

Part I. Concentrations

1. Definition of a solution

A solution is a homogeneous mixture of two or more components. It consists of a majority solvent (which dissolves) and one or more minority solutes (the dissolved substances). If the solvent is water, it is called an aqueous solution. We distinguish between liquid solutions and solid solutions.

1.1. Liquid solutions

A liquid solution is a homogeneous mixture in which the solvent is a liquid. The solute can be a gas, a liquid, or a solid, but the solvent is always liquid: saline solution (salt dissolved in water), sugar solution (sugar dissolved in water).

1.2. Solid solutions

A solid solution is a homogeneous mixture in which the solvent is a solid. The solute can be another solid, a gas, or a liquid. Solid solutions are often called alloys when they involve metals, such as bronze (an alloy of copper and tin), or stainless steel (an alloy of iron and carbon).

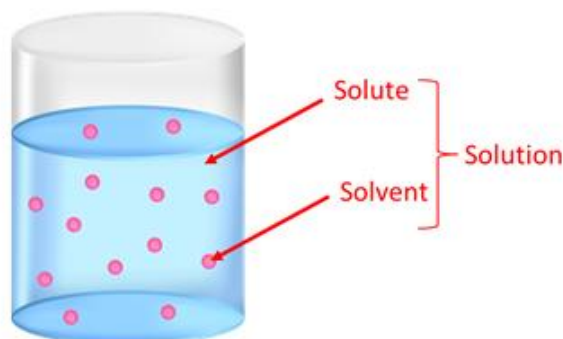


Fig. I.1. Solution

2. Expressions of concentrations

The most commonly used measures to express concentration are described below.

2.1. Mass concentration C_m

The mass concentration or weight percentage of a solution represents the mass of solute per unit volume of solution, expressed in g/L.

$$C_m = t_p = \frac{\text{masse of solute}}{\text{Volume of solution}} \quad \text{Eq. (I.1)}$$

Example 1

5 g of copper sulfate (CuSO_4) is dissolved in 400 mL of water. What is the mass concentration of copper sulfate?

Solution

$$C_m = t_p = \frac{\text{masse of solute}}{\text{Volume of solution}} = \frac{m_{\text{CuSO}_4}}{V_{\text{solution}}}$$

$$C_m = t_p = \frac{5}{400 \times 10^{-3}} = 12.5 \text{ g/L}$$

2.2. Molar concentration C_M

Molarity or molar concentration of a chemical species in solution represents the number of moles of solute per liter of solution (mol/L).

$$M = C_M = \frac{\text{number of moles of solute}}{\text{Volume of solution}} \quad \text{Eq. (I.2)}$$

Example 2

An aqueous solution of iron (III) chloride is prepared by dissolving 4.5 g of solute in a volume of 100 mL.

Calculate the molar concentration C_M of FeCl_3 .

Given: $M_{(\text{FeCl}_3)} = 162 \text{ g/mol}$

Solution

$$M = C_M = \frac{\text{number of moles of solute}}{\text{Volume of solution}}$$

$$n = \frac{m}{M} = \frac{4,5}{162} = 0.027 = 2,7 \cdot 10^{-2} \text{ mol}$$

So :

$$C = \frac{m}{V} = \frac{2,7 \cdot 10^{-2}}{100 \cdot 10^{-3}} = 0.27 \text{ mol /L}$$

2.3. Relationship between molar concentration and mass concentration

With M as the molar concentration, we can derive the relationship between mass concentration and molar concentration

$$C_m = C_M \times M \quad \text{Eq. (I.3)}$$

2.4. Equivalent concentration or Normality N

It is defined as the number of equivalents of solute per liter of solution. The concept of normality is sometimes used to simplify calculations in titration problems (eq/L).

$$N = C_N = \frac{\text{total number of gram - equivalents of solute}}{\text{total volume of solution}} = \frac{n_{eq}}{V} \quad \text{Eq. (I.4)}$$

2.5. Relationship between normality and molarity

Normality (N) and molarity (M) are two ways of expressing the concentration of a solution. They are related by the following relationship:

$$N = M \times n_{\text{equivalents per mole}} = M \times Z \quad \text{Eq. (I.5)}$$

1. For Acids, an equivalent is the quantity of acid that gives 1 mole of (H⁺) ions.

HCl can give 1 proton (H⁺)



So **Z = 1**

If the molarity of HCl is 1 M, So the normality will be: N=1 M×1=1 N

H₂SO₄ can give 2 protons (H⁺)



So **Z = 2**

If the molarity of H₂SO₄ is 1 M, So the normality will be: N=1 M×2=2N

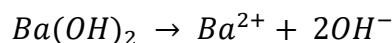
2. For bases, an equivalent is the quantity of base that provides 1 mole of (OH⁻) ions.

NaOH



Z= 1, so the normality will be: N= M

Ba(OH)₂



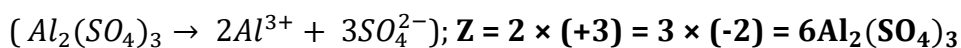
Z= 2, so, **C_N = 2 × C_M**

3. For Redox reactions, an equivalent is the quantity of a substance that gives or accepts 1 mole of electrons.

MnO₄⁻ ($MnO_4^- + 5e^- + 8H^+ \leftrightarrow Mn^{2+} + 4H_2O$); **Z = 5** so, **C_N = 5 × C_M**

($Cr_2O_7^{2-} + 6e^- + 14H^+ \leftrightarrow 2Cr^{3+} + 7H_2O$); **Z = 6** so, **C_N = 6 × C_M**

4. For salts an equivalent corresponds to the number of metal atoms in their valence state.



Example 3

Calculate the normality of a solution prepared by dissolving 4.9 g of sulfuric acid (H₂SO₄) in 250 mL of solution.

Given: M(H₂SO₄) = 98 g/L

Solution

Since sulfuric acid is diprotic (H₂), its equivalent factor is 2

1. Calculate the number of moles:

$$n = \frac{m}{M} = \frac{4.9}{98} = 0.05 \text{ mol}$$

2. Calculate the number of equivalents:

$$n_{eq} = n \times f = 0.05 \times 2 = 0.10 \text{ eq}$$

3. Calculate the normality:

$$N = \frac{n_{eq}}{V} = \frac{0.10}{250 \times 10^{-3}} = 0.40 \text{ eq/L} = 0.40N$$

2.6. Molal concentration or molality C_{molal}

Molality or molal concentration is defined as the number of moles of solute contained in one kilogram of solvent (mol/kg).

$$C_{molal} = \frac{\text{number of moles of solute}}{\text{mass of solvent (kg)}} \quad \text{Eq. (I.6)}$$

Example 4

We have 250 mL of a sulfuric acid solution (H₂SO₄) prepared from 15 g of sulfuric acid. Calculate the normality of this solution. The molar mass of H₂SO₄ is M = 98 g/mol.

Solution

1. Calculate the number of moles (n) of sulfuric acid:

$$n_{H_2SO_4} = \frac{m_{H_2SO_4}}{M_{H_2O}} = \frac{m_{H_2SO_4}}{M_{H_2SO_4}} = \frac{15g}{98g/mol} = 0.153 \text{ mol}$$

2. Determine the molarity of the solution

$$M = \frac{n_{H_2SO_4}}{V_{H_2O}} = \frac{m_{H_2SO_4}}{M_{H_2SO_4}} = \frac{0.153}{250 \cdot 10^{-3}} = 0.612 \text{ mol/L}$$

3. The relationship between normality (N) and molarity (M) is given by: N=Z×M

Since sulfuric acid is diprotic, it can release 2 protons (2H⁺), so, Z = 2

$$N = 2 \times M = 2 \times 0.612 = 1.224 \text{ N} \left(\frac{eqg}{L}\right)$$

2.7. Mass percentage

The mass percentage is the ratio between the mass of the solute (the dissolved substance) and the total mass of the solution or mixture, multiplied by 100 to express the result as a percentage (%).

$$P_m = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 100 \quad \text{Eq. (I.7)}$$

Example 5

What is the mass percentage of solute in each of the following solutions?

a. 4.12 g of NaOH in 100 g of water.

b. 5 mL of ethanol ($\rho = 0.789 \text{ g/mL}$) in 50 g of water.

Solution

a. Calculation of the mass percentage of the solute (NaOH)

$$P_m = \frac{m_i}{m_T} \times 100$$

$$m_i = m_{\text{NaOH}} = 4,12 \text{ g}$$

$$m_T = m_{\text{NaOH}} + m_{\text{H}_2\text{O}} = 4,12 + 100 = 104,12 \text{ g}$$

$$P_m = \frac{4,12}{104,12} \times 100 = 3,95 \%$$

b. Calculation of the mass percentage of the solute (ethanol)

$$P_m = \frac{m_i}{m_T} \times 100$$

$$m_i = m_{\text{C}_2\text{H}_5\text{OH}}$$

$$\text{Since } \rho = \frac{m}{V} \rightarrow m_{\text{C}_2\text{H}_5\text{OH}} = \rho_{\text{C}_2\text{H}_5\text{OH}} \times V_{\text{C}_2\text{H}_5\text{OH}}$$

$$m_{\text{C}_2\text{H}_5\text{OH}} = 0.789 \times 5 = 3.945 \text{ g}$$

$$m_T = m_{\text{C}_2\text{H}_5\text{OH}} + m_{\text{H}_2\text{O}} = 3,945 + 50 = 53,945 \text{ g}$$

$$P_m = \frac{3,945}{53,945} \times 100 = 7.31 \%$$

2.8. Volume percentage

The volume percentage is the ratio between the volume of the solute (the dissolved substance or one of the components of the mixture) and the total volume of the mixture, multiplied by 100 to express the result as a percentage.

$$P_v = \frac{\text{volume du soluté}}{\text{total volume of solution}} \times 100 \quad \text{Eq. (I.8)}$$

Exemple 6

Carbon dioxide (CO₂) represents 0.04 % of the volume of inhaled air. Upon exhalation, it occupies 4.5 mL of air.

- Express and calculate the volume percentage of carbon dioxide in exhaled air.
- Compare this value to that in inhaled air and conclude.

Solution

- Express and calculate the volume percentage of CO₂ in exhaled air.

The volume percentage of a gas is given by:

$$P_v(\text{CO}_2) = \frac{P_{\text{CO}_2}}{P_{\text{air}}} \times 100 = \frac{4,5}{100} \times 100 = 4,5 \%$$

- Compare with inhaled air and conclude

On remarque que $P_{\text{CO}_2}(\text{expiré, Exhaled air}) > P_{\text{CO}_2}(\text{inspiré, Inhaled air})$

This is a consistent result since, during respiration, the body releases carbon dioxide.

2.9. Mole fraction

The mole fraction (x_i) of a component is expressed as the ratio of (n_i) (the number of moles of that component) to the total amount of substance (n_T) (the total number of moles in the solution):

$$n_T = n(\text{solvent}) + n(\text{solute})$$

Since both n_i et n_T are expressed in moles, the mole fraction x_i is dimensionless.

$$X_i = \frac{n_i}{n_T} = \frac{n_i}{\sum_i n_i} \text{ with } \sum_i x_i = 1 \quad \text{Eq. (I.9)}$$

Example 7

Calculate the mole fraction of glycine (C₂H₅NO₂) in an aqueous solution of molality 14 mol/kg.

Solution

From the definition of molality, we can say that 1 kg of solvent (H₂O) contains 14 mol of glycine.

id : $n(\text{glycine}) = 14 \text{ mol}$ and $m(\text{H}_2\text{O}) = 1 \text{ kg} = 1000 \text{ g}$

- Calculate the number of moles of water in 1 kg:

$$n_{\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} = \frac{1000}{18} = 55.55 \text{ mol}$$

So, the total number of moles in solution

$$n_{\text{Total}} = n_{\text{C}_2\text{H}_5\text{NO}_2} + n_{\text{H}_2\text{O}} = 14 + 55.55 = 69.55 \text{ mol}$$

- Calculate the mole fraction of glycine:

$$X_{\text{glycine}} = \frac{n_{\text{glycine}}}{n_T} = \frac{14}{69.55} = 0.2$$

3. Calculate the mole fraction of water:

Since : $\sum_i x_i = 1$

So : $X_{glycine} + X_{H_2O} = 1 \rightarrow X_{H_2O} = 1 - X_{glycine} = 1 - 0.2 = 0.8$

2.10. Mass fraction

The mass fraction (w_i) of a component is expressed as the ratio of its mass (m_i) to the total mass (m_T) of the solution. Since both (m_i) and (m_T) are expressed in grams, the mass fraction (w_i) is dimensionless.

$$w_i = \frac{m_i}{m_T} = \frac{m_i}{\sum_i m_i} \quad \text{with} \quad \sum_i w_i = 1 \quad \text{Eq. (I.10)}$$

Example 8

If a mixture contains 20 g of salt dissolved in 80 g of water, calculate the mass fraction of salt.

Solution

Mass percentage of salt

$$w_{sel} = \frac{m_{sel}}{m_T} = \frac{m_{sel}}{\sum_i m_i} = \frac{m_{sel}}{m_{sel} + m_{eau}} = \frac{20}{20 + 80} = 0,2 = 20\%$$

To calculate the mass percentage of water, we can subtract directly

$$\sum_i w_i = 1 \rightarrow w_{sel} + w_{H_2O} = 1 \rightarrow w_{H_2O} = 1 - w_{sel} = 0.8 = 80\%$$

2.11. PPM

PPM (parts per million) is a concentration unit used to measure very small amounts of solute in a mixture or solution. It expresses the quantity of a substance (the solute) relative to one million units of the total mixture (usually the solvent). Both mass and volume can be used to express PPM.

$$C_{PPM}(\text{mass}) = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

$$C_{PPM}(\text{volume}) = \frac{\text{volume de solute}}{\text{volume of solution}} \times 10^6$$

Example 9

In a natural spring water sample, there are 2 g of mineral salts in 10 kg of solution. What is the concentration in ppm?

Solution

$$C_{PPM} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

$$m_{\text{solute}} = 2g$$

$$m_{\text{solution}} = 10 \text{ kg} = 10 \cdot 10^3 = 10000 \text{ g}$$

$$C_{PPM} = \frac{2}{10000} \times 10^6 = 200 \text{ ppm}$$

Part II. Conductimetry

Conductimetry is an electrochemical technique used to measure the electrical conductivity of a solution, which indicates its ability to conduct electrical current due to the presence of ions. This method provides valuable information about the ionic properties of solutions, concentration, and chemical reactions such as dissociation equilibria, acid-base titrations, and complex formation.

1. Ion mobility

Ion mobility is defined as the rate at which an ion moves under the influence of an electric field. It is influenced by several factors, including the ion's size, charge, and the properties of the surrounding solvent. Ion mobility plays a crucial role in the ionic conductivity of a solution, as it directly affects the speed at which ions contribute to charge transport.

2. Electrolytes

An electrolyte is a substance that, when dissolved in a solvent (usually water), dissociates into ions (cations, which are positively charged, and anions, which are negatively charged), allowing the solution to conduct electricity. There are two types of electrolytes.

a. Strong electrolytes: They completely dissociate into ions in solution, allowing for high conductivity. Examples include sodium chloride (NaCl), sulfuric acid (H₂SO₄), and sodium hydroxide (NaOH).

b. Weak electrolytes: They partially dissociate, leaving an equilibrium between the ions and the undissociated molecules. This results in lower conductivity. Examples include acetic acid (CH₃COOH) and ammonia (NH₃).

3. Electroneutrality of solutions

A solution is electrically neutral if the sum of the concentrations of the positively charged species (cations) equals the sum of the concentrations of the negatively charged species (anions):

$$\sum (Z_{\text{cation}} \times C_{\text{cation}}) = \sum (Z_{\text{anion}} \times C_{\text{anion}}) \quad \text{Eq. (I.13)}$$

Where:

C_{cation} : Molar concentration of the cations.

Z_{cation} : Charge of the cations.

C_{anion} : Molar concentration of the anions.

Z_{anion} : Charge of the anions.

Example 10

Verify the electroneutrality of a solution containing Na_3PO_4 at a concentration of 0.1 M and NaCl at a concentration of 0.5 M.

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4. Conduction of electrolyte solutions

4.1. Conductance

The conductance (**G**) of a solution is a quantity that reflects the ability of a material or solution to allow the passage of electric current. It is expressed in Siemens (S). Conductance is equal to the inverse of resistance.

$$G = \frac{1}{R} \quad \text{Eq. (I.14)}$$

Where: G: is the conductance (in siemens, S).

R : is the resistance (in ohms, Ω).

4.2. Conductance in electrolyte solutions

The conductance measured for a solution depends not only on the intrinsic properties of the solution but also on the geometry of the measurement cell. To determine the conductance, it is necessary to have:

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

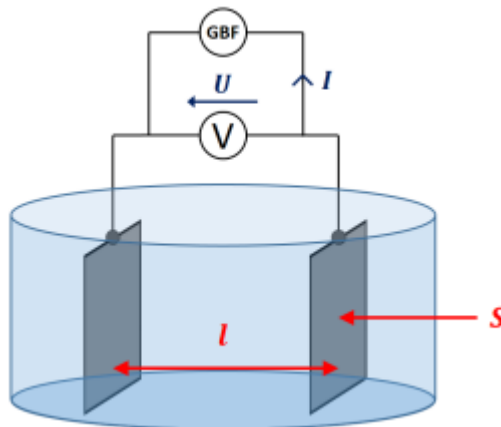


Fig. I.2. Schematic of a conductometric cell

The conductance G is proportional to the ratio S/L , called the geometric factor of the conductometric cell. The proportionality coefficient σ corresponds to the conductivity of the solution and is expressed in $S \cdot m^{-1}$.

$$G = \sigma \frac{S}{L} \quad \text{Eq. (I.15)}$$

Where:

G: The conductance (in siemens, S)

S: The surface area of the cell electrodes (m^2)

L: The distance between the plates (m)

σ : The conductivity ($S \cdot m^{-1}$)

The conductivity (σ) can be expressed as a function of the measured conductance by rearranging Equation (I.15), and the following relationship is obtained:

$$\sigma = G \frac{L}{S} = G \times K, \text{ with } K = \frac{L}{S} \quad \text{Eq. (I.16)}$$

Where K represents the cell constant.

4.3. Conductivity and ionic mobility

The electrical conductivity (σ) of an electrolytic solution depends on concentration, charge, and mobility of the ions present in the medium.

Ionic mobility (u_i) is defined as the speed at which an ion (i) moves when subjected to an electric field of unit strength. Ions that are smaller or carry higher charges usually move faster, and therefore contribute more to the total conductivity of the solution. The relationship between electrical conductivity and ionic mobility is given by the following equation:

$$\sigma = F \sum_i C_i Z_i u_i \quad \text{Eq. (I.17)}$$

Where:

σ : is the conductivity (S/m).

C_i : is the molar concentration of ion i (mol/m^3).

Z_i : is the charge number of ion i .

u_i : is the ionic mobility of ion i ($m^2/V \cdot s$).

F: is the Faraday constant ($\approx 96,500 \text{ C/mol}$).

4.4. Ionic molar conductivity

The ionic molar conductivity of an ion is a measure of its ability to carry an electric charge when present in solution. It is expressed in $S \cdot m^2/mol$, and directly related to the ionic mobility (u_i) through the following equation:

$$\lambda_i = Z_i u_i F \quad \text{Eq. (I.17)}$$

Where:

λ_i : is the ionic molar conductivity of ion (i) ($S \cdot m^2/mol$).

Z_i : is the valence (or charge) of ion i.

u_i : is the ionic mobility of ion i ($m^2/V \cdot s$).

F : is the Faraday constant ($\approx 96,500 C/mol$).

4.5. Relationship between conductivity and ionic molar conductivity

The conductivity of a solution (σ) can also be expressed in terms of the ionic molar conductivity of the different species present in the solution. It is given by the following relationship:

$$\sigma = \sum_{i=1}^n \lambda_i C_i \quad \text{Eq. (I.18)}$$

Where:

σ : Conductivity of the solution (S/m).

λ_i : Molar conductivity of ion i ($S \cdot m^2/mol$).

C_i : Molar concentration of ion i (mol/m^3).

4.6. Conductivity cell

A conductivity cell is a device used to measure the electrical conductivity of a solution. It is employed in conductimetry, an analytical technique that determines the ionic concentration of a solution by measuring its ability to conduct electric current.

4.7. Kohlrausch's law

Kohlrausch's Law establishes a simple and additive relationship between the total molar conductivity of a solution and the ionic molar conductivities of its different constituents. This law is particularly valid at infinite dilution.

At a given temperature, the molar conductivity of a solution is equal to the sum of the individual contributions of the ionic molar conductivities of the ions present. It is mathematically expressed as follows:

$$\sigma = \sum_{i=1}^n Z_i \cdot \lambda_i \cdot C_i \quad \text{Eq. (I.19)}$$

Where:

σ : Conductivity of the solution (S/m).

Z_i : Charge number of ion i.

λ_i : Ionic molar conductivity of ion i (S.m²/mol).

C_i : Concentration of ion i (mol/m³).

Part III. Conductometric titration

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 point of a titration is determined by measuring the conductance of the mixture. A solution's electrical conductivity is attributed to its ions.

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.

2. Evolution of the chemical system

Fig. I.3. illustrates the principle of the conductometric titration and the different stages of the reaction.

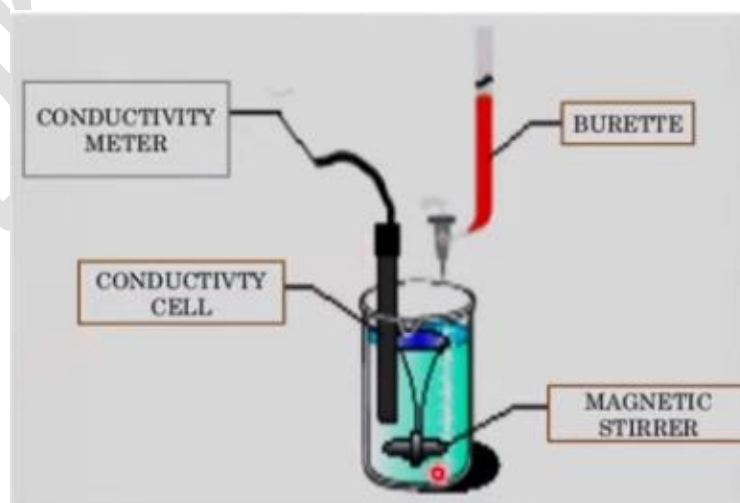


Fig. I.3. Schematic for a conductometric titration

CHAPTER I. Generalities on Solutions

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, because 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.4). 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 (V_E).

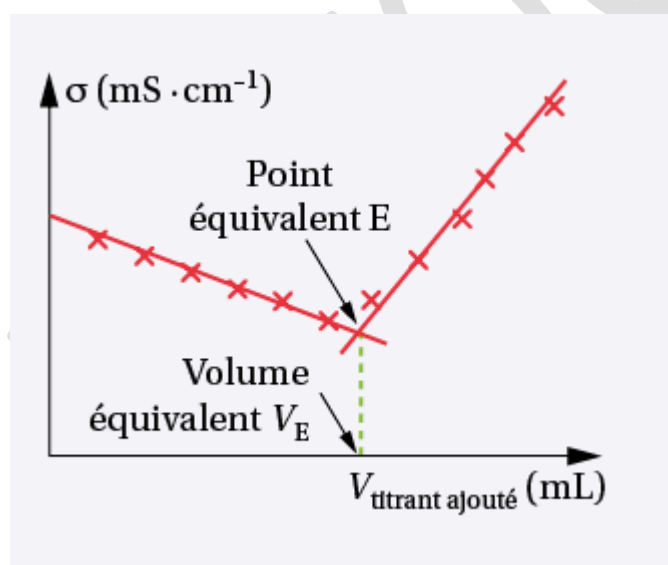


Fig. I.4. Conductometric titration curve $\sigma = f(V)$

Before the equivalent point

At this stage, the acid remains in excess, resulting in a higher concentration of H^+ ions compared to OH^- ions in the solution. The solution contains an excess of H^+ ions, Cl^- ions, and a small amount of Na^+ ions (from the base). As a result, the conductivity (σ) decreases.

At the equivalent point

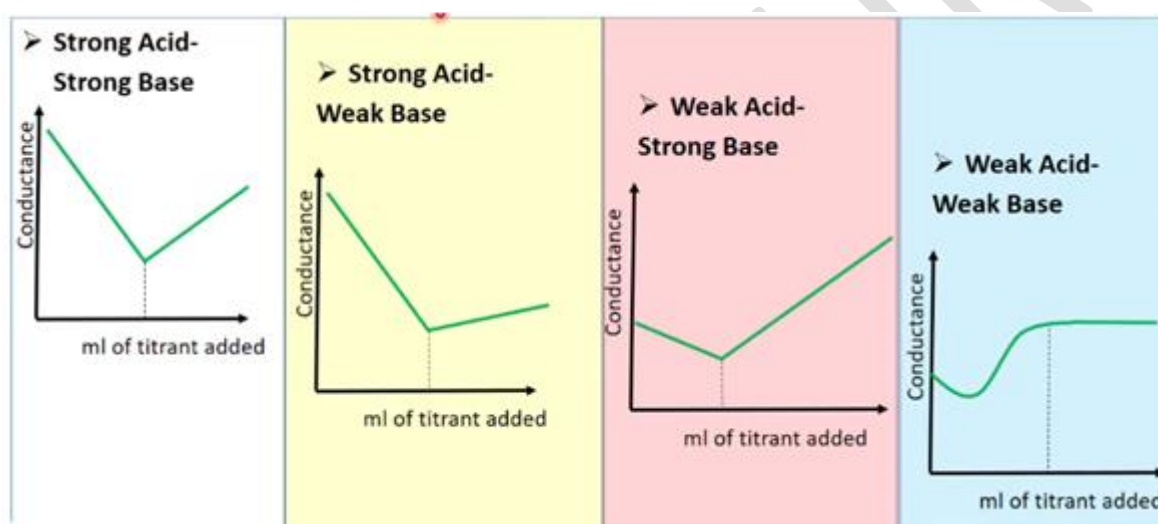
At this stage, the acid is fully neutralized, resulting in a solution composed of Na^+ , Na^+ , and Cl^- ions, indicative of a neutral solution. The conductivity (σ) reaches its minimum value. At this point, the amounts of acid and base are stoichiometrically equivalent, meaning they

have completely neutralized each other, and no H^+ ions remain in excess. The solution contains only Na^+ and Cl^- , products of the neutralization reaction between the acid and the base, forming a neutral solution.

After the equivalent point

Beyond the equivalence point, the base is in excess, resulting in the presence of OH^- ions in the solution, as the base has not yet been neutralized. The solution now contains Na^+ , Cl^- , and an excess of OH^- ions. The conductivity (σ) increases linearly with the addition of more base, as the OH^- ions contribute significantly to the solution's conductivity.

3. Different type of conductometric titration curve



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