

1. Definition of a Solution

A solution is a mixture of two or more components. The major component is called the solvent, and the minor component(s) are called solute(s).

$$\text{SOLUTION} = \text{SOLUTE} + \text{SOLVENT}$$

There are liquid solutions and solid solutions. A solution is called aqueous when the solvent is water. This is particularly true for solutions in all living systems.

A solution is said to be saturated with a given component when it contains the maximum amount of that component that the solvent can dissolve.

2. Expressions of Solute Proportion:

The most commonly used quantities to express a composition are listed below.

❖ Mole Fraction

Let n_i be the amount of substance of any given component i in the solution. The mole fraction x_i of this component is expressed by the ratio of n_i to the total amount of substance n (total number of moles):

$$x_i = \frac{n_i}{n} = \frac{n_i}{\sum_i n_i} \text{ avec } \sum_i x_i = 1$$

n_i and n are expressed in moles. x_i is dimensionless.

Example:

We dissolve 15g of ethanoic acid CH_3COOH and 11g of hydrochloric acid HCl in one liter of water ($M = 18 \text{ g/mol}$).

- Calculate the mole fraction of CH_3COOH and HCl in %.
- Calculate the mass percentage of the solution.

Solution:

$$n_{CH_3COOH} = \frac{m_{CH_3COOH}}{M_{CH_3COOH}} = 0.25 \text{ mole}$$

$$n_{HCl} = \frac{m_{HCl}}{M_{HCl}} = 0.30 \text{ mole}$$

$$n_{H_2O} = \frac{m_{H_2O}}{M_{H_2O}} = 55.55 \text{ mole}$$

Mole Fraction of CH₃COOH :

$$f_{CH_3COOH} = 100 \times \frac{n_{CH_3COOH}}{n_{H_2O} + n_{CH_3COOH} + n_{HCl}} = 0.45 \%$$

Mole Fraction of HCl :

$$f_{HCl} = 100 \times \frac{n_{HCl}}{n_{H_2O} + n_{CH_3COOH} + n_{HCl}} = 0.53 \%$$

Mass Percentage of CH₃COOH

$$f_{CH_3COOH}^m = 100 \times \frac{m_{CH_3COOH}}{m_{H_2O} + m_{CH_3COOH} + m_{HCl}} = 1.46\%$$

Mass Percentage of HCl

$$f_{HCl}^m = 100 \times \frac{m_{HCl}}{m_{H_2O} + m_{CH_3COOH} + m_{HCl}} = 1.07\%$$

❖ Mass Fraction

Let **m_i** be the mass of a component **i** in the solution. The mass fraction **w_i** of this component is expressed by the ratio of its mass to the total mass mmm of the solution.

$$w_i = \frac{m_i}{m} = \frac{m_i}{\sum_i m_i} \text{ avec } \sum_i w_i = 1$$

m_i and m are expressed in the same unit of mass. w_i is dimensionless. In practice, the mass percentage is mostly used:

$$P(\%) = w_i \times 100 (\%)$$

Example:

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

❖ Mass Concentration C_p :

The mass concentration or gravimetric C^M of a solution is the mass of a solute contained in a unit volume of the solution.

$$C_p = \frac{\text{masse of solution}}{\text{volume of solution}}$$

C_p as g.L^{-1} si *masse(i)* Is a g and V at a L.

Example 2: We mix 500 cm^3 of a glucose solution at 7g/L with 2 liters of water. What is the mass concentration of the solution?

In 500 $\text{cm}^3 = 0.5$ liters, we have: $C_p = 7 = m \text{ solute} / 0.5$

$m \text{ solute}(\text{glucose}) = 7 \times 0.5 = 3.5 \text{ g}$

Final volume of the solution:

$V \text{ final solution} = V \text{ glucose} + V \text{ water}$

$= 0.5 + 2 = 2.5 \text{ liters}$

Thus, the mass concentration is: $C_p \text{ solution} = \frac{m \text{ glucose}}{V \text{ solution finale}}$

$C_p \text{ solution} = \frac{3.5}{2.5} = 1.4 \text{ g / l}$

❖ Molar Concentration or Molarity (C_M):

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

$$C_M = \frac{\text{Number of moles of solute}}{\text{volume of solution}}$$

It is usually expressed in moles per liter (mol.L^{-1}). In the international system (MKS), molarity is expressed in moles per cubic meter (mol.m^{-3}).

❖ Molal Concentration or Molality (C_m):

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

$$C_m = \frac{\text{Number of moles of solute}}{\text{total mass of the solvent}}$$

Or $C_m = \frac{m \text{ solute}}{m \text{ solvent}} \text{ (mol/kg)}$

Exemplel 3 :

We dissolve 4.5g of NaCl (58.5g/mol) in 500 cm^3 of distilled water. Calculate C_M and C_m .

Remarks:

In the case of sufficiently diluted aqueous solutions, molarity and molality are numerically equal ($C_M = C_m$). Indeed, under these conditions, the mass of one liter of solution is practically equal to the mass of one liter of water (1 kg).

$$C_M = \frac{n}{V_{\text{solvent}}} = \frac{\frac{m}{M}}{V_{\text{sol}}} = \frac{\frac{4.5}{58.5}}{0.5} = 0.154 \text{ mole/l}$$

$$C_m = 0.154 \text{ mole / kg .}$$

In other words, for an ionic solution, the equivalent concentration $C_{eq}(i)$ of an ionic species i is equal to the product of the ionic molar concentration C_i and the absolute value of the ion's valence Z_i , such that:

$$C_{eq} = C^M(i) |Z_i| \text{ (Eq l}^{-1}\text{)}$$

For a solution containing several different ionic species, the equivalent concentration is equal to the sum of the equivalent concentrations of the anionic and cationic forms.

$$C_{eq} = \sum_i C^{M-}(i) |Z_i^-| + \sum_j C^{M+}(j) |Z_j^+|$$

According to the principle of electro-neutrality, we have:

$$\sum_i C^{M-}(i) |Z_i^-| = \sum_j C^{M+}(j) |Z_j^+|$$

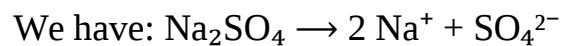
It follows that:

$$C_{eq} = 2 \sum_i C^{M-}(i) |Z_i^-| = 2 \sum_j C^{M+}(j) |Z_j^+|$$

Example:

Let's consider a solution of Na_2SO_4 (142 g/mol) obtained after dissolving a mass of $m = 14.2$ g of Na_2SO_4 crystals in 500 ml of water.

Calculate the equivalent concentration of the solution.



The molarity of the solute Na_2SO_4 is given by:

$$C_{\text{Na}_2\text{SO}_4}^M = \frac{n_{\text{Na}_2\text{SO}_4}}{V} = \frac{\frac{m_{\text{Na}_2\text{SO}_4}}{M_{\text{Na}_2\text{SO}_4}}}{V} = \frac{\frac{14.2}{142}}{0.5} = 0.2 \text{ mol l}^{-1}$$

By definition, the equivalent concentration of the solution is given by:

$$C_{eq_{\text{Na}_2\text{SO}_4}} = C_{eq_{\text{Na}^+}} + C_{eq_{\text{SO}_4^{2-}}} = C_{\text{Na}^+}^M |Z_{\text{Na}^+}| + C_{\text{SO}_4^{2-}}^M |Z_{\text{SO}_4^{2-}}|$$

Whith : $Z_{\text{Na}^+} = 1$ and $Z_{\text{SO}_4^{2-}} = -2$

$$C_{Na^+}^M = 2 C_{Na_2SO_4}^M = 0.4 \text{ mol l}^{-1}$$

$$C_{SO_4^{2-}}^M = C_{Na_2SO_4}^M = 0.2 \text{ mol l}^{-1}$$

we find: $C_{eq} \text{ } Na_2SO_4 = 0.8 \text{ Eq. l}^{-1}$

❖ **Osmolar concentration (Osmolarity) C^O :**

Osmosis is a diffusion phenomenon observed when two liquids of different concentrations are separated by a permeable membrane. It is represented by the symbol C^O :

$$C^O = i \times C^M \text{ (osmole/l)}$$

This is the ratio of all undissociated molecules and ions in a solution to the volume of the solution.

$$C^O = \frac{n_{osm}}{V} = \frac{n_{ion}}{V} + \frac{n_{nondiss}}{V} \text{ osmole/l}$$

Considering a weak electrolyte solution with a dissociation coefficient α and molar concentration C^M in a solvent volume V , we seek the relationship between osmolar concentration and molar concentration. Each molecule of this solute dissociates into v^+ positive ions and v^- negative ions.

$$C^M = \frac{n_{initial}}{V}$$

$$C^o = \frac{n_{\text{osmol}}}{V}$$

$$C^0 = \frac{n_{\text{ions}} + n_{\text{nondiss}}}{V}$$

$$\begin{aligned} n_{\text{ions}} &= n_{\text{cations}}^{\text{ions}+} + n_{\text{anions}}^{\text{ions}-} = \nu_+ \alpha n_{\text{init}} + \nu_- \alpha n_{\text{init}} \\ &= (\nu_+ + \nu_-) n_{\text{diss}} = \nu n_{\text{diss}} = \alpha \nu n_{\text{init}} \end{aligned}$$

$$n_{\text{nondiss}} = n_{\text{initial}} - n_{\text{diss}} = n_{\text{initial}} - \alpha n_{\text{initial}} = (1 - \alpha) n_{\text{initial}}$$

$$\begin{aligned} C^0 &= \frac{n_{\text{ions}} + n_{\text{nondiss}}}{V} = \frac{\nu \alpha n_{\text{init}} + (1 - \alpha) n_{\text{initial}}}{V} \\ &= \frac{n_{\text{init}} (\alpha \nu + 1 - \alpha)}{V} = (1 + \alpha(\nu - 1)) C^M \end{aligned}$$

$$C^o = (1 + \alpha(\nu - 1)) C^M$$

$$i = 1 + \alpha(\nu - 1)$$

$$C^0 = i C^M$$

Knowing that:

i = Van't Hoff ionization coefficient

$$i = 1 + \alpha(\nu - 1)$$

α = dissociation rate of the molecule.

$\alpha=1$: total dissociation.

$\alpha=0$: no dissociation.

$0 < \alpha < 1$: partial dissociation.

ν = number of ions released per dissociated solute molecule.

Ionic concentration or ionarity [ions] or Clions

$$[Ions] = \alpha \nu_{ion} C_M \text{ iongram/mol or mol of ion/L.}$$

- α = dissociation coefficient
- ν_{ion} = number of ions provided by each molecule upon dissociation

Example:



Equivalent concentration C_{eq} :

For an ion i with ionic concentration $[i]$ and valence Z_i , we have:

Unit: equivalent gram/L or mol of equivalent/L

- ν_{ion} is the number of ions provided by each molecule upon dissociation.
- $|Z_i|$ = Electrovalence of the solute molecule

Example:

Given that the molar concentration of $\text{CaCl}_2 = 2 \text{ mol/L}$ with a dissociation coefficient $\alpha = 1$,
Calculate the equivalent concentration of positive and negative ions. What can we conclude?

Solution:



$$C_{ca^{++}}^{eq} = |Z_{ca^{++}}| \quad [Ca^{++}] = |Z_{ca^{++}}| \alpha \nu_{Ca^{++}} C^M = 2 \times 1 \times 1 \times 2 = 4 \text{ Eqg / l}$$

$$C_{cl^-}^{eq} = |Z_{cl^-}| \quad [Cl^-] = |Z_{cl^-}| \alpha \nu_{cl^-} C^M = 1 \times 1 \times 2 \times 2 = 4 \text{ Eqg / l}$$

❖ **Ionic force of a solution:**

This is a numerical value characterizing the state of the solution. It is dimensionless and is generally denoted by μ and given by the formula:

$$\mu = \frac{1}{2} \sum_i C_i^M Z_i^2$$

Where:

μ = The ionic strength is dimensionless.

C_i = Molarity of the solution

Z_i = Charge of the ions present in the solution

The ionic strength allows the quantification of the ionic crowding in a solution, taking into account the effect of interionic interactions of all ions, such as molecular attractions or repulsions.

Example:

We take 1 mole of CaCl_2 with 2 moles of NaCl in a volume of 1 liter; calculate the ionic strength of the solution.

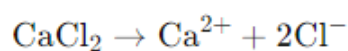


To calculate the ionic strength of the solution, we can use the formula:

$$\mu = \frac{1}{2} \sum_i C_i^M Z_i^2$$

1. For CaCl_2 :

When dissolved, CaCl_2 dissociates into 1 Ca^{2+} ion and 2 Cl^- ions:



- Concentration of $\text{Ca}^{2+} = 1 \text{ M}$
- Charge $Z_{\text{Ca}^{2+}} = +2$
- Concentration of $\text{Cl}^- = 2 \text{ M}$
- Charge $Z_{\text{Cl}^-} = -1$

2. For NaCl:

NaCl dissociates into 1 Na^+ ion and 1 Cl^- ion:



- Concentration of $\text{Na}^+ = 2 \text{ M}$
- Charge $Z_{\text{Na}^+} = +1$
- Concentration of $\text{Cl}^- = 2 \text{ M}$
- Charge $Z_{\text{Cl}^-} = -1$

$$Z_{\text{Ca}^{++}} = +2 \quad \text{et} \quad Z_{\text{Cl}^-} = -1$$

$$[\text{Ca}^{++}] = \nu_{\text{Ca}^{++}} \alpha C^{\text{M}} = 1 \times 1 \times 1 = 1 \text{ ion g/l}$$

$$[\text{Na}^+] = \nu_{\text{Na}^+} \alpha C^{\text{M}} = 1 \times 1 \times 2 = 2 \text{ ion g/l}$$

$$[\text{Cl}^-]_{\text{NaCl}} = \nu_{\text{Cl}^-} \alpha C^{\text{M}} = 1 \times 1 \times 2 = 2 \text{ ion g/l}$$

$$[\text{Cl}^-]_{\text{CaCl}_2} = \nu_{\text{Cl}^-} \alpha C^{\text{M}} = 2 \times 1 \times 1 = 2 \text{ ion g/l}$$

$$\begin{aligned} \mu &= \frac{1}{2} [Z_{\text{Na}^+}^2 [\text{Na}^+] + Z_{\text{Cl}^-}^2 [\text{Cl}^-] + Z_{\text{Ca}^{++}}^2 [\text{Ca}^{++}] + Z_{\text{Cl}^-}^2 [\text{Cl}^-]] \\ &= \frac{1}{2} [(1)^2 \cdot 2 + (1)^2 \cdot 2 + (2)^2 \cdot 1 + (-1)^2 (2)] \\ &= \frac{1}{2} [2 + 2 + 4 + 2] = 5 \end{aligned}$$

The ionic strength of the solution containing 1 mole of CaCl_2 and 2 moles of NaCl in 1 liter is 5

3. Solubility of a solute in a solvent

Solubility is the maximum amount of substance that can dissolve in a given volume of water. The solubility of a pure substance depends, for a given temperature, on the structure of the compound and the nature of the solvent.

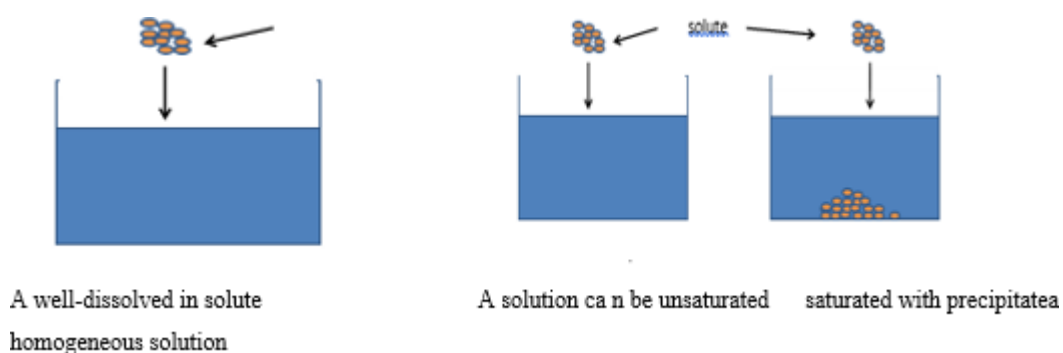
To define the solubility product for a saturated solution (which, by definition, is a solution in dynamic equilibrium with undissolved solute), we define an equilibrium constant that is related to the solubility constant.

A piece of sugar placed in water disappears into it, and we say it dissolves; therefore, sugar is soluble.

However, if you put a large amount of sugar into a small volume of water, not all of the sugar will dissolve: the sugar solution is said to be saturated.

The solubility S of an ionic crystal (a slightly soluble salt) in water is the number of moles of the ionic compound that can dissolve in a liter of solution, expressed in mol/L.

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



3.1 Dissociation Coefficient

It is the ratio of the number of moles of solute molecules that have dissociated to the initial number of moles of molecules. It is a dimensionless number. The degree of ionization is between 0 and 1.

$\alpha = 1$ for a strong electrolyte solution

$\alpha < 1$ for a weak electrolyte solution

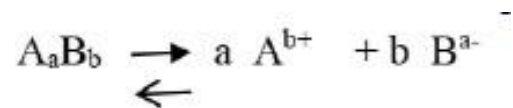
When a solute is dissolved in a defined volume of solvent, there is a concentration limit beyond which no more solute can be dissolved. This is the maximum solubility. The solubility depends on several factors: temperature, pH, etc.

3.2 Factors affecting solubility:

- **Temperature:** Generally, solubility increases with temperature.

- **pH:** pH affects solubility if the ions are acids or bases.
- **Complexation:** The formation of successive complexes with ions in various precipitates increases the solubility of these ions.
- **Presence of a common ion:** The solubility of a slightly soluble salt decreases in the presence of a substance when both substances share a common ion.

A weak solution is obtained by the dissociation of a solute in the following form:



The equilibrium constant for this solution is given by Ostwald's law, which can be written as:

$$K = \frac{[A^{b+}]^a [B^{a-}]^b}{(A_a B_b)_{\text{nondiss}}}$$

We define the solubility constant **K_s** using this equation:

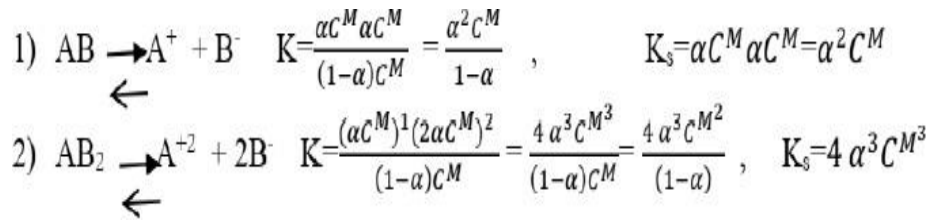
$$K_s = [A^{b+}]^a [B^{a-}]^b \quad \Rightarrow \quad K_s = K (A_a B_b)_{\text{nondiss}}$$

Let C^M be the molar concentration of the electrolyte $A_a B_b$

$$[A]^{b+} = a \alpha C^M \quad ; \quad [B]^{a-} = b \alpha C^M$$

$$\begin{aligned} (A_a B_b)_{\text{nondiss}} &= \frac{n_{(A_a B_b) \text{ nondiss}}}{V} = \frac{n_{\text{init}} - n_{\text{diss}}}{V} \\ &= \frac{n_{\text{int}} - \alpha n_{\text{int}}}{V} = \frac{(1-\alpha)n_{\text{int}}}{V} = (1-\alpha)C^M \\ K &= \frac{(a\alpha C^M)^a \cdot (b\alpha C^M)^b}{(1-\alpha)C^M} \end{aligned}$$

Exemple :



4. Electrical Properties

When a potential difference (U) is applied across two parallel plates immersed in an ionic solution, an electric current (I) can be recorded. In this case, the solution is conductive with an electrical resistance (R).

4.1 Current Flow

Liquids such as oil, pure water, and glucose or urea solutions allow little or no passage of electric current. In contrast, aqueous ionic solutions conduct electric current.

The electrical resistance R of an electrolytic solution with resistivity ρ placed in a container of length l and cross-sectional area S is given by the expression:

$$R = \rho \frac{l}{S}$$

Where:

- [R]: Ohm (Ω)
- [ρ]: $\Omega \cdot \text{m}$
- [l]: m
- [S]: m^2

Since the transport of current in an electrolytic solution is ensured by all the ions, its conductivity primarily depends on:

- The number of ions present, i.e., their concentrations;
- The specific characteristics of the ions (their charge and mobility).

The electrical conductivity χ is expressed in $\Omega^{-1} \cdot \text{m}^{-1}$. It is the inverse of resistivity:

$$\chi = \frac{1}{\rho}$$