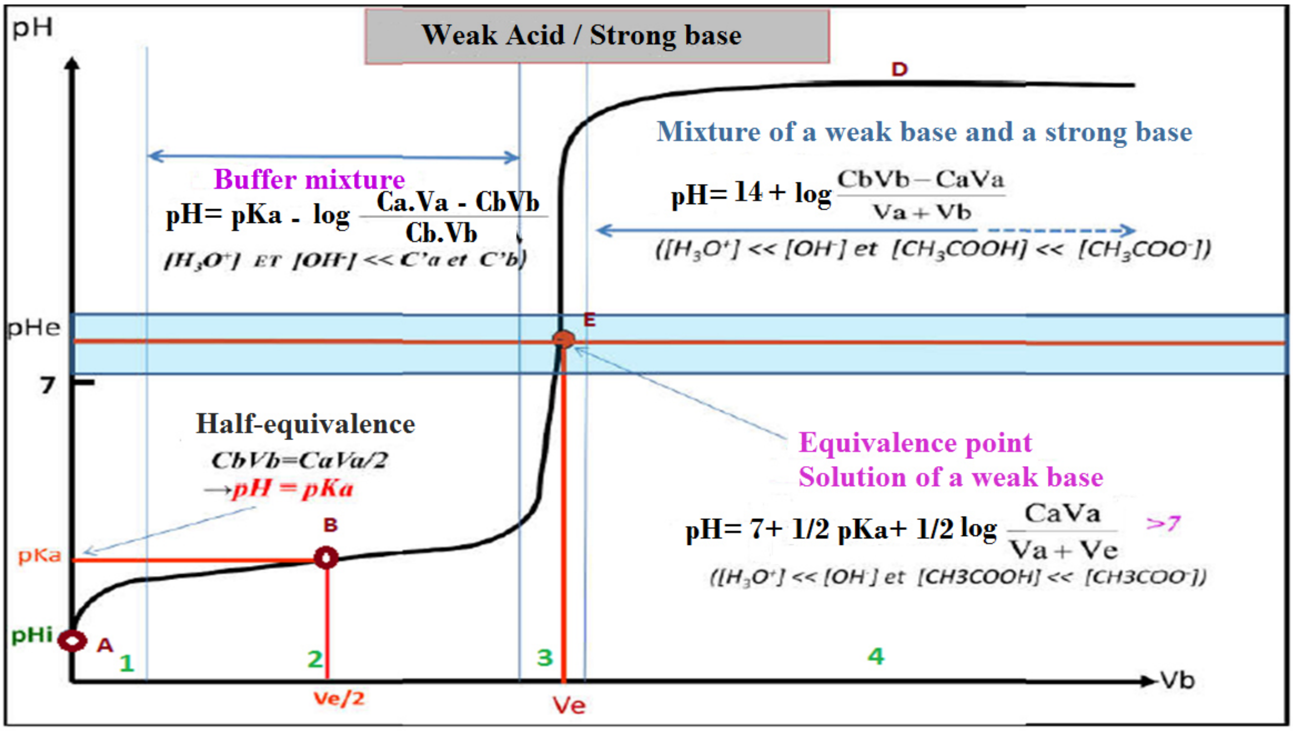
Weak acid (CH_3COOH) :

Va=10mL of a concentration Ca =10 mol.L^{-1}

Strong base (NaOH) :

Of a volume Vb of concentration Cb = 10 mol.L^{-1}

Balanced reaction: $CH_3COOH + Na^+ ,OH^- \rightarrow CH_3COO^- , Na^+ + H_2O$



The choice of colored indicators is more limited. We will have to use indicators turning into a basic environment such as Phenolphthalein [8,2 – 10].

The neutralization curve can be summarized on the following points :

- **Point A :** We are in the presence of a solution of a weak acid ⟹ **pH= ½ pKa – ½ log Ca** ;

Ca= [CH_3COOH]

- **Zone 2 :** corresponds to a buffer mix (CH_3COOH/CH_3COO^-)

$$\boxed{pH = pKa - \log Ca/Cs}$$

Ca: Concentration of the acetic acid remaining in solution.

Cs: Concentration of the acetate formed.

Calculation of Ca : **Calculation of Cs :**

$$Ca = [CH3COOH] = \frac{CaVa - CbVb}{Va+Vb} \qquad Cs = [CH3COO-] = \frac{CbVb}{Va+Vb}$$

$$\boxed{pH = pKa - \log \frac{CaVa - CbVb}{CbVb}}$$

- **Point B :** corresponds to the half-equivalence **: Ca = Cs ⇒ pH = pKa (half neutralisation).**

- **Zone 3 :** turning zone ⇒ observation of the pH jump.

- **Point E :** it's the equivalence point. (Ca.Va = Cb.Vb). We are in presence of a basic salt: (hydrolysis de CH_3COO^-)

$$\boxed{pH = 7 + ½\, pKa_{,CH3COOH} + ½ \log C}$$

- **Zone 4 :** we are in the presence of an excess of a strong base (Vb > VE)

- **Point D :** It is situated after the equivalence point⇒ $[OH-] = \frac{CbVb - CaVa}{Va+Vb}$

pH = 14 – pOH ⇒ $\boxed{pH = 14 + \log \frac{CbVb - CaVa}{Va+Vb}}$

Remark :

Influence of weak acid strength

The lower the pKa of a couple, the stronger the acid of this couple and the lower the initial pH of the solution. Thus, the pH jump to equivalence is greater if the acid has a low pKa.

Influence of adding water

As we saw above in the paragraph on the influence of concentration, adding water causes:

- An increase in the initial pH because the acid is more diluted.
- A less significant jump in pH at the equivalence;

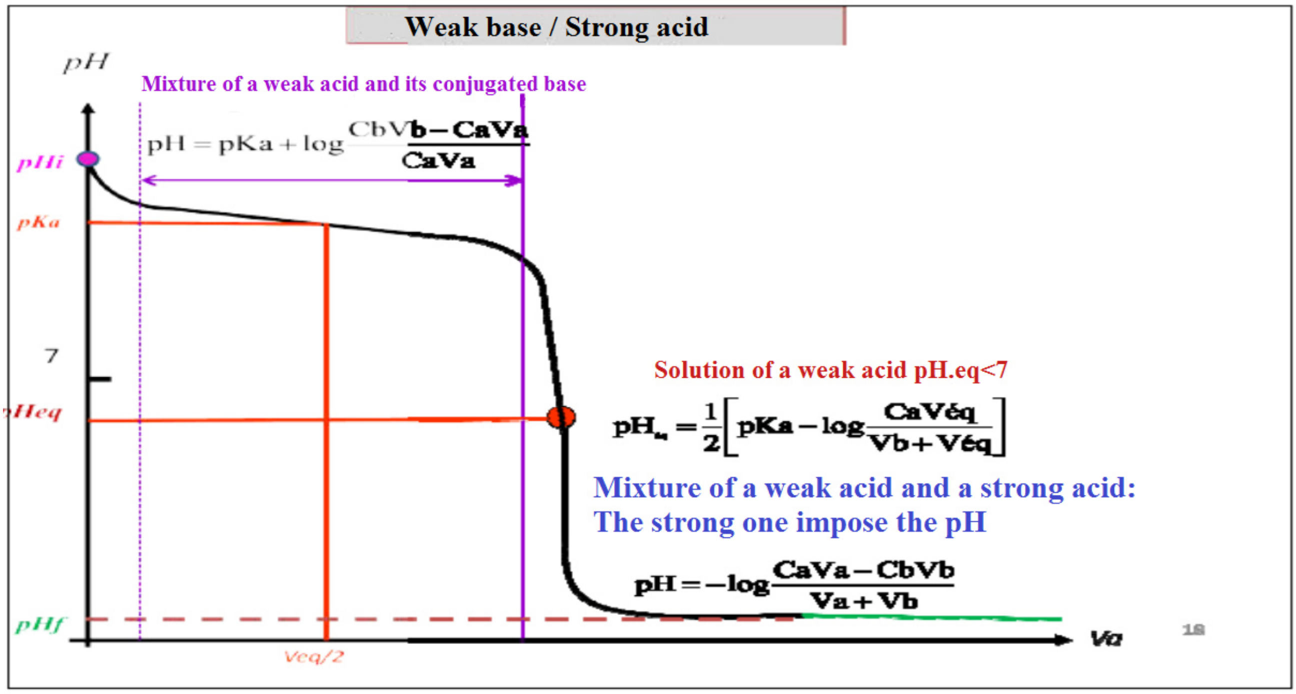
Warning: the more water you add, the more difficult it is to precisely determine the equivalence.

VIII.4 Neutralization of a weak base by a strong acid

When titrating a weak base with a strong acid, we find the previous curve but reversed and the colored indicators used are those changing in an acidic environment.

Example : Titration of NH_3 by HCl

$$NH_3 + HCl \longrightarrow NH4^+ + Cl^- + H_2O$$



- **Initially**: we are in the presence of a weak basic solution

  The pH of the environment is the pH of a weak base :

  $\boxed{pH = 14 - 1/2\ pKb + ½ \log Cb}$ with **Cb = [NH3]₀**

- **In the semi-neutralization zone**: corresponds to a buffer mix

  $\boxed{pH = 14 - pKb + \log Cb/Cs}$

  Cb = [NH_3] remaining in solution

  Cs = [NH_4^+]

- **At the point of half neutralization**: (V_{HCl} = 1/2 V_E) ⇒ Cb = Cs ⇒ $\boxed{pH = 14 - pKb}$
- **At the equivalent point** : (V_{HCl} = V_E) ⇒ $n_{NH3} = n_{HCl}$

We are in presence of an acid salt: (hydrolyde de NH_4^+)

$\boxed{pH = 7 - ½\ pKb,NH_3 - ½ \log C}$

- **After the equivalence** : (V_{HCl} > V_E) There is an excess of Hydrochloric acid ⇒ n Acid solution

$\boxed{pH = -\log Ca'}$ with $Ca' = \frac{CaVa - CbVb}{Va+Vb}$

IX. APPLICATION EXERCICES

Exercise 01 :

Consider the pka of the following acid-base couples in water:

HCl/Cl^- = **-6** HF/F^- = **3, 2** HNO_3/NO_3^- = **-4** $HClO/ClO^-$ = **7,5**

1. Which acids are subject to the leveling effect in water? Can we classify them in the scale of acidity in relation to water? Justify.
2. Write the acid-base reaction corresponding to each of these acids in water.
3. We consider another solvent, methanol CH_3OH, specify the behavior of the acids HCl and HNO_3 in this solvent knowing that their pKa are respectively equal to **1,2** and **3,2**, justify.

- Write for each acid the reaction that takes place in this solvent.
- Give the expression for the acidity constant in each case.

pKa data of reference pairs : (H_3O^+/H_2O = **-1,74**) , (H_2O/OH^- =**15,74**)
($CH_3OH_2^+/CH_3OH$ = **-1,38**) , (CH_3OH/CH_3O^- = **17,98**).

Exercise 02 :

A solution of HCOOH formic acid whose pKa is **3.8** has a pH equal to **2.3**.

1. Calculate the concentrations of the different species present in solution**.**
2. What is the value of the dissociation coefficient ⍰ of formic acid in this solution?
3. If we add **25** ml of pure water to **50** ml of this solution, what are the new values of pH and ⍰? What can we conclude?

Exercise 03 :

What is the final pH obtained by mixing:

1. **20 ml** of HNO_3 solution **$1,5.10^{-2}$ mol/l** with **20 ml** of HCl solution **10^{-2} mol/l** and **60 ml** of distilled water ?
2. **20 ml** of HCl **10^{-2}** M with **20 ml** of monochloroacetic acid **10^{-1}** M ?
3. **25 ml** of formic acid **10^{-1}** M with **50 ml** of acetic acid **10^{-2}** M ?
4. **10 ml** of NaOH **10^{-3}** M with 10 ml of ammonia NH_3 **10^{-1}** M ?
5. **50 ml** of HBr solution **0,1 M, 20 ml** of HNO_3 solution **0,05 M** and **100 ml** of KOH solution **0,2 M** ?

Data : $Ka_{CH2ClCOOH}$= **1,41 ; 10^{-3}** . **Data :** Ka_{HCOOH}= **1,58 . 10^{-4}** ; **Data :** $Ka_{CH3COOH}$= **1,8 . 10^{-5}**

Exercise 04 :

1. What mass of pure chloroacetic acid should be used to prepare **150 ml** of a solution (**A**) **0.08M** of this acid. We give: $M_{ClCH2COOH}$= **94,5 g** , $pKa_{ClCH2COOH}$ = **2,9**.
2. Calculate the pH of the solution (**A**).
3. Solution (**B**) is prepared by taking **75 ml** of solution (**A**) and adding **25 ml** of a **0.12 M** KOH potassium hydroxide solution.
   - **a)** Calculate the concentrations of the acid and its conjugate base in solution (**B**).
   - **b)** Calculate the pH of the solution (**B**).

4. Prepare solution (**C**) by taking **100 ml** of solution (**B**) and adding **100 ml** of a **10^{-3}M** HCl solution**.**

a) Calculate the pH of the **solution (C).**
b) Compare the pH values of solutions **(B)** and **(C).**

What can we conclude

- **Exercice 06 :**

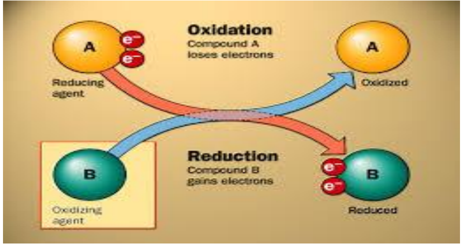
A solution **S** is prepared by mixing **500 ml** of formic acid HCOOH at **0.15 mol/l** (pKa = **3.8**) and **700 ml** of sodium formlate HCOONa at **0.1 mol/l.**

1. Calculate the pH of solution **S**

2. Calculate the variation in pH, when we add **10^{-3} moles** of HCl to **100 ml** of this solution **S** (we consider that there is no change in volume).

CHAPTER III : OXYDATION-REDUCTION REACTIONS

I DEFINITIONS



In redox reactions, there is an exchange of electrons between chemical species:

An oxidant : chemical species capable of capturing one or more electrons. **Ex** : $Fe^{3+} + 1\ e^- \longleftrightarrow Fe^{2+}$

A reductant : chemical species capable of releasing one or more electrons.
Ex: $Fe^{2+} \longleftrightarrow Fe^{3+} + 1\ e^-$

Oxidation represents a loss of electrons which results in an increase in DO**.**

Reduction represents a gain of electrons which results in a reduction in DO**.**

An oxidant and a reducer are said to be **conjugated** and form a redox couple (denoted **Oxidizer/Reducer**) if they can be linked by a **redox half-equation**:

$$\text{Oxidant} + ne^- \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftarrows}} \text{Reductant}$$

$$\text{Reduction : } Ox + n\,e^- \rightarrow Red$$

$$\text{Oxidation : } Red \rightarrow Ox + n\,e^-$$

Examples :

Redox couple	Oxidant	Half redox equation	Reductant
$H^+_{(aq)} / H_{2\,(g)}$	H^+ : Hydrogen ion	$2H^+_{(aq)} + 2e^- \rightleftarrows H_{2\,(g)}$	H_2 : Dihydrogen
$O_{2\,(g)} / H_2O_{(\ell)}$	O_2 : Dioxygen	$O_{2\,(g)} + 4H^+_{(aq)} + 4e^- \rightleftarrows 2H_2O_{(\ell)}$	H_2O : Water
$MnO_4^-{}_{(aq)} / Mn^{2+}{}_{(aq)}$	MnO_4^- : Permanganate ion	$MnO^-_{4\,(aq)} + 8H^+_{(aq)} + 5e^- \rightleftarrows Mn^{2+}_{(aq)} + 4H_2O_{(\ell)}$	Mn^{2+} : Manganese ion

A **redox reaction** is an electron transfer reaction between an oxidant and a reductant of different couples. The products of the reaction are the **conjugated forms** of the reactants. The reaction equation is:

$$\begin{array}{lll} Ox_1 + n_1\,e^- \rightleftarrows Red_1 & \times n_2 & (\textit{couple } Ox_1/Red_1) \\ \quad Red_2 \rightleftarrows Ox_2 + n_2\,e^- & \times n_1 & (\textit{couple } Ox_2/Red_2) \\ \hline n_2\,Ox_1 + n_1\,Red_2 \rightarrow n_2\,Red_1 + n_1\,Ox_2 & & \text{Exchange of } n_1 \times n_2 \text{ electrons} \end{array}$$

Example : Redox reaction in a fuel cell

$$\begin{array}{rll} O_{2\,(g)} + 4H^+_{(aq)} + 4e^- \rightleftarrows 2H_2O_{(\ell)} & (\times 1) & \text{Couple } O_{2\,(g)} / H_2O_{(\ell)} \\ H_{2\,(g)} \rightleftarrows 2H^+_{(aq)} + 2e^- & (\times 2) & \text{Couple } H^+_{(aq)} / H_{2\,(g)} \\ \hline O_{2\,(g)} + 2H_{2\,(g)} \rightarrow 2H_2O_{(\ell)} & & \end{array}$$

II STRENGTH OF AN OXIDANT AND REDUCER

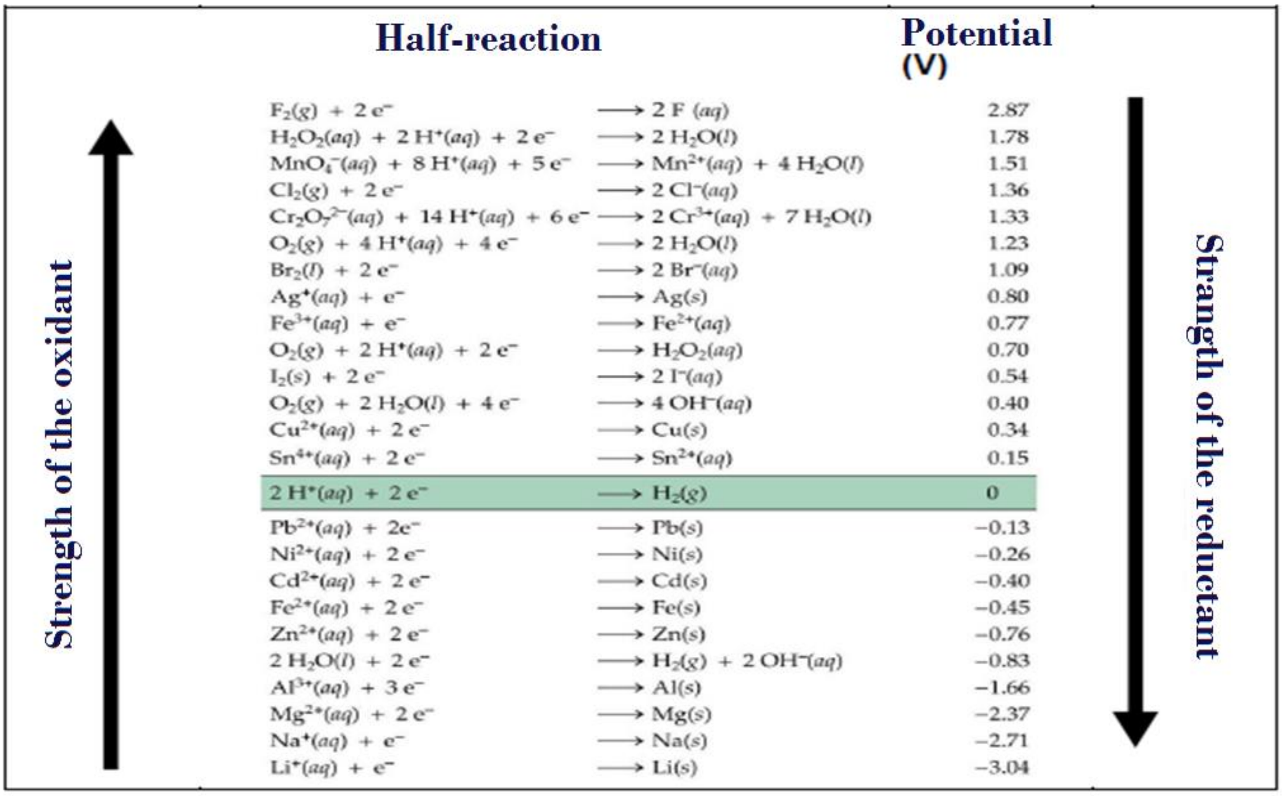
- In a redox couple, the **oxidant** is more stronger as it easily fixes electrons.

Oxidant + n e- ⟺ reductant (direction 1 favored or the reaction is directed to the right).

- A **reductant** is more stronger the more it easily releases electrons (direction 2 favored or to the left)

The stronger an oxidant, the weaker the associated reductant and vice versa (Table)

Classification of oxydants and reductants in fonction of their strength



Half-reaction		Potential (V)
$F_2(g) + 2e^-$	$\longrightarrow 2\,F\,(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

- The **stronger** the oxidant in a couple, the **higher** its potential.
- It is the oxidant of the couple with **the highest potential** which spontaneously oxidizes the reducer of the couple with **the lowest potential**. Thus, in a list of redox couples classified by decreasing value of their potentials, each one can oxidize all those which come after it.

III THE OXYDATION DEGREE

III.1 Definition

An element, involved in a molecule or in an ion, can present itself in **different oxidation states** depending on the number and nature of the elements to which it is linked.

The oxidation state is the **fictitious charge** carried by an element in a chemical compound. The degree of oxidation is **related to the electronegativity of an element**, i.e. the number of **electrons it loses or gains** when it engages with a molecule or an ion.

- ### III.2 Determination of the oxidation degree

In the case of polyatomic substances, information on the exact distribution of charges in the molecule is almost always lacking. However, we can determine the **DO** from the following conventional rules

Chemical species	Rule for calculating the oxydation degree	Examples
Simple bodies	D.O. = 0	Sn, C, Cl_2, S, Cu, Na, O_3
Molecules	Σ algebraic of D.O. = 0	$KMnO_4$; $K_2Cr_2O_7$; H_2SO_3
Simple ion	The D.O = the algebraic value of the electric charge of this ion	S^{2-} → -2 Cl^- → -1 Al^{3+} → +3
Polyatomic ion	Σ algebraic of D.O. = Z (charge of the ion)	MnO^{4-} ; SO_4^{2-} ; HPO_4^{2-}
Hydrogen	D.O = +1 except in hydrides metallic where the D.O = -1	HNa → -1 for H HK → -1 for H Mg H_2 → -1 for H
Oxygen	The D.O = -2 , except in the peroxides Where the D.O = -1	Na_2O_2, H_2O_2, R-O-O-R
Halogens	The D.O = -1 except when they are associated directly to the oxygen we attribute (-2) to the oxygen and we calculate then the D.O of the halogen	AgBr ; $CaCl_2$; IO_3^-; $[AuCl_4]^-$; NaF
Alkalin metal	The D.O = +1	Li ; K ; Na
Alkaline earth metal	The D.O = +2	Ca, Mg ; Ba

All other oxidation degrees are calculated so that the algebraic sum of the oxidation degrees is equal to the charge that the chemical compound carries.

Example 1 :

- Calculate the oxydation degree of the chlorine in the following compounds:

ClO^-, ClO_2^-, ClO_3^-, ClO_4^-

- The same goes for iodine and bromine, except for fluorine which is more electronegative than oxygen.

- Calculate the D.O of Mn and S in different compounds:

Compounds : Mn Mn^{2+} MnO $Mn(OH)_2$ MnO_2 MnO^{2-} $KMnO_4$

Compounds : H_2S SO_2 $Na_2S_4O_6$ S H_2SO_4 $Na_2S_2O_3$ SO_3

Example 2 :

Let be the reaction: $ClO^- + NO_2^- \Leftrightarrow NO_3^- + Cl^-$

Is it an ox-red reaction? If yes describe the transfer of electrons.

IV REDOX REACTIONS

A redox reaction can take place either:

- Between two chemical compounds in solution:

Example : $Ce^{4+} + Fe^{2+} \Leftrightarrow Ce^{3+}$ Fe^{3+} (**Chemical reaction**)

- Between a chemical compound and an electrode with a well-chosen potential (**electrochemical reaction**).

Depending on its potential, the electrode can fix or release electrons.

A redox reaction happens betwen an oxidant and a reductant.

In the example : $\mathbf{Cu^{2+} + Zn \Leftrightarrow Cu + Zn^{2+}}$ and in the direct sens of the equilibrium, Zn acts as a reducing agent (it reduces Cu^{2+} to Cu) and Cu^{2+} acts as an oxidizing agent (it oxidyzes Zn to Zn^{2+}) The two couples oxidant / reductant (called redox couples) involved in the reaction are therefore Cu^{2+}/ Cu et Zn^{2+}/ Zn.

Generally, a redox reaction takes place between two redox couples **(Ox1 /Red1)** and **(Ox2 / Red2).**

- The reaction is favored in **direction 1**(to the right) if **Ox1** is **stronger than Ox2** and **Red2** is **stronger than Red1**.
- It should be noted that the strength of an oxidant and a reducer depends on several parameters in particular : **the concentrations, the pH of the environment, T and P.**

Example of calculation: Based on the classification in Table 1, specify whether or not the following reactions are possible

1. $F + Fe^{2+} \rightarrow$?

2. $Cu^{2+} + Mn^{2+} \rightarrow$?

3. $Sn^{2+} + Zn^{2+} \rightarrow$?

V BALANCE OF A REDOX EQUATION

Balancing a redox equation is done by following the coming steps:

- Determine the DO of the atom having undergone oxidation or reduction. .
- Determine the number of electrons involved.
- Write the electronic half-equations separately.
- Balance these equations against charges if necessary using H^+ or HO^- ions.
- Balance the masses using H_2O molecules.
- Write the overall reaction by combining the two electronic half-equations and respecting the law of conservation of electrons.

Example of calculation :

Balance the following redox reactions:

$\mathbf{ClO_2 + BH_4^- \Leftrightarrow Cl^- + HBO_2 + H^+}$ (in acidic environment)

$\mathbf{IO_3^-(aq) + Cr(OH)_3 \Leftrightarrow CrO_4{}^{2-}(aq) + I^-(aq)}$ (in basic environment)

$\mathbf{Fe^{3+} + I^- \Leftrightarrow Fe^{2+} + I_2}$

Reaction of disproportionation (dismutation)

It is a reaction during which the same species undergoes both oxidation and reduction.

$2Cu^+ \rightleftharpoons Cu^{2+} + Cu$

$Cl_2 + 2OH^- \rightleftharpoons Cl^- + ClO^- + H_2O$

$2H_2O_{2(aq)} \rightleftharpoons 2H_2O_{(l)} + O_{2(g)}$

VI ELECTRODE POTENTIAL AND OPERATION OF A BATTERY

VI.1 Electrode potential

The redox potential, also called redox potential, is a thermodynamic quantity which measures the oxidizing or reducing power of a redox system. It is expressed in volt unit (**V**) and denoted **E(Ox/Red).** The measurement of a redox potential of a couple is done experimentally measured under normal conditions of P and T (**P = 1 atm**, **T = 25°C**) compared to a reference which is conventionally the couple $\mathbf{H^+/ H_2}$. The latter constitutes what is called a hydrogen electrode.

Example : A silver wire dipping into a solution of AgNO3 : $\mathbf{Ag \Leftrightarrow Ag+ + 1\ e^-}$

The Ag+/Ag couple has a very specific redox potential. Experimentally we cannot measure a potential but rather a potential difference (P.D)

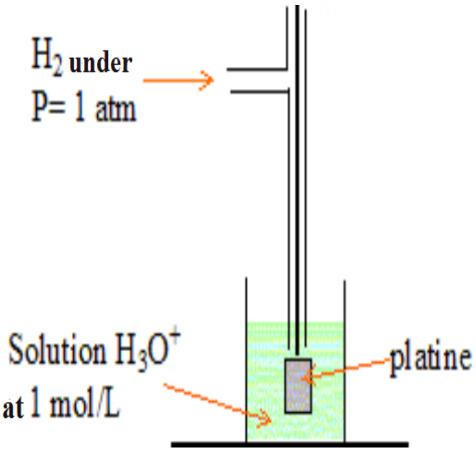
To be able to measure this P.D, two Redox systems are required:
Red1 ⟺ Ox1 + ne (a half cell)
Ox2 + ne ⟺ Red2 (a half cell).

By connecting the two half-cells by an electrically conducting wire, a battery is formed whose electromotive force (e.m.f.) is measurable.

To be able to compare the potentials of several redox systems with each other, it is necessary to measure their e.m.f., relative to the same reference couple.

Le couple Ag+/Ag a un potentiel redox bien précis. Expérimentalement on ne peut pas mesurer un potentiel mais plutôt une différence de potentiel (d.d.p.)

- By convention we took the couple **H^+/H_2** as a reference couple and we assigned it the zero volt potential, under well-defined conditions: T= **25°C**, PH2 = **1 atm** and $[H^+]$ = **1 mol/L** ⟹ pH = **0**

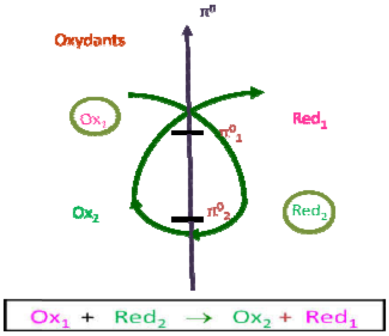


This half-cell constitutes a reference electrode, called a **standard hydrogen electrode (S.H.E.)**

By convention: **$E°(H^+/H_2)$ = 0, 00 V**

The more reductive a system is, that is to say the more it is able to oxidize by releasing electrons, and the smaller its redox potential.

Conversely, a system is the most oxidizing, that is to say capable of reducing itself by capturing electrons, when its redox potential is high. We note the standard potential of a redox couple E0 (Ox / Red).



Examples : E^0 (Cu^{2+} / Cu) = +0,34 V, E^0 (Pb^{2+} / Pb) = -0,13 V.

The values of the E^0 potentials are of very practical use for predicting a redox reaction between two couples. The couple with the highest E^0 corresponds to the strongest oxidizer, to the one with the lowest E^0 corresponds to the strongest reducer. In the previous example, Cu^{2+} is the strongest oxidant and Pb is the strongest reducer. The spontaneous reaction between these two couples is therefore:

$$Pb + Cu^{2+} \longrightarrow Pb^{2+} + Cu$$

The Hydrogen electrode has some disadvantages for maintaining the defined conditions.
There are other reference electrodes, such as the saturated calomel electrode and the chloride silver electrode whose electrode potential is more stable.

VI.2 Different types of electrodes

There are four main types (or species) of electrodes:

a)- Electrodes of the first type

1. Electrode made of a metal in equilibrium with one of its ions in solution

Examples :

- An Ag wire dipping into a solution containing Ag^{+}.
- A Cu wire dipping into a solution containing Cu^{2+}

2. Electrode consisting of a gas bubbling in a solution containing an ion common with one of the constituents of this gas.

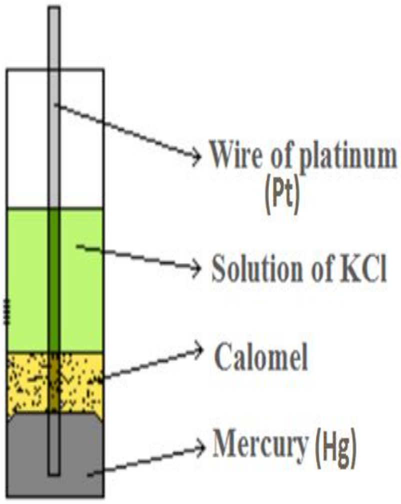
Examples :

- Cl_2 bubbling in a solution containing Cl^-

- H_2 bubbling in a solution containing H^+

b)- Electrodes of the second type

1. Electrode made of a metal in equilibrium with one of its poorly soluble salts



Example 1 : Saturated calomel electrode (SCE): **Pt/Hg/Hg₂Cl₂/Cl**

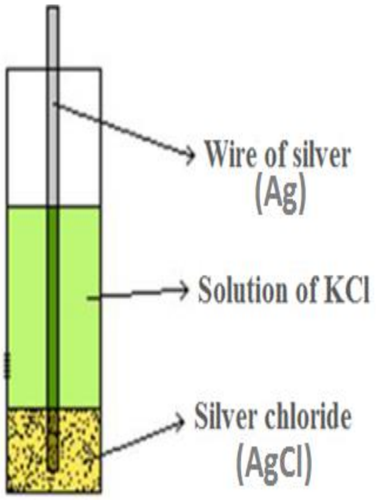
The electronic half equation of the redox couple **Hg_2Cl_2 (s)/Hg(l)** is written:

$$\mathbf{Hg_2Cl_2 (s) + 2e \Leftrightarrow 2Hg(l) + 2Cl^-}$$

$E_{SCS} = E° + 0.06/2 \text{ Log}(1/[Cl^-]^2)$

If we take a saturated solution of KCl ⇒ $[Cl^-]$ = constant

⇒ E_{SCS} = constant = **0.246 v**



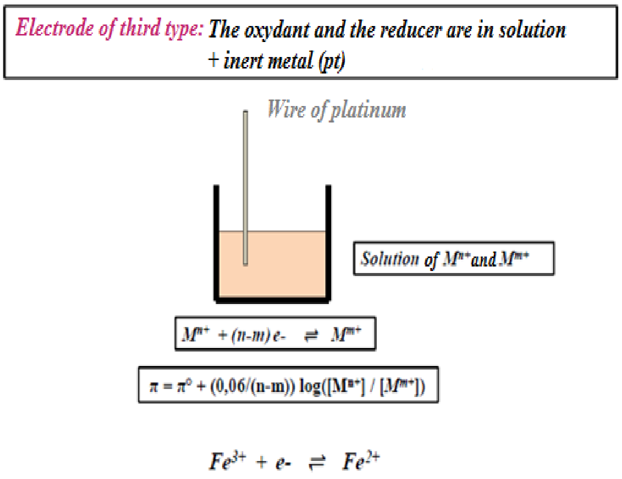
Example 2: Electrode of silver chloride: **$Ag/AgCl/Cl^-$**

The electronic half equation of the redox couple **AgCl(s)/Ag(s)** is written: **$AgCl (s) + 1e \Leftrightarrow Ag(s) + Cl^-$**

$E_{SCS} = E° + 0.06 \text{ Log}(1/[Cl^-])$

If we take a saturated solution of KCl ⇒ $[Cl^-]$ = constant

⇒ E_{SCS} = **+0.199 v**



c)- Electrode of third type (or redox electrodes)

Electrode made of an inert metal immersed in a solution containing the forms Ox and Red of a redox couple

Example : Platinum electrode dipping into a solution containing the couple **Fe^{3+}/Fe^{2+}**

d)- Electrodes of fourth type (or specific electrodes) :

These electrodes measure the activity of a given ion.

Example : Electrode specific to hydrogen ⇨ measuring the pH of a solution

The specific hydrogen electrode is a combined electrode:

Glass Electrode (Potential proportional to pH) + **Reference Electrode** (Fixed Potential) ⇨ we read directly a d.o.p., **proportional to the pH of the solution**.

- ## VI.3 Standard electrode potential

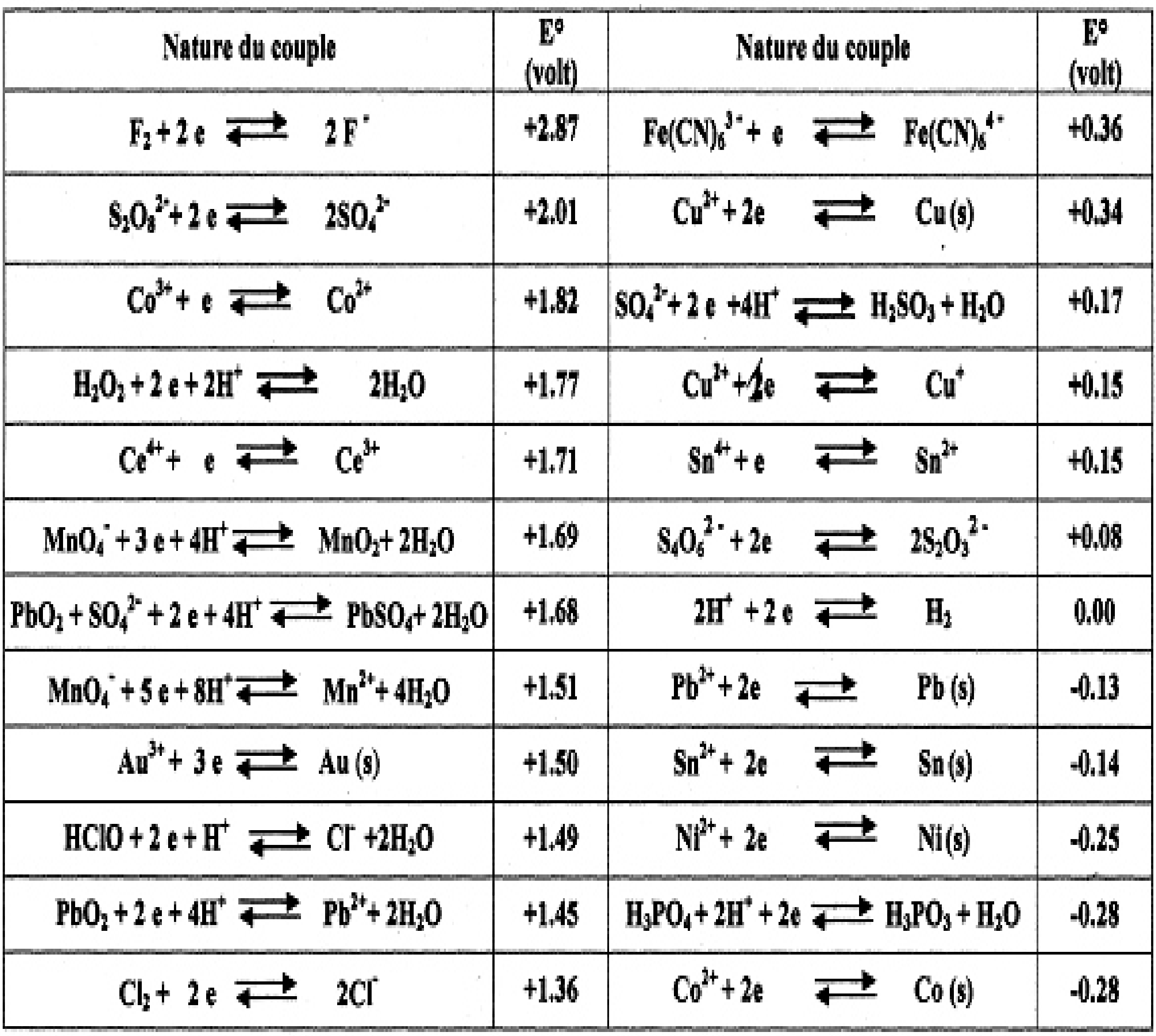
The electrode potential E depends on many parameters (temperature, pressure, concentrations, pH). We define the standard electrode potential E° measured under standard conditions for which the concentrations are **1 mol/l**, the pressure **P = 1 atm** and the temperature **T = 25°C**.

How to measure the standard potential of a redox couple?

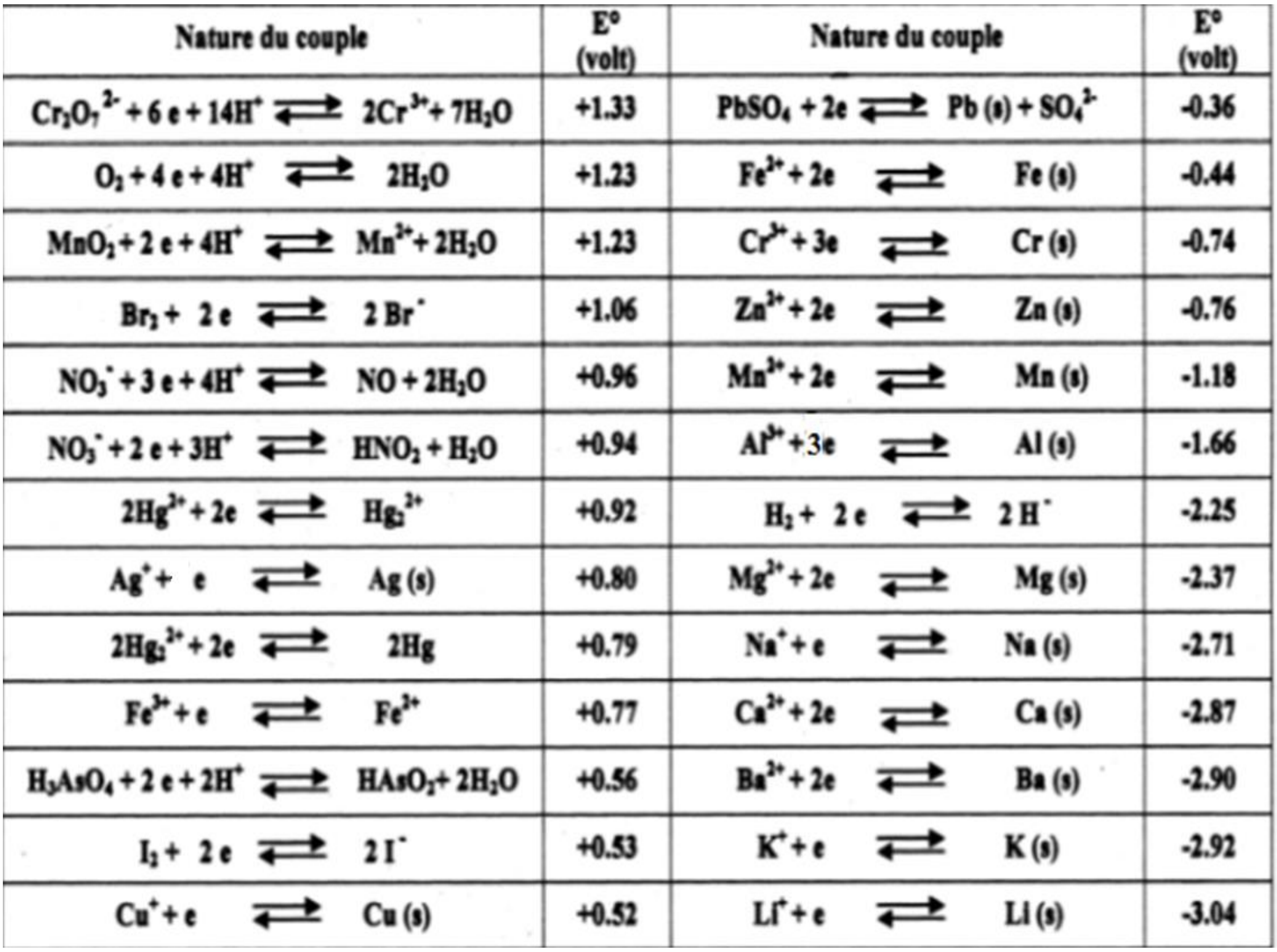
To measure the standard potential of a redox couple, we make a cell and introduce a reference redox couple (e.g. hydrogen electrode) into half-cell I. We connect the hydrogen electrode to the electrode of half-cell II, of the redox couple to be studied.

The **emf**, displayed on the voltmeter, corresponds to the redox potential of the couple in half-cell II.

The standard potentials of the main Redox couples are grouped in the following tables.

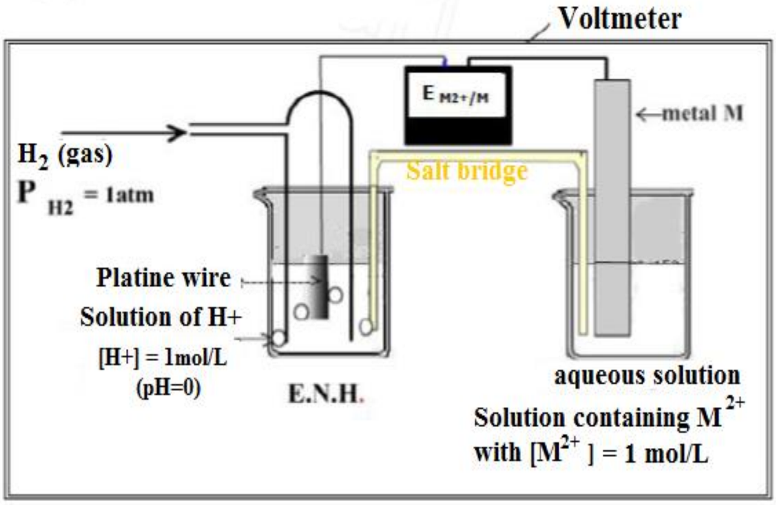


Nature du couple	E° (volt)	Nature du couple	E° (volt)
$F_2 + 2e \rightleftarrows 2F^-$	+2.87	$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$	+0.36
$S_2O_8^{2-} + 2e \rightleftarrows 2SO_4^{2-}$	+2.01	$Cu^{2+} + 2e \rightleftarrows Cu(s)$	+0.34
$Co^{3+} + e \rightleftarrows Co^{2+}$	+1.82	$SO_4^{2-} + 2e + 4H^+ \rightleftarrows H_2SO_3 + H_2O$	+0.17
$H_2O_2 + 2e + 2H^+ \rightleftarrows 2H_2O$	+1.77	$Cu^{2+} + \cancel{2}e \rightleftarrows Cu^+$	+0.15
$Ce^{4+} + e \rightleftarrows Ce^{3+}$	+1.71	$Sn^{4+} + e \rightleftarrows Sn^{2+}$	+0.15
$MnO_4^- + 3e + 4H^+ \rightleftarrows MnO_2 + 2H_2O$	+1.69	$S_4O_6^{2-} + 2e \rightleftarrows 2S_2O_3^{2-}$	+0.08
$PbO_2 + SO_4^{2-} + 2e + 4H^+ \rightleftarrows PbSO_4 + 2H_2O$	+1.68	$2H^+ + 2e \rightleftarrows H_2$	0.00
$MnO_4^- + 5e + 8H^+ \rightleftarrows Mn^{2+} + 4H_2O$	+1.51	$Pb^{2+} + 2e \rightleftarrows Pb(s)$	-0.13
$Au^{3+} + 3e \rightleftarrows Au(s)$	+1.50	$Sn^{2+} + 2e \rightleftarrows Sn(s)$	-0.14
$HClO + 2e + H^+ \rightleftarrows Cl^- + 2H_2O$	+1.49	$Ni^{2+} + 2e \rightleftarrows Ni(s)$	-0.25
$PbO_2 + 2e + 4H^+ \rightleftarrows Pb^{2+} + 2H_2O$	+1.45	$H_3PO_4 + 2H^+ + 2e \rightleftarrows H_3PO_3 + H_2O$	-0.28
$Cl_2 + 2e \rightleftarrows 2Cl^-$	+1.36	$Co^{2+} + 2e \rightleftarrows Co(s)$	-0.28



Nature du couple	E° (volt)	Nature du couple	E° (volt)
$Cr_2O_7^{2-} + 6e + 14H^+ \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33	$PbSO_4 + 2e \rightleftharpoons Pb(s) + SO_4^{2-}$	-0.36
$O_2 + 4e + 4H^+ \rightleftharpoons 2H_2O$	+1.23	$Fe^{2+} + 2e \rightleftharpoons Fe(s)$	-0.44
$MnO_2 + 2e + 4H^+ \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23	$Cr^{3+} + 3e \rightleftharpoons Cr(s)$	-0.74
$Br_2 + 2e \rightleftharpoons 2Br^-$	+1.06	$Zn^{2+} + 2e \rightleftharpoons Zn(s)$	-0.76
$NO_3^- + 3e + 4H^+ \rightleftharpoons NO + 2H_2O$	+0.96	$Mn^{2+} + 2e \rightleftharpoons Mn(s)$	-1.18
$NO_3^- + 2e + 3H^+ \rightleftharpoons HNO_2 + H_2O$	+0.94	$Al^{3+} + 3e \rightleftharpoons Al(s)$	-1.66
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	+0.92	$H_2 + 2e \rightleftharpoons 2H^-$	-2.25
$Ag^+ + e \rightleftharpoons Ag(s)$	+0.80	$Mg^{2+} + 2e \rightleftharpoons Mg(s)$	-2.37
$2Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	+0.79	$Na^+ + e \rightleftharpoons Na(s)$	-2.71
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77	$Ca^{2+} + 2e \rightleftharpoons Ca(s)$	-2.87
$H_3AsO_4 + 2e + 2H^+ \rightleftharpoons HAsO_2 + 2H_2O$	+0.56	$Ba^{2+} + 2e \rightleftharpoons Ba(s)$	-2.90
$I_2 + 2e \rightleftharpoons 2I^-$	+0.53	$K^+ + e \rightleftharpoons K(s)$	-2.92
$Cu^+ + e \rightleftharpoons Cu(s)$	+0.52	$Li^+ + e \rightleftharpoons Li(s)$	-3.04

Diagram of the device for measuring the standard potential of a redox couple



By convention the e.m.f. **$\Delta E = E2 - E1$** with:
E2 : potential of the platinum electrode of the redox Couple studied
E1 : potential of the hydrogen electrode

If **$\Delta E > 0$** $\Longrightarrow$ the electrons flow towards the compartment (II) and the current flows towards the compartment (I) We can therefore say that the Redox couple studied is more oxidizing than the couple H^+/H_2

If **$\Delta E < 0$** $\Longrightarrow$ the electrons flow towards the compartment (I) and the current flows towards the compartment (II).

We can therefore say that the Redox couple studied is less oxidizing than the couple H^+/H_2.

$$\boxed{E_1 = 0 \Longrightarrow \Delta E = E_2}$$

General speaking :

- A substance can only oxidize another substance if its oxidizing power is higher, that is to say if it has a higher electrode potential.
- A substance can only reduce another substance if its reducing power is higher, that is, its electrode potential is lower.
- **Standard electrode potentials allow us to conclude whether a reaction is possible or not.**

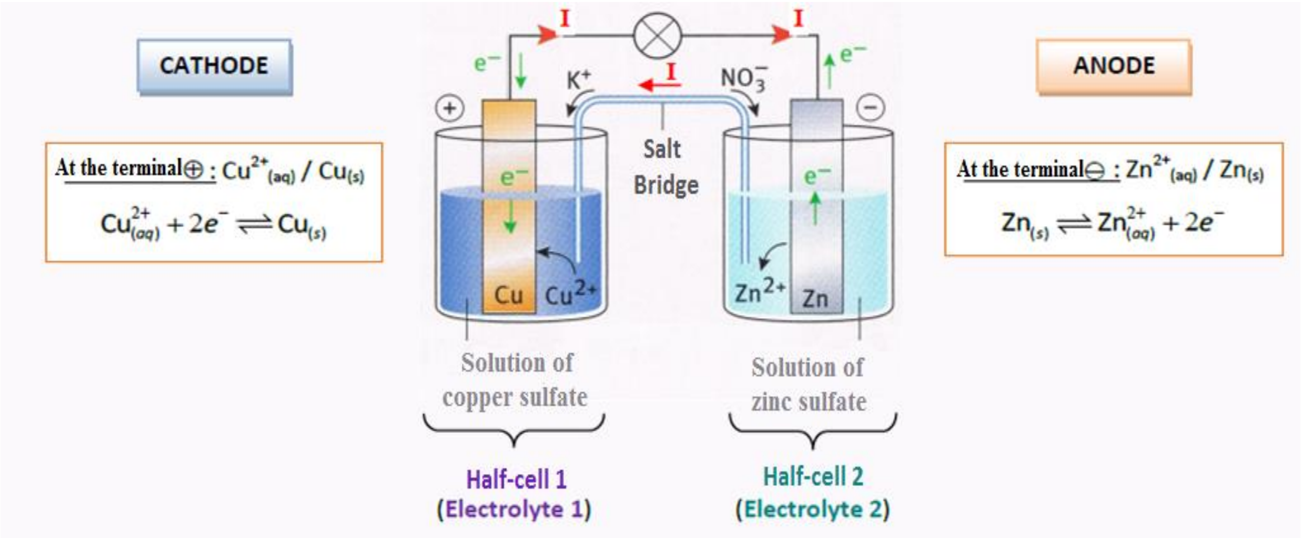
Example : We give the redox potentials: $E°_{F2/F^-}$ = **+2.87v** ; $E°_{Cl2/Cl^-}$ = **+1.40v** ; $E°_{Br2/Br^-}$= **+1.06v** ; $E°_{PbO2/Pb^{2+}}$ = **+ 1.46v**.

1. Among these couples, which one reacts spontaneously with Pb2+ ? Justify your answer.
2. Write the half reactions and deduce the overall reaction.

VI.4 Creation of an electrochemical cell

A battery converts chemical energy into electrical energy.
The electrochemical cell is one of the important applications of redox reactions. To build it, simply choose two redox couples involved in a spontaneous redox reaction and design an electrical circuit so that each couple constitutes an electrode; the anode and the cathode. The figure below illustrates an example of an electrochemical cell:

Cu^{2+} / Cu: E1° = + **0.34 v** and Zn^{2+} / Zn: E2°= **- 0.76 v**



Terminal ⊕ (REDUCTION)		Terminal ⊖ (OXIDATION)
Copper blade soaking in copper(II) sulfate solution ($Cu^{2+}_{(aq)} + SO^{2-}_{4\,(aq)}$) Reaction at the electrode $\boxed{Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}}$	**Salt bridge** potassium nitrate or ammonium nitrate gel	Zinc slide soaking in zinc(II) sulfate solution ($Zn^{2+}_{(aq)} + SO^{2-}_{4\,(aq)}$) Reaction at the electrode $\boxed{Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-}$

Global Redox reaction

$$\boxed{Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}}$$

Daniell’s battery diagram

- Two moles of electrons are exchanged during the reaction between one mole of copper(II) ions and one mole of zinc atoms.

- The salt bridge used generally consists of an aqueous solution of a very soluble salt (KNO_3 in the previous figure). It serves to ensure the transport of ions to the two electrodes to maintain the electroneutrality of the solutions. The latter lose their electroneutrality following the increase in Cu^{2+} ions at the cathode and the decrease in Zn^{2+} ions at the anode.

- The electric wire is used to transport electrons from the anode to the cathode, which produces an electric current detected by a voltmeter.

- The conventional representation of an electrochemical cell corresponds to writing the chemical species constituting the anode, separated by a slache, followed by a double slache symbolizing the electrolytic bridge.

We then write the chemical species constituting the cathode, also separated by a slache. In the example above, the conventional writing is as follows:

$$\underbrace{\mathbf{Fe\,(s)\,/\,Fe^{2+}\,(aq)}}_{\text{Half-cell: anode (pole -)}}\ \mathbf{//}\ \underbrace{\mathbf{Cu^{2+}\,(aq)\,/Cu\,(s)}}_{\text{Half-cell: cathode (pole +)}}$$

VI.5 Nernst equation

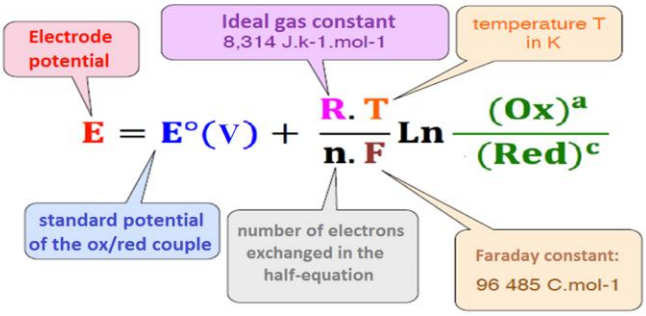
The potential taken by an electrode soaking in a solution depends on the couple studied but also on the activities (concentrations or pressures for the gases) of the species involved in the couple.

Let's take a look at the reaction: $\mathbf{Co + Ni^{2+} \Leftrightarrow Co^{2+} + Ni}$
Under standard conditions the balance is moved in direction 1 (to the right)

However, experience shows that if $[Ni^{2+}] = 0.01$ M and $[Co^{2+}] = 1$M, the reaction takes place in direction 2, we must therefore establish a relationship between the concentrations and the e.m.f. **This is the Nernst equation.**

The Nernst equation gives the potential of a redox couple engaged in an oxidation or reduction half-reaction compared to its standard potential.

For a half-reaction of the form: $a\,Ox + ne^- \Longleftrightarrow c\,Red$ at T = 25 °C



$$E = E°(V) + \frac{R.T}{n.F} Ln \frac{(Ox)^a}{(Red)^c}$$

[Ox] and [Red] : respective concentrations of the oxidized and reduced forms in mole/L.

By replacing these constants by their values in the Nernst equation and passing from the natural logarithm to the decimal logarithm, we arrive at the following expression:

$$\boxed{E = E^0 + \frac{0,059}{n} \log([Ox]^a / [Red]^c)}$$

If [Ox] = [Red] = 1M ⟹ **E = E°** (standard conditions)

VII RELATIONSHIP BETWEEN THE POTENTIALS OF STANDARD ELECTRODES AND THE EQUILIBRIUM CONSTANT

Let be 2 Redox couples: **Ox1 /Red1** and **Ox2 / Red2**. We make 2 half-cells with these Redox couples and we connect them by an electrically conducting wire.

If **Ox1** is **stronger** than **Ox2** and **Red2** is **stronger** than **Red1** then:

$$(Ox1 + n_1e \Leftrightarrow Red1) \times n_2$$

$$(Red2 \Leftrightarrow Ox2 + n_2e) \times n_1$$

$$n_2Ox1 + n_1\,Red2 \Leftrightarrow n_2Red1 + n_1Ox2$$

$$\boxed{K = ([Ox2]^{n1}.\ [Red1]^{n2}) \big/ ([Ox1]^{n2}.\ [Red2]^{n1})}$$

The potential possibilities of the 2 electrodes will be:

$E1 = E1° + 0.06/n_1 \log [Ox1]/[Red1]$

$E2 = E2° + 0.06/ n_2 \log [Ox2] / [Red2]$

$\Delta E = E1 - E2 \Leftrightarrow \Delta E = \Delta E° - 0.06/n_1.n_2. \log K$

At the equilibrium no current passes ⟹ **ΔE = 0 ;** so we have :

$$\boxed{\mathbf{Log\ K = n_1.n_2.\ \Delta E°/0.06}}$$

$n_1.n_2 = n =$ number of e^- involved in the overall reaction

$$\boxed{\mathbf{\Rightarrow \log K = n.\ \Delta E°/0.06}}$$

VIII INFLUENCE OF PH ON THE ELECTRODE POTENTIAL

If the redox reaction involves H+ protons, the redox potential depends on the pH.

Example: Let be the half-cell made up with the couple: MnO_4^- / Mn^{2+}

$MnO_4^- + 8H^+ + 5e- \Longleftrightarrow Mn^{2+} + 4H_2O$

$E = E° + RT/nF \ln [MnO_4^-]. [H^+]^8/ [Mn^{2+}]$

$E = E° + 8\ RT/nF \ln [H^+] + RT/nF \ln [MnO_4^-\ ] /[Mn^{2+}]$

Using the decimal logarithm, RT/F = 0,06 and n = 5, we can write:

$E = E° + 8/5\ .\ 0,06 \log [H^+] + 0,06/5 \log [MnO_4^-\ ] / [Mn^{2+}]$

$E = E° - 8/5\ .\ 0,06\ pH + 0,06/5 \log [MnO_4^-\ ] / [Mn^{2+}]$

We put: E°' = E° - 8/5 . 0,06 pH ⟹ $\boxed{\mathbf{E°' = E° - k\ pH}}$

- **E°'** is called apparent standard potential; it characterizes the Redox couple for a given pH.

- The **more acidic** the environment and the greater the potential ⟹ **the higher** the oxidizing power of the couple.

IX ELECTROLYSIS

IX.1 Definition

Electrolysis is the reverse process of the electrochemical cell:

A battery transforms chemical energy into electrical energy. It's a spontaneous reaction.

Electrolysis imposes a higher voltage on the battery to promote a given reaction.

Unlike the electrochemical battery, electrolysis is a non-spontaneous reaction **(forced reaction**). Electrolysis plays an important role in the manufacturing and purification of many products (Al, Na, NaOH, H_2, Cl_2, etc.) and in the electrodeposition of a metallic layer on another metal.

Example :
Electrolysis of molten NaCl (with carbon electrodes)
At the anode : $2Cl^- \Leftrightarrow Cl_2 + 2e^-$
At the cathode: $2Na^+ + 2e^- \Leftrightarrow 2Na$
Overall reaction: $2NaCL\ (l) \longrightarrow 2Na\ (l) + Cl_2$

The quantities of substances transformed during electrolysis are calculated based on Faraday's law.

IX.2 Faraday law

The mass of a substance produced or transformed at a given electrode is proportional to the quantity of electricity Q passing through it, **Q = I.t**

Q : quantity of electricity (Cb)
I : intensity (A)
t : time of electrolysis (s)
The charge carried by a mole of electrons is called the faraday.

$\boxed{\mathbf{1F = 96500\ cbs}}$

Application exercise:

If a current of 2.5A flows through a $ZnSO_4$ solution for 60 minutes, what is the mass of zinc deposited at the cathode? $M_{Zn} = 65.37$ g

X REDOX TITRATION

Redox reactions are used to determine the unknown concentration of an oxidant or reducer. The principle is the same as for acid-base reactions.

The determination of the equivalent point is done:

- By a colored indicator.
- Or by a potentiometer which indicates the potential jump in the vicinity of the point.

If the colors of the Ox and Red forms of a redox couple are different, this couple can serve as an indicator.

X.1 Normality of an oxidizing solution

An oxidizing solution is said to be n times normal (**nN**) if in a reaction it can fix **n** moles of **é per liter**

Example 1:

$MnO_4^- + 5\,e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

A normal $KMnO_4$ solution should contain **1/5** mole of $KMnO_4$ per liter of solution.

X.2 Normality of a reducing solution

A reducing solution is called n normal (**nN**) if in a reaction it can release **n** moles of **é per liter**.

Example 2 :

$I_2 + 2\,e^- \longrightarrow 2\,I^-$

A normal solution of KI should contain one mole of KI per liter..

X.3 Determination of an unknown concentration

Example: Dosage of a volume **V_1** of ferrous ions solution (Fe^{2+}) of an unknown concentration **C_1**, by permanganate ions (MnO_4^-) of a known concentration **C_2** **.**

$MnO_4^-(aq) + 5\,Fe^{2+}(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$

At the equivalent point we have: **$N_1.V_1=N_2.V_2$**

N_1 : normality of ferrous ions solution (Fe^{2+})
V_1 : volume of the ion solution (Fe^{2+}) ; **V_2 :** volume of the ions solution (MnO_4^-)
N_2 : normality of the permanganate ions solution (MnO_4^-)

Where : $C_1.V_1 = 5\,C_2.V_2$ $\Rightarrow C_1 = 5\,C_2.V_2 / V_1$

XIAPPLICATION EXERCICES

• Exercise 01:

We have these two couples: **$Ni^{2+}/Ni(s)$; ($E^0 1$= - 0,25 V** and **$Co^{2+}/Co(s)$; ($E^0 2$= - 0,28 V)**

- Determine the direction of the reaction for the following concentrations:

1- [**Ni^{2+}**]= **10^{-3} M** and [**Co^{2+}**]= **10^{-3} M**

2- [**Ni^{2+}**]= **10^{-4} M** and [**Co^{2+}**]= **10^{-1} M**

• Exercise 02:

A/ we give the following table of some normal redox potentials:

Couple	Ba^{2+}/Ba	Mg^{2+}/Mg	Zn^{2+}/Zn	Fe^{2+}/Fe	H^+/H_2	Cu^{2+}/Cu	Fe^{3+}/Fe^{2+}	Ag+/Ag
E°(v)	-2.9	-2.37	-0.76	-0.44	0.00	+0.34	+0.77	+0.80

A.1/ Which one of the metal ions is displaced by all the other metals ?

A.2/ With which metal will the reaction be most complete? Write the reactions.

A.3/ Which of these metals are acid resistant?

B/ We immerse a copper blade in a solution of ferrous sulfate (**$FeSO_4$**) and another in a solution of silver nitrate (**$AgNO_3$**).

B.1/ What do we observe?

B.2/ Why do we obtain ferrous chloride **$FeCl_2$** and not ferric chloride **$FeCl_3$** by the action of hydrogen chloride on iron?

• Exercise 03:

The first half cell is constituted of a platine electrode dipping into a solution of acidified potassium permanganate (**K^+; MnO_4^-**) in which the concentrations are :[**MnO_4^-**]=**0,010 mol/L** ;
[Mn^{2+}]= 0,020 mol/L ; [H_3O^+]= 0,010 mol/L

The other half cell is a silver electrode dipping into a solution of silver nitrate **(Ag^+,NO_3^-) [Ag]= 0,10 mol/L.** The study is done at 25°C.

1- Express then calculate the potential values E_1 and E_2 of each half-cell.

2- Specify the polarity of the electrodes.

3- Calculate the value of the E.M.F of the cell at the beginning of the operation (running).

4- Write the overall equation of the chemical reaction when the cell (battery) is charging. Precise the oxidizing and the reducing species.

We give: **$E^0(MnO_4^-/Mn^{2+})$ = +1,51 V** ; **$E^0(Ag^+/Ag)$= + 0,80 V.**

• Exercise 04:

We want to make a metallic deposit of nickel on an iron object. To do this, we carry out the electrolysis of a solution of nickel (II) sulfate. The object to be covered constitutes one of the electrodes. The other electrode is unassailable: a gaseous release of oxygen is observed there.

1) Should the iron object constitute the cathode or the anode? Show the connections to be made on a diagram.
2) Write the electronic half-equations of the reactions at the electrodes as well as the balance equation of electrolysis
3) What is the mass of nickel deposited on the iron object after **45 minutes** of electrolysis at an intensity of **1.8 A**.
4) What is the mass of oxygen produced? M_{Ni} = **58.7 g**

- **Exercise 05:**

We create the following cell consisting of two compartments separated by a salt bridge.

The first compartment contains **100ml** of a solution of silver nitrate **$AgNO_3$** with a concentration of **0.7M** into which a silver wire is immersed.

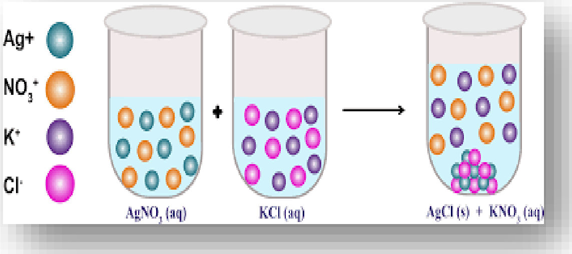
The second compartment contains a platinum wire in 100ml of a mixture of ferrous sulfate **$FeSO_4$ 0.7M** and ferric sulfate **$Fe_2(SO_4)_3$ 0.7M**.

1) Give the diagram of the battery indicating:
- Polarity, the direction of electrons and current, the half-reactions which take place at each electrode as well as the overall reaction.
2) Calculate the potential of each electrode when the battery begins to discharge and the electromotive force (e.m.f.).
3) The battery is charged until the e.m.f. is zero; what will be the concentrations of the ions in solution in each compartment of the battery.

Data: E° (Ag^+/Ag)= **0.80** V; E° (Fe^{3+}/Fe^{2+}) = **0.77** V.

CHAPTER IV : PRECIPITATION REACTIONS

I INTRODUCTION



A solubility equilibrium reflects the partial dissociation of a salt that is poorly soluble in solution. Generally, a salt can be defined as an ionic compound consisting of cations and anions forming an electrically neutral product. These ions can be mineral (chloride Cl^- like KCl) or organic (acetate CH_3COO^- like CH_3COONa), monatomic or polyatomic.

II SOLUBILITY AND SOLUBILITY PRODUCT

• II.1 Solubility

The molar (or mass) solubility of a compound is the maximum number of moles (or mass) that can be dissolved in one liter of solution.

$$s\ (mol/L) = n / V \qquad ; \qquad s\ (g/L) = m / V$$

When a heterogeneous equilibrium is established between the solid and its ions in solution, the solution is said to be saturated.

$$AgCl_{(S)} \underset{precipitation}{\overset{dissolution}{\rightleftharpoons}} Ag^+_{(aq)} + Cl^-_{(aq)}$$

- ➢ A salt is insoluble or poorly soluble if its solubility is less than 0.01 M.
- ➢ A salt is slightly soluble if its solubility is between 0.01 M and 0.1 M
- ➢ A salt is soluble if its solubility is greater than 0.1 M or 10 g/L.

A solution is said to be saturated if it contains the maximum quantity of solute that it can dissolve.

The concentration of a saturated solution is therefore equal to the solubility value.

• II.2 Solubility ptoduct

The study of dissolution-precipitation equilibria is a direct application of the general laws of equilibria. The equilibrium constant in this case is called Solubility product Ks (P or Kps).

Example : Calculation of the solubility of AgCl in pure water knowing that Ks = 1,7 10^{-10} at 25 °C.

$AgCl_{(solide)}$	⇆	$Ag^+_{(aq)}$	+	$Cl^-_{(aq)}$
n		0		0
n-s		s		s

$$Ks = [Ag+].[Cl^-] = s^2$$

Where : $s = (Ks)^{1/2} = 1,3\ 10^{-5}$ mol/l

Or more: $1,3\ 10^{-5} . 143,5 = 1,9\ 10^{-3}$ g/l $(M_{AgCl} = 143,5$ g/mol).

For a formula body A_nB_m, in accordance with what we saw for the equilibrium constants:

$$A_nB_{m(solid)} \leftrightharpoons nA^{+m}_{(aq)} + mB^{-n}_{(aq)} \qquad K_s = [A^{+m}]^n . [B^{-n}]^m$$

Example 1 :

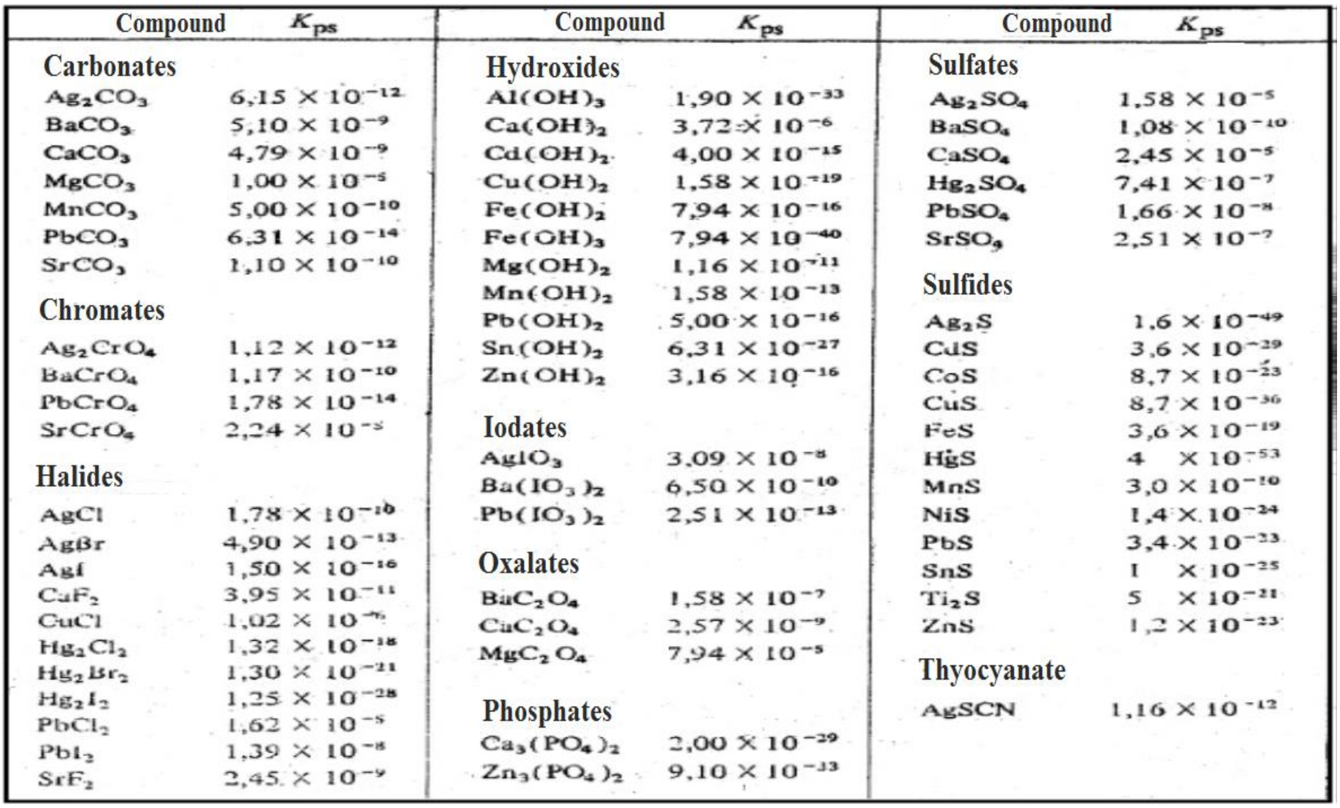
Calculate the solubility of $Mg(OH)_2$ if $Ks_{(Mg(OH)2)}$ = **5.10^{-12}** and $M_{Mg(OH)2}$ = **53.8 g/mol**

Example 2 :

At T = 25°C, the solubility of $BaSO_4$, S = **2.5 10^{-3} g/l**. Calculate its solubility product Ks.

M_{BaSO4}= **233 g/mol**.

In the following table, the solubility products of some poorly soluble salts (at 25°C) are grouped together.



Compound	K_{ps}
Carbonates	
Ag_2CO_3	$6{,}15 \times 10^{-12}$
$BaCO_3$	$5{,}10 \times 10^{-9}$
$CaCO_3$	$4{,}79 \times 10^{-9}$
$MgCO_3$	$1{,}00 \times 10^{-5}$
$MnCO_3$	$5{,}00 \times 10^{-10}$
$PbCO_3$	$6{,}31 \times 10^{-14}$
$SrCO_3$	$1{,}10 \times 10^{-10}$
Chromates	
Ag_2CrO_4	$1{,}12 \times 10^{-12}$
$BaCrO_4$	$1{,}17 \times 10^{-10}$
$PbCrO_4$	$1{,}78 \times 10^{-14}$
$SrCrO_4$	$2{,}24 \times 10^{-5}$
Halides	
$AgCl$	$1{,}78 \times 10^{-10}$
$AgBr$	$4{,}90 \times 10^{-13}$
AgI	$1{,}50 \times 10^{-16}$
CaF_2	$3{,}95 \times 10^{-11}$
$CuCl$	$1{,}02 \times 10^{-6}$
Hg_2Cl_2	$1{,}32 \times 10^{-18}$
Hg_2Br_2	$1{,}30 \times 10^{-21}$
Hg_2I_2	$1{,}25 \times 10^{-28}$
$PbCl_2$	$1{,}62 \times 10^{-5}$
PbI_2	$1{,}39 \times 10^{-8}$
SrF_2	$2{,}45 \times 10^{-9}$
Hydroxides	
$Al(OH)_3$	$1{,}90 \times 10^{-33}$
$Ca(OH)_2$	$3{,}72 \times 10^{-6}$
$Cd(OH)_2$	$4{,}00 \times 10^{-15}$
$Cu(OH)_2$	$1{,}58 \times 10^{-19}$
$Fe(OH)_2$	$7{,}94 \times 10^{-16}$
$Fe(OH)_3$	$7{,}94 \times 10^{-40}$
$Mg(OH)_2$	$1{,}16 \times 10^{-11}$
$Mn(OH)_2$	$1{,}58 \times 10^{-13}$
$Pb(OH)_2$	$5{,}00 \times 10^{-16}$
$Sn(OH)_2$	$6{,}31 \times 10^{-27}$
$Zn(OH)_2$	$3{,}16 \times 10^{-16}$
Iodates	
$AgIO_3$	$3{,}09 \times 10^{-8}$
$Ba(IO_3)_2$	$6{,}50 \times 10^{-10}$
$Pb(IO_3)_2$	$2{,}51 \times 10^{-13}$
Oxalates	
BaC_2O_4	$1{,}58 \times 10^{-7}$
CaC_2O_4	$2{,}57 \times 10^{-9}$
MgC_2O_4	$7{,}94 \times 10^{-5}$
Phosphates	
$Ca_3(PO_4)_2$	$2{,}00 \times 10^{-29}$
$Zn_3(PO_4)_2$	$9{,}10 \times 10^{-33}$
Sulfates	
Ag_2SO_4	$1{,}58 \times 10^{-5}$
$BaSO_4$	$1{,}08 \times 10^{-10}$
$CaSO_4$	$2{,}45 \times 10^{-5}$
Hg_2SO_4	$7{,}41 \times 10^{-7}$
$PbSO_4$	$1{,}66 \times 10^{-8}$
$SrSO_4$	$2{,}51 \times 10^{-7}$
Sulfides	
Ag_2S	$1{,}6 \times 10^{-49}$
CdS	$3{,}6 \times 10^{-29}$
CoS	$8{,}7 \times 10^{-23}$
CuS	$8{,}7 \times 10^{-36}$
FeS	$3{,}6 \times 10^{-19}$
HgS	4×10^{-53}
MnS	$3{,}0 \times 10^{-10}$
NiS	$1{,}4 \times 10^{-24}$
PbS	$3{,}4 \times 10^{-33}$
SnS	1×10^{-25}
Ti_2S	5×10^{-21}
ZnS	$1{,}2 \times 10^{-23}$
Thyocyanate	
$AgSCN$	$1{,}16 \times 10^{-12}$

When is balance reached?

The equilibrium between a solid and its solubilized ions is reached when the dissolution rate is equal to the precipitation rate.

How do we achieve this balance?

This balance can be obtained:

- by the dissolution of a solid in a solvent

Example: $BaSO_4$ (s) ⟺ Ba^{2+}(aq) + SO_4^{2-}(aq)

- Or by the precipitation of a solid from its solubilized ions.

Example: $Ba(NO_3)_2 + Na_2(SO_4) \Longleftrightarrow Ba(SO_4)_{(s)} + 2NaNO_3$

In reality, it is the ionic particles which react with each other and the reaction is as follows:

$$\mathbf{Ba^{2+}{}_{(aq)} + 2\ NO_3^-{}_{(aq)} + 2Na^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} \Leftrightarrow Ba(SO_4)_{(s)} + 2\ NO_3^-{}_{(aq)} + 2Na^+{}_{(aq)}}$$

We can clearly see that the essential change is the formation of the $BaSO_4$ precipitate, the other ions are still in solution. It would therefore be correct to represent this equilibrium by the following reaction:

$$\mathbf{Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \Leftrightarrow Ba(SO_4)_{(s)}}$$

This equilibrium equation does not change whatever the origin of Ba^{2+} and SO_4^{2-}.

The following table lists the main electrolytes with their water solubilities

Alkaline metal ions Li^+, Na^+, K^+	All soluble compounds
Hydronium ions, H_3O^+	All soluble compounds
Ammonium ions NH_4^+	All soluble compounds
Nitrates, NO_3^-	All soluble compounds
Acetates, CH_3COO^-	Soluble compounds, except with Ag^+
Chlorides, Cl^- **Bromides, B^{r-}** **Iiodides, I^-**	Soluble compounds, except with Ag^+, $Pb^{2+,}$ $Hg^{2+}$and Cu^+
Sulfates, SO_4^{2-}	Soluble compounds, except with ca^{2+}, $Be^{2+,}$ Ba^{2+} and Pb^{2+}
Sulfides, S^{2-}	Soluble compounds, with Li^+, K^+, Na^+, H_30^+, NH_4^+, Be^{2+} , Mg^{2+}, $Ca^{2+}$and $Ba^{2+.}$ Insoluble compounds with all the others.
Hydroxides , OH^-	Soluble compounds, with Li^+, K^+, Na^+, H_30^+, NH_4^+, Sr^{2+} and $Ba^{2+.}$ Insoluble compounds with all the others.
Phosphates, PO_4^{3-} **Carbonates, CO_3^{2-}** **Sulphites, SO_3^{2-}**	Soluble compounds, with Li^+, K^+, Na^+, H_30^+ and NH_4^+ Insoluble compounds with all the others.

The previous table allows you to predict whether a precipitation reaction can take place or not.

Example 1: Is there any precipitation when mixing:

1. NH_4Cl and KNO_3
2. $CaCl_2$ and $K_2C_2O_4$

Answer :

1. No precipitation since the 4 probable salts are all soluble NH_4Cl, NH_4NO_3, KNO_3 and KCl.
2. There is possibility of precipitation of CaC_2O_4

Example 2: Calculation of the solubility

What is the solubility S of $Ca_3(PO_4)_2$ at T=25°C ? $Ks = 10^{-26}$

Let's write the reaction: $\mathbf{Ca_3(PO_4)_2(s) \longrightarrow 3Ca^{2+} + 2PO_4^{3-}}$

t = 0	0	0
Equilibre	3S	2S

$Ks = [Ca^{2+}]^3 . [PO_4^{3-}]^2 = (3S)^3 (2S)^2 = 27 S^3 x 4 S^2 = 108. S^5$

$\rightarrow S = (Ks/108)^{1/5}$ (avec $Ks = 10^{-26}$) ⇨ $\boxed{\mathbf{S = 2, 5\ 10^{-6}\ mole/L}}$

The solubility S of a solid is **variable**. Thus, the addition of a common ion from a more soluble solid **reduces the solubility** of the initial solid.

IIICALCULATION OF THE SOLUBILITY OF A SOLID IN A SOLUTION

To calculate the solubility S of a solid AB, it's necessary to:

1. Write the reaction and deduce the equilibrium constant Ks

$\mathbf{AB(s) \Leftrightarrow A^+ + B^-}$ $\quad\quad Ks = [A^+].[B^-]$

2. Calculate the quotient (or initial product $\mathbf{P_i}$) $\mathbf{Q = [A^+]_o .[B^-]_o}$

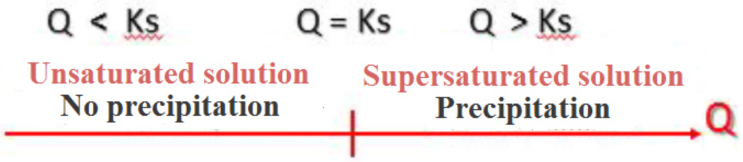
3. If **Q < Ks** ⟹ The solution is **unsaturated**, there is no solid, equilibrium is not achieved. To achieve balance you must:

- Either Add common ions using soluble salts.
- Either dissolve part of the AB salt.

4. If **Q = Ks** ⟹ Equilibrium is established: beginning of appearance of solid. The solution is said to be **saturated**.

5. If **Q > Ks** ⟹ the system evolves in the direction of precipitation: the excess of ions forms the solid. The solution is said to be **supersaturated** to reach equilibrium it is necessary to precipitate AB.

6. Calculate the concentrations of the different species at equilibrium



Example :

We make the mixture of two highly soluble salts; 10 mL of an aqueous salt solution $AgNO_3$ 0,1 M and 10 mL of a salt solution NaCl 0,1 M.

- Is there a precipitation?
- What will be the concentrations of the species in solution?

We give $K_{s,AgCl} = 1.78 . 10^{-10}$

IV FACTORS INFLUENCING THE SOLUBILITY OF A POORLY SOLUBLE SALT

IV.1 The commun ion effect

The shift in solubility equilibria obeys Le Châtelier's principle. Thus, if a highly soluble salt containing a common ion, such as KCl/NaCl, is added to a saturated $PbCl_2$ solution, the Cl^- concentration increases. For the solubility product relationship to remain verified, it will be necessary to consume Pb^{2+} ions, by partially precipitating $PbCl_2$

Example : Calculate the solubility of PbI_2 in :

- Pure water.
- A solution of potassium iodide KI, 0,1M.
- A solution of lead nitrate $Pb(NO_3)_2$, 0,1 M.

We give $Ks_{(PbI2)} = 1.39 \cdot 10^{-8}$

Answer :

- **Solubility in pure water**

$\mathbf{PbI_{2(s)} \rightleftarrows Pb^{2+}_{(aq)} + 2I^-_{(aq)}}$; $Ks = [Pb^{2+}][I^-]^2 = s.(2s)^2 = 4s^3$ $\quad s = \left(\frac{Ks}{4}\right)^{1/3}$

t=0 a 0 0

Eq a-S S 2S **$s = 1.51 \cdot 10^{-3}$ mol/L**

- **Solubility in KI solution; 0,1M**

$KI \rightarrow K^+ + I^-$;

And $\mathbf{PbI_{2(s)} \rightleftarrows Pb^{2+}_{(aq)} + 2I^-_{(aq)}}$; $[I^-] = c + 2s'$;

t=0 0 C $Ks = s'.(c+2s')^2$; so : $s' = \left(\frac{Ks}{C^2}\right)$

Eq s' C+2s' $s' < s$ and $s \ll c \rightarrow s' \ll c$ **$S' = 1.39 \cdot 10^{-6}$ mol/L**

- **Solubility $Pb(NO_3)_2$ solution ; 0,1M**

$Pb(NO_3)_2 \rightarrow Pb^{2+} + 2NO_3^-$

And $PbI_{2(s)} \rightleftarrows Pb^{2+}_{(aq)} + 2I^-_{(aq)}$; $[Pb^{2+}] = c + s''$;

t=0 C 0 $Ks = (c + s'').(2s'')^2$; $s'' = \left(\frac{Ks}{4C}\right)^{1/2}$

Eq C+s'' 2s'' $s'' < s \rightarrow s'' \ll c$ **$S'' = 1.86 \cdot 10^{-4}$ mol/L**

The presence of a common ion in the solution reduces the solubility of the salt.

The effect of the common ion is comparable to the effect of a strong acid on the dissociation of a weak acid.

IV.2 Effect of temperature

The solubility of a compound depends on the value of the solubility product Ks of the compound and the value of Ks depends on the temperature T according to Van 't Hoff's law:

- In general, dissolution is an endothermic reaction ⟹ **ΔH > 0** ⟹ solubility **increases** as the **temperature increases**.
- Sometimes the dissolution is an exothermic reaction ⟹ **ΔH < 0** ⟹ the solubility **decreases** as the **temperature increases**.

Example :

Case of $CaSO_4$ which is less soluble when T increases, which explains the phenomenon of scaling in boilers, water heaters, etc.

IV.3 Effect of pH

If the species resulting from the dissolution of the poorly soluble salt have acid-base properties, the solubility will depend on the pH.

Example 1 :

What is the solubility of Fe $(OH)_2$ **:**

- In pure water.
- In HCl solution **0.1 mole/l** ?
- In a buffer solution of a **pH = 6** ?

We give : **Ks,** $_{Fe\,(OH)_2}$ **= 7.94 . 10**$^{-16}$

Example 2 :

Which of the following ionic solids is the least soluble? **:**

- AgCl pKs= **9,7**
- Ag_2CrO_4 pKs= **12**
- $PbBr_2$ pKs= **6,6**
- PbI_2 pKs= **7,9**

V APPLICATION EXERCICES

- **Exercise 01 :**

Consider a solution containing a metal ion M^{2+} of concentration C.

a) From what pH do we obtain the precipitation of this metal ion in the form hydroxide? We give K_s, the solubility product of this hydroxide $M(OH)_2$.

b) In an equimolecular mixture of ions: Ca^{2+}, Cu^{2+}, pb^{2+} and Mg^{2+}, of concentration C=**1mole/l**. In what order do these ions precipitate in the form of hydroxides when the pH is increased?

	$Ca(OH)_2$	$Cu(OH)_2$	$Pb(OH)_2$	$Mg(OH)_2$
Ks	**$3,72.10^{-6}$**	**$1,58.10^{-19}$**	**5.10^{-16}**	**$1,16.10^{-11}$**

c)
Represent the different salts on an axis graduated in pH

- **Exercise 02:**

A/ Consider the following poorly soluble salts: CaF_2, $CuCl$, $AgBr$, $Mg(OH)_2$
Which of these salts are more soluble in an acidic environment than in water. Justify.
B/ Calculate the solubility of magnesium hydroxide
B1/ In pure water
B2/ In an aqueous solution of nitric acid (HNO_3) with a concentration of **0.01 mol/L.**
We give: Ks, $Mg(OH)_2$= $1.16\ 10^{-11}$

- **Exercise 03:**

A precipitate contains **4.60g** of Zinc oxalate and **3.37g** of Magnesium oxalate. How much water should we use to remove the Magnesium from the precipitate?
What is then the mass of dissolved Zinc oxalate?
We give: Zn: **65.4**; Mg:**24.3**; C:**12**; O:**16** ; $pKS_{,ZnC2O4}$=**8.8** ; $pKS_{,MgC2O4}$= **4.1**

- **Exercise: 04**

Consider a solution containing a metal ion Fe^{3+} with a concentration $C_0=10^{-2}$ **mol/L**.
a) Determine the pH limit for precipitation of $Fe(OH)_3$, knowing that $pKs(Fe(OH)_3))=38$.
b) On an axis graduated in pH, position the areas of predominance of Fe^{3+} ions and the $Fe(OH)_3$.

- **Exercise 05:**

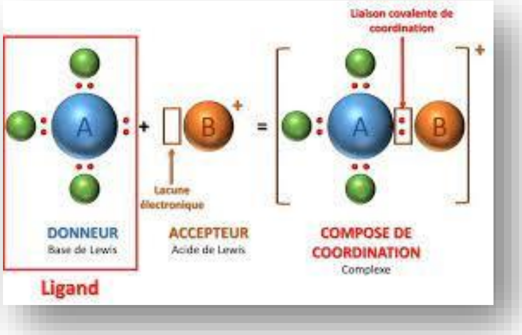
Ag^+ ions are added to a solution that contains Cl^- and I^- ions, both at a concentration of **0.01M**.

1) Which salt, precipitates first? Justify your answer.
2) Calculate the concentration of Ag^+, when the first salt begins to precipitate.
3) Calculate the concentration of the anion of the first precipitate, when the second salt begins to precipitate.

We give: $Ks_{AgCl}= 2,8 \cdot 10^{-10}$; $Ks_{AgI}= 8,5 \cdot 10^{-17}$

CHAPTER V : COMPLEXATION REACTIONS

I DEFINITIONS



A complex is a chemical species **$[M(aL)x(nL)y]^q$** in which there is a metal cation (M^{n+}) linked to one or more anions or neutral molecules.

- The metal cation (M^{n+}) is called central ion. It is an electron acceptor. (These are Lewis acids)

- Anions or molecules (L) are called **ligands** or **coordinates**. They are electron donors. (These are Lewis bases)

Indeed, alongside ordinary compounds such as $Al_2(SO4)_3$, $FeSO_4$ and $Fe(CN)_2$, we encounter compounds whose structure is more complex such as Mohr's salt: $(NH_4)_2Fe(SO_4)_2.6H_2O$, potassium ferrocyanide: $K_4[Fe(CN)_6].3\,H_2O$, etc.

These compounds are obtained by union of salt molecules with acids, bases or other salts of simpler composition:

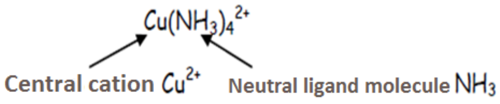
Example 1:

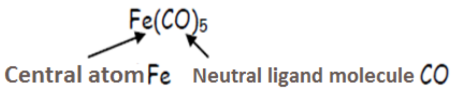
$(NH_4)_2\,SO_4 + FeSO_4 \Leftrightarrow (NH_4)_2Fe(SO_4)_2$

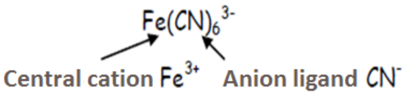
Example 2:

$[Ag(NH_3)_2]^+$: Ag^+ is the central ion and NH_3 is the ligand.

$[Ag(S_2O_3)_2]^{3-}$: Ag^+ is the central ion and $S_2O_3^{2-}$ the ligand.







II STRUCTURE OF A COMPLEXE

II.1 Formula of a complexe

$$\boxed{[M\,(aL)_x(nL)_y]^q}$$

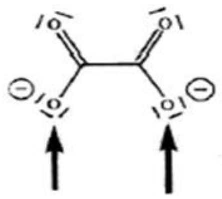
M : central atom
La : anionic ligands and **x** : number of anionic ligands
Ln : neutral ligands and **y** : number of neutral ligands
Q : The total charge of the complex

- The number of bonds that the coordinator ion can establish is called the coordination number or coordination index.
- A ligand that attaches to the central atom or ion using a single doublet is *monodentate*.

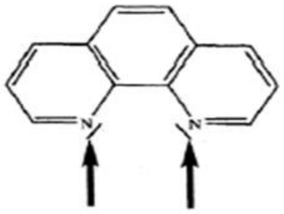
- A ligand that attaches to the central atom or ion using two doublets is *bidentate.*

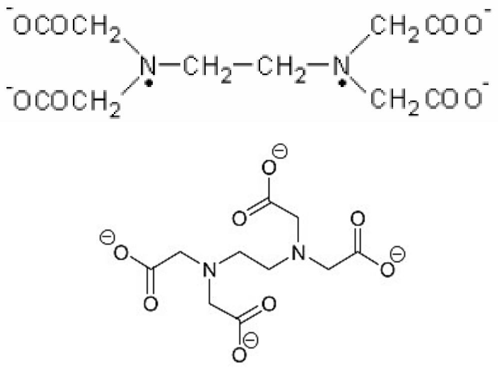
Example :

oxalate Ion



orthophenanthroline





Ethylene Diamine Tetraacetic acid (EDTA)

- ➢ A ligand that attaches to the central atom or ion using several doublets is ***polydentate.***

- The formula for a complex is noted in square brackets, with the possible charge placed outside.
- A complex can be positively charged, negatively charged or neutral.
- The total charge of the complex ion is the algebraic sum of the charges of all the constituents of the complex.
- A complex is perfectly soluble in water when it is globally charged differently from a precipitate.

Application :

Calculate the charge of the central ion in the following complexes:

$[Cu(NH_3)_4]^{2+}$; $[HgI_4]^{2-}$; $[Fe(CO)_5]$; $Na_2[Co(NO_2)_6]$

II.2 coordination index

Central ions	Coordination index
Ag^+, Cu^+, Au^+	2
Cu^{2+}, Hg^{2+}, Au^{2+}, Cd^{2+}, pb^{2+}, pt^{2+}, pd^{2+}	4
Fe^{2+}, Fe^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Al^{3+}, Zn^{2+}, Pt^{4+}	6
Ca^{2+}, Sr^{2+}, Ba^{2+}	8

Example: Give the different coordinations of :

$[Fe(CN)_6]^{4-}$; $[Cu(NH_3)_4]^{2+}$; $[Cu(H_2O)_6]^{2+}$

- ➢ In general, the coordination number is between 2 and 12 and varies with the nature of the ligands, notably their size (n decreases if the size of the ligand increases)
- ➢ For the same central atom, the coordination index varies from one complex to another.

II.3 The most encountered ligands:

a) **Neutral molecules :** H_2O, NH_3, CO, NO…

b) The anions : CN^-, NO_2^-, Cl^-, Br^-, I^-, OH^-....

II.4 Name of some mineral coordinates :

Ligand	Nomenclature	Ligand	Nomenclature	Ligand	Nomenclature
H^-	Hydride	CO_3^{2-}	Carbonate	SO_4^{2-}	Sulfato
O^{2-}	Oxo	CN^-	Cyano	H_2O	Aqua
OH^-	Hydroxo	$C_2O_4^{2-}$	Oxalate	NH_3	Ammine
S^{2-}	Thio	SCN^-	Thiocyanato	CO	Carbonyl
I^-	Iodo	NH_2^-	Amido	NO	Nitrosyl
Br^-	Bromo	N_3^-	Nitrido	EDTA	Ethylenediaminetetraacetato
Cl^-	Chloro	NO_3^-	Nitrato	$S_2O_3^{2-}$	Thiosulfate
F^-	Fluoro	NO_2^-	Nitrito		

III NOMENCLATURE

1. We name the ligands then the central metal.
2. If the complex is positively or negatively charged, its name is ended by the word « Ion ».
3. The name of a neutral ligand is retained. (Except “aqua” for H_2O and “ammine” for NH_3).
4. The name of a negative ligand ends with the letter «o». (e.g. Chloro or Cyano).
5. The number of ligands is specified by a prefix: di, tri, tetra, penta, hexa...
6. The name of the positive anion is written before the name of the negative anion.
7. If the complex has zero or positive charge, the central ion or atom has the name of the corresponding element.
8. If the complex is negatively charged, the ending “ate” is added to the name of the corresponding central element.
9. The name of the complex ends with the number of charges carried by the central metal (its oxidation number), indicated in Roman numerals.

Example:

Name the following complexes:

$[Fe(CO)_5]$, $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{3-}$, $[Al(H_2O)_6]^{3+}$, $[Ag(Cl)_2]^-$, $[Cu(H_2O)_6]^{2+}$, $[Ni(CN)_4]^{2-}$.

IV APPLICATION OF THE COMPLEXATION REACTION

1. Maintaining certain ions in solution, preventing them from precipitating

Example :
Maintaining Ca^{2+} in solution, preventing it from precipitating as $CaCO_3$ in boilers.

2. Recovery of noble metals

The noble metals Ag and Au are oxidized and complexed by cyanide ions:

$$Ag^+_{aq} + 2CN^- \rightleftarrows Ag(CN)_2^- \quad \textbf{Because} \quad E_0(Ag(CN)_2^-/Ag) = -0.44 \ll E'_0$$

$$Au^+_{aq} + 2CN^- \rightleftarrows Au(CN)_2^- \quad \textbf{Because} \quad E_0(Au(CN)_2^-/Au) = -0.61 \ll E'_0$$

3. Coloring pigments:

Ferric potassium ferrocyanide ($KFe^{III}[Fe^{II}(CN)_6]$, Prussian blue), is used as a pigment.

4. Electroplating baths :

The metals to be deposited electrochemically are first maintained in concentrated solution in the form of complexes: $Au(CN)_2^-$, $Ni(CN)_4^-$

5. Anti-tumor chemistry (Cancer)

Use of Cis-$[Pt(NH_3)_2Cl_2]$. It ensures the exchange between Cl^- ligands and the nitrogen atoms of DNA, which are responsible for cellular reproduction.

6. Traitement of heavy metal poisoning

Example : Lead poisoning
$Pb^{2+} + Ca\text{-}Y^{2-} \Rightarrow Ca^{2+} + Pb\text{-}Y^{2-}$
EDTA alone cannot be used because it will fix all the calcium in the body.

7. Concealment of certain annoying ions which could distort the characterization assay of another ion

Example : Concealment of Cu^{2+} by complexing it with CN^-, before searching for $Cd^{2+,}$, because both precipitate in the presence of H_2S :

$Cu^{2+} + H_2S \Leftrightarrow CuS$ (Black) $+ 2H^+$
$Cd^{2+} + H_2S \Leftrightarrow CdS$ (Yellow) $+ 2H^+$

8. The quantitative identification of certain ions which give very colored complexes

By colorimetric determination, the quantity of the complex formed is determined and the quantity of the ion to be determined is deduced.

Examples:
Use of chelates such as EDTA (Y^{4-}) to measure certain elements
$\mathbf{(Ca + Mg) + Y^{4-} \longrightarrow Ca\,Y^{2-} + Mg\,Y^{2-}}$
$Fe^{3+} + SCN^- \leftrightarrow FeSCN^+$ Red ; visible if $C > 10^{-5,5}$

What is the difference between a precipitaion reaction and a reaction of complexation?

The principal difference is their solubility:

- In a precipitation reaction there is an equilibrium between the solid and the ions which constitute it.
- In a complexation reaction all the constituents are in a dissolved state.

V STABILITY OF COMPLEXES

The stability of a complex depends on its structure. It increases with the charge of the central ion. This stability is measured by its **formation constant** or **stability constant.**

V.1 Complexation equilibrium constant

a) The global constant of formation of a complex (or stability constant)

The global constant of formation or stability, noted **β**, is the constant linked to the written equilibrium in the direction of formation of the complex.

$M + nL \Leftrightarrow ML_n$ (I) (example $[Cu(NH_3)_4]^{2+}$)

The global constant of stability: $\boxed{\beta_n = [MLn]/[M].[L]^n}$

Example :

$Cr^{3+} + 4OH^- \leftrightarrow Cr(OH)_4^-$ $\beta 4 = \frac{[Cr(OH)4-]}{[Cr3+].[OH-]*4}$

The **higher βn** ⇒ the more stable the complex ⇒ the weaker the dissociation (the concentration of the constituents is low) ⇒ The complexe is said to be **perfect.**

b) The global constant of dissociation of a complex

The constante of dissociation **K_D** of a complex is the written equilibrium constant in the direction of destruction of the complex and the formation of the metal and **free ligands.**

$ML_n \Leftrightarrow M + nL$ $\boxed{K_D = 1/\beta n = [M].[L]^n/[MLn]}$

The **higher KD** (the greater the concentrations of the constituents) ⇒ the more unstable the complexe ⇒ the complex is said to be **unperfect.**

By analogy with the acid-base reactions:

- We define: $\boxed{PK_D = -\log K_D = \log \beta_n}$
- and: **pM = -log [M]**

Knowing that $[M] = K_d . [ML_n]/[L]^n \Longrightarrow \boxed{pM = pK_D + \log [L]^n/[MLn]}$

- We define $\boxed{pL = -\log [L]}$ $\Longrightarrow$ $\boxed{pL = 1/n\,(pK_D + \log[M]/[MLn])}$

c) Successives formation constant

When with one only type of ligand (L), Mn^+ can form several complexes ML_n (n>1) or polydentate complexes we say that we have successive complexes. The stability and the dissociation constants of these complexes are linked.

$M + L \Leftrightarrow ML$ (I) $Kf_1 = [ML]/[M].[L]$

$ML + L \Leftrightarrow ML_2$ (II) $Kf_2 = [ML_2]/[ML].[L]$

$ML_2 + L \Leftrightarrow ML_3$ (III) $Kf_3 = [ML_3]/[ML_2].[L]$

$ML_{(n-1)} + L \Leftrightarrow ML_n$ (n) $Kf_n = [ML_n]/[ML_{(n-1)}].[L]$

When combining the n reactions, we obtain the overall reaction : $M + nL \Leftrightarrow ML_n$

of constant βn $\boxed{\beta_n = [ML_n] / [M].[L]^n}$

$\boxed{\beta n = \prod_{i=1}^{n} Kfi} \Rightarrow \boxed{Log\beta n = \sum_{i=1}^{n} Log\ Kfi} \Rightarrow \boxed{Log\beta n = \sum_{i=1}^{n} pKdi}$

Likewise, the dissociation of a complex having n identical ligands involves n successive equilibria and the Kd_i can also be determined.

- ## V.2 Area of predominance: Ligand exchange

A complex can exchange both its metal ion (M) and a ligand (L). Depending on the nature of the exchange, we can establish a predominance diagram graduated in **pM = -Log[M]** or in **pL =-Log[L].**

a)- Ligand exchange :

Let be the equilibrium : $ML_{(n-1)} + L \Leftrightarrow ML_n$ ($MLn / ML_{(n-1)}$ donor/receiver couple)

$Kf_n = [ML_n]/[ML_{(n-1)}].[L] \Longrightarrow pL = \log Kf_n + \log[ML_{(n-1)}]/[MLn]$

$\Longrightarrow pL = pKd_n + \log[ML_{(n-1)}]/[ML_n]$

Reminder:

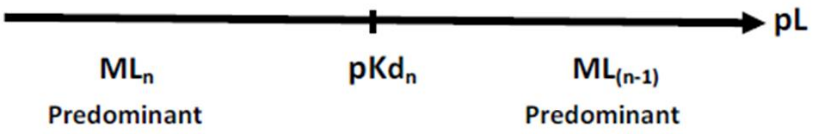
This is the same reasoning as for acid-base reactions (H^+ proton exchange) except that here we have a ligand exchange.

pH = pKa + log [A-]/[AH]

- If pH = pKa ⟹ [A-] = [AH]
- If pH > pKa ⟹ [A-] > [AH] ⟹ the base is predominant
- If pH < pKa ⟹ [A-] < [AH] ⟹ the acid is predominant

If $pL > pKd_n \Longrightarrow [ML_{(n-1)}] > [ML_n] \Longrightarrow$ Predominance of $[ML_{(n-1)}]$

If $pL < pKd_n \Longrightarrow [ML_{(n-1)}] < [ML_n] \Longrightarrow$ Predominance of $[ML_n]$

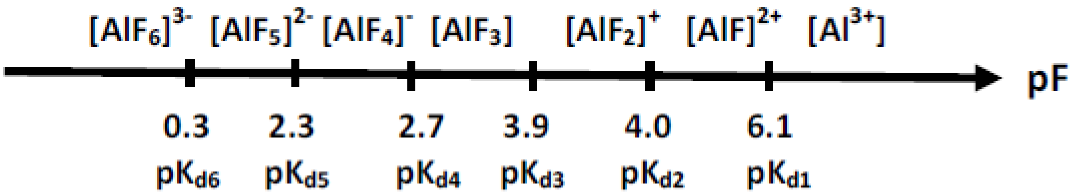


In the case of a polycomplexation, it is necessary to superimpose the predominance diagrams of the different couples, to have the complete predominance diagram.

Example :

The Al^{3+} ion forms with the F^- ions the following complexes: $[AlF]^{2+}$; $[AlF_2]^+$; $[AlF_3]$; $[AlF_4]^-$; $[AlF_5]^{2-}$ et $[AlF_6]^{3-}$, the successive constants are: $\log Kf_1 = 6.1$; $\log Kf_2 = 4.0$; $\log Kf_3 = 3.9$; $\log Kf_4 = 2.7$; $\log Kf_5 = 2.3$ and $\log Kf_6 = 0.3$.

- Draw the graduated predominance diagram in pF= -logF.
- Knowing that $\log Kf_i = Pkd_i$, we can establish the following predominance diagram:



b)- Exchange of central ion : same reasoning as for ligand exchange.

V.3 Calculation of metal and ligand concentrations

Consider a complex ML_n of concentration $\mathbf{C_0}$ and the global dissociation constant $\mathbf{K_D}$

By analogy with acid-base reactions, three cases can arise:

- If the complex is **very stable** $\Longrightarrow$ **β_n is very large** $\Longrightarrow$ **K_D is very low** $\Longrightarrow$ the concentrations of the constituents are very low $\Longrightarrow$ we can **neglect [M]** in front of $[ML_n]$.
- If the complex is **moderately stable** $\Longrightarrow$ [M] and $[ML_n]$ have comparable values, **none** is neglected.
- If the complex is very **unstable** $\Longrightarrow$ **β_n is very weak** $\Longrightarrow$ **K_D is very large** $\Longrightarrow$ the concentrations of the constituents are very high $\Longrightarrow$ we can **neglect $[ML_n]$** in front of [M].

Calculation of the concentration [L] :

$ML_n \Leftrightarrow M + nL$ $\qquad K_D = 1/\beta n = [M].[L]^n / [ML_n]$

t_0	$\mathbf{C_0}$	**0**	**0**
t_{eq}	$\mathbf{C_0 - x}$	**x**	**nx**

(I)

$[M] = x$

$[L] = nx \Longrightarrow x = [L]/n = [M]$

Conservation of matter of the metal ion: $C_0 = [M] + [ML_n]$

If the complexe is stable we can write: $C_0 = [ML_n]$ (we neglect [M] in front of C_0)

$K_D = [L]^{n+1}/nC_0 \Longrightarrow$ $\boxed{[L] = \sqrt[n+1]{n.KD.C0}}$

$$\boxed{pL = \frac{1}{n+1}\,(pKD - \log n.C0)}$$

If n=1 :

$$\boxed{pL = \frac{1}{2}\,(pKD - \log C0)}$$

(Similar formula to a weak acid)

Calculation of the concentration [M] :

According to the equation **(I),** we have :

$x = [M]$

$[L] = nx \Longrightarrow [L] = n\,[M] \Longrightarrow [L] = n\,[M]$

$$\boxed{KD = \frac{[M].[L]^n}{[MLn]} = \frac{[M].(n[M])^n}{[MLn]} = \frac{n^n.[M]^{n+1}}{C0}} \Longrightarrow \boxed{[M] = \sqrt[n+1]{KD.\frac{C0}{n^n}}}$$

$$\boxed{pM = \frac{1}{n+1}\,(pKD - \log\frac{C0}{n^n})}$$

Si n=1 :

$$\boxed{pM = \frac{1}{2}\,(pKD - \log C0)}$$

V.4 Prediction of reactions

a) Case of a single central atom and several ligands

Example 1: Fe^{3+} in the presence of : **I^-** and **Br^-**

When the I^- and Br^- ligands are present at identical concentrations, Fe^{3+} reacts with the anion which leads to the formation of the most stable complex.
Two reactions are possible:

$Fe^{3+} + Br^- \rightleftharpoons [FeBr]^{2+}$ pKD,$[FeBr]^{2+}$ = - 0,15

$Fe^{3+} + I^- \rightleftharpoons [FeI]^{2+}$ pKD,$[FeI]^{2+}$ = 2,85

It is the most stable complex (lowest KD ⟹ highest pKD) that is formed. It corresponds to $[FeI]^{2+}$ whose pKD = 2.85

Example 2:

if we add the ligand $C_2O_4^{2-}$ to a solution which contains the red complex $[FeSCN]^{2+}$ The color disappears. Explain
We give : $K_f[FeSCN]^{2+}$= **$10^{2.2}$** et $K_f[Fe\ C_2O_4]^+$ = **$10^{9.4}$**

This is explained by an exchange of ligands according to the following reaction:

$[FeSCN]^{2+} + C_2O_4^{2-} \rightleftharpoons [Fe\ C_2O_4]^+ + SCN^-$

If we calculate the equilibrium constant Kc :

$$\boldsymbol{Kc = \frac{[Fe\ C2O4]+.[SCN-\ ]}{[FeSCN]2+.[C2O42-]} = \frac{Kf[Fe\ C2O4]+}{Kf[FeSCN]2+} = \frac{10^{\ 9,4}}{10^{\ 2,2}} = 10^{\ 7,2} \gg 1}$$

b) Case of a ligand and two cations

Example:

Br^- in the presence of **Fe^{3+}** and **Cu^{2+}**
pKD$[CuBr]^+$ = **-0,07** , pKD$[FeBr]^{2+}$= **-0,15**

It's $[CuBr]^+$ which is formed:
$[FeBr]^{2+} + Cu^{2+} \rightleftharpoons [CuBr]^+ + Fe^{3+}$

The reaction is done in direction 1 (towards the right)

Even if the $[FeBr]^{2+}$ complex is already formed, it can be destroyed and release Fe^{3+}, by adding Cu^{2+} which forms a more stable complex with Br^-.

V.5 Internal factors influencing the stability of complexes:

There are internal factors and external factors:

- **Internal factors:** Nature of the coordination and nature of the coordinating ion.
- **External factors:** Presence of another coordinator, Presence of another coordination, PH, dilution, etc.

a)- Nature of the coordinator or central ion:

The smaller the central ion is, more highly charged and with low electropositivity, the more stable the complex will be.
Very electropositive alkalis do not give complexes, while transition metals give the most stable complexes.

b)- Nature of the coordination or ligand:

The more the ligands are electron donors ⟹ strong bases according to Lewis, the more stable the complex will be.

For chelates, stability increases with:
- The number of cycles
- The number of atoms constituting the cycle (the optimum stability is obtained with C5 and C6 cycles)
-When the number of chelator molecules coordinated with the central ion increases.

c)- Influence of the pH of the solution

In general, ligands have a basic character and can therefore react in the presence of an acid.
Two cases can arise:

- If the ligand is the conjugate base of a strong acid (Ex ; Cl^-, NO_3,...) ⇒ the pH has no influence on the complexation equilibrium.
- If the ligand is the conjugate base of a weak acid (Ex ; $C_2O_4^{2-}$, CH_3COO^-,...) ⇒ the pH has an influence on the complexation equilibrium.

- ✓ **By hydrolysis of the ligand**

  $L + H_2O \rightleftharpoons LH^+ + OH^-$ (EX. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$)

$$Kb = \frac{[LH+].[OH-]}{L}$$

- ✓ **By adding an acid**

  $L + H_3O^+ \rightleftharpoons LH^+ + H_2O$ (EX. $C_2O_4^{2-} + H_3O^+ \rightleftharpoons H_2C_2O_4 + H_2O$)

Example :

Let be a solution containing the complex $[FeF]^{2+}$; KD =**10^{-5}**, what happens if we add strong acid to it?

We have two consecutive reactions:

$[FeF]^{2+} \rightleftharpoons Fe^{3+} + F^-$ (KD) (I)

$F^- + H_3O^+ \rightleftharpoons HF + H_2O$ (1/ Ka) (II)

$[FeF]^{2+} + H_3O^+ \rightleftharpoons Fe^{3+} + HF + H_2O$ K = KD / Ka (III) $KD = \frac{[Fe3+].[F-]}{[FeF]2+}$

If we add H_3O^+ ⇒ $[F^-]$ decreases, which leads to an increase in the ratio:

$\frac{Kd}{[F-]} = \frac{[Fe3+]}{[FeF]2+}$ ⇒ **increased dissociation of the complex**

VI APPLICATION EXERCICES

- **Exercise 01:**

A/ Name the following complexes :

(a) $K_3[CrF_4O]$ **(b)** $[Cr(H_2O)_6]Cl_3$; **(c)** $[Fe(NH_3)_5H_2O]^{2+}$

(d) $Na_3[Fe(CN)_6]$ **(e)** $[PtBr_2(NH_3)_2]$ **(f)** $[CoCl_2(NH_3)_4]$ Cl

B/ Write the formulas of the following complexes :

a. Tetrachlorocobaltate (II) ion.
b. Pentacyanocarbonylferrate (II) ion.
c. Ammonium hexafluoronickelate (IV).
d. Pentaaquahydroxoaluminium(III) ion.
e. Potassium tetrafluorooxochromate (III).
f. Tetraamminedichlorocobalt(III) chloride.

- **Exercise 02:**

a) Copper hydroxide **$Cu(OH)_2$** is redissolved by the addition of ammonia. For what ?

b) The dissociation constant of **$[Ag(NH_3)_2]^+$** is **6.10^{-8}**, that of **$[Ag(CN)_2]^-$** is **4.10^{-20}**. In which complex is the **Ag^+** ion most hidden?

c) The solubility product of AgCl is **$K_s = 10^{-10}$**. What are the constants of the following equilibria:

$$AgCl\,(s) + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^-$$

$$AgCl\,(s) + 2CN^- \rightleftarrows Ag(CN)_2^- + Cl^-$$

d) Compare the solubilities of AgCl (in moles/l):

- In pure water
- In an excess of **1N** ammonia solution.
- In an excess of **1N** cyanide solution.

- **Exercise 03:**

The **Cu^{2+}** ion forms with **NH_3**, four successive complexes whose respective formation constants are: $\log K_{f1}$= **4.1**, $\log K_{f2}$= **3.5**, $\log K_{f3}$= **2.9** and $\log K_{f4}$= **2.1.**

We send gaseous ammonia (**NH_3**) into a solution initially containing **Cu^{2+}** ions with a concentration of **0.1 mol/L** and we stop when the concentration of free **NH_3** in the solution stabilizes at the value of **0.5 mol/L**.

1. Give the structure of the four successive complexes and their nomenclature.
2. Plot the predominance diagram as a function of **pNH3**.
3. Which of the complexes is the majority? justify your answer.
4. Write the overall reaction for the formation of the majority complex.
5. Calculate the numerical value of the overall formation constant of this complex. What can we conclude?
6. Calculate the concentration of **Cu^{2+}** at equilibrium.

• Exercise 04:

A solution is produced initially containing ferric ions at **10^{-3} M** and thiocyanate ions at **0,1 M**. The dissociation constant of $[Fe(SCN)[^{2+}$ **K_{d1} = 0,01**.

a) What are the final concentrations of **Fe^{3+}, SCN^-** and **$[Fe(SCN)]^{2+}$**.

b) What minimum quantity of NaF must be added to **10 ml** of the initial solution to completely eliminate the red coloring of $[Fe(SCN)]^{2+}$ (we will assume that the red coloring disappears if $[Fe(SCN)^{2+}] <$ **3.10^{-6}**)

The dissociation constant of **$[FeF]^{2+}$** is K_{d2} = **$10^{-5,5}$**.

We give: M_{NaF} = **42g**

• Exercise 05:

To a clear solution of **Al^{3+}** ions, sodium hydroxide (**NaOH** crystals) is added at constant volume.

First of all, a precipitate of aluminum hydroxide **$Al(OH)_3$** is formed which redissolves in an excess of **OH^-** ions, forming the complex ion **$[Al(OH)_4]^-$**

1. Write the two equilibrium reactions of formation and dissolution of the compound **$Al(OH)_3$** in the presence of **OH^-** ions.

2. Express the equilibrium constant for each reaction, the precipitation and the dissolution if $Al(OH)_3$ giving the complex ion **$[Al(OH)_4]^-$.**Calculate the numerical value of each equilibrium constant.

3. What are the pOH values of the beginning and end of precipitation when the pOH of the solution varies from 14 to 1, If the initial concentration $[Al^{3+}]$ =**10^{-3} M**.

4. Deduce the domains of predominance of the $[Al^{3+}]$ and $[Al(OH)_4]^-$ ions, as well as the domain of existence of the $Al(OH)_3$ precipitate. Represent these three domains on an axis oriented pOH.

Data: pKs,$Al(OH)_3$ = 33 ; $\beta_4 = 10^{35}$

REFERENCES

1- Chimie tous en PCSI, B.Fosset, éditions Dunod-2010.

2- Chimie générale, J.Hill, R.J.Petrucci, éditions ERPI-2008.

3- Chimie générale, P.A. Rock, McQuarrie, D.Allan, éditions De Boeck-1992.

4- Chimie des solutions, S. Mathé, éditions Dunod-2017.

5- Chimie analytique (Chimie des solutions), M.Beljean-Leymarie, J.-P.Dubost, M. Galliot-Guiley, éditions Masson-2006.

6- Chimie des solutions, J.W. Hill, R.H. Petrucci, M.Dion, M.Lamoureux, éditions ERPI-2004.

7- Tous les exercices de chimie MPSI-PTSI, S.Beaumont, éditions EdiScience-2007.

8- Cours de cinétique chimique, C.Vanhaverbeke, Université Joseph Fourier de grenoble, Année universitaire 2011-2012 .