Algerian People's Democratic Republic

Ministry of Higher Education and Scientific Research

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Faculty of Sciences and Technology

Course Handout

Intended for students of the 2nd year Process Engineering

Chemistry of solutions

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PREFACE

This course is intended for second year students engineering process.it provides a comprehensive introduction to the fundament principles of Chemistry of solutions, organized into five chapters

The course encompasses the core componenets of the official curriculum in solution chemistry, specifically tailored to this level of study.it is developed based on established reference materials in the field and incorporates selected pratical applications to reinforce theoretical concepts.

The primary objective of this course is to enable students to acquire a solid mastery of solution chemistry. By the expected to be capable of performing the necessary calculations and providing accurate interpretations essential for thorough understanding of phenomena occurring in solutions.

Furthermore, the course aims to establish a strong conceptual foundation for analyzing the mechanisms governing equilibrium in aqueous systems.

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Chapter I
The solutions

I.1 Definition of solution

- **Solution**: A homogeneous mixture, in the gaseous, liquid, or solid phase, of at least two substances.
- **Solvent**: The component present in the largest amount and found in the same physical state as the solution.
- **Solute**: Any substance that can be dissolved in the solvent.

When the solvent used is water, this solution is called an ***aqueous solution***.

I.2 The concentration of solution

The most commonly used quantities to express a composition of solute are listed below:

I.2.1 Molar fraction

n_i be the amount of substance of any component i in the solution. The ***molar fraction x_i*** of this component is expressed as the ratio of n_i to the total amount of substance n (total number of moles).

$$x_i = \frac{n_i}{n} = \frac{n_i}{\sum n_i} \; with \; \sum_i x_i = 1$$

n_i and n is expressed in mol , x without dimension

I.2.2 Mass fraction

m_i be the mass of a component i in the solution. The ***mass fraction w_i*** of this component is expressed as the ratio of its mass to the total mass m of the solution:

$$w_i = \frac{m_i}{m} = \frac{m_i}{\sum m_i} \; with \; \sum_i w_i = 1$$

We use usually the mass percentage: P (%) = w_i ×100

Example: A concentrated commercial solution of nitric acid at 70% contains 70 g of HNO_3 in 100 g of solution, which means 70 g of HNO_3 for 30 g of water.

I. 2.3 Mass concentration t_P

The mass concentration or **weight percent** t_P of a solution is the mass of a solute contained in one unit of volume of the solution.

$$t_p = \frac{mass\ of\ solute}{Volume\ of\ solution}$$

t_P is expressed in g/l; mass in g and volume in L.

I.2.4 Molar concentration: molarity

Molarity or molar concentration of a solution is the number of moles of a solute contained in one unit of volume of the solution.

$$C_M = \frac{number\ of\ mole\ of\ \ solute}{Volume\ of\ solution}$$

It is usually expressed in moles per liter ($mol.L^{-1}$).

I.2.5 Molality or molal concentration C_m

Molality is the number of moles of a solute contained in one kilogram of solvent.

$$C_m = \frac{number\ of\ mole\ of\ \ solute}{mass\ \ of\ solvent}$$

Molality is expressed in the MKS system in moles per kilogram ($mol.kg^{-1}$).

If the solution contains multiple solutes, the molality of the solution is given for each of the solutes present in the solution.

I.2.6 Equivalent concentration or Normality

The concept of normality is sometimes used to simplify calculations in titration problems. The normality or equivalent concentration of a solution is the number of gram equivalents of solute contained in one unit of volume of the solution.

$$C_N = \frac{number\ of\ equivalent\ gram\ of\ solute}{Volume\ of\ solution} = \frac{n'}{V}$$

It is usually expressed in gram equivalents per liter of solution (Eq.g/L).

a) ***Cas of acid- base***:

Let's consider a solution containing a solute that dissociates, producing n_a anions carrying a charge of Z_a and n_c cations carrying a charge of Z_c.

$$C_{n_c}A_{n_A} \rightarrow n_C C^{Z_C} + n_A A^{Z_A}$$

$n' = n_A \times \ |Z_A| \times n = n_C \times Z_C \times n$ n: number of mole of solute

n': number of equivalent gram of solute

The relation between the normality and morality:

$$\boxed{n' = n_A \times \ |Z_A| \times n = n_C \times Z_C \times n} \Rightarrow \boxed{C_N = n_A \times Z_A \times C_M = n_C \times Z_C \times C_M}$$

Note :

The chemical equivalent represents the number of negative (-) or positive (+) charges involved in a reaction. It is the number of electric charges associated with an ion in solution. An ion has a charge Z in absolute value.

Example :

$HCl \rightarrow H^+ + Cl^-$ Z=1

$H_2SO_4 \rightarrow 2\,H^+ + SO_4^{-2}$ Z= 2

b) ***Cas of oxidation-reduction***

$$\boxed{\boldsymbol{C_N = x \times C_M}}$$

x : is the number of moles of electrons that is captured (or released) by one mole of the considered substance (the oxidizing agent or the reducing agent).

Example:

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

X=5 $\rightarrow \boldsymbol{C_N = 5 \times C_M}$

$$CrO_7^{2-} + 6e^- + 14H^+ \rightleftarrows 2Cr^{3+} + 7H_2O$$

X=6 → $\boldsymbol{C_N = 6 \times C_M}$

I.3 The dilution

Dilution involves preparing a solution with a lower concentration from a stock solution.

- Method: Using a pipette, introduce a determined volume of the stock solution into a volumetric flask, and add water until the marked line.
- Basic observation: The number of moles of solute present in the diluted solution is the same as in the sample of the stock solution taken.
- Dilution problems can therefore be solved using an algebraic method with the formula:

$$C_{conc} \times V_{conc} = C_{dil} \times V_{dil}$$

I.4 Aqueous solution of ionic compounds

The solute decomposes into ions;

- The forces that cause the dissolution of ionic solids are dipole-dipole forces (ion-dipole, to be precise in this case).
- We then refer to the ***solvation sphere*** of water (or hydration sphere) which orients its positive pole towards the anions and its negative pole towards the cations. Therefore, a polar solvent is required to dissolve an ionic compound.(figure I.1)

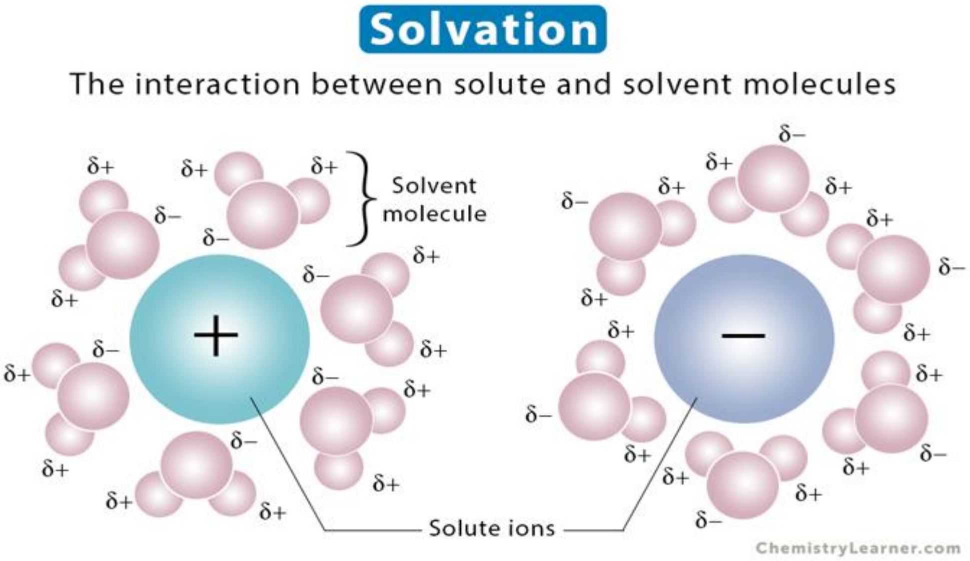


Figure I.1: Solvation mechanism

I.4.1 Activity of solution

When a chemical species (ion or molecule) is in solution, solute-solvent and solute-solute interactions occur. The availability of the chemical species for a reaction may then appear very different from its concentration in the solution. We introduce the notion of activity of a solution, which corresponds to the effective concentration of the solution.

The ***activity*** for the chemical species "i" is denoted as "a_i" and is expressed as:

$$\mathbf{a_i = C_i \, . \, f_i}$$

where:

f_i: the activity coefficient, which ranges between 0 and 1. It equals 1 for ideal solutions.

C_i: the concentration

- Activity is without dimension.
- For diluted solutions (less than 10^{-3} mol/l), activity is close to concentration.
- For pure substances and the solvent, activity is equal to 1.

I.5 Conductometry

I.5.1 Electrolyte solutions

Electrolytic solution: a solution that allows the passage of an electric current.

- Aqueous solutions of ionic compounds are ***good conductors***; the charged particles that move are ions.
- Ions carry an electric charge through the solution; ***anions*** (-) are attracted to the anode, and ***cations*** (+) are attracted to the cathode**.**

I.5.2 The Arrhenius theory

• Svante Arrhenius hypothesized that certain substances, such as NaCl and HCl, dissociate ***into cations and anions when dissolved in water.***

• The ions produced in this way allow electricity to flow through the solution.

• **Electrolyte**: a solute that produces enough ions to make a solution conductive.

• This is the theory of electrolytic dissociation.

I.5.3 Types of electrolytes

• ***Strong electrolyte***: a solute that **dissociates** almost **completely** or completely into ions in solution. Good conductor (NaCl, HCl, $KMnO_4$).

• ***Non-electrolyte***: a solute that ***does not dissociate***, or only very weakly, into ions in solution. It mostly remains in molecular form. Does not conduct electricity (CH_3CH_2OH).

• ***Weak electrolyte***: a solute that ***is partially ionized*** in solution. Current can flow, but a weak electrolyte is a poor conductor (CH_3COOH).(figure I.2)

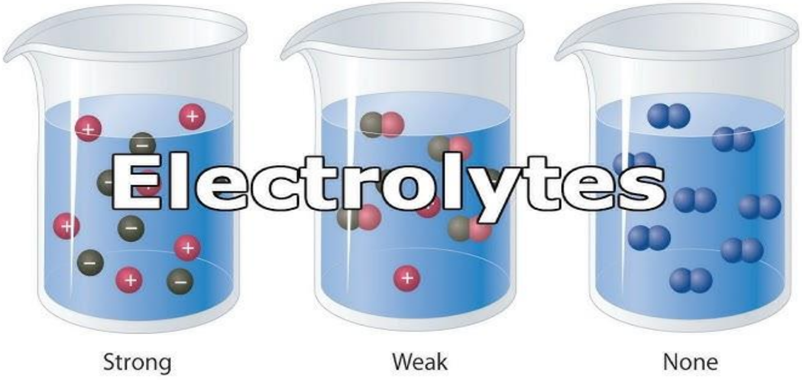


Figure I.2: Types of electrolytes

I.5.4 Ionic Mobility

In general, substances that react at the electrodes can be carried in three different ways:

- **Migration**: Transport of ions under the influence of an applied electric field.
- **Diffusion**: Mode of transport due to concentration differences in the solution, where a concentration gradient is established.
- **Convection**: A macroscopic transport process in which dissolved substances or ions are carried ,along by the overall movement of the fluid.

The mobility of an ion is defined as the velocity of the ion per unit of electric field (E):

$$\boldsymbol{u_i = \frac{V_i}{E}}$$

I.5.5 Conduction of electrolyte solutions

I.5.5.1 Conductance and conductivity

An ionic solution is conductive. It is the presence of ions, which gives the solution its conductive character.

To determine the conductance of an ionic solution, we need:

- ✓ An alternating current generator,
- ✓ A conductometric cell, consisting of two parallel metal plates, with surface area S and separated by a distance L (figure I.3).
- ✓ A voltmeter measuring the voltage across the two plates of the conductometric cell,
- ✓ An ammeter measuring the current intensity of the alternating current.

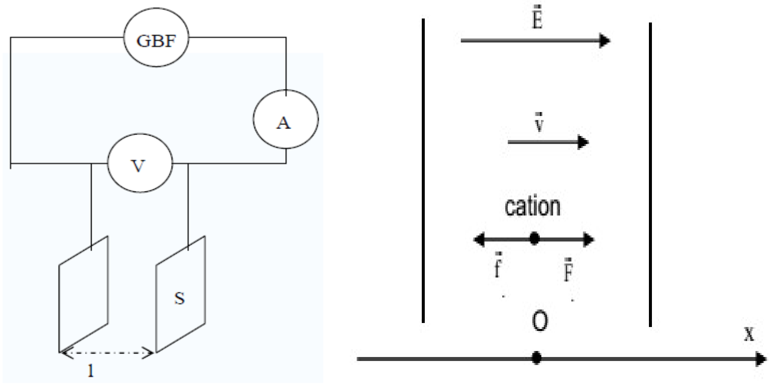


Figure I.3: Conductometric cell

In this way, we can determine the **resistance** R of the portion of the aqueous solution between the two electrodes. This resistance is calculated using ***Ohm's law***.

$$\boxed{\mathbf{R = \frac{U}{I}}}$$

The resistance is expressed in ***ohms*** (Ω) if the voltage is in **volts** (V) and the current is in **amperes** (A).

This resistance characterizes the portion of the solution between the two electrodes that "resists" the passage of current. We can then define a quantity that would be the inverse of the resistance; it would characterize the ability of the portion of the solution to conduct electric current... this quantity is called **conductance**, denoted **G**, and is defined by:

$$\boxed{\mathbf{G = \frac{1}{R} = \frac{I}{U}}}$$

Conductance is then expressed in **siemens** (S), which is equivalent to Ω^{-1}.

Experience 01:

We use the same electrolyte for two experiments:

- We modify the distance L between the electrodes: the conductance G decreases.
- We modify the surface area S of the electrodes while keeping L constant: the conductance G increases.

$$\boxed{\mathbf{G} = \boldsymbol{\kappa} \times \frac{\mathbf{S}}{\mathbf{L}}} \Rightarrow \boxed{\mathbf{G} = \frac{\boldsymbol{\sigma}}{\boldsymbol{\gamma}}}$$

With **γ** being the cell constant (m^{-1}) and σ in $S.m^{-1}$.

Cell constant γ depends on the characteristics of the conductometric cell and is given by: **l** in meters and **S** in square meters.

κ (kappa**)** is defined as a quantity that characterizes the ability to conduct current, not just for the portion between the two electrodes but for the entire solution, this quantity is the **conductivity** of the solution, denoted **κ**.

I.5.5.2 Ionic conductivity κ_i

Each ion in the electrolyte contributes to the passage of current. However, each ion does not contribute in the same way; thus, we define a quantity that reflects the ability of each ion to "carry" the current; this quantity is the ionic conductivity, denoted $\boldsymbol{\sigma_i}$ (where i designates an ion).

For any ionic solution, the conductivity of the solution is the sum of the ionic conductivities of the present ions, which can be mathematically expressed as:

$$\boxed{\boldsymbol{\kappa} = \sum \boldsymbol{\kappa_i}}$$

Example: the contribution of the ion Na^+ in a sodium chloride solution will be denoted as σ_{Na^+}. The contribution of the chloride ion Cl^- will be denoted as σ_{Cl^-}

The conductivity σ of the sodium chloride solution will then be the sum of the ionic conductivities of all the ions present in the solution.

For sodium chloride, we will have: $\kappa = \kappa_{Na^+} + \kappa_{Cl^-}$

The ionic conductivity σ_i depends on the concentration of ion i:

As [i] increases, κ_i increases.

$$\boxed{\boldsymbol{\kappa_i = \lambda_i . C_i}}$$

where [i] is the concentration of ion i in mol/m³. The molar conductivity of ion i is expressed in **mS·m²·mol⁻¹.**

$$\boxed{\boldsymbol{\kappa = \sum \lambda_i . C_i}}$$

We have also: $\boldsymbol{\kappa_i = F.|Z|.C_i.\mu_i}$

with **κ**= Σ **κ**$_i$ = F · Σ |Zi| · Ci · μi. With F =96500 coloumb/mol.

$$\boxed{\boldsymbol{\kappa = \sum \kappa_i = \sum \lambda_i . C_i = F.\sum |Z_i| \mu_i . C_i}}$$

This formula expresses **Kohlrausch's law** (Kohlrausch's law was established in 1874 by Friedrich Kohlrausch)

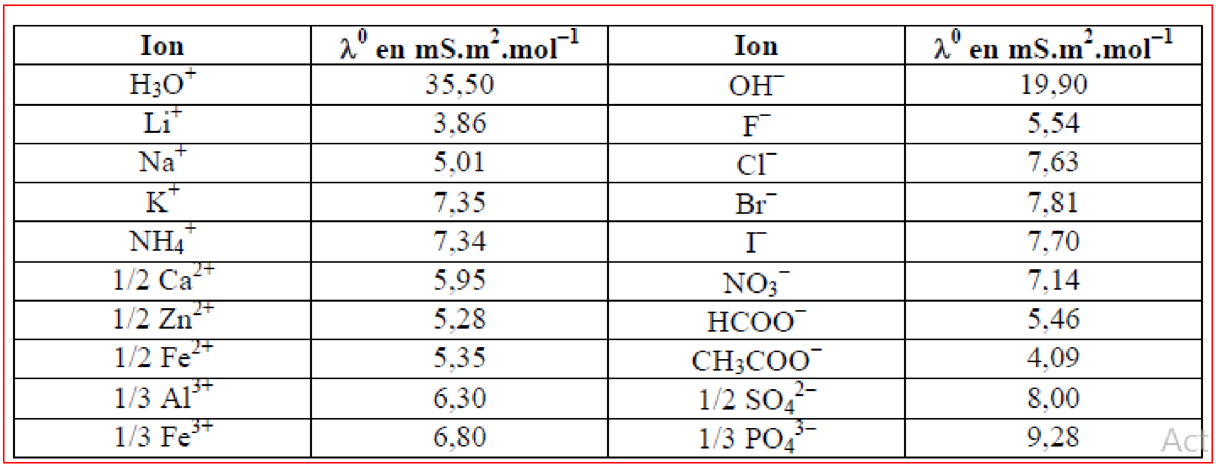
I.5.5.3 Limiting molar ionic conductivity:

For an infinitely diluted solution, meaning when $c_i \to 0$, the molar ionic conductivity approaches a limiting value: $\lambda_i \to \lambda_i (\infty)$, which is called the limiting molar ionic conductivity.

It has a characteristic value for an ion in a given solvent and at a specified temperature. Therefore, it is a tabulated value. Thus, for dilute solutions:

$$\boxed{\boldsymbol{\kappa_i = \sum_i \lambda_i^0 \, c_i}}$$

Table I.1 : Limiting molar ionic conductivity of some ions



Ion	λ^0 en mS.m^2.mol^{-1}	Ion	λ^0 en mS.m^2.mol^{-1}
H_3O^+	35,50	OH^-	19,90
Li^+	3,86	F^-	5,54
Na^+	5,01	Cl^-	7,63
K^+	7,35	Br^-	7,81
NH_4^+	7,34	I^-	7,70
1/2 Ca^{2+}	5,95	NO_3^-	7,14
1/2 Zn^{2+}	5,28	$HCOO^-$	5,46
1/2 Fe^{2+}	5,35	CH_3COO^-	4,09
1/3 Al^{3+}	6,30	1/2 SO_4^{2-}	8,00
1/3 Fe^{3+}	6,80	1/3 PO_4^{3-}	9,28

I.5.5.4 Molar conductivity:

1. **In terms of the limiting molar ionic conductivities:**

Let the electrolyte be A_xB_y

$$A_xB_y \rightarrow xA^{Z+} + yB^{Z-}$$

$$\boxed{\Lambda\left(A_xB_y\right) = x\lambda(A^{Z+}) + y\lambda(B^{Z-})}$$

2. **In term of the concentration of the electrolyte and σ.**

a) <u>Strong electrolyte</u>

A_xB_y	$\rightarrow$	xA^{Z+} +	yB^{Z-}
C_0		0	0
0		xC_0	yC_0

$[C_{A_x}]$ =n $[CA_xB_y]$; $[C_{B_y}]$= n $[CA_xB_y]$

$$\begin{aligned} \kappa_i = \sum\lambda_i . C_i &= \lambda(A^{Z+}).\lfloor A^{z+}\rfloor + \lambda(B^{z-}).\lfloor B^{z-}\rfloor \\ &= \lambda_{A^{Z+}} x\, C_0 + \lambda_{B^{Z-}}\, y\, C_0 \\ &= \lfloor xA_{Z+} + y\, B_{Z-}\rfloor C_0 \end{aligned}$$

$$\boxed{\boldsymbol{\kappa} = \Lambda\left(\boldsymbol{A_xB_y}\right) \times \lfloor \boldsymbol{C_0} \rfloor}$$

Experimentally

Kohlrausch's law describes the behavior of electrolytes, particularly strong electrolytes, for a concentration ranging from 0.01 M to infinite dilution:

$$\boxed{\Lambda_i = \sum\lambda_i = \Lambda_i^0 - K\sqrt{C}}$$

Λ_0 is the limiting equivalent conductivity at infinite dilution. To calculate it, we use the law of independent ion migration in the form:

$$\Lambda^\circ = \lambda_+ + \lambda_-$$

The plot $\wedge_c = f\left[\sqrt{C}\right]$ (Figure I.4)

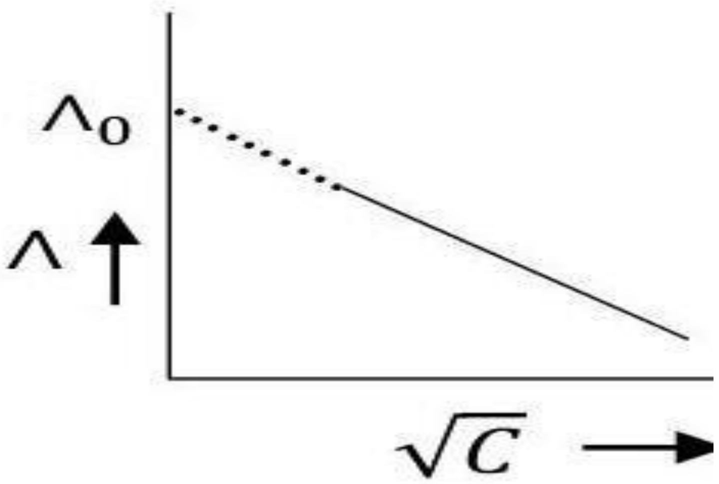


Figure I.4: Variation of the equivalent conductivity of a strong electrolyte as a function of concentration

b) <u>**Weak electrolyte**</u>

$$\begin{array}{cccc} A_xB_y & \rightarrow & xA^{Z+} + & yB^{Z-} \\ C_0 & & 0 & 0 \\ 0 & & x\alpha C_0 & y\alpha C_0 \end{array}$$

$[C_{A_x}]$ =n α $[CA_xB_y]$; $[C_{B_y}]$= n α $[CA_xB_y]$

$$\kappa_i = \sum \lambda_i . C_i = \lambda(A^{Z+}).\lfloor A^{z+} \rfloor + \lambda(B^{z-}).\lfloor B^{z-} \rfloor$$

$$= \lambda_{A^{Z+}} x\ \alpha\ C_0 + \lambda_{B^{Z-}}\, y\ \ \alpha C_0$$

$$= \lfloor xA_{Z+}\ + y\ B_{Z-} \rfloor\, \alpha C_0$$

$$\boldsymbol{\kappa = \wedge\left(A_xB_y\right) \times \alpha\lfloor C_0 \rfloor}$$

Therefore, C → 0, then α → 1:

$$\Lambda \rightarrow \Lambda^0 = (\ X\lambda_A^0\ + Y\ \lambda_B^{\circ})$$

μ_i approaches its limiting value μ_i^0 and consequently $\lambda_i = F\,|Z_i|\,\mu_i \rightarrow \lambda_i^0 = F|Zi|\mu_i^0$.when the dilution is infinite, the weak electrolyte is completely dissociated, and behaves like a strong electrolyte.

Experimentally, one can use conductivity measurements as a function of concentration to estimate K_a. As:

$$\frac{1}{\boldsymbol{\Lambda}} = \frac{1}{\boldsymbol{\Lambda^0}} + \frac{\boldsymbol{\Lambda_c}}{\boldsymbol{K_a}\,(\boldsymbol{\Lambda^0})^2}$$

This is ***Ostwald's dilution law***. The graph of $1/\Lambda$ as a function of Λ_c allows us to obtain the value of $1/\Lambda^0$ at concentration c = 0 (given by the y-intercept) and the value of K_a (given by the slope).(Figure I.5)

$$K_a = \frac{\alpha^2 . c}{1 - \alpha}$$

Since α is the degree of ionization, it is given by: $\alpha = \Lambda_c / \Lambda^o$.

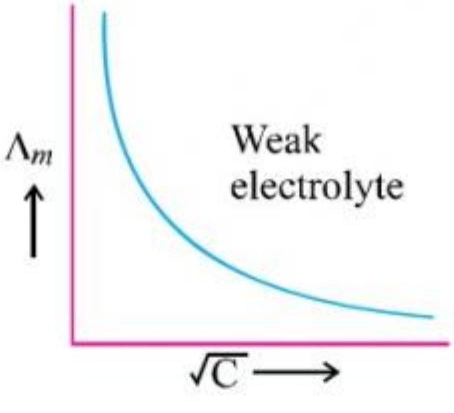


Figure I.5: Variation of the equivalent conductivity of a weak electrolyte as a function of concentration

I.6 Conductometric measurements

Conductivity measurements allow determining the concentration of ions present in the solution. They are widely used in chemistry for:

- Titrations,
- Determinations of chemical kinetics,
- Determinations of thermodynamic equilibrium constants (solubility product).

I.6.1 Conductometric dosage

Conductometric titration is an electrical measurement method that determines the concentration of an electrolyte by measuring conductance at various stages of titration with another standard electrolyte. It is a type of titration, in which the end of a titration is determined by measuring the conductance of the mixture. A solution's electrical conductivity is attributed to its ions.

I.6.1.1 Principle

Conductometric titrations are based on the principle that the conductance of a solution depends on both the number and the mobility of ions present. This method is particularly suitable for electrolyte solutions, in which conductivity is determined by the presence of mobile ions.

More ions → more charge carriers → higher conductivity.

A conductivity meter measures the conductance of the solution by passing an electric current through electrodes immersed in the beaker. A solution with higher conductivity will produce a higher current reading on the conductivity meter.

During the titration, the type and concentration of ions change, and therefore the conductivity of the solution also changes.

I.6.1.2 Evolution of the chemical system

Figure. I.6. illustrates the principle of the conductometric titration and the different stages of the reaction.

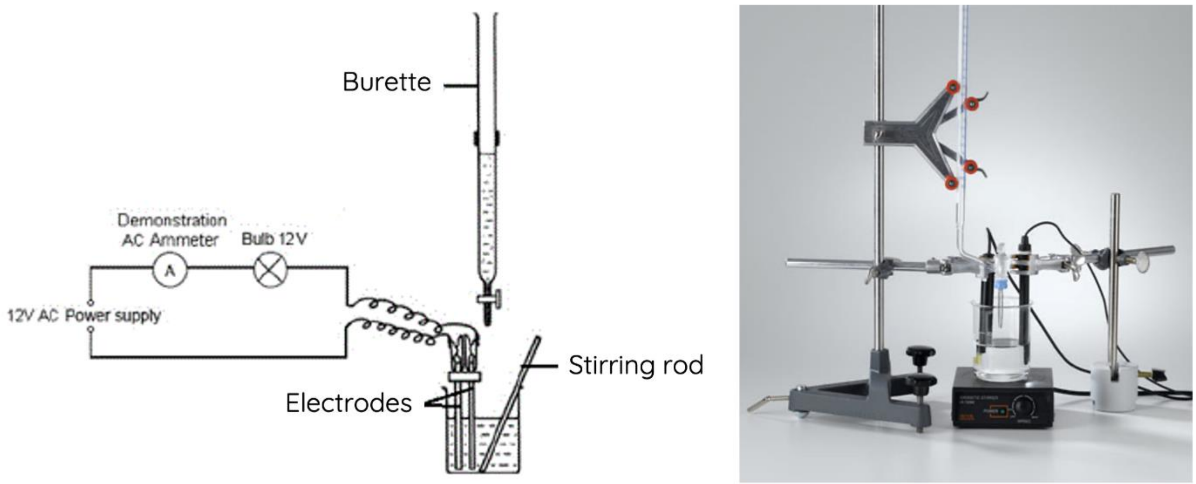


Figure I.6 : Conductometric titration apparatus

When an electrolytic solution (titrant solution) is added from a burette to another electrolytic solution, the conductivity of the solution changes when an ionic reaction occurs between these solutions. When one ion replaces another, the conductivity of the solution changes.

- If high-mobility ions, such as hydrogen ions (H^+), are replaced by lower-mobility ions, such as sodium ions (Na^+), the conductance of the solution decreases, beacause conductance depends on both the number of ions and their mobility.
- Similarly, if low-mobility ions are replaced by high-mobility ions during the reaction, the conductance of the solution increases. The basic principle of conductometry (conductivity) titration is that ions of one mobility are replaced by ions of another mobility, causing the conductance of the solution to change during the reaction.

The conductometric titration curve is obtained by plotting the conductivity (σ) of the solution against the volume of titrant (V) added from the burette, typically at intervals of 1 mL. Thus, a titration curve $\sigma = f(V)$ is constructed (Fig. I.7).The equivalence point (E) is determined from the point of inflection or the intersection of the linear segments of the curve, and the corresponding x-coordinate gives the equivalence volume (VE).

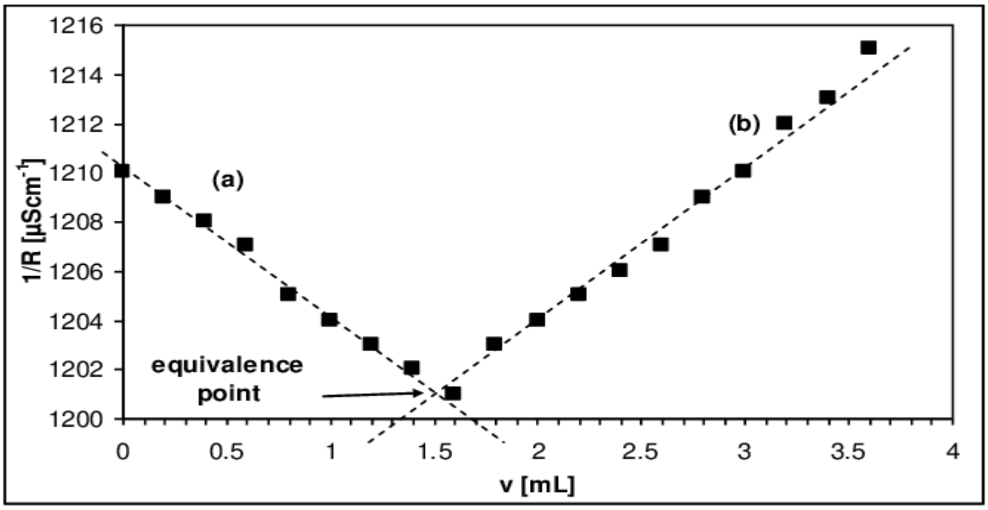


Figure I.7: Variation of the conductivity with respect to volume (titration curve)

I.7 Application exercises

Exercise 01:

The density of the sulfuric acid solution in a car battery is 1.83 g/cm³ at 25 °C, and this solution contains 33.3% of H_2SO_4 by mass.

1) What is the mass of one liter of the solution?
2) How much H_2SO_4 is there in one liter of the solution?
3) What is the molarity of the solution?
4) What is the molality of the solution?
5) What is the molar fraction of H_2SO_4 in the solution?

Solution:

1) Calculate the mass of one liter of the solution

We have $\rho_{solution} = 1.83\ g\ /cm^3$

$$\rho_{solution} = \frac{m_{sol}}{V_{sol}} \Rightarrow m_{sol} = \rho_{sol} \text{ x } V_{sol}$$

$$= 1.83 \text{ x } 1000$$

$$\boldsymbol{m_{sol} = 1830\ g}$$

2) Calculate the mass of H_2SO_4

We have 33.3 % of H_2SO_4 by mass

$$\begin{cases} 33.3 \text{ g } H_2SO_4 \longrightarrow 100 \text{ g of solution} \\ m(H_2SO_4) \longrightarrow 1830 \text{ g of solution} \end{cases}$$

⇨ $m\,(H_2SO_4) = \frac{1830\ x\ 33.3}{100}\frac{1830\ x\ 33.3}{100}$

$$\mathbf{m\,(H_2SO_4) = 609.39\ g}$$

3) Calculate the molarity of the solution

$$\text{Molarity}= \frac{Number\ of\ mole\ of\ solution}{Volumeof\ solution}$$

$$C_M = \frac{n_{\text{H2 SO4}}}{V_{sol}} = \frac{m_{\text{H2 SO4}}}{M_{\text{H2 SO4}}V_{sol}}$$

$$\mathbf{C_M = \frac{609.39}{1\ x\ 98} = 6.218\ mol\ /\ l}$$

$$\mathbf{Molarity = 6.218\ M}$$

4) Calculate the molality of the solution

$$\text{Molality} = \frac{Number\ of\ mole\ of\ solute\ (mol)}{Volumeof\ solvent\ (Kg)}$$

$$\text{Molality} = \frac{m_{H2SO4}}{M_{H2SO4} \times m_{solvent}}$$

$$= \frac{609.39}{98\ x\ (1830\ x10^{-3})}$$

Molality = 3.39 mol / Kg

$$\mathbf{Molality\ \approx 3.40\ mol\ /\ Kg}$$

5) Calculate the mass fraction of H_2SO_4 in the solution

$$\text{Mass fraction X} = \frac{mass\ of\ solute}{mass\ of\ solute + mass\ of\ solvent}$$

$$= \frac{609.39}{609.39+1830} = \frac{609.39}{2439.39}$$

Mass fraction X = 0.24

<u>Exercise 02:</u>

The resistance of a conductivity measurement cell is R = 100 Ω at 18°C. When it is filled with a 0.2 N NH_4Cl solution.

1) Calculate the cell constant (ɣ) if the specific conductivity **κ** of NH_4Cl is 0.0164 $S \cdot cm^{-1}$ and the specific conductivity of water (solvent) is $8.10^{-6}\ \Omega^{-1} \cdot cm^{-1}$.

2) If this cell is filled with a 0.2 N hydrochloric acid (HCl) solution, a resistance of R= 200 Ω is found. Calculate the equivalent conductivity ($\wedge$eq)of this electrolyte

<u>Solution:</u>

We have :

$$\begin{cases} [NH_4Cl] = 0.2\ N \\ R = 100\Omega \end{cases}$$

1) **Calculate the cell constant:**

κ (NH4Cl)= 0.0164 S.Cm^{-1}

κ (solvent) = 8.10-6 Ω^{-1}.Cm^{-1}

$$\mathrm{K} = \frac{\gamma}{R} \Rightarrow \gamma = \ \mathrm{K(solution)}.R$$

In other hand we have :

κ (solution) = κ (solvent) + κ (Solute)

= 0.0164 + 8.10^{-6}

κ (solution) = 0.0164 S.Cm^{-1}

ɣ= R. κ = (0.0164).(100) = 1.64 Cm^{-1}

ɣ = 1.64 Cm^{-1}

2) **Calculate the equivalent conductivity of HCl**

We have : [HCl] = 0,2 N

$$\Lambda_{eq} = \frac{1000.\mathrm{K}_{HCl}}{C}$$

We need to calculate the κ (HCl)

$$\mathrm{K}_{HCl} = \frac{\gamma}{R}$$

Same cell →same cell constant ɣ

$$\mathrm{K}_{HCl} = \frac{\gamma}{R} = \frac{1.64}{200} = 8{,}2\ \times 10^{-3}\ \Omega^{-1}.Cm^{-1}$$

$$\Lambda_{eq} = \frac{1000.\mathrm{K}_{HCl}}{C} = \frac{1000.\ 8{,}2.10^{-3}}{200} = 41\ \Omega^{-1}.Cm^{2}\ .eq^{-1}$$

$$\boldsymbol{\Lambda_{eq} = 41\ \Omega^{-1}.Cm^{2}\ .eq^{-1}}$$

Chapter II

Acids and bases

II.1 Definitions

II.1.1 Theory of Brönsted-Lowry

This theory is based on the concept of proton exchange and on the fact that protons do not exist in a free state in solution.(fig II.1)

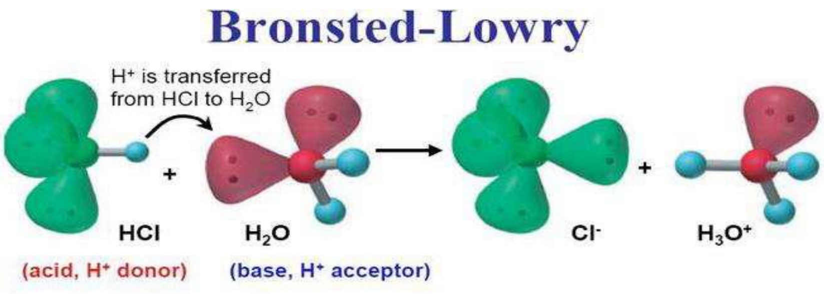


Figure II.1: Brönsted-Lowry acid-base reaction

II.I.2 Definition of ARREHENIUS (1887)

- ✓ An ***acid*** is a substance that releases the $\mathbf{H^+}$ ion (hydrogen ion = proton) into water.
- ✓ A ***base*** is a substance that releases the $\mathbf{OH^-}$ ion (hydroxide ion) into water.

II.1.2.1 Conjugate acid-base pairs.

To every acid corresponds a conjugate base, and to every base corresponds a conjugate acid, which allows the definition of acid-base pairs.(table II.1)

Table 1I.1 : Acids and conjugate bases

Acids	**Conjugate Base**
HF	F^-
HBr	Br^-
HNO_3	NO_3^-
$HC_2H_3O_2$	$C_2H_3O_2^-$
H_2SO_4	HSO_4
H_2O	OH^-

II.1.3 Definition of LEWIS

An even broader definition of acids and bases ,was proposed by ***Lewis*** in the 1920, and his definitions are as follows (Fig II.2):

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

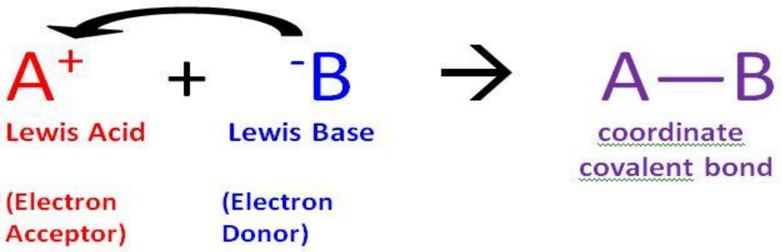


Figure II.2: LEWIS acids and bases

II.2 Reaction with water

These equilibria are purely theoretical because the proton released by the acid, must necessarily be captured by a base. Similarly, for a base to manifest there must be a proton donor.

Examples:

$$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$$

$$NH_4^+ + H_2O \leftrightarrows H_3O^+ + NH_3$$

$$HCOOH + H_2O \leftrightarrows H_3O^+ + HCCO^-$$

II.3 The acidity constant

For a conjugate pair **AH/A⁻**, the acidity constant $\mathbf{K_a}$ is defined by:

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

The value of K_a depends only on the conjugate pair HA/A⁻. The $\mathbf{pK_a}$ is more commonly used than K_a: $\boldsymbol{pK_a = -\log K_a}$ Therefore, $\boldsymbol{K_a = 10^{-pK_a}}$

II.4 Ostwald's dilution law

Ostwald’s law is a law concerning acid-base reactions in water, which states that dilution increases the dissociation of the acid (and the protonation of the base).

For a weak acid, denoted as **HA**, it reacts with water as follows:

$$\mathbf{HA + H_2O \leftrightarrows A^- + H_3O^+}$$

We set [HA] = c - x = c (1 – α), and $[H_3O^+] = [A^-] = x = c\alpha$.

α : is the *degree of dissociation*.

We then have the **acidity constant K_a**:

$$\mathbf{K_a = \frac{x^2}{C-x} = \frac{C\alpha^2}{1-\alpha}}$$

α approaches 1 if and only if ***K_a/c increases***, since Ka is a constant. Therefore, the dissociation of the acid increases as c decreases, meaning with dilution.

For a weak base denoted as B–, it reacts with water as follows:

$$\mathbf{B^- + H_2O \leftrightarrows BH + OH^-}$$

We set [B–] = c – x = c (1-β), and [OH–] = [BH] = x = cβ,

where **β** is the ***degree of protonation***.

As before, we obtain:

$$\mathbf{K_b = \frac{x^2}{C-x} = \frac{c\,\beta^2}{1-\beta}}$$

Similarly, β approaches 1 if and only if K_b/c increases, since K_b is a constant; thus, the base becomes more protonated as it is diluted.

II.5 Dissociation of water

$$\mathbf{H_2O_{(l)} + H_2O_{(l)} \leftrightarrows H_3O^+{}_{(aq)} + OH^-{}_{(aq)}}$$

Pure water is a poor conductor of electricity. Applying the law of mass action to this equilibrium:

At 25°C, 1 liter of water:

$$[OH^-]\ [H_3O^+] = 10^{-14} = K_e$$

This constant is called the **ionic product of water**. (K_e varies with temperature)

Note: In any aqueous solution, the ionic product remains constant at a given temperature:

- A ***neutral*** solution has $[OH^-] = [H_3O^+] = 10^{-7}$ mol/L at 25°C.
- An **acidic** solution has $[OH^-] < [H_3O^+]$.
- A **basic** solution has $[OH^-] > [H_3O^+]$.

II.6 Strength of acids and bases

The strength of an acid or a base is its tendency to donate or accept one or more protons more or less easily.(Fig II.3)

- ✓ An acid or base is **strong** if the dissociation reaction in water is **complete**.
- ✓ An acid is **weak** if its dissociation reaction in water is **incomplete**, thus limited to an ***equilibrium***.

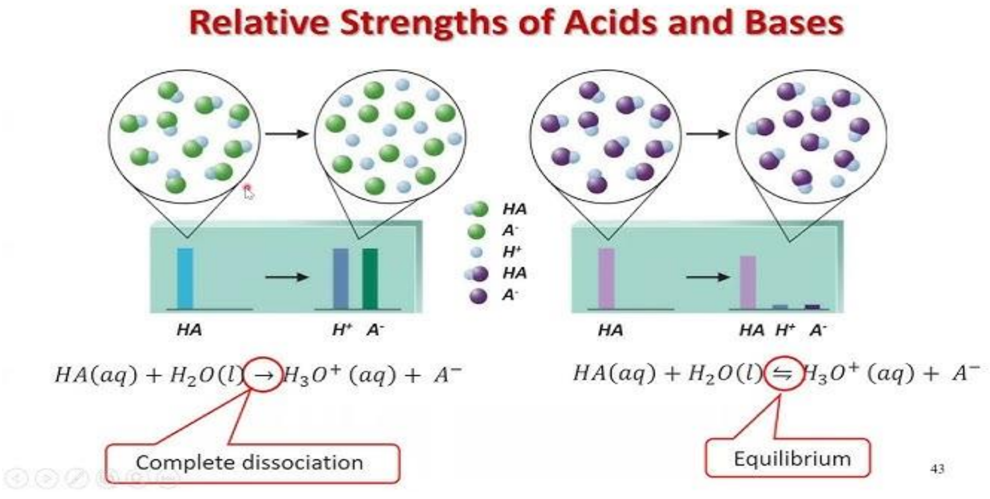


Figure II.3: Relative strengths of Acids and Bases

<u>Let be an acid HA</u>:

$$\mathbf{HA + H_2O \leftrightarrows A^- + H_3O}$$

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

- If K_a is very high, the reaction is complete, and the acid is completely dissociated; this will be a strong acid.

$$\mathbf{HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-}$$

We use a single arrow to indicate that the acid is completely dissociated.

- If K_a is low, the dissociation of the reaction is partial, and the acid is weak.

$$\mathbf{HF + H_2O \leftrightarrows H_3O^- + F^-}$$

We use a double arrow to indicate the equilibrium.

Let a base B:

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

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

- If K_b is very high, the reaction is complete, and the base is strong.

$$\mathbf{RO^- + H_2O \rightarrow ROH + OH^-}$$

A single arrow indicates a ***complete reaction***,

- If K_b is low, the reaction is partial, and the base is weak.

$$\mathbf{CN^- + H_2O \looparrowright\leftrightarrows HCN + OH^-}$$

A double arrow indicates a ***partial reaction***.

II.7 Relation between K_a and K_b of an acid-base pair

Consider this reaction:

$$\mathbf{HA + H_2O \rightleftharpoons A^- + H_3O^+} \qquad Ka = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$\mathbf{A^- + H_2O \rightleftarrows HA + OH^-} \qquad K_b = \frac{[HA][OH^-]}{A^-}$$

$$\mathbf{K_aK_b = \frac{[H_3O^+][A^-][HA][OH^-]}{[HA][A^-]} = [H_3O^+][OH^-] = K_e}$$

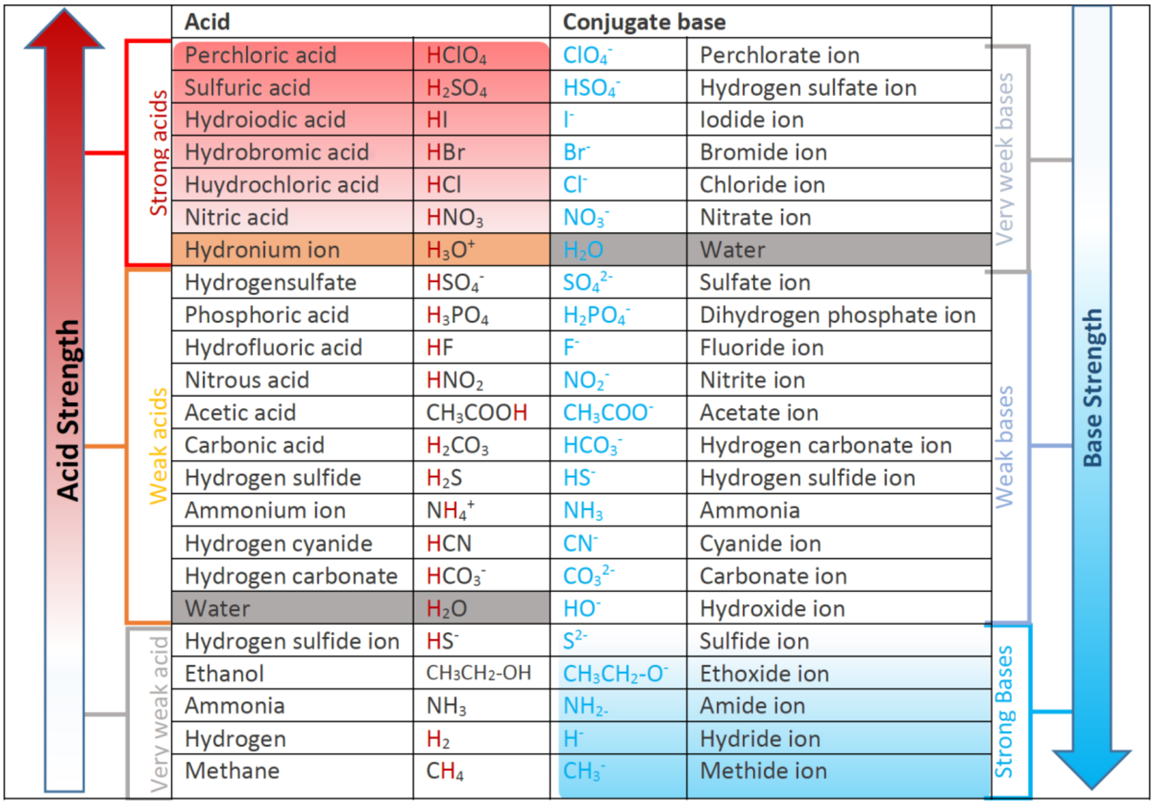
This indicates that a stronger acid corresponds to a weaker conjugate base, given that K_e remains constant. Conversely, a weaker acid is associated with a stronger conjugate base.

We define:

$$pK_a = -\log K_a \qquad\qquad pK_b = -\log K_b$$

$$K_a.K_b = K_e \qquad\qquad pK_a + pK_b = pK_e$$

- As an **acid** becomes more dissociated (**stronger**), its $\mathbf{K_a}$ **constant increases**, resulting in a lower pK_a.
- As a **base** becomes **stronger**, its $\mathbf{K_b}$ **value rises**, leading to a lower pK_b.



Acid		Conjugate base	
Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion
Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion
Hydroiodic acid	HI	I^-	Iodide ion
Hydrobromic acid	HBr	Br^-	Bromide ion
Huydrochloric acid	HCl	Cl^-	Chloride ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Hydrogensulfate	HSO_4^-	SO_4^{2-}	Sulfate ion
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
Hydrofluoric acid	HF	F^-	Fluoride ion
Nitrous acid	HNO_2	NO_2^-	Nitrite ion
Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion
Carbonic acid	H_2CO_3	HCO_3^-	Hydrogen carbonate ion
Hydrogen sulfide	H_2S	HS^-	Hydrogen sulfide ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrogen cyanide	HCN	CN^-	Cyanide ion
Hydrogen carbonate	HCO_3^-	CO_3^{2-}	Carbonate ion
Water	H_2O	HO^-	Hydroxide ion
Hydrogen sulfide ion	HS^-	S^{2-}	Sulfide ion
Ethanol	$CH_3CH_2\text{-}OH$	$CH_3CH_2\text{-}O^-$	Ethoxide ion
Ammonia	NH_3	NH_{2-}	Amide ion
Hydrogen	H_2	H^-	Hydride ion
Methane	CH_4	CH_3^-	Methide ion

Figure II.4 : Relative Strength of acids and bases

- ✓ The strongest acids are at the top of the table.
- ✓ The weakest bases are located at the top because a stronger acid corresponds to a weaker base.
- ✓ The pairs framed as H_2O/H_3O^+ and H_2O/OH^- indicate that these are the strongest acids and bases that can be found in solution.

II.8 Acid-base role of water: H_2O is an ampholyte

1) <u>With an acid, water undergoes the acid-base reaction</u>:

$$\mathbf{AH + H_2O \rightleftarrows A^- + H_3O^+}$$

The first pair is AH/A^-. The second pair is therefore H_3O^+/H_2O. Water (H_2O) is thus the conjugate base of the acid H_3O^+. The two half-reactions occurring are:

$$\left.\begin{aligned} &AH \leftrightarrows A^- + H^+ \\ &H_2O + H^+ \leftrightarrows H_3O^+ \end{aligned}\right\} \qquad \mathbf{HA + H_2O \leftrightarrows A^- + H_3O^+}$$

2) <u>With a base, water undergoes the acid-base reaction:</u>

$$\mathbf{B + H_2O \rightleftharpoons BH^+ + OH^-}$$

The first pair is H_2O / OH^-. The second pair is therefore BH^+ / B. Water (H_2O) is thus the conjugate acid of the base OH^-. The two half-reactions occurring are:

$$\left.\begin{aligned} &H_2O \rightleftharpoons OH^- + H^+ \\ &B + H^+ \rightleftharpoons BH^+ \end{aligned}\right\} \qquad \mathbf{B + H_2O \rightleftharpoons BH^+ + OH^-}$$

II.8.1 Autoprotolysis of Water

Pure water contains hydronium ions (H_3O^+) and hydroxide ions (OH^-) formed by the reaction, known as the autoprotolysis of water, represented by the equation:

Indeed, water, being an ***ampholyte***, can react according to the following reactions:

$$\begin{array}{c} \mathbf{H_2O \rightleftharpoons OH^- + H^+} \\ \mathbf{H_2O + H^+ \rightleftharpoons H_3O^+} \\ \hline \mathbf{2H_2O \rightleftharpoons H_3O^+ + OH^-} \end{array} \qquad \mathbf{K = K_e = [H_3O^+] \times [OH^-]}$$

The electrical neutrality of pure water implies that $[H_3O^+] = [OH^-]$.

At 25 °C, pH = 7, meaning $[H_3O^+] = [OH^-] = 10^{-7}$ mol·L⁻¹.

The ionic product K_e is associated with the value pK_e by the formula: $\mathbf{pK_e = -\log K_e}$.

II.9 Forecasting Acid-Base Reactions Using pKa

Consider the acid-base reaction

$$\mathbf{A_1 + B_2 \rightleftarrows B_1 + A_2}$$

The equilibrium constant for this reaction is written as:

$$\boldsymbol{k = \frac{[B_1][A_2]}{[A_1][B_2]} = \frac{K_{a_1}}{K_{a_2}} = 10^{pK_{a_2} - pK_{a_1}}}$$

The reaction is quantitative if **K >> 1**, meaning if $\boldsymbol{K_{a_1} \gg K_{a_2}}$ or even $\boldsymbol{pK_{a_1} \gg pK_{a_2}}$

A reaction is considered complete (quantitative) if $\mathbf{K \geq 10^4}$, thus $\boldsymbol{pK_{a_2} \gg pK_{a_1} \geq 4}$.

II.9.1 Gamma Rule

✓ If we place the two pairs on a graduated pK_a scale, the reaction that occurs best in solution, called the predominant reaction, is that between the strongest acid and the strongest base among the two pairs, resulting in the formation of the weakest acid and base. (Fig II.5)

✓ In contrast, the reverse reaction occurs hardly at all, and the mixture of $B_1 + A_2$ is stable.

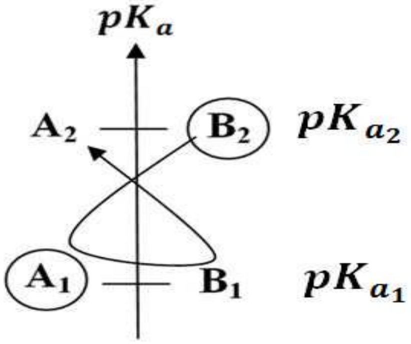


Figure II.5: Gamma rule

II.10 pH of solution

II.10.1 Concept of pH:

The pH of a solution is defined as the negative logarithm (base 10) of the activity of the ions present in the solution:

II.10.2 pH Scale:

- ✓ At 25°C, the pH of pure water is 7.
- ✓ At 25°C, an acidic solution will therefore have a **pH below 7** ($[H_3O^+] > 10^{-7}$ mol·L⁻¹) and a basic solution will have a **pH above 7** ($[H_3O^+] < 10^{-7}$ mol·L⁻¹). (Fig II.6)

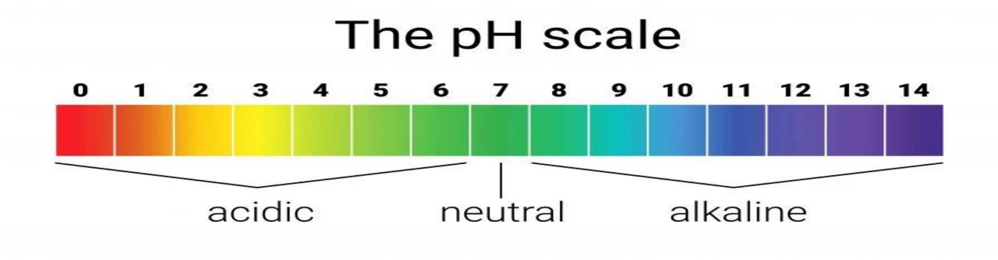


Figure II.6: The pH scale

II.10.3 Calculation of pH in aqueous medium

Using logarithms: - log (a · b) = log a + log b ;- log (a/b) = log a - log b ;- log (1/a) = -log a

II.10.3.1 pH of a Strong Acid:

We write the equilibrium reactions of the species:

$$\mathbf{HA + H_2O \leftrightarrows A^- + H_3O^+}$$

At t=0 C 0 0

At t_{eq} 0 C C

At equilibrium, we will have: $[H_3O^+] = C$ Thus

$$\boxed{\mathbf{pH = -\log C}}$$

II.10. 3.2 pH of a Strong Base:

$$\boldsymbol{B + H_2O \rightarrow BH^+ + OH^-}$$

T=0 C ex 0 0

T=Teq 0 ex C C

Since B is a strong base, it dissociate completely in water :

If [B]= C →[B] = $[OH^-]$ = C

By definition pOH= - log = $[OH^-]$ and knowing thar pH+ pOH = 14 →pH = 14- pOH

Thus:

$$\boxed{\mathbf{pH = 14 + log\ C' = pK_e + log_{10}[H_3O^+]}}$$

II.10.3.3 pH of Weak acids

Consider an acid HA in solution at a concentration C_a:

$$\mathbf{HA + H_2O \leftrightarrows A^- + H_3O^+}$$

The acid dissociation constant is given by : $Ka = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$

According to the law of conservation of mass

$$C = [AH] + [A^-] and\ [AH] \gg [A^-], [AH] + [A^-] \approx [AH] \rightarrow \boldsymbol{C} = [\boldsymbol{AH}]$$

According to the electroneutrality law:

$$\sum positive\ charge = \sum negative\ charge \longrightarrow [H_3\,O^+] = [A^-] + [OH^-]$$

The medium is acidic :

$$[H_3O^+] \gg [OH^-] \rightarrow [H_3O^+] \gg [OH^-] \rightarrow K_a = \frac{[A^-][H_30^+]}{[AH]}$$

$$\rightarrow K_a.C = [H_3O^+]^2 \rightarrow [H_3O^+] = (K_a.C)^2 \rightarrow -log_{10}[H_3O^+] = -\,log_{10}(K_a.C)^{1/2}$$
$$= \frac{1}{2}(-log_{10}K_a - \log C) = {}^1\!/_2\ (pK_a - \log C)$$

Therefore, the pH of the weak acid:

$$\boxed{\boldsymbol{pH = \frac{1}{2}pK_a - \frac{1}{2}\log C}}$$

II.10.3.4 PH of weak bases

Consider a base B in solution at a concentration C_b:

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

The basicity constant is given by

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

According to the law of conservation of mass

$$C = [B] + [BH^+] and\ [B] \gg [BH^+], [B] + [BH^+] \approx [B] \rightarrow \boldsymbol{C} = [\boldsymbol{B}]$$

According to the electroneutrality law

$$\sum positive\ charge = \sum negative\ charge \longrightarrow [OH^-] = [BH^+] + [H_3O^+]$$

The medium is basic :

$$[OH^-] \gg [H_3O^+] \rightarrow [H_3O^+] = [BH^+] \rightarrow K_b = \frac{[BH^+][0H^-]}{[B]}$$

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

$$\boldsymbol{pOH = \frac{1}{2}\,(pK_b - log_{10}C)}$$

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

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

$$\boldsymbol{pH = \frac{1}{2}pK_a + \frac{1}{2}pK_e + \frac{1}{2}log\ C}$$

$$\boldsymbol{pH = 7 + \frac{1}{2}\,(pK_a + log_{10}\,C)}$$

II.10.3.5 pH of mixed solutions

II.10.3.5.1 pH of Mixture of strong acid and strong base

Strong acid AH exp: HCl; HNO_3; concentration C_a and volume V_a

Strong base B exp :NaOH ; KOH concentration C_b and volume V_b

The new concentrations are: $C'_a = \frac{C_a V_a}{V_T}$ $C'_b = \frac{C_b V_b}{V_T}$

If $C'_a > C'_b$ $pH = -\log(C'_a - C'_b)\ with\ pH \leq 6.5$

If $C'_a = C'_b$ $pH = 7$

If $C'_a < C'_b$ $pH = -\log(\frac{K_e}{C'_b - C'_a})\ with\ pH \geq 6.5$

II.10.3.5.2 Mixture of two strong acids AH_1 and AH_2

Consider a mixture of two strong acids AH1 (C_1) and AH2 (C_2)

In aqueous solution, both strong acids are completely dissociated:

$$AH_1 + H_2O \rightarrow A_1^- + H_3O^+$$

$$AH_2 + H_2O \rightarrow A_2^- + H_3O^+$$

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

We calculate the new concentrations of AH1 and AH_2:

$$C'_1 = \frac{C_1 V_1}{V_T} \quad C'_2 = \frac{C_2 V_2}{V_T}$$

$$\boxed{\boldsymbol{pH = -\log(C'_1 + C'_2)}}$$

$$[H_3O^+] = C'_1 + C'_2$$

This relation is avaible if

$$\boldsymbol{[H_3O^+] \geq 10\,[OH^-]\ so\ pH \leq 6.5}$$

II.10.3.5.3 Mixture of strong acid (AH_1) and weak acid (AH_2)

Strong acid (AH 1): completely dissociates

$$AH_1 + H_2O \rightarrow A_1^- + H_3O^+$$

Weak acid (AH 2): partially dissociates

$$AH_2 + H_2O \rightarrow A_2^- + H_3O^+$$

With equilibrium constant:

$$K_a = \frac{[A_2^-][H_3 0^+]}{[AH_2]}$$

Because the strong acid (AH 1) dissociates completely, it produce a large concentration of H_3O^+ this shifts the equilibrium of the weak acid to the left (Le Châtelier's principle), suppressing its dissociation even more.

As a result, the contribution of (AH 2) to ($[H_3O^+]$) is negligible compared to that of (AH 1).

So the total hydronium concentration $[H_3O^+]= [H_3O^+]\ (from\ AH\ 1)+ [H_3O^+]\ (from\ AH\ 2)$

Since: $[H_3O^+]\ (from\ AH\ 2)$ is very small

So: $[H_3O^+] = [H_3O^+]\ (from\ AH\ 1) = C_{AH\ 1}$

By definition:

$$\boldsymbol{pH = -\,log_{10}\ [H_3O^+] = -log_{10}\ (C_{AH1})}$$

II.10.3.5.4 Mixture of two weak acids (AH $_1$) and (AH $_2$)

Weak acid (AH 1): completely dissociates

$$AH_1 + H_2O \rightarrow A_1^- + H_3O^+$$

Weak acid (AH_2): partially dissociates

$$AH_2 + H_2O \rightarrow A_2^- + H_3O^+$$

With equilibrium constants:

$$K_{a,AH1} = \frac{[A_1^-][H_3 0^+]}{[AH_1]}$$

$$K_{a,AH2} = \frac{[A_2^-][H_3 0^+]}{[AH_2]}$$

Since both acids are weak **: x=[** H_3O^+**]**

Since both acids are weak **: (x << [** H_3O^+**])** ,we can approximate **:**

$$\boldsymbol{[AH_1] \approx C_{AH1} \ , [AH_2] \approx \ C_{AH2}}$$

From equilibrium constants

$$K_{a,AH1} = \frac{[A_1^-][H_30^+]}{[AH_1]} \quad \Rightarrow [A_1^- \,] = \frac{K_{a\ AH1} \times C_{AH1}}{x}$$

$$K_{a,AH2} = \frac{[A_2^-][H_30^+]}{[AH_2]} \quad \Rightarrow [A_2^- \,] = \frac{K_{a\ AH1} \times C_{AH1}}{x}$$

$$\boldsymbol{X = \frac{K_{a,AH1} \ \times C_{AH1}}{X} + \frac{K_{a,AH2} \ \times C_{AH2}}{X}}$$

$$X^2 = \ K_{a,AH1} \ \times C_{AH1} + K_{a,AH2} \times C_{AH2}$$

$$[H_3O^+] = \sqrt{K_{a,AH1} \times C_{AH1} + K_{a,AH2} \times C_{AH2}}$$

By definition:

$$\boldsymbol{pH = \ -log_{10}\,[H_3O^+] \ \rightarrow pH = \ -\frac{1}{2}\ log_{10}\,(K_{a,AH1} . C_{AH1} + \ K_{a,AH2}\ . C_{AH2})}$$

II.10.3.5.5 Mixture of two strong bases

Each strong base dissociates completely in water

$$B_1 \ + H_2O \rightarrow B_1H^+ + OH^- \qquad\qquad B_2 \ + H_2O \rightarrow B_2H^+ + OH^-$$

Since both bases are strong , they fully dissociated, releasing hydroxide ions (OH-) inti the solution

Let :

- C_{B1}: molar concentration of the first strong acid
- C_{B2}: molar concentration of the second strong acid

Because dissociation is complete:

$$[OH^-]_{B1} \ = C_{B1} \, , [OH^-]_{B2} = C_{B2}$$

Thus , the total hydroxide ion concentration in the mixture is :

$$[OH^-] = C_{B1} + C_{B2}$$

By definition :

$$pOH = -\, log_{10}\, [OH^-]$$

Substituting the total concentration:

$$pOH \;= -log_{10}\,(\, C_{B1} + C_{B2})$$

We have : $pH + pOH = 14 \quad \rightarrow pH \;= 14 - pOH$

$$pH = 14 - (\, log_{10}\,(C_{B1} + C_{B2})$$

$$\boldsymbol{pH = 14 + \frac{1}{2}\, log_{10}\,(\, C_{B1} + C_{B2})}$$

II.10.3.5.6 Mixture of strong base and weak base

Since B1 is a strong base , it dissociate completely in water;

B2 is a weak base , it dissociates partially in water**:**

$$B_1 \; + H_2O \rightarrow BH_1^+ + OH^- \qquad\qquad B_2 \; + H_2O \; \leftrightarrows BH_2^+ + OH^-$$

With :

$$K_B = \frac{[BH_2^+][0H^-]}{[B_2]}$$

Since , the strong base completely dissociates , it produced a large concentration of hydroxide (OH^-)

This increases the [OH^-] in the solution and therefore suppresses the dissociation of the weak (Le chatelier’s principle).

Hence ; the contribution of the weak base B_2 to [OH^-] is negligible compared to that of the strong base B2

The total hydroxide is :

$$[OH^-] = [OH^-]_{B1} + [OH^-]_{B2} \approx [OH^-]_{B1} \quad THUS\ [OH^-] = C_{B1}$$

$$pOH = -log_{10}[OH^-] = -log_{10}(C_{B1})$$

And using the relation **: pH+pOH = 14**

We obtain : $pH = 14 - pOH = 14 - (-log_{10}\ C_{B1})$

$$\boldsymbol{pH = 14 + \frac{1}{2}\ log_{10}\ (C_{B1}\ )}$$

II.10.3.5.7 Mixture of two weak bases (B1) and (B2)

$$B_1 + H_2O \rightarrow BH_1^+ + OH^- \qquad B_2 + H_2O \leftrightharpoons BH_2^+ + OH^-$$

$$K_B = \frac{[BH^+][0H^-]}{[B]}$$

At typical dilute conditions $[B] \approx C_B\ and\ [OH^-] \ll C_B$ we have :

$$[OH^-] \approx \sqrt{K_B C_B}$$

For two weak bases in the same solutions, their hydroxide contributions add

$$[OH^-] = \sqrt{k_{b1}C_{B1} + K_{b2}C_{B2}}$$

And $K_a\,K_b = k_w$, using $pOH = -log_{10}[OH^-]\ and\ pH + pOH = 14\ \ (at\ 25°C)$

$$pH = 14 - (-\frac{1}{2}\ log_{10}(K_{b1}C_{b2} + K_{b2}C_{b2}\ ) = 14 + \frac{1}{2}\ log\ _{10}\ (K_{b1}C_{B1} + K_{b2}C_{B2}\ )$$

We can substitute $K_b\ by\ \frac{K_w}{K_a}$

$$pH = 14 + \log K_W + \frac{1}{2}\log\ \ (\frac{C_{B1}}{K_{a,B2}} + \frac{C_{B2}}{K_{a,B2}}$$

Since $K_W = -\log 10^{-14} = -14 \Rightarrow$

$$\mathbf{pH = 7 + \frac{1}{2}\log_{10}\left(\frac{C_{B1}}{K_{a,B1}} + \frac{C_{B2}}{K_{a,B2}}\right)}$$

II.10.3.6 pH of polyacids and polybases

The common diacids and polyacids are weak. Furthermore, we generally observe that:

$$k_{a1} > k_{a2} > k_{a3} \Rightarrow pk_{a1} < pk_{a2} < pk_{a3}$$

When $\boldsymbol{\Delta pk_a = |pk_{a2} - pk_{a1}| \geq 2}$

- We consider the first acidity for a polyacid (the small value of pka)
- We consider the first basicity for a polybases (the highest value of pka)

II.10.3.7 pH of an amphoteric solution

An amphoteric substance can act both as an acid and a base :

It can therefore donate or accept a proton ,leading to two equilibria

$$AH_2^+ \rightleftharpoons AH + H_3O^+ \qquad (K_{a1})$$

$$AH \rightleftharpoons A^- + H_3O^+ \ (K_{a2})$$

At equilibrium, for the amphoteric species AH, we have two acid dissociation constants:

$$K_{a1} = \frac{[AH][H_30^+]}{[AH_2^+]}$$

$$K_{a2} = \frac{[A^-][H_30^+]}{[AH]}$$

At the isolectric point the concentration AH_2^+ of and $A^-$are appoximately equal :

$$[AH_2^+] = [A^-]$$

Multiply both equations we find :

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

$$\boldsymbol{pH = -\,log_{10}\ [H_3O^+] = -\frac{1}{2} log_{10}\ (K_{a1} \,.\, K_{a2})}$$

$$\boldsymbol{pH = \frac{1}{2}\ (pK_{a1} + pK_{a2})}$$

Thus, the pH is ***independent of the concentration***:

$$\boxed{\boldsymbol{pH = \frac{1}{2} pK_{a1} + \frac{1}{2} pK_{a2}}}$$

II.10.3.8 pH of salt of an aqueous solution

When a salt dissolves in water, it dissociates into its ions.
Depending on whether those ions come from strong or weak acids/bases, they may or may not react (hydrolyze) with water, which affects the pH.

Acide + Base ⟶ Salt + H_2O

1) Salt of strong acid and strong base

NaCl (from NaOH and HCl):

$$NaOH + HCl \rightarrow H_2O + NaCl$$

The resulting salt (NaCl) dissociates completely into (Na+) and (Cl-) ions, which are neutral and do not react with water.

$$NaCl \rightarrow Na^+ + Cl^-$$

Na^+ and Cl^- do not exhibit any acid-base characteristics; the solution is neutral with a **pH of 7.**

2) Salt of strong acid and weak base

NH_4Cl (from NH_3 and HCl)

$$NH_3 + HCl \rightarrow NH_4Cl$$

In water, NH4Cl dissociate completely

$NH_4Cl \rightarrow NH_4^+ + Cl^-$ **Dissociation**

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ **Hydrolysis**

Cl^- **is indifferent** in water.

Since, the conjugate base of the strong acid is a base of zero strength, and the conjugate acid of the weak base is a weak acid, The pH is that of the weak acid NH_4^-

$$\boldsymbol{pH = \frac{1}{2}pK_a + \frac{1}{2}logC_a}$$

3) Salt of weak acid and strong base

CH_3COONa (from CH_3COOH and NaOH)

$$CH_4COOH + NaOH \rightarrow CH_3COONa + H_2O$$

In aqueous solution, sodium acetate dissociates completely:

$CH_3COONa \rightarrow CH_3COO^- + Na^+$ **Dissociation**

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ **Hydrolysis**

Na^+ is ***indifferent*** in water.

Since, Na^+ is the cation of a strong base it does not hydrolyse, while the CH_3COO^- the conjugate base of the weak acid (CH_3COO) undergoes hydrolysis. So, the pH is that of the weak base CH_3COO^-:

$$\boldsymbol{pH = -\,log_{10}\ [H_3O^+] = 7 + \frac{1}{2}\ (pKa + \ log_{10}\ (C_0)}$$

4) Salt of weak acid and weak base

Example: let the salt CH_3COONH_4 be in water: $[CH_3COONH_4] = C_0$

$$NH_+ + CH_3COOH\ \ + CH_3COONH_4$$

In water, ammonium acetate dissociates completely:

$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+$ Dissociation of the salt

(1) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $K_1 = Ka = 10^{-9.25}$

(2) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ $K_2 = 10^{-9.25}$

(3) $NH_4^+ + CH_3COO^- \rightleftharpoons NH_3 + CH_3COOH$ $K_3 = 10^{-4.5}$

Among these three reactions, the one that will occur preferentially is the one with the largest equilibrium constant; thus, it is reaction (3) since $K_3 >> (K_2 = K_1)$:

$$\mathbf{NH_4^+ + CH_3COO^- \rightleftharpoons NH_3 + CH_3COOH}$$

t=0:	C_0	C_0	0	0
at equilibrium:	C_0 - X	C_0 - X	X	X

We observe that at equilibrium: $[NH_4^+] = [CH_3COO^-]$ and $[NH_3] = [CH_3COOH]$

=> $$K_a = \frac{[NH_3]\times[H_3O^+]}{NH_4^+}\ ;\ K_b = \frac{[CH_3COO^-]\times[H_3O^+]}{[CH_3COOH]}$$

$$\rightarrow K_a \times K_a' = \frac{[CH_3COO^-]}{[CH_3COOH]} \times \frac{[NH_3]}{[NH_4^4]}]\ \times [H_3O^+]^2\ = \frac{1}{2}\ (pK_a\ + pK_a'\ ) \Longrightarrow$$

$$[H_3O^+] = \sqrt{K_a \times K_a'}\quad \rightarrow$$

$$\boldsymbol{pH = -\,log_{10}\ [H_3O^+] = \frac{1}{2}(\,pK_a + pK_a')}$$

II.11 Buffer solutions

pH plays a very important role in many chemical and biochemical reactions. Many reactions can only occur if the pH of the medium is maintained within certain limits, sometimes very narrow. For example, blood pH is buffered at 7.4 (7.39 ± 0.015) at 37°C: outside of these limits, serious disturbances occur.

1) Definition

A solution exhibits a buffering effect if its **pH varies very little**:

- ✓ upon the addition of small amounts of hydronium ions H_3O^+ or hydroxide ions OH^-;
- ✓ upon moderate dilution.

The pH of the buffer solution is given by the ***Henderson-Hasselbalch*** equation:

$$pH = pk_{a+}\log\frac{[A^-]}{[AH]}$$

II.12 Acid-Base Titration

II.12.1 Definition

An acid-base titration involves a complete acid-base reaction between the analyte to be measured and a titrant with a known concentration. It consists of reacting the solution to be analyzed (the titrated solution of unknown concentration) with a solution containing the titrant (the reagent whose concentration is known).(Fig II.7)

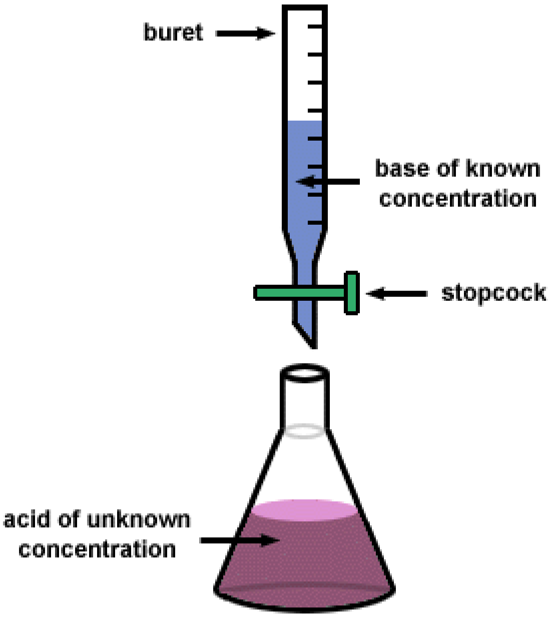


Figure II.7: Schematic of acid-base titration

II.12.2 Equivalence

During a titration, the titrant solution is added to the beaker, and before equivalence is reached, the titrated reagent is in excess in the beaker. Then, there comes a moment when the titrated reagent is completely neutralized by the titrant; this is the ***equivalence point***. At this precise moment, the ***amounts of the titrant*** and the **titrated reagent** in the beaker are ***equal***.

For a titration to be experimentally feasible, a change must be observed at equivalence:

- ✓ In a colorimetric titration, a ***color change*** is observed.
- ✓ In a pH-metric titration, a sudden ***change in pH*** is observed.

II.12.3 Titration of a strong acid by a strong base

Example : titration of NaOH by HCl (Fig II.8)

$$\mathrm{HCl}\ (aq)+ NaOH(aq)\rightarrow NaCl\ (aq)+H_2O\ (l)$$

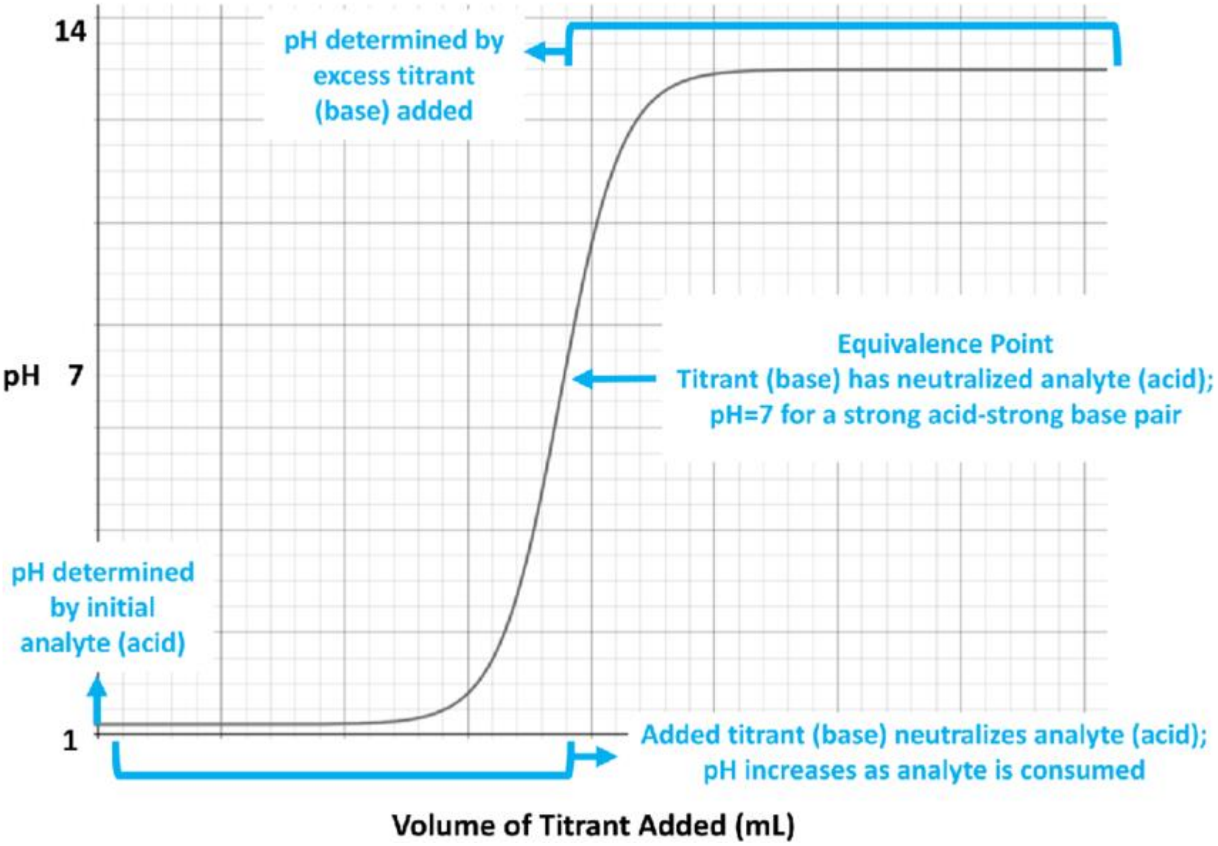


Figure II.8: Titration of strong acid by a strong base curve

The strong acid and strong base dissociate completely in water.

$$\mathrm{AH} \quad + \quad \mathrm{BOH} \rightarrow \quad \mathrm{AB} + H_2O$$

The titration curve can be divided into three distinct parts:

Before the equivalence point

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

$$[H_3O^+] = \frac{C_aV_a - C_bV_b}{V_a + V_b}$$

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

At the equivalence point

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

$C_a·V_a = C_b·V_b$ ($[H_3O^+] = [OH^-]$). At this point, pH=7 at 25°C.

After the equivalence point

After the equivalence point, Ca·Va is less than Cb·Vb ($[OH^-] > [H3O^+]$). The OH^- ions react with all the H_3O^+ ions to form water, leaving in solution an amount of OH^- ions equal to $C_b·V_b–C_a·V_a$.

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

$$pOH = -\log[OH^-] = -log_{10}\left(\frac{C_aV_a - C_bV_b}{V_a + V_b}\right)$$

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

II.12.4 Titration of a weak acid by a strong base

Example :(Fig II.9)

$$CH_3CO_2\,(aq) + OH^-(aq) \rightarrow CH_3CO_2^-\,(aq) + H_2O\,(l)$$

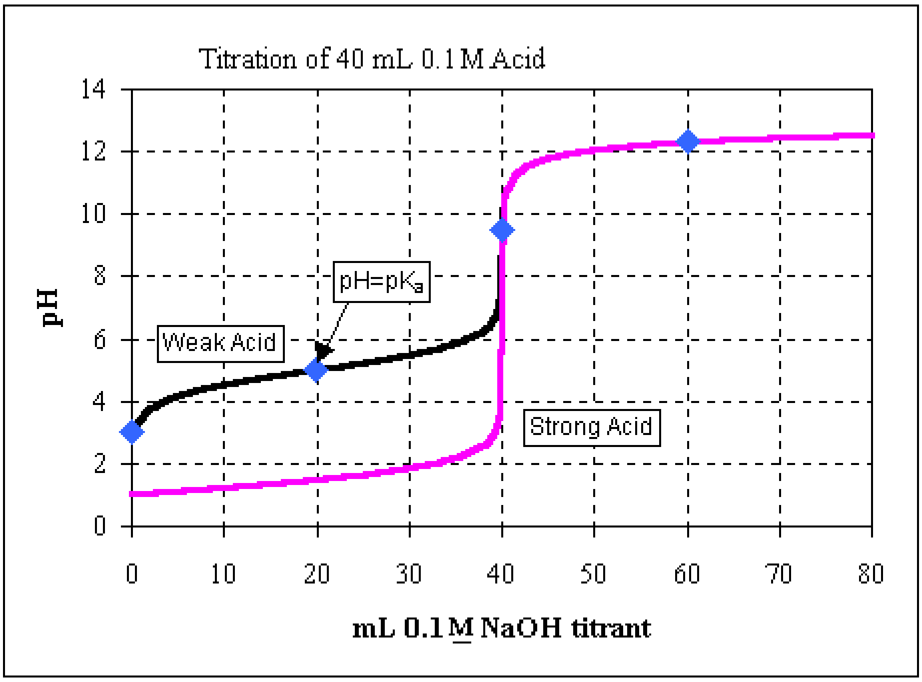


Figure II.9: Titration of weak acid by a strong base curve

II.12.5 Titration of a strong acid with a weak base

Example: titration of NH_3 with HCl (Fig II.10)

$$NH_3(aq) + HCl\,(aq) \rightarrow NH_4Cl\,(aq)$$

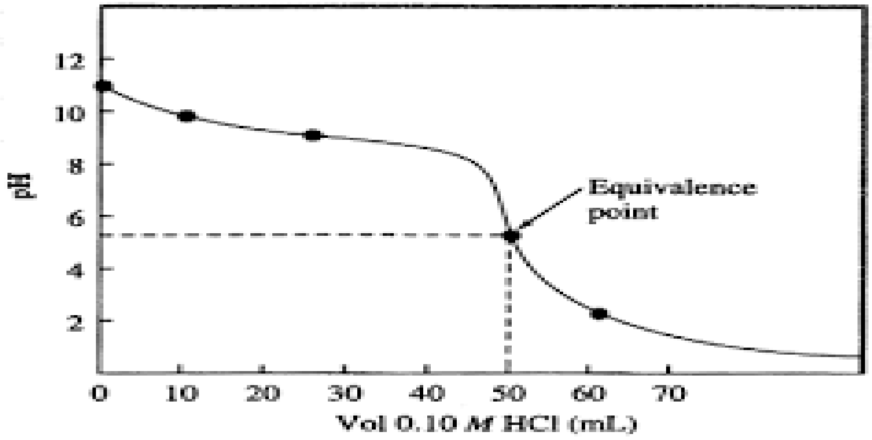


Figure II.10: Titration of strong acid by a weak base curve

II.13 DOSAGE PH-METRIC

This is a titration carried out with a pH meter: we study the variations in pH of the reaction medium.(Fig II.10)

II.13.1 Experimental setup

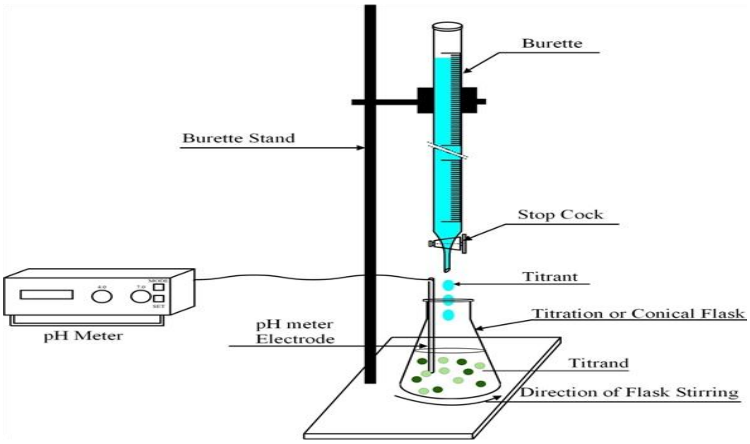


Figure II.11: Experimental setup of dosage pH-metric

II.13.2 Principle

A very precise volume, measured using a graduated pipette, of the solution to be titrated is placed in a beaker. Distilled water is added so that the glass electrode is properly immersed in the solution. The pH values are recorded based on the volume of titrant solution added using the graduated burette.

II.13.3 pH-Metric Titration Curve:

We measure the **pH** of the solution as a function of the **volume** of sodium hydroxide solution added. (Fig II.12)

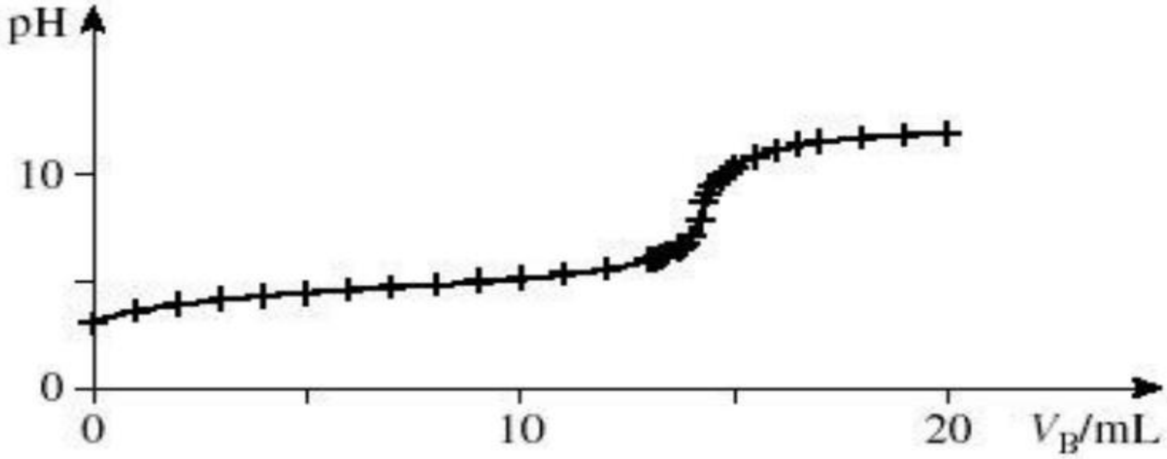


Figure II.12 : pH-Metric Titration Curve

II.13.4 Identification of the Equivalence Point:

- ✓ Tangent Method

- ✓ Derivative Curve Method

II.13.4.1 Tangent Method:

(To be used when the curve is plotted on graph paper) .Two tangents are drawn on either side of point E that are parallel to each other. The line parallel to these two tangents and equidistant from them intersects the curve at the equivalence point E.

II.13.4.2 Derivative Curve Method (to be used when the curve is plotted on a computer)

The derivative curve of the function pH = f(V_b) features a peak whose apex has an x-coordinate of $\mathbf{V_b = V_b}$ **equivalent**.

II.14. COLORIMETRIC TITRATION

1. Device

The same experimental setup is used, except that a pH meter is not needed; instead, we add 3 drops of a ***colored indicator*** to the Erlenmeyer flask.(fig II.13)

2. Principle

In an acid-base colorimetric titration, the observable aspect is the color of the solution. The color change at the equivalence point is caused by the transition of an acid-base color indicator introduced in very small quantities.

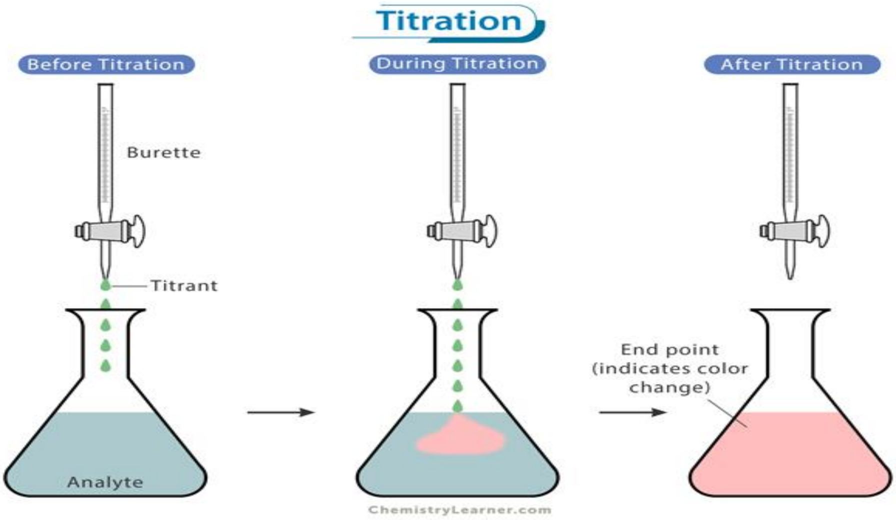
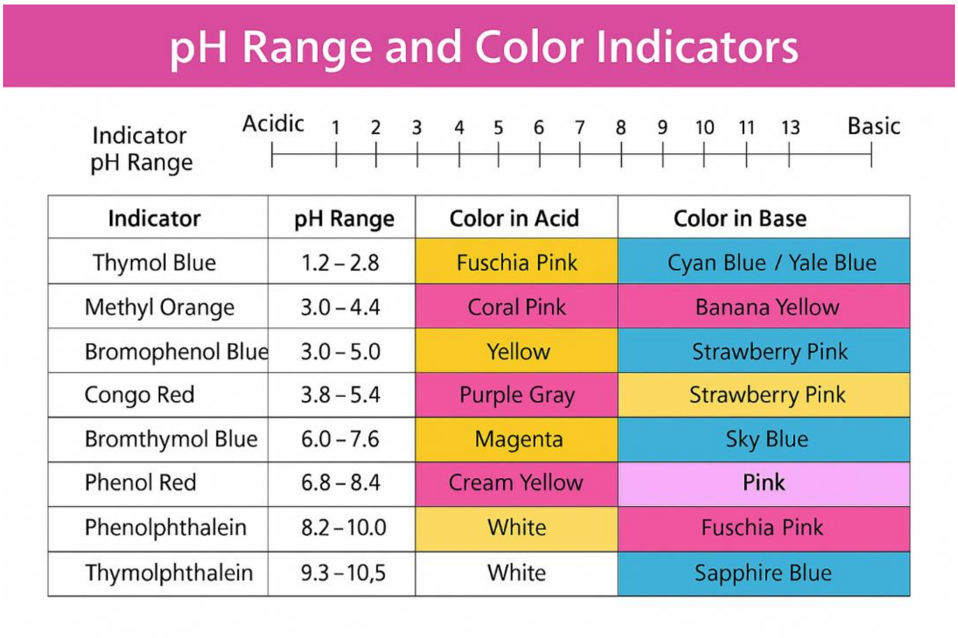


Figure II.13: Colorometric titration device

3.Choice of the Colored Indicator

Colored indicators (or acid-base indicators) are molecules that have the ability to change color depending on the acidity (in the Brønsted sense) of their surrounding environment. By extension, the pH indicator is a chemical detector of the hydronium (or oxonium) ion H_3O^+.

Their syntheses most often lead to solids, and colored indicators are typically used in very small amounts in a solvated state in aqueous solutions. Therefore, a few drops can significantly color a solution, and the color will be sensitive to the pH values it takes on.(Fig II.14)



pH Range and Color Indicators

Indicator	pH Range	Color in Acid	Color in Base
Thymol Blue	1.2 – 2.8	Fuschia Pink	Cyan Blue / Yale Blue
Methyl Orange	3.0 – 4.4	Coral Pink	Banana Yellow
Bromophenol Blue	3.0 – 5.0	Yellow	Strawberry Pink
Congo Red	3.8 – 5.4	Purple Gray	Strawberry Pink
Bromthymol Blue	6.0 – 7.6	Magenta	Sky Blue
Phenol Red	6.8 – 8.4	Cream Yellow	Pink
Phenolphthalein	8.2 – 10.0	White	Fuschia Pink
Thymolphthalein	9.3 – 10,5	White	Sapphire Blue

Figure II.14 : pH range and color indicator

II.15 Application Exercises

Exercise 01:

a) 3.23 g of HNO_3 is introduced into water. The volume of the resulting solution is 450 mL. What is the pH of this solution knowing that HNO_3 is a strong monoacid.

b) What is the pH of an aqueous solution of sodium hydroxide NaOH at 8.10^{2} M?

c) We dissolved 0.07 mole of acetic acid (CH_3COOH) in 500 ml of solution.

What is the pH of the solution knowing that 15 molecules of acetic acid per 1000 are dissociated (acetic acid is a weak monoacid)?

Calculate the acidity constant K_a of this acid.

Solution:

1) **pH of so**lution HNO_3

$HNO_3 \rightarrow H^+ + NO^{3-}$

HNO3 is a strong acid

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

$$C = \frac{n}{V} = \frac{m}{M.V} = \frac{3{,}23}{63 \times 0{,}45} = 0{,}14\ mol/l$$

$$\boldsymbol{pH = -log\ C = -\ log_{10}\ [H_3O^+] = -log\ (0,14) = 0,94}$$

pH = 0,94

2) **pH** of NaOH

NaOH is a strong acid ;so

$$pH = 14 + \log C = 14 + \log (8.10^{-2})$$

pH = 12,9

3) **pH** of CH_3COOH

CH3COOH is a weak acid so :

pH = -log C

$$C = \frac{n}{V} = \frac{0{,}07}{500} = 14\ mol/l$$

15 molecules dissociated → 1000 molecules → $\alpha = \frac{15}{1000} = 0{,}015$

$$pH = -\log[H_3O^+] = -\log(C_0\alpha) = -\log(14 \times 0.015)$$

pH = 2,67

Calculate K_a :

$$K_a = \frac{\alpha^2.C}{1-\alpha} = \frac{(0.015^2\ ).14}{1-0.015} = 3{,}198.10^{-5}$$

Exercise 02:

We mix 50 mL of an aqueous solution of CH_3COOH (1 mol/L) with 50 mL of a solution of CH_3COONa (0.1 mol/L). pK_a of CH_3COOH/CH_3COO^- = 4.7.

1) What do we call this solution?

2) Calculate the pH of this solution

Solution:

$$CH_3COOH \begin{cases} 50\ ml \\ C = 1M \end{cases} \quad + \quad CH_3COONa \begin{cases} 50\ ml \\ C = 0{,}1M \end{cases}$$

pK_a (CH_3COOH/CH_3COO^-) = 4.7

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

1) we called this solution “ ***Buffer solution***” because we have a mixture that contains Acid (CH_3COOH) with its conjugate base ($CH3COO^-$)

2) Calculate the pH of solution

Equation of HENDERSON :

$$pH = pK_a + \log\frac{[Base]}{[Acid]}$$

$$pH = 4{,}7 + \frac{\frac{0{,}1 \times 50}{100}}{\frac{1 \times 50}{100}} = 4{,}8$$

pH= 4,8

Chapter III

Oxidation and Reduction

III.1 Definitions

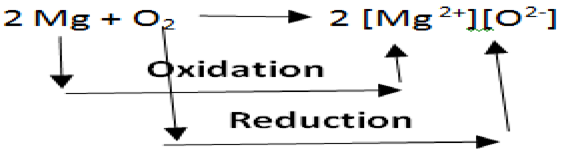
At different times, ***oxidation*** and ***reduction (redox)*** have had different, Compare the following definitions:

Oxidation is:	**Reduction** is:
➢ Gaining oxygen	•Losing oxygen
➢ Losing hydrogen	•Gaining hydrogen
➢ Losing electrons (+charge increases)	•Gaining electrons (+ charge decreases)

Oxidation and reduction are opposite reactions. They are also paired reactions:

In order for one to occur, the other must also occur simultaneously.

While the first two definitions of oxidation-reduction are correct, the most useful definition Is the third involving the gain or loss of electrons.



1) An Oxidant (Oxidizing Agent)

An **oxidant**, is a chemical species that **gains one or more electrons** in a reaction, causing another species to lose electrons. When an oxidant gains electrons, it gets **reduced**.

Example :

$$Cu^{2+} + 2e^- \rightarrow Cu$$

2) A Reductant (Reducing Agent)

A **reductor**, is a chemical species that is capable of **donating one or more electrons** in a reaction, when a reductant loses electrons, it gets **oxidized**.

Example:

$$Al \rightarrow Al^{3+} + 3e^-$$

3) Redox Couple (Oxidant / Reductant)

A **redox couple** consists of an **oxidant** and a **reductant** that correspond to each other in a half-reaction. The species **Ox** and **Red** form a **redox couple**, written as **Ox/Red**.

$$\text{Oxidant} + ne^- \leftrightarrow \text{Reductant}$$

Examples:

Fe^{3+} / Fe^{2+} Couple

$$\mathbf{Fe^{3+} + e^- \leftrightarrow Fe^{2+}}$$

In this redox couple :

Fe^{3+} (ferric ion) is the **oxidant** (it can gain an electron to become Fe^{2+}).

Fe^{2+} (ferrous ion) is the **reductant** (it can donate an electron to become Fe^{3+}).

III.2 Determination of oxidation number

The **oxidation number (NO)** (also called the **oxidation state**) of an atom in a compound is the **number of electrons,** an atom has gained or lost compared to its neutral (uncombined) state.

a) The oxidation number of an element in its elemental form is 0 (zero):

Example: H, O, Cu, Co → **NO = 0**

b) In ***compounds***, the oxidation number of ***hydrogen*** is almost always **+1,** The most common exception occurs when hydrogen combines with metals; In this case the oxidation number of hydrogen is typically –1.

Example

H_2 : NO (H) = 0.

Hydrogen in compounds with non-metals (H_2O, HCl) : NO (H) = +1.

Hydrides (NaH, KH, LiH) : NO (H) = -1 (hydrogen is bonded to metals that are more electropositive).

c) The oxidation number of ***oxygen*** is almost **+2**. However, there are exceptions depending on the specific bonding environment of oxygen.

Examples:

F_2O → NO (F) = -I and NO (O) =+II

H_2O_2 → NO (H) = +I and NO(O) = -I

d) When two atoms of the **same element** combine to form a molecule, and no charge is present on the molecule (neutral combination), the **oxidation number** of each atom in the molecule is **zero**.

Example

F_2, Br_2, Cl_2 → **NO = 0**

e) For a complex ion, the ***sum*** of the positive and negative oxidation numbers of all elements in the ion ***equals the charge on the ion***.

Example

Sulfate ion (SO_4^{2-}) : ΣNO = NO(**S**) + 4×NO(**O**) = -2 → NO(**S**) = +6

f) For an electrically neutral compound, the sum of the positive and negative oxidation numbers of all elements in the compound equals zero.

Example

NH_3 : ΣNO = N.O(N) + 3 × N.O(H) = 0

II.3 Balancing Redox Reaction

Every chemical reaction must be balanced according to the "Law of conservation of mass". The chemical equations which involve oxidation and reduction can also be balanced with the help of the following methods

- ***Oxidation number method.***
- ***Ion electron method*** (or half reaction method)

III.3.1 Ion electron method (or half reaction method):

It is based on the Principle that the electrons lost during oxidation half reaction in a particular redox reactions is equal to the electrons gained in the reduction half reaction. The method is called ***half reaction method***. The balancing is completed in the following steps:

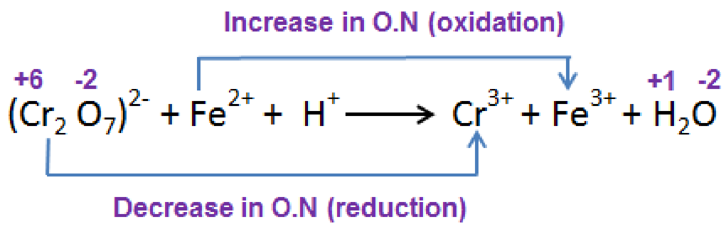
Example: Balance the chemical equation by ion-electron method:

$$\mathbf{Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow Cr^{3+} + Fe^{3+} + H_2O}$$

Step-1 : Write the oxidation number of each atom in the skeleton

$$(\overset{+6}{Cr}_2\ \overset{-2}{O}_7)^{2-} + Fe^{2+} + H^{+} \longrightarrow Cr^{3+} + Fe^{3+} + \overset{+1}{H}_2\overset{-2}{O}$$

Step-2 : Find out the species involved in the oxidation and reduction half reactions:



Step-3 : Balancing oxidation half reaction:

As oxidation number increases 1, add one e⁻ on the product side to balance change in O.N.

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

Step-4 : Balancing reduction half reaction:

The decrease in oxidation number per Cr atom is 3 and the total decrease in O.N for two Cr atoms is 6. Therefore, add $6e^-$ on the reactant side. In order to balance O atoms add 7 H_2O molecules on the product side then balance H atoms by adding 14 H^+ on reactant side.

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Step-5 : Adding the two half reactions:

$$\begin{array}{c} [\,Fe^{2+} \longrightarrow Fe^{3+} + e\,] \times 6 \\ Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \\ \hline Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \end{array}$$

III.4 Practical realization of redox reactions

The transfer of electrons between two redox couples can occur via two different pathways:

III.4.1 Direct Electron Transfer (Chemical Pathways)

The reagents are brought into direct contact: a zinc sheet Zn(s) is immersed in a solution of Cu^{2+}. (Fig III.1)

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

$K = 1.9 \times 10^{37} >>> 10^4$ → Total reaction.

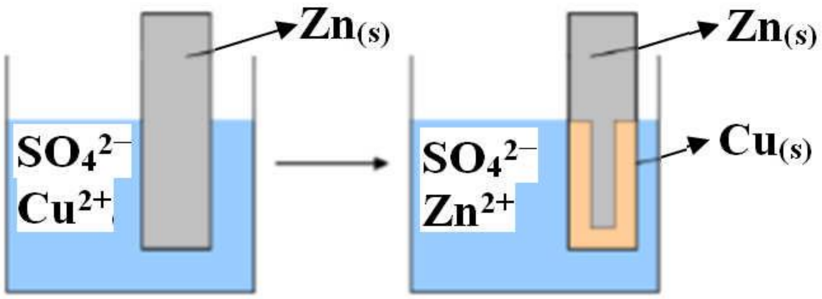


Figure III.1: Electrochemical cell (**Direct electron transfer)**

III.4.2 Indirect Electron Transfer (Electrochemical Pathways)

The two half-reactions occur in two distinct compartments connected to each other by an electrical conductor. Together, they form an electrochemical cell. There are two types:

- Galvanic Cell (Battery): spontaneous (natural) reactions.
- Electrolysis Cell: forced reaction using an electric energy source; the direction is opposite to that of the corresponding galvanic cell (battery).

III.4.2.1 Galvanic Cells (Batteries)

An electrochemical battery is a generator that converts chemical energy from a spontaneous (natural) redox reaction into electrical energy.

III.4.2.2 The Daniell Cell

British chemist ***John Daniell*** invented this cell in 1836. It consists of an anode (a zinc strip immersed in a $ZnSO_4$ solution) and a cathode (a copper strip immersed in a $CuSO_4$ solution).

1)Construction of the cell

- Two metallic electrodes, Zn and Cu, are immersed in solutions of Zn^{2+} ($ZnSO_4$) and Cu^{2+} ($CuSO_4$), respectively.
- The electrochemical generator, called a cell, is formed by two half-cells connected by a salt bridge.
- The salt bridge, or electrolytic junction, ensures electrical conduction between the compartments through the migration of ions (cations move in the direction of the electric current in the bridge, while anions move in the opposite direction) and maintains electroneutrality of the solutions in both compartments.(Fig III.2)

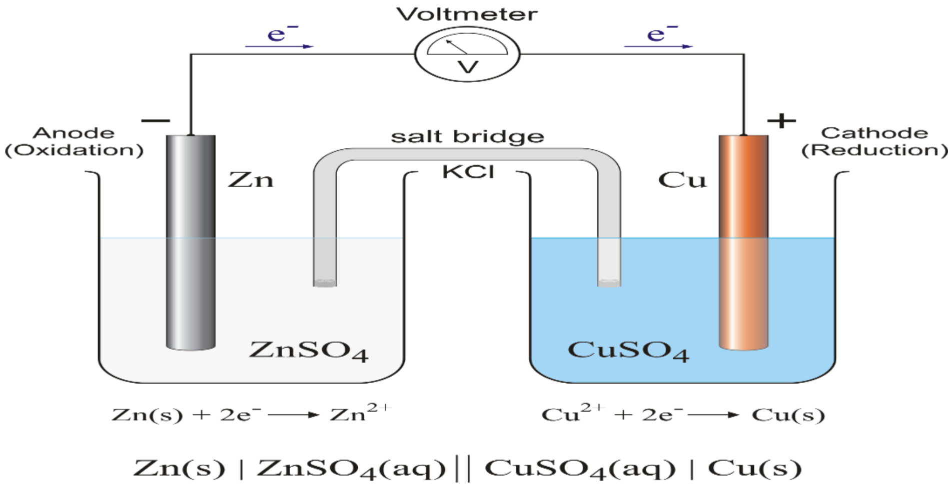


Figure III.2 : Schematic of a Daniell cell

2) Operation of a Battery:

When a battery is part of a closed electrical circuit, it acts as a generator. It causes the flow of electric current in this circuit because there is a spontaneous but indirect transfer of electrons between the reducing agent of one half-cell, here zinc, and the oxidizing agent of the other half-cell, here Cu^{2+} ions.

- At the positive terminal (the cathode), the oxidizing agent Cu^{2+} is reduced:

$$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$$

- At the negative terminal (the anode), the reducing agent Zn is oxidized:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$$

- The equation of the reaction describing the operation of the battery is the same as that which describes the spontaneous evolution of the system. It corresponds to a progression in the direct sense of the redox reaction equation:

$$Cu^{2+}(aq) + Zn(s) = Cu(s) + Zn^{2+}(aq)$$

- If we allow the battery to operate long enough, we observe an ***increase*** in ***mass*** at the copper electrode while the zinc electrode becomes thinner (***decrease in its mass***).

Role of the Salt Bridge

- Allows the flow of current within the cell.
- Maintains electrical neutrality in the solutions (by the migration of Na^+ cations in the direction of the electric current within the bridge, and SO_4^{2-} anions in the opposite direction).

The formal representation of this cell is:

$$\ominus \ \mathbf{Zn} / \mathbf{Zn}^{2+} // \mathbf{Cu}^{2+} / \mathbf{Cu} \ \oplus$$

3) Electromotive Force (E.M.F.) of a Battery:

Each battery is characterized by an electromotive force E and an internal resistance r.

✓ The value of the electromotive force (E.M.F.) E depends on the redox couples that make up the battery, as well as the concentration of the aqueous solutions used.

✓ The internal resistance r depends on the concentration of the aqueous solutions used and the surface area of the submerged electrodes.

Ohm's Law for a Battery in "Generator" Convention: E is called the electromotive force (E.M.F.) of the battery, measured in volts (V). E > 0.

The E.M.F. E is measured using a voltmeter connected to the terminals of the battery when it is not delivering any current (I = 0 A) (switch open): if I = 0, then U1 = E.

E is equal, at all times, to the positive difference in potential between the electrodes of the battery.

$$\boldsymbol{E = E_{cathode} - E_{Anode} = E_{+} - E_{-} = E_{CU^{+2}/Cu} - E_{Zn^{+2}/Zn}}$$

Note: The E.M.F. of a depleted battery is zero ($E = E_{cathode} - E_{anode} = 0$).

III.4.2.3 Electrolysis cell

An ***electrolytic cell*** can be defined as an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction. Electrolytic cells are electrochemical cells that can be used for the electrolysis of certain compounds. For example, water can be subjected to electrolysis (with the help of an electrolytic cell) to form gaseous oxygen and gaseous hydrogen. This is done by using the flow of electrons (into the reaction environment) to overcome the activation energy barrier of the non-spontaneous redox reaction.

The three primary components of electrolytic cells are:

- Cathode (which is negatively charged for electrolytic cells)
- Anode (which is positively charged for electrolytic cells)
- Electrolyte

The electrolyte provides the medium for the exchange of electrons between the cathode and the anode. Commonly used electrolytes in electrolytic cells include water (containing dissolved ions) and molten sodium chloride.(Fig III.3)

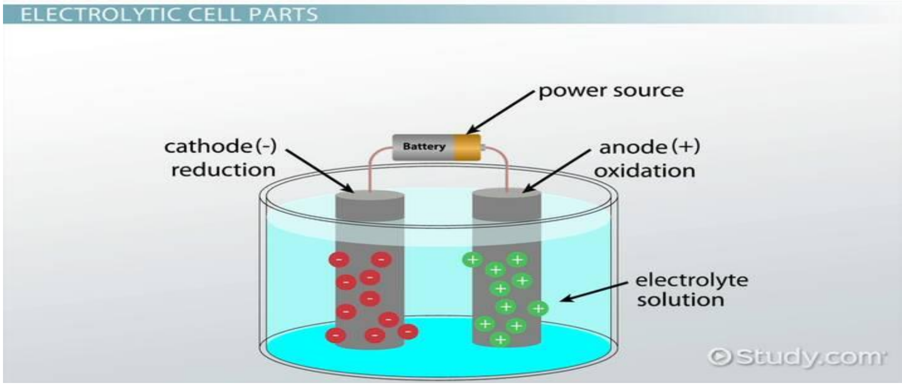


Figure III.3: Electrolysis cell shematic

a) Quantity of electricity delivered by a galvanic or electrolysis cell

The quantity of electricity delivered by a battery over a duration Δt is defined as the absolute value of the electric charge Q that has been transferred between the two electrodes during this time.

$$\boxed{Q = I \times \Delta t}$$

Where: I: current intensity in A; Δt: duration in s; Q: quantity of electricity in C (Coulombs).

Note: If the duration Δt is expressed in hours, then Q is obtained in A.h (ampere-hours).

b) Maximum quantity of electricity delivered by a battery:

The maximum quantity Q_{max} of electricity delivered by the battery is the amount of electricity delivered from the moment of its manufacture until the point at which its equilibrium state (final state) is reached. The battery is then considered depleted.

$$Q_{max} = N_{max}(e^-) \times e = n_{max}(e^-) \times N_a \times e^- = n_{max}(e^-) \times F = z \times x_{max} \times F$$
$$\text{avec } (F = N_A \times e^- = 96\ 485\ C \times mol^{-1}$$

N max(e^-) : The maximum number of electrons that can be transferred from one electrode to another;

nmax(e^-) : The maximum number of moles of electrons that can be transferred from one electrode to another;

Z: The stoichiometric number associated with the electrons transferred in the redox reaction equation;

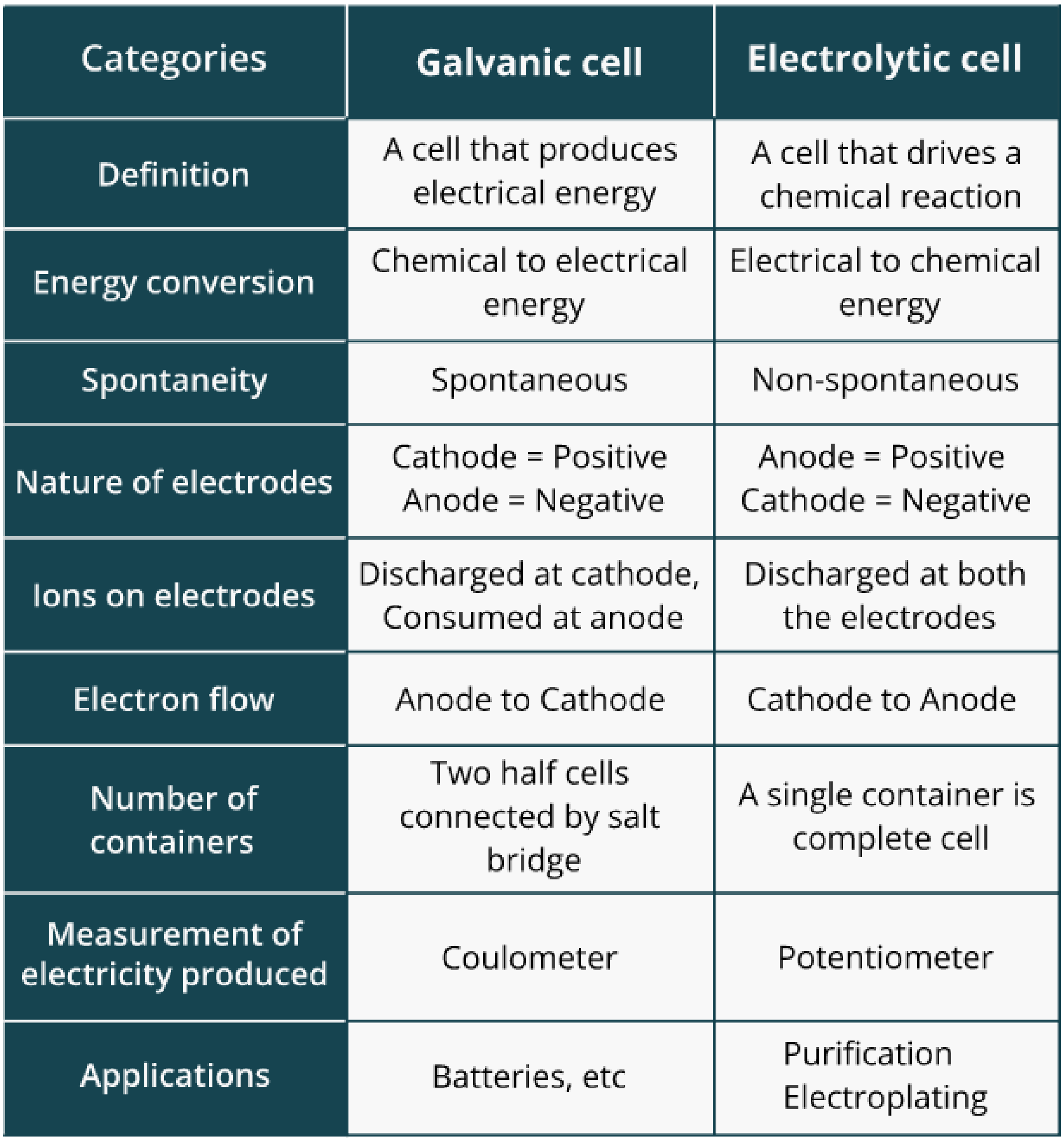
xmax : The maximum extent of reaction in moles;

F : The Faraday constant.

III.4.2.4 Difference between cell electrolysis and galvanic cell

The table II.1 resume the difference between cell electrolysis and galvanic cell

Table III.1: Difference between cell electrolysis and galvanic cell



Categories	Galvanic cell	Electrolytic cell
Definition	A cell that produces electrical energy	A cell that drives a chemical reaction
Energy conversion	Chemical to electrical energy	Electrical to chemical energy
Spontaneity	Spontaneous	Non-spontaneous
Nature of electrodes	Cathode = Positive Anode = Negative	Anode = Positive Cathode = Negative
Ions on electrodes	Discharged at cathode, Consumed at anode	Discharged at both the electrodes
Electron flow	Anode to Cathode	Cathode to Anode
Number of containers	Two half cells connected by salt bridge	A single container is complete cell
Measurement of electricity produced	Coulometer	Potentiometer
Applications	Batteries, etc	Purification Electroplating

III.5 Nernst Equation:

The formula that allows us to predict the variation of the electromotive force (EMF) with concentration and pressure is expressed in the form of an equation discovered by the German chemist ***Walther Nernst***.

We know from thermodynamics how ΔG_r varies with composition:

$\Delta G_r = \Delta G_r° + RT \ln Q$, where Q is the reaction quotient.

$\Delta G_r = - n F E$ and $\Delta G_r° = - n F E°$, leading to: $- n F E = - n F E° + RT \ln Q$.

Or, by dividing both sides by – n F:

$$\mathbf{E = E° - (RT/nF) \ln Q.}$$

For the half-reaction: Ox + n e– ⇌ Red.

$$E_{ox/_{Red}} = E^0{}_{ox/red} - \frac{RT}{nF} ln \frac{a_{Red}}{a_{ox}} \Rightarrow E_{\frac{ox}{red}} = E°_{\frac{ox}{red}} + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{Red}} \Rightarrow E_{ox/red} = E°_{ox/red} + \frac{2.3\,RT}{nF} \log \frac{a_{ox}}{a_{red}} = E°_{ox/red} + \frac{0.059}{n} \log \frac{a_{ox}}{a_{red}}$$

Because: F = 1 Faraday = 96,500 C; R (Ideal Gas Constant) = 8.31 SI units;

T (ambient temperature in Kelvin) = 298 K;

E: Redox potential;

E°: Standard potential, a characteristic constant of the considered couple (Ox/Red);

n: the number of electrons exchanged during the reaction.

III.6 Prediction of Redox Reactions:

The direction of the reaction between two redox couples can be approximately predicted by comparing their standard potentials $E_1°$ and $E_2°$. Let's take a graduated vertical graph in E°.(Fig III.4).

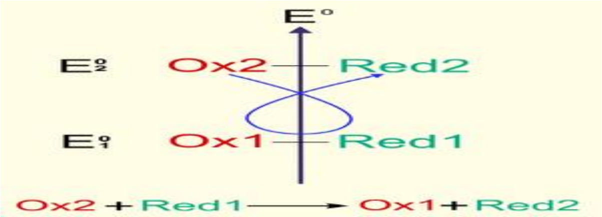


Figure III.4 : Gamma rule

In accordance with the gamma rule, the predominant reaction occurs between the strongest oxidant (Ox1) and the strongest reductant (Red2) to produce the weakest oxidant (Ox2) and the weakest reductant (Red1).

The half-equations for the electron transfer are written as follows:

$$(Red_2 \rightarrow n_2\, e^- + Ox_2) \times n_1$$

$$\underline{(Ox_1 + n1\, e^- \rightarrow Red_1) \times n_2}$$

$$n_2\, Ox_1 + n_1\, Red_2 \rightarrow n_1\, Ox_2 + n_2\, Red_1.$$

III.7 Types of Electrodes

There are several types of electrodes used in electrochemistry, primarily distinguished by their role in the reaction and their material.

III.7.1 Reference Electrode

A reference electrode is a half-cell with a constant and well-defined electrochemical potential, used in electrochemical measurements to provide a stable reference point.

It allows researchers to measure the potential of a second electrode, known as the working electrode, by forming a galvanic cell and focusing on the reaction occurring at the working electrode rather than on the entire cell. (Fig III.5)

III.7.1.1 The Standard Hydrogen Electrode (SHE)

The Standard Hydrogen Electrode (SHE) is the primary reference electrode in electrochemistry, used to define the zero point of the electrode potential scale. All other electrode potentials are measured relative to it.

Composition and Structure:

The SHE consists of a platinum electrode coated with platinum black to increase (augmenter) surface area, immersed in a 1 M H^+ solution (usually HCl), and continuously bubbled with pure hydrogen gas at a pressure of 1 atm. Half-Cell Reaction:

III.7.1.2 The Saturated Calomel Electrode (SCE)

The saturated calomel electrode (SCE) is a type of reference electrode commonly used in electrochemical measurements.

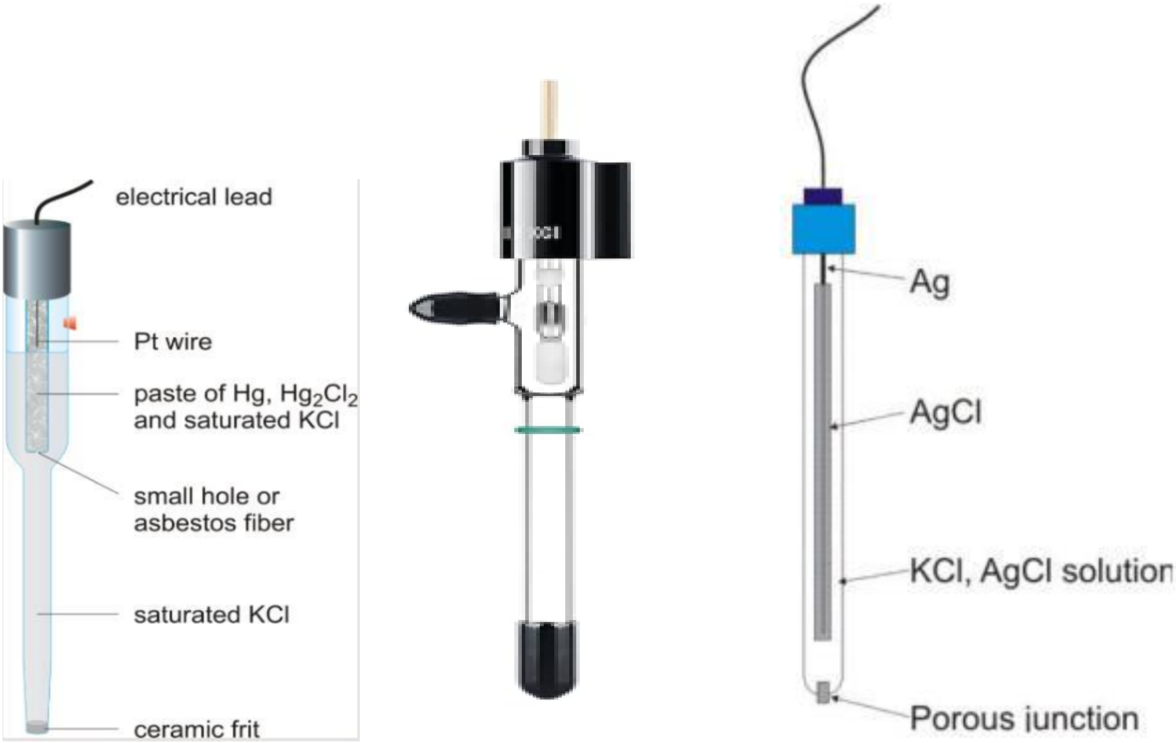
It consists of mercury (Hg) in contact with a paste of mercurous chloride (Hg_2Cl_2, or calomel) and a saturated potassium chloride (KCl) solution. This combination produces a stable and reproducible potential, making it ideal as a reference point for measuring other electrode potentials.

III.7.1.3 The Silver/Silver Chloride (Ag/AgCl) Electrode

The silver/silver chloride (Ag/AgCl) electrode is a reliable reference electrode in electrochemistry, used to provide a stable and well-defined potential in aqueous solutions.

It consists of a silver wire coated with solid silver chloride, immersed in a potassium chloride (KCl) solution. This configuration ensures a stable and reproducible ionic contact between the solid and liquid phases.

Because of its simplicity, stability, and non-toxicity (compared to the saturated calomel electrode), the Ag/AgCl electrode is widely used in laboratories and field applications.



Standard Hydrogen Electrode (SHE)

Saturated Calomel Electrode (SCE)

Silver/Silver Chloride (Ag/AgCl) Electrode

Figure III.5 : Type of reference electrodes

III.7.2 Working electrode

The working electrode is the main electrode in an electrochemical cell where the reaction of interest occurs—either oxidation or reduction. It is the electrode whose potential is controlled and measured relative to a reference electrode. It is an essential component of a three-electrode system, which also includes a reference electrode and a counter (auxiliary) electrode.

The working electrode allows the study of electron transfer reactions by applying a specific potential or current. It serves as the active surface where electrochemical reactions take place, such as metal dissolution, corrosion, deposition, or inhibitor adsorption.

III.7.2.1 Platinum electrode (Pt)

Frequently used in electrochemical studies where the reacting substance is non-conductive, such as during oxygen oxidation or hydrogen reduction. Platinum is chosen for its excellent chemical inertness, electrical conductivity, and resistance to corrosion, making it ideal for serving as an inert electrode in many redox systems.

III.7.2.2 Graphite electrode

Commonly employed in a wide range of applications because it is inexpensive, chemically stable, and mechanically robust. Graphite electrodes are especially suitable for experiments involving organic compounds or aqueous electrolytes, and are often used in battery research, electrocatalysis, and corrosion studies.

III.7.3 Auxiliary electrode (or counter electrode*)*

The auxiliary electrode, also known as the counter electrode, is an essential component of an electrochemical cell. It is used together with the working electrode and the reference electrode to complete the electrical circuit.

It allows the current to pass through the electrolyte while ensuring that the reaction of interest occurs only on the working electrode. Its main role is to balance the current flowing through the cell to maintain charge neutrality.

III.7.3.1 Platinum (Pt)

Widely used because of its high conductivity, chemical inertness, and corrosion resistance. 2. Graphite or glassy carbon

Cost-effective and stable alternatives, suitable for both aqueous and organic electrolytes.

III.7.3.2 Nickel or stainless steel

Commonly used in industrial or large-scale electrolysis systems.

III.8 Application exercises

<u>Exercise 01:</u>

a) Balance the following redox reactions in acidic medium

$H_3ASO_4 + H_2C_2O_4 \leftrightarrows CO_2 + HASO_2$ $\qquad$ $Cr_2O_7^{-2} + CH_3OH \rightleftarrows Cr^{3+} + HCOOH$

b) Balance the following redox reactions in basic medium

$IO_3^- + Cr(OH)_3 \rightleftarrows CrO_4^{2-} + I^-$ $\qquad$ $MnO_4^- + MnO_2 \leftrightarrows MnO_4^{2-}$

Solution :

a) In acidic medium

1) $H_3AsO_4 + H_2C_2O_4 \leftrightarrows CO_2 + HAsO_2$

Calculate the oxidation number for $As\ in\ H_3AsO_4$

O.N = 3(1) +X +4(-2) = 0 → X= V

Calculate the oxidation number for $AS\ in\ HAsO_2$

1+ X + 2(-2) = 0 → X(AS) = III

So $H_3AsO_4\ is\ the\ oxydant$ 1 → $CO_2\ is\ the\ oxydant$ 2

$HAsO_2\ is\ the\ reductant$ 1 → $H_2C_2O_4$is the reductant 2

$$half\ reaction\ of\ reduction\ H_3AsO_4 + 2\ H^+ + 2\ e^- \leftrightarrows HAsO_2 + 2H_2O$$

$$half\ reaction\ of\ oxidation\ \ H_2C_2O_4 + \leftrightarrows 2CO_2 + 2H^+ + 2e^-$$

$$overall\ reaction\ H_3AsO_4 + H_2C_2O_4 \leftrightarrows 2CO_2 + HAsO_2$$

2)$Cr_2O_7^{-2} + CH_3OH \rightleftarrows Cr^{3+} + HCOOH$

Calculate the oxidation number $of\ Cr\ in\ \ Cr_2O_7^{-2}\ and\ Cr^{3+}$

$\mathrm{Cr_2O_7^{-2}}$: $2\ \mathrm{X} + 7(-2) = \ -2\ \ \rightarrow \mathrm{X} = \mathrm{VI}$

$\mathrm{Cr^{3+}}$: X = III

$\mathrm{Cr_2O_7^{-2}}$ is the the oxydant 1 → $\mathrm{Cr^{3+}}$ is the reductant 1

$$2 \times (\mathrm{Cr_2O_7^{-2}} + 14\ \mathrm{H^+} + 6\ \mathrm{e^-} \rightleftarrows \mathrm{Cr^{3+}} + 7\mathrm{H_2O})$$

$$3 \times (\mathrm{CH_3OH} + \mathrm{H_2O} \rightleftharpoons \mathrm{HCOOH} + 4\mathrm{H^+} + \ 4\mathrm{e^-})$$

$$2\mathrm{Cr_2O_7^{-2}} + \mathrm{CH_3OH} + 16\ \mathrm{H^+} \rightleftarrows 2\mathrm{Cr^{3+}} + 3\mathrm{HCOOH} + 11\mathrm{H_2O}$$

1) IN basic medium

$$IO_3^- + Cr(OH)_3 \rightleftarrows CrO_4^{2-} + I^-$$

Calculate the oxidation number $of\ Cr\ in\ Cr(OH)_3\ and\ CrO_4^{2-}$

$$Cr(OH)_3 : X + 3(-2) + 3(1) \rightarrow X = VI$$

$$CrO_4^{2-} : X + 4(-2) = -2 \rightarrow X = IV$$

$Cr(OH)_3$ *is the oxidant* 1 → IO_3^- *is the reductant* 2

CrO_4^{2-} *is the reductant* 1 → I^- *is the oxidant* 2

$$2 \times (Cr(OH)_3 + OH^- \rightleftarrows CrO_4^{2-} + 3e^- + 4H^+)$$

$$IO_3^- + 6H^+ + 6e^- \leftrightharpoons I^- + 3H_2O$$

$$IO_3^- + 2Cr(OH)_3 + 4\,OH^- \rightleftarrows 2CrO_4^{2-} + I^- + 5H_2O$$

<u>Exercise 02:</u>

We construct a galvanic cell with the two half-cells A and B.

Half-cell A: consisting of a silver sheet (Ag) immersed in 40 mL of a silver nitrate solution ($AgNO_3$) with a concentration of 10^{-1} mol·L^{-1}.

Half-cell B :consisting of a manganese (Mn) sheet immersed in 20 mL of a manganese sulfate ($MnSO_4$) solution with a concentration of 2×10^{-3} mol·L^{-1}.

1) Indicate the cathode and the anode. Calculate the electromotive force (EMF) of this cell.

2) Draw the diagram of this cell, indicating the positive and negative terminals, the direction of electron and current flow, and the electrode reactions naming the cathode and anode.

3) What is the overall cell equation?

4) Calculate the equilibrium constant (k).

SOLUTION:

1) Indicate the cathode and the anode

Half cell A:

$$\boldsymbol{Ag^+ + 1e^- \leftrightharpoons Ag}$$

Equation of NERNST:

$$E = E°_{ox/red} + \frac{0.059}{n}\log\frac{a_{ox}}{a_{red}} = E°_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{[Ag^+]}{[Ag]}$$

We have :

$E°_{\frac{Ag^+}{Ag}} = 0.80\ V$; [Ag] = 1; $[Ag^+] = 10^{-1}\frac{mol}{l}$

$$E_{Ag^+/Ag} = E°_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{[Ag^+]}{[Ag]} = 0.80 + 0.059\ log\ (0.1) = 0.74\ V$$

Half cell B:

$$Mn^{2+} + 2e^- \leftrightharpoons Mn$$

Equation of NERNST:

$$E_{Mn^{+2}/Mn} = E°_{ox/red} + \frac{0.059}{n}\log\frac{a_{ox}}{a_{red}} = E°_{Ag^+/Ag} + \frac{0.059}{1}\log\frac{[Mn^{2+}]}{[Mn]}$$

We have :

$E°_{\frac{Mn^{2+}}{Mn}} = -1.03\ V$; [Mn] = 1; $[Mn^{2+}] = 2.10^{-3}\frac{mol}{l}$

$$E_{Mn^{+2}/Mn} = E°_{Mn^{+2}/Mn} + \frac{0.059}{1}\log\frac{[Mn^{2+}]}{[Mn]} = 0.80 + 0.059\ log\ (0.02) = -1.05\ V$$

We observe that :

$$E_{Ag^+/Ag} > \quad E_{Mn^{+2}/Mn} \rightarrow$$

Silver electrode is the cathode →Reduction

Manganese electrode is the anode→Oxidation

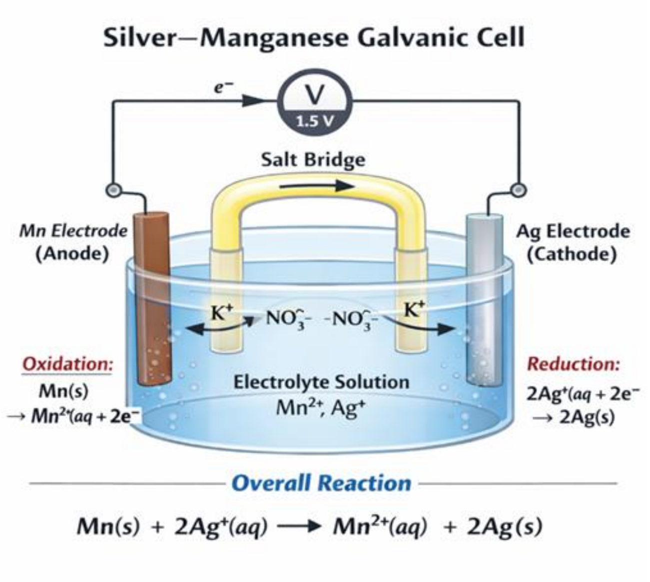
Calculate the Electromotive force of the cell (EMF)

EMF= E (cathode) – E(Anode) $= E_{Ag^+/Ag} - E_{Mn^{+2}/Mn}$

= 0.74 – (-1.05) = 1.79 Volt

EMF = 1.79 volt

2) Draw the diagram of this cell



3) The overall reaction -

$$2 \times (Ag^{+} + 1e^{-} \leftrightharpoons Ag)$$

$$Mn \leftrightharpoons Mn^{2+} + 2e^{-}$$

$$Mn\,(s) + 2Ag^{+}\,(aq) \leftrightharpoons Mn^{+2}\,(aq) + Ag\,(s)$$

2) Calculate the equilibrium constant

At equilibrium ,the electromotive force is equal to 0;EMF=0

EMF =0 →ΔE=0

$$E^{\circ}{}_{Ag^{+}/Ag} - E^{\circ}{}_{Mn^{+2}/_{Mn}} + 0.03\ log\ \frac{[Ag^{+}]^{2}}{[Mn^{+2}]} = 0$$

$$\Delta E^{0} + 0.03 \log \frac{1}{K} = 0$$

$$\log \frac{1}{K} = \frac{-\Delta E^{0}}{0.03} = -\frac{0.79-(-1.03)}{0.03} \rightarrow \log k = +\frac{1.83}{0.03} \rightarrow K = 10^{61}$$

Chapter IV

The solubility

IV.1 Concept of solubility-saturation

For any solute dissolved in a defined volume of solvent, there exists at a given temperature a limit of concentration, beyond which the substance can no longer be dissolved; this is the maximum concentration = solubility.(Fig IV.1)

Figure IV.1: Homogeneneous/heterogeneous solution

IV.2 Definition of solubility

The solubility **(S)** of a chemical species in pure water is the maximum amount that can be dissolved in 1 L of pure water at the considered temperature. The solubility is expressed in **mol/l** or **g/L** .

Examples at 20°C for ionic solids:

- $NaCl_{(s)}$: S = 6 mol/l= 350 g/l
- $Ca(OH)_2(s)$: S= 1.3. 10^{-2} mol/l = 0.96 g/l
- $PbI_2(s)$: S= 1.35.10^{-3}mol/l = 626 mg/l
- AgCl(s): S = 10^{-5} mol /l = 1.4 mg/l

Examples at 25°C:

- For NaCl: S = 6 mol/l = 352 g /l NaCl is considered **very soluble**.
- For AgCl:S = 10^{-5} mol/l = 1.4 mg/l. AgCl is considered **very poorly soluble**.

A chemical species is considered poorly soluble when S < **10^{-2} mol/l**

IV.3 Precipitation Reaction

A **precipitation reaction** is a type of chemical reaction in which two aqueous solutions combine to form an insoluble solid, known as a **precipitate**. This reaction occurs when the ions in the two solutions interact and create a compound that cannot dissolve in water, resulting in the formation of a solid.

IV.4 Solubility product (K_s)

For a solid ionic compound C_nA_m dissolving in water, The saturated solution of an ionic compound is the site of the following heterogeneous equilibrium.

$$C_nA_m \quad \leftrightarrows nC^{m+} + mA^{n-}$$

Transformation in ***direction 1*** is ***dissolution***, while transformation in ***direction 2*** is ***precipitation***, or crystallization of the solid within the solution.

$$[C^{m+}] = nS \;\; ; \;\; [A^{n-}] = mS$$

The apparent solubility product K_S , commonly used, is expressed in molar concentrations.

$$K_S = [C^{m+}]^n \; [A^{n-}]^m$$

K_S depends on ***temperature*** and ionic strength. Ks is often expressed in the form of pK_S

$$pK_S = -log_{10}K_S \;\; ; \;\; K_S \; = 10^{-pK_S}$$

A high Ks corresponds to a more soluble compound, whereas a low pKs indicates greater solubility.

IV.4.1 Relation between molar solubility (S) and solubility product (Ks)

Case 1. ***An ionic compound of type XY*** **(1:1)**

An ionic compound XY is made up of a cation X^+ and an anion Y^-, each with a stoichiometric coefficient equal to 1.

Example:

Consider the ionic compound silver chloride (AgCl), dissolves in water according to the equilibrium. Given the solubility product Ks(AgCl) $=1.8 \times 10^{-10}$, calculate the molar solubility.

$$AgCl\ (s) \leftrightarrows \; Ag^+(aq) + \; Cl^-(aq)$$

	$AgCl\ (s)$	$Ag^+(aq)$	$Cl^-(aq)$
T=0	S	0	0
Teq	0	S	S

$$K_S = [Ag^+][Cl^-] = (S).(S) = S^2 \Rightarrow S = \sqrt{K_S} \Rightarrow S = \sqrt{1.8 \times 10^{-10}}$$
$$= \mathbf{1.34 \times 10^{-5}}\ \boldsymbol{mol/l}$$

Case 2.: ***An ionic compound of type*** **X_2Y (2:1)**

In this case the dissolution equation gives cation $2X^+$ and an anion Y^-.

Example:

Consider that the silver carbonate (Ag_2CO_3) dissolves in water according to the following equilibrium. Given the value of K_S for Ag_2CO_3 : Ks = 8.1×10^{-12}, Calculate the molar solubility **(S)** (mole.L-1)

$$Ag_2CO_3(s) \leftrightarrows 2Ag^+(aq) + CO_3^{-2}\ (aq)$$

T=0	S	0	0
Teq	0	2S	S

$$K_S = [Ag^+]^2\ [CO_3^{-2}] = (2S)^2\ (S) = 4S^3 \rightarrow S = \left(\frac{K_S}{4}\right)^{\frac{1}{3}} = \sqrt[\frac{1}{3}]{\frac{K_S}{4}} \rightarrow S = 1.26 \times 10^{-4}\ mol/l$$

Case 3: ***An ionic compound of type*** **X_aYb**

The dissolution of an ionic compound with the general formula XaYb is represented as:

This means that for every mole of XaYb that dissolves, **a** moles of X^{b+} (cation) and **b** moles of Y^{a-} (anion) are produced.

Example:

Consider that the magnesium phosphate $Mg_3(PO_4)_2$ dissolves in water according to the following equilibrium. Given the value of Ks for $Mg_3(PO_4)_2$: Ks = 1×10^{-24}, Calculate the molar solubility **(S)** (mole.L^{-1})

$$Mg_3(PO_4)_{2\,(S)} \leftrightarrows 3Mg^{2+}\ (aq) + 2PO_4^{+3}(aq)$$

T=0	S	0	0
Teq	0	3S	2S

$$K_S = (Mg^{2+})^3\ (PO_4^{+3})^2 = (3S)^3\ (2S)^2 \rightarrow S = \sqrt[5]{\frac{k_S}{108}} = 4 \times 10^{-6} mol/l$$

IV.5 Condition for Forming a Precipitate

IV.5.1 Dissolution of a Sparingly Soluble Salt

Example: Calcium hydroxide ($Ca(OH)_2(s)$) is added to water.

Three possibilities:

- If the amount of substance per liter $\frac{n}{v} < S$: Everything dissolves, resulting in a liquid phase, and ***no precipitate*** forms.
- The amount of substance per liter $\frac{n}{v} = S$: The formation of the first grain of precipitate .**beginning of precipitation.**
- If the amount of substance per liter $\frac{n}{v} > S$ **:** Not everything dissolves; there is a liquid phase plus a solid phase (a precipitate).

  The liquid phase is a saturated solution.

IV.5.2 Formation of a Sparingly Soluble Salt by Mixing Two Solutions

Three scenarios can be observed when mixing solution S1 containing a completely soluble salt AB (AB → A + B) with solution S2 also containing a completely soluble salt CD (CD → C + D)

1) If **$P_i = [A^+] [B^-] < Ks$** , there is no precipitation, resulting in a single phase.

2) If **$P_i = [A^+] [B^-] = K_S$** , we are at the limit of precipitation, resulting in a saturated solution.

3) If **$P_i = [A^+] [B^-] > K_S$**, precipitation of the salt will occur, resulting in two phases: a solid phase (precipitate) and a liquid phase (saturated solution, where $[A^-][B^+] = Ks$

The ionic product $P_i = [A^+][B^-]$ is an expression identical to K_s, but it takes into account the concentrations of the components in the solutions.

IV.6 Factors Influencing the Solubility of a Compound

IV.6.1 Effect of Temperature

$$\mathbf{A_nB_{m\,aq} \rightleftarrows nA^{m+}_{aq} + nB^{n-}_{aq}}$$

We accept Van't Hoff's law:

$$\frac{dlnK_S}{dT} = \frac{\Delta H_r^0}{RT^2} \Rightarrow LnK_S(T_2) - lnK_S(T_1) = \frac{\Delta H_r^0}{R} \times (\frac{1}{T_1} - \frac{1}{T_2})$$

ΔH: the standard enthalpy of reaction at 298 K

R : Ideal gas constant

In most cases, the dissolution of an electrolyte is an endothermic process. As a result, the solubility constant (Ks) generally increases with temperature (T), making solubility a rising function of temperature.

Solubility usually increases with temperature

IV.6.2 Effect of common ion

For example, consider the dissolution of silver chloride in a hydrochloric acid solution with a molar concentration of 0.1 M. Since hydrochloric acid is a strong acid, it completely dissociates into cations H^+ and Cl^- anions. Silver chloride dissociates according to the following reaction:

$$AgCl_s \leftrightarrows Ag_{aq}^+ + Cl_{aq}^-$$

Qualitatively, using Chatelier's principle, it can be shown that an increase in chloride ions (therefore to the right of the equilibrium) causes a shift of the equilibrium to the left. The presence of chloride ions decreases the solubility of silver chloride.

The presence of common ion decrease the solubility

IV.6.3 Effect of pH

pH is involved if the ions C^{n+} or A^{m-} are acids or bases. It is necessary to consider the acid-base equilibria with a constant K_a for example, the carbonates of alkaline earth metal ions. In this case, solubility increases if the pH decreases.

Example:

Consider the equilibrium for silver acetate dissolution

$$CH_3COOAg\ (s) \leftrightarrows Ag^+(aq) + CH_3COO^-\ (aq)$$

$$CH_3CO_2^-(aq) + H_3O^+ \leftrightarrows CH_3CO_2H + H_2O$$

$$K_S = [Ag]^+ \times [CH_3CO_2^-] \,;\; K_a = \frac{[CH_3CO_2^-] \times [H_3O^+]}{[CH_3CO_2H]} \;;$$

$$S = [Ag^+] = [CH_3CO_2^-] + [CH_3CO_2H]$$

$$S = [Ag^+] = [CH_3CO_2^-] + \frac{[CH_3CO_2^-] \times [H_3O^+]}{K_a} = [CH_3CO_2^-] \times \left(1 + \frac{[H_3O^+]}{K_a}\right)$$

$$[CH_3CO_2^-] = \frac{S}{1 + \frac{[H_3O^+]}{K_a}} \Longrightarrow [Ag]^+ \times [CH_3CO_2^-] = S = S \times \frac{S}{1 + \frac{[H_3O^+]}{K_a}} = \frac{S^2}{1 + \frac{[H_3O^+]}{K_a}}$$

$$= K_S$$

$$S = \sqrt{K_S(1 + \frac{[H_3O^+]}{K_a}}$$

If the pH decrease ,[H_3O^+] increase which mean the solubility increase

IV.6.4 Effect of complexation:

The formation of successive complexes with ions present in various precipitates increases the solubility of these ions.

The solubilty increase with the formation of complexe

IV.7 Application exercises

Exercise 01:

1) What mass of magnesium fluoride (MgF_2) can be dissolved :

a) In 200 ml of pure water

b) In 200 ml of water containing 5 g of magnesium chloride ($MgCl_2$)

Data: K_s (MgF_2) = 7,08 .10^{-9} ; M(MgF_2) =62 g/mol ; M($MgCl_2$) = 95 g/mol ;pka (HF/F^-=3.2)

Solution:

1) **Calculate the mass of (MgF_2) dissolved in** :
a) **200 ml of pur water**

We have:

$$MgF_2 \rightleftharpoons Mg^{+2} + 2F^-$$

T=0	S	0	0
Teq	0	S	2S

$$K_S = [Mg^{+2}]\,[F^-]^2 = (S)(2S)^2 = 4S^3 \rightarrow S = \left(\frac{K_S}{4}\right)^{\frac{1}{3}} = \sqrt[\frac{1}{3}]{\frac{K_S}{4}} = \sqrt[\frac{1}{3}]{\frac{7.08 \times 10^{-9}}{4}} \rightarrow$$

$$S = 1.2 \times 10^{-3}\ mol/l$$

$$S = \frac{n}{V} = \frac{m}{M \times V} \Rightarrow m = S \times M \times V \longrightarrow m = 1.2 \times 10^{-3} \times 62 \times 0.2 = 0.015\ g$$

$$\boldsymbol{m = 0.015\ g}$$

b) 200 ml of water containing 5 g of magnesium chloride ($MgCl_2$)

We have

$$MgF_2 \rightleftharpoons Mg^{+2} + 2F^-$$

T=0	S	C	0
Teq	0	S'+C	2S'

$$K_S = [Mg^{+2}]\,[F^-]^2 = (S' + C)(2S')^2$$

We can assume that (S) is very small compared to C (**S'<< C**). We can then write

$$K_S = (C)(2S')^2 \rightarrow S' = \sqrt{\frac{K_S}{4C}} \ldots\ldots\ldots\ldots 1$$

Calculate the concentration of $MgCl_2$:

$$C = \frac{n}{V} = \frac{m}{M \times V} = \frac{5}{95 \times 0.2} = 0.263\,\frac{mol}{l}$$

By replacing the values of C and K_s in formula 1 we find :

$$\boldsymbol{S' = 8.2 \times 10^{-5}\ \frac{mol}{l}}$$

$$S' = \frac{n}{V} = \frac{m}{M \times V} \Rightarrow m = S' \times M \times V \longrightarrow m = 8.2 \times 10^{-5} \times 62 \times 200 \times 10^{-3} = 1 \times 10^{-3}\ g$$

$$\boldsymbol{m = 1 \times 10^{-3}\ g}$$

We observe that: **S'<S : the solubility decrease in presence of common ion**

Exercise 02:

We mix 50 ml of a 0.05 M NaF solution with 50 ml of a 0.1 M $Mg(NO_3)_2$ solution.

1) Is there a formation of a MgF_2 precipitate?

***Data*:** $PK_s(MgF_2) = 8.15$.

Solution :

The condition for precipitation is: $P_i \ ionic\ product\ > K_S\ \ solubility\ product$

$$MgF_2 \rightleftharpoons Mg^{+2} + 2F^-$$

$$P_i = [Mg^{+2}]_0\,[F^-]_0^2$$

We have : $[F^-] = [Na^+] = \frac{C_1 \times V_1}{V_T} = \frac{0.05 \times 50}{100} = 0.025\, mol/l$

$$[Mg^{+2}] = [F^-] = \frac{C_2 \times V_2}{V_T} = \frac{0.1 \times 50}{100} = 0.05\, mol/l$$

So $P_i = [Mg^{+2}]_0\,[F^-]_0^2 = 0.05 \times (0.025)^2 = 3.1 \times 10^{-5}$

$$K_s = 10^{-pKs} = 10^{-8.5} = 7 \times 10^{-9}$$

$$P_i > K_S$$

There is a formation of precipitate

Chapter V

Complexes

V.1 Definition

A complex is a polyatomic chemical species **ML_n** soluble in water. It consists of a central metal atom or cation **M**, surrounded by **n** molecules or ions **L**, called ligands.

V.1.1 The central element (M)

The central element is a metallic atom or cation, which can be a transition metal cation from the d-block (Fe^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}) or a cation from the alkali or alkaline earth metals in the s-block (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}). The metal center, characterized by electron deficiencies, functions as a Lewis acid, meaning it can accept at least one pair of electrons.

V.1.2 Ligands (L)

Ligands are species that have at least one lone pair of electrons on an atom that is either formally or partially negatively charged, making them Lewis bases. Ligands can be classified into two categories :

Anionic ligands : These carry a negative charge when not coordinated to the metal (e.g., Br^{-}, HO^{-}, etc.).

Neutral ligands : These have no net charge (H_2O, NH_3, etc.).

V.2 Complex Formula

The formula of a complex is written inside square brackets, beginning with the central atom (**M**), followed by the **anionic ligands**, and concluding with the **neutral ligands**.

$$[\boldsymbol{M}(\boldsymbol{L})_{\boldsymbol{n}}]^{\boldsymbol{X}+}$$

Where:

M : the central metal atom or ion.

L : the ligands bound to the metal.

n : number of ligands coordinated to the metal.

x : indicates the overall charge of the complex, which depends on the charges of the central metal and the ligands.

Examples:

$$Fe^{2+} + \ 6CN^{-} \rightarrow [Fe(CN)_6]^{4-}$$

$$Cu^{2+} + \ 4NH_3 \rightarrow [Cu(NH)_3]^{2+}$$

$$Central\ cation + ligand\ \rightarrow complex$$

V. 3 Nomenclature of Complexes

V.3.1 Rules

- The name of the complex is written as a single word.

- If the complex [**ML**] is not neutral (anion or cation), it is preceded by the word "**ion**."

- Ligands (**L**) are listed in alphabetical order, followed by the central element (**M**).

The number of monodentate ligands is indicated by prefixes such as **di-**, **tri-**, **tetra-**, **penta-**, **hexa-**, etc.

- The number of polydentate ligands is indicated by prefixes such as **bis-**, **tris-**, **tetrakis-**, **pentakis-**, etc.

- For anionic complexes, the metal's name ends with the suffix "-ate."

- The oxidation state of the central element is indicated in Roman numerals at the end of the complex name.

Prefix-Ligand Names + Metal Name + (Oxidation State)

V. 3.2 Names of Ligands

The name is derived from the name of the molecule or ion.

V.3.2.1. Anionic Ligands : The suffix "**o**" is added.

Examples

Monodentate Anionic Ligands

- Cl^- : chloro
- I^- : iodo
- F^- : fluoro
- H^- : hydride
- CN^- : cyano
- OH^- : hydroxo
- SO_4^{2-} : sulfate
- SCN^- : thiocyanato
- NO_2^- : nitrito

Polydentate Anionic Ligands

- $S_2O_3^{2-}$: thiosulfato
- $C_2O_4^{2-}$: oxalato
- $C_6H_4(COO)_2$: phthalato

V.3.2.2 Neutral (Molecular) Ligands Examples

Monodentate Neutral Ligands

- H_2O : aqua
- NH_3 : ammine
- CO : carbonyl
- NO : nitrosyl
- CH_3NH_2 : methylamine

Polydentate Neutral Ligands

- en : ethylenediamine

V.3.3 Names of complexes

Complexes can either be neutral (no overall charge), cationic (positively charged), or anionic (negatively charged), depending on the metal's charge and the nature of the ligands involved.

V.3.3.1 Neutral complexes

These complexes do not carry a net charge. The total charge is balanced between the central metal ion and the ligands ($[Ni(CO)_4]$).

V.3.3.2 Non-neutral Complexes

These complexes carry a net charge, which can either be positive (cationic) or negative (anionic), depending on the charges of the metal ion and the ligands ($[Cu(H_2O)_6]^{2+}$), ($[Fe(CN)_6]^{4-}$).

Example:

Let's consider the complex $[Cu(NH_3)_4]^{2+}$

Name of the Ligands: The ligand is **ammine**, since NH_3 is a neutral ligand.

Name of the Metal: The metal is **copper** (Cu).

Oxidation State of the Metal: The oxidation state of copper in this complex is +2, so it is written as copper (II).

All Together: The name of the complex is **tetraamminecopper(II) ion.**

V.3.3.3 Case of a complex salt:

The name of the complex salt follows the general rule of naming salts : the anion is named first, followed by the cation.

Example :

$K_3[Fe(CN)_6]$: Potassium hexacyanoferrate(III)

Cation K^+, The potassium ions are named first as "potassium" since they are outside the coordination sphere.

Anionic Complex: $[Fe(CN)_6]^{3-}$

Ligands: Cyanide (CN^-) ligand with the prefix hexa- for six ligands → Hexacyano.

Metal: Iron (Fe) is part of an anionic complex, so the name changes to ferrate.

Oxidation State: Iron is in the +III

So the complete Name is Potassium **hexacyanoferrate(III)**

$[Cr(NH_3)_4]Cl_3$: Tetramminechromium(III) chloride.

V.3.3.4 Case of Multiple Ligands:

When a complex contains multiple ligands, the nomenclature follows specific rules to ensure clarity and consistency.

- The central metal is named after all the ligands have been listed.
- If the complex is an anion, the metal name will end with "ate" (e.g., ferrate for iron).
- The oxidation state of the metal is written in Roman numerals in parentheses after the metal name (e.g., Cu(II)).

Example:

$[Cu(CO)_2Cl_2]$ dicarbonyldichlorocopper(II)

$[Co(H_2O)_3I_3]$: tris(aqua)triiodocobalt(III)

Note :

For anionic complexes, the metal's name is modified to end with "-ate" and for some metals, the Latin-derived name is used :

- Iron → Ferrate
- Copper → Cuprate
- Silver → Argentate
- Gold → Aurate

V.4 Formation of a complex

The formation of a complex involves the process where a central metal ion forms bonds with ligands (molecules or ions) through coordination interactions

V.4.1. Formation Constant

The overall formation constant is the equilibrium constant associated with the formation equilibrium of the complex MLn. This equilibrium constant is denoted as βn.

For the complex **$[Ag(NH_3)_2]^+$**, its formation equilibrium is written as:**.**

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

Therefore : $K_f = \frac{[Ag(NO)_{3_2}]^+}{[Ag^+][NH_3]^2}$

Kf is the overall formation constant or stability constant; it is denoted as **β** or **Kf**. It characterizes the formation equilibrium of the complex.

Kf increase→ The more stable complex

Note : The formation of the complex is complete if : **Kf ≥ 104**

V.4.2 Dissociation Constant

This is the equilibrium constant associated with the dissociation equilibrium of the complex. This equilibrium constant is denoted as **Kd**.

$$K_d = \frac{1}{K_f} = \frac{[Ag^+][NH_3]^2}{\left[Ag(NO)_{3_2}\right]^+}$$

It is also observed that : $pKd = -\log Kd = \log Kf$

V.4.3 Successive Formation Constants of Complexes

Successive formation constants (also called **stability constants**) are equilibrium constants that describe the stepwise formation of metal-ligand complexes. They are denoted as K1, K2, K3,…, representing each step where an additional ligand binds to the central metal ion.

When a metal ion Mn+ forms a complex with a ligand L, the reaction can be described step by step.

First step

$$M + L \leftrightarrow ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \leftrightarrow ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \leftrightarrow ML_3 \quad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

The equilibrium constants can further be extended for the attack of n number of ligands as given bellow.

$$ML_{n-1} + L \leftrightarrow ML_n \quad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Where K_1,K_2, K_3……Kn are the equilibrium constants for different steps

Typically, the successive constants decrease in magnitude : $K_1 > K_2 > K_3$. This reflects the fact that adding more ligands becomes less favorable as the complex becomes more saturated.

The **overall formation constant** (βn) for a complex [MLn] is the product of the successive constants : $\beta n = K_1 \cdot K_2 \cdot K_3 \cdots Kn$

Example :

For the complex $[Cu(NH_3)4]2^+$, the successive formation constants might be:

$K_1 = 4.5\times10^3$, $K_2 = 2.8\times10^3$, $K_3 = 1.5\times10^3$, $K_4 = 7.9\times10^2$

V.4.4 Stability of complexes

The stability of complexes is closely related to the formation constant of a complex, which is a quantitative measure of the tendency of a metal ion to bind with a given ligand to form a complex.

Note : The complex is more stable when **Kf** is larger

Example :

$$Fe^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-} \qquad K_f = 10^{24}$$

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^{4+} \qquad K_f = 10^{27.1}$$

The complex **$[Fe(CN)_6]4^-$** is more stable than **$[Ag(NH_3)_2]^+$**, because Kf for **$[Fe(CN)_6]_4^-$** is greater than Kf for **$[Ag(NH_3)2]^+$**.

V.4.5 Effect of pH on Complexes

The **pH** of a solution plays a critical role in determining the availability of ligands with ionizable functional groups (**OH^-**, **NH_2**) for coordination to a metal center.

- **At low pH :** Protonation of ligands reduces the availability of lone pairs, decreasing complex stability or preventing complexation.

- **At high pH :** Deprotonation enhances ligand basicity, making them stronger donors and increasing complex stability.

Example : Glycine (NH_2CH_2COOH)

At low pH, Glycine exists in the form $NH_3^{+\cdot}$ Both the amino group (NH_2) and carboxylic group (COOH) are protonated, so glycine cannot coordinate to a metal ion.

- **At neutral pH**, Glycine exists in the form $NH_3^+CH_2COO^-$. The amino group (NH_2) is protonated to NH_3^+ while the carboxylic group (COOH) is deprotonated to COO^-, so partial coordination is possible via the COO^- group.
- **At high pH**, Glycine exists in the form $NH_2CH_2COO^-$. Both the amino group (NH_2) and carboxylic group (COO^-) are deprotonated. Complete coordination is possible via both NH_2 and COO^-, allowing glycine to act as a bidentate ligand.

V.5 Some application of complexes

Complexes play a crucial role in various scientific, industrial, and biological fields due to their unique properties. Here are some examples of the applications of complexes in different domains:

V.5.1 Analytical Chemistry

a) ***Complexometric Titration :*** Determination of Ca^{2+} and Mg^{2+} in hard water using EDTA complex with metal ions are used to accurately measure the concentrations of metals in solutions.

- **Metal Indicators *:*** as Eriochrome Black T as an indicator for alkaline earth metals.

b) Biology and Medicine

- ***Metalloenzymes:*** Many essential enzymes contain metal complexes , such as Hemoglobin ($Fe^{2+)}$ transports oxygen in blood.
- ***Medical Treatments:*** Some complexes are used as drugs, such as Cisplatin $[PtCl_2(NH_3)_2]$ a complex used in cancer therapy.

c) Agriculture

Complexes are used as Fertilizers**,** as Iron-EDDHA complexes are used to treat iron deficiency (chlorosis) in plants.

d) Environment

- **Water Treatment**: Complexes, such as those formed by chelating agents, are used to remove heavy metals from wastewater, example: EDTA is used to remove Pb^{2+} , Hg^{2+}, etc.
- **Pollution Reduction:** Catalytic complexes are used in catalytic converters to reduce vehicle exhaust emissions such as the Rhodium and platinum complexes.

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