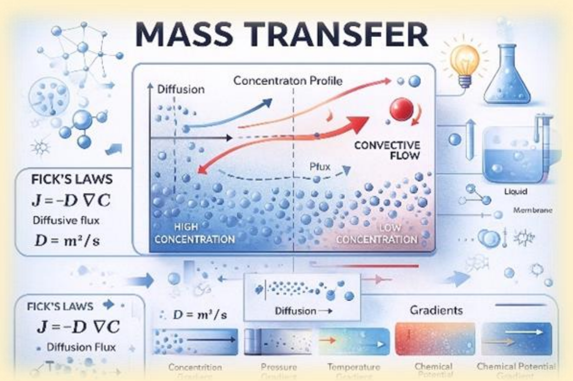
Chapter IV: Diffusion in solids



IV.1. Introduction:

Diffusion in solids is the process of mass transport by atomic motion, which tends to homogenize a material. This phenomenon is due to thermal agitation and defects in the crystal lattice, such as vacancies, and is much slower than in liquids or gases. Diffusion is governed by laws such as Fick's law and the Arrhenius law, and its rate increases with temperature and time. It has numerous applications, including surface hardening of metals and doping of semiconductors.

IV.2. Fundamental principles:

- **Atomic motion:** The atoms of solids, although relatively bound, can move by "jumping" from one position to another. This movement is facilitated by temperature and the existence of defects in the crystal lattice, such as vacancies.
- **Homogenization:** Diffusion is an irreversible process that occurs from areas of high concentration to areas of low concentration, with the aim of achieving a homogeneous distribution.
- **Temperature dependence:** A high temperature provides the kinetic energy needed for atoms to overcome energy barriers and move more easily. Diffusion is generally negligible at room temperature but becomes significant at temperatures close to the melting point.

Applications

- **Materials processing:** Diffusion is fundamental in processes such as carburizing (surface hardening of steels) and nitriding.
- **Semiconductor manufacturing:** It is used to introduce impurities (doping) into silicon crystals in order to modify their electrical properties.
- **Alloys and welds:** It allows different metals to be mixed to form alloys or to perform diffusion welds.
- **Corrosion protection:** It can be used to create protective coatings.

IV.3. Basic concepts:

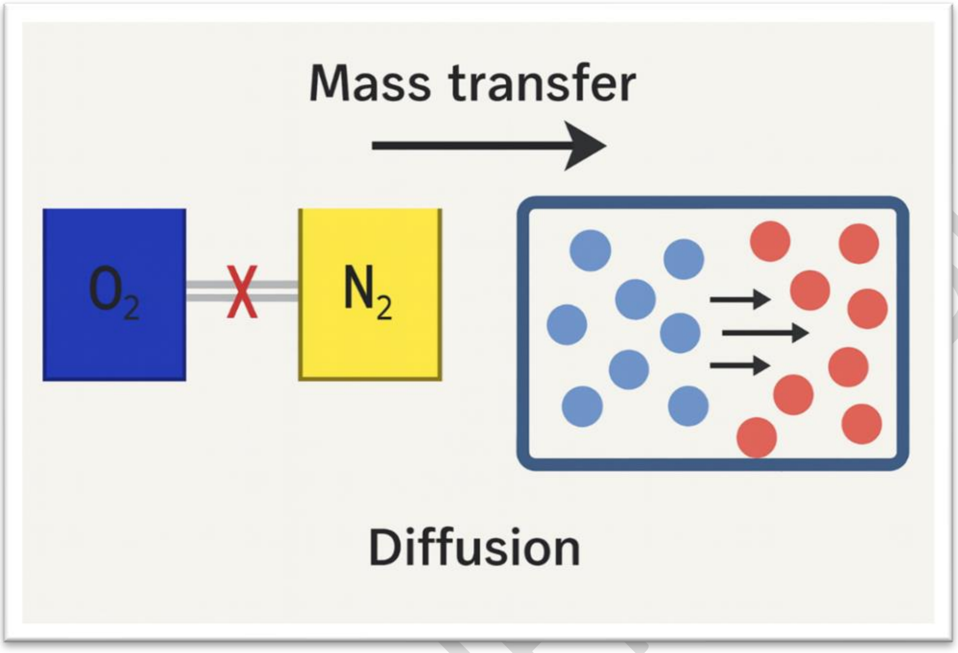
Mass transfer plays a very important role in the basic unit operations implemented during the **processing of food or biological products :** (drying, salting, sweetening, absorption, adsorption, crystallization, extraction, distillation, ...).

✓ During these operations, mass transfer is classically **the limiting factor in the speed of the process,** although heat transfer and product flow can also be involved.

✓ Material transfer also plays a very important role **in product packaging** and storage **:** transfer of moisture, gases, and flavor compounds through the packaging material.

✓ Mass transfer consists of the migration of compounds within a phase or between phases. This migration results from a change in the equilibrium of a system caused by one of the potential difference(s): difference in concentration of a species from one point to another, difference of temperature and/or pressure difference.

✓ Any potential difference leads to a spontaneous evolution towards uniformity: a difference in concentration of a compound between two points in a system therefore leads to a transfer of matter until uniformity of concentration is reached.



When considering mass transfer, two cases must be distinguished, depending on whether the transfer occurs within a single phase or between two partially or totally immiscible phases. Furthermore, each phase can be mobile or stationary.

Within a phase (mobile or stationary)

Mass (or matter) transfer

- **Between phases (mobile or not)**
- **Between phases (mobile or not)**

IV.4. Diffusion:

Diffusion is a slow process: molecules migrate in a solid or in a fluid considered as stationary (laminar flow).

Example: diffusion of sugar molecules, dispersion by molecular agitation along random trajectories between water molecules.

✓A sugar cube in a cup of coffee. It begins to melt and spreads throughout the cup by diffusion.

- Sugar molecules immersed in coffee try to make their way through the liquid molecules.
- The diffusion results from a difference in concentration: when the sugar melts, the sugar concentration, which was highest at the bottom of the cup and zero at the surface, will change more or less rapidly, and all the coffee will eventually be sweetened.

IV.4.1. **Mobile phase:**

In contrast, in the case of a mobile phase, the transport by diffusion of the constituents is not due solely to **molecular diffusion** but also to **turbulent diffusion (convection).**

Convection: Convection is a rapid process: molecules are carried along in a natural or forced fluid current (natural or forced and mixed convection).

Natural convection:

Mixed convection:

Example: stirring with a spoon is forced convection.

IV.5. Balance equations for a mixture:

a) Definitions of Amount of Substance, Concentrations and Mass Flux Densities:

We will consider here a mixture of gases or a solution (consisting of a solvent and one (constituent which we will denote A) or of several constituents or even a suspension of particles.

The concentration of the various constituents can be expressed in different ways.

Mass	**Molar**
Mass of component A: m $_A$ (kg)	Quantity of substance of component A: n $_A$ (mol)
Mass concentration: ρ(kg/ m^3)	Molar concentration: c (mol/ m^3)
$\rho = \frac{m_A}{V}$	$\rho = \frac{n_A}{V}$
Mass fraction	**Mole fraction**
$\varpi_A = \frac{m_A}{m_T} = \frac{m_A}{\sum_i m_i} = \frac{\rho_A}{\rho_T}$	$X_A = \frac{n_A}{n_T} = \frac{n_A}{\sum_i n_i} = \frac{c_A}{c_T}$
Average mass velocity of mixing in fixed axes (mass barycentric velocity):	**Average molar mixing velocity in fixed axes (barycentric molar velocity):**
$\vec{v} = \frac{1}{\rho}\sum_i \rho_i \vec{v_i}$	$\vec{v}^{\,*} = \frac{1}{c}\sum_i c_i \vec{v_i}$
Mass diffusion rate:	**Molar diffusion rate:**
This is the diffusion rate of A relative to the mixing rate:	$\vec{v}^{\,*'}{}_A = \vec{v}_A - \vec{v}^{\,*}$
$\vec{v}\,'{}_A = \vec{v}_A - \vec{v}$	

Mass transfer rate: quantity of matter transferred per unit of time:

$$q=\frac{m_A}{t}$$

$$q^*=\frac{m_A}{t}$$

Flux density:

$$n_A=\rho_A\times V_A$$

$$N_A=c_A\times V_A$$

Diffusion mass flux density:

$$J_A=\rho_A\times V_A'$$

Molar diffusion flux density:

$$J_A^*=c_A\times V_A^{*'}$$

- **Application:**

$$\sum_i \overrightarrow{J_i}=\sum_i \overrightarrow{J_i^*}=0$$

$$\overrightarrow{N}_A=c_A\times\overrightarrow{V}_A=c_A\left(\overrightarrow{V}_A^{*'}+\overrightarrow{V}^*\right)$$

$$\overrightarrow{N}_A=\overrightarrow{J}_A+X_A\sum_i\overrightarrow{N}_i$$

- ($\overrightarrow{J}_A$) : Diffusion flux density.
- ($X_A\sum_i\overrightarrow{N}_i$) : Convection or transport flux density.

$$\overrightarrow{n}_A=\overrightarrow{J}_A+\varpi_A\sum_i\overrightarrow{n}_i$$

$\vec{V}_i$: Velocity of species i. Indeed, any point in space at the given instant (Eulerian variable) can be characterized by its local concentration as well as its absolute local velocity, that is to say, relative to a fixed frame of reference:

IV.5. Fick diffusion law for a mixture:

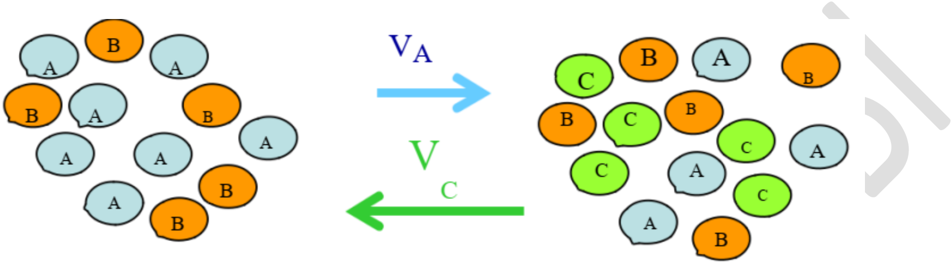


Figure II.1: Schematic representation of molecular diffusion.

Molecular diffusion is a spontaneous movement of molecules (atoms or ions) from regions where their concentration is high to areas where it is lower, or even zero.

Under the influence of the concentration difference (driving force), mass transfer occurs until the concentrations (of species A, B and C) become homogeneous again, that is, equal in both regions. The transfer then ceases.

IV.5.1. Fick's First Law:

For the calculation of a diffusive flux, assume that the diffusion of matter results solely from a concentration gradient. In reality, diffusion can also result from a temperature gradient, a pressure gradient, or an external force. However, in most cases, these effects are negligible, and the dominant driving force is the concentration gradient.

IV.5.2. Fick's diffusion law for a mixture:

Fick's equation is the law that governs molecular diffusion when it is caused solely by a concentration gradient. General formula - vector representation (flux along the 3 spatial directions):

$$\vec{J}_A = -D_{AM}\,\overrightarrow{grad}(\rho_A)$$

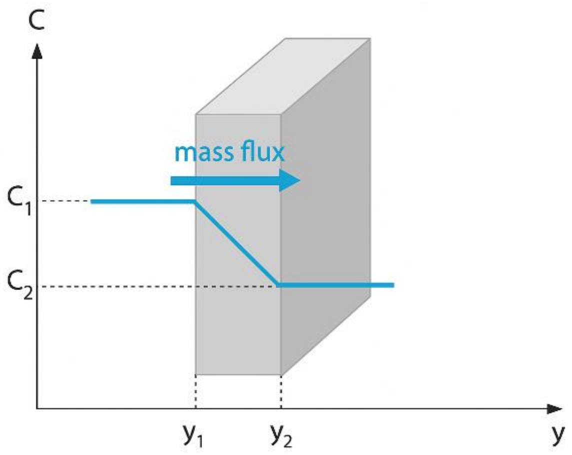
$$\vec{J}^*_A = -D_{AM}\,\overrightarrow{grad}(c_A)$$

If c and ρare constants:

$$J_A = \rho_A \times V'_A = -\rho D_{AM}\,grad(\varpi_A)$$

$$J^*_A = \rho_A \times V^{*'}_A = -cD_{AM}\,grad(X_A)$$

IV.5.2. Fick's diffusion law for a mixture: Formula for a unidirectional flux (here along the y-axis):



$$J_A = -D_{AM}\frac{d\rho_A}{dy} = -D_{AM}\frac{\Delta\rho_A}{\Delta y}$$

$$J^*_A = -D_{AM}\frac{dc_A}{dy} = -D_{AM}\frac{\Delta c_A}{\Delta y}$$

J_A : J^*_A : Diffusion flux of A (kg.m $^{-2.}$ s $^{-1}$ or mol.m $^{-2}$ .s $^{-1)}$

D_{AM} : Diffusion coefficient (diffusivity) of A in mixture M (m².s⁻¹)

IV.5.3. Diffusion coefficient D_{AB} :

✓The diffusion coefficient is defined for a compound in a medium: D_{AM} is the diffusion coefficient of compound A in medium M.

- **It depends on pressure and temperature:** Diffusion coefficients can be found in the literature or calculated using correlations.

Typical values of D_{AB} :

- A and B gas: 20°C: $D_{\mathbf{AB}} = 1$ to $2 \times 10^{-5}\ m^2/s$; (higher values if A or B = H_2)
- Liquids A and B: 20°C: $D_{AB} = 0.2$ to $2 \times 10^{-9}\ m^2/s$
- Gas in solid: 20°C: $D_{AB} = 10^{-12}$ to $10^{-14}\ m^2/s$ increases greatly with T
- Solid in solid: 20°C: $D_{AB} = 10^{-34}$ to $10^{-19}\ m^2/s$ increases significantly with temperature

IV.5.4.Fick's Second Law:

second **law** describes how the **concentration of a diffusing constituent changes over time** in a medium. It is used when the concentration **changes over time** , unlike Fick's first law (which only applies to the steady state).

General form of Fick's second law

one-dimensional diffusion (along the x-axis):

$$\frac{\partial c}{\partial x} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x} \right)$$

For the case where the diffusion coefficient is constant:

$$\frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2}$$

Or :

- C(x,t): concentration of the diffusant (mol/m³)
- t : time (s)
- D : diffusion coefficient (m²/s)
- X: Broadcasting Directorate

IV.6. Origin: combination of the 1st law + mass balance:

The first law:

$$\mathbf{J} = -\mathbf{D}\frac{\partial \mathbf{c}}{\partial \mathbf{x}}$$

Mass balance in an elementary volume:

$$\frac{\partial \mathbf{c}}{\partial \mathbf{t}} = -\mathbf{D}\frac{\partial \mathbf{J}}{\partial \mathbf{x}}$$

$$\frac{\partial \mathbf{c}}{\partial \mathbf{x}} = \frac{\partial}{\partial \mathbf{x}}\left(\mathbf{D}\frac{\partial \mathbf{c}}{\partial \mathbf{x}}\right)$$

IV.7. Special cases:

✓ Diffusion in a semi-infinite solid:

If the surface is suddenly brought to a concentration of Cs:

$$\mathbf{c}(\mathbf{x},\mathbf{t}) = \mathbf{c}_s\,\mathrm{e}\mathbf{rfc}\left(\frac{\mathbf{x}}{2\sqrt{\mathbf{Dt}}}\right)$$

Widely used in metallurgy and diffusion in membranes.

✓ Diffusion through a flat membrane of length L:

$$\frac{\partial \mathbf{c}}{\partial \mathbf{x}} = \frac{\partial}{\partial \mathbf{x}}\left(\mathbf{D}\frac{\partial \mathbf{c}}{\partial \mathbf{x}}\right)$$

Subject to conditions:

- $C(0,t)=C_1$

- C(L, t) = C $_2$
- **Meaning of the diffusion coefficient D:**

✓ Larger **D** → rapid diffusion

✓ Depends on temperature (Arrhenius law)

$$\mathbf{D} = \mathbf{D}_0 \exp\left(-\frac{\mathbf{E_a}}{\mathbf{RT}}\right)$$

Total flux = diffusion + convection

$$\vec{\mathbf{N}}_A = \vec{\mathbf{J}}_A^* + \vec{\mathbf{T}}_A^* = \vec{\mathbf{J}}_A^* + \mathbf{X}_A \sum_i \mathbf{N}_i$$

Diffusive flux of A:

$$\vec{\mathbf{J}}_A^* = -\mathbf{D}_{AB} \frac{\Delta \mathbf{c}_A}{\Delta \mathbf{y}}$$

Convective flux from A : $\vec{\mathbf{T}}_A^* = \mathbf{c}_A \vec{\mathbf{V}}^{*'}$

Thus, the total mass flux is written as:

$$\mathbf{n}_A = \mathbf{J}_A + \mathbf{T}_A = \mathbf{J}_A + \varpi_A \sum_i \mathbf{n}_i$$

IV.8. Generalized mass balance equation:

The objective of mass balance is to **describe the evolution of the concentration of a species A** in a mixture, **as a function of time and position in space.**

In other words, we are trying to **determine the concentration profile.**

1. Principle of mass balance on a volume element

We consider a small elementary volume:

dv=Δx Δy Δz

The principle of conservation of mass is applied to this volume:

$$\text{Entrées} - \text{Sorties} \pm \text{Production par réaction} + \text{Accumulation} = 0$$

This leads to the general equation:

$$\mathbf{div}\left(\vec{\mathbf{N}}_{\mathbf{A}}\right) \pm \mathbf{r}_{\mathbf{A}} + \frac{\partial \mathbf{c}_{\mathbf{A}}}{\partial \mathbf{t}} = 0$$

Or:

- $\vec{\mathbf{N}}_{\mathrm{A}}$: total molar flux of species A (mol·m^{-2}·s^{-1})
- $\mathbf{r}_{\mathbf{A}}$: rate of production or consumption due to a reaction (mol·m^{-3}·s^{-1})
- c_{A} : concentration of A (mol·m^{-3})

- **Case without reaction and in steady state:** If:

- There is no **chemical reaction** → $\mathbf{r}_{\mathbf{A}} = 0$
- The state is **stationary** → $\frac{\partial \mathbf{c}_{\mathbf{A}}}{\partial \mathbf{t}} = 0$

Then the equation simplifies:

$$\mathbf{div}\left(\vec{\mathbf{N}}_{\mathrm{A}}\right) = 0 \Rightarrow \frac{\partial \mathbf{N}_{\mathbf{Ax}}}{\partial \mathbf{x}} + \frac{\partial \mathbf{N}_{\mathbf{Ay}}}{\partial \mathbf{y}} + \frac{\partial \mathbf{N}_{\mathbf{Az}}}{\partial \mathbf{z}} = 0$$

This is the general balance equation for diffusion

IV.9. Typical problem: diffusion in a binary mixture A–B:

We generally seek to calculate **the concentration profile of A,** in a binary medium consisting of A and B.

a) Equimolar diffusion (stationary medium):

Assumption:

NA+NB= 0

The flows balance out → the mixture does not move globally.

This case often corresponds to reactions where stoichiometries compensate for fluxes.

b) Diffusion of A in a stagnant (inert) gas B:

Assumption:

$N_B = 0$

A diffuses in a medium where B is totally immobile. This is the classic case of membranes, gas films, boundary layers, etc.

IV.10. Problem: Stationary diffusion in a binary medium AB:

Objective: To find the concentration profile of A in a mixture AB

Hypotheses:

- **a)** Steady state: $\frac{\partial}{\partial t} = 0$
- **b)** Unidirectional diffusion: $N_A = 0$ and $N_B = 0$
- **c)** Medium at constant total pressure, temperature and concentration: P=cts, c=cts and T = cts
- **d)** Constant diffusion coefficient : $D_{AB} = cst$
- **e)** No chemical reaction.

Case 1: Equimolar diffusion (stationary medium): NA + NB = 0, the mixture does not move, there is no convection, only diffusion

Equation of the total flux: for space A:

$$N_A = J_A^* + x_A \sum_i N_i$$

As :

$$\sum_i N_i = N_A + N_B = 0$$

The second part disappears, therefore:

$$N_A = J_A^*$$

Or :

$$J_A^* = -cD_{AB}\frac{dy_A}{dz}$$

So:

$$N_A = -cD_{AB}\frac{dy_A}{dz}$$

Special cases: Stationary diffusion:

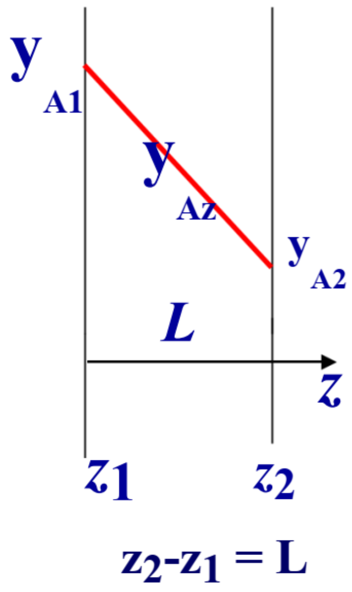
$$N_A\,dz = -cD_{AB}\,dy_A$$

$$\int_{z_1}^{z_2} N_A\,dz = -cD_{AB}\int_{y_{A1}}^{y_{A2}} dy_A$$

$$\int_{z_1}^{z_2} N_A\,dz = -cD_{AB}\int_{y_{A1}}^{y_{A2}} dy_A$$

$$N_A = -cD_{AB}\frac{y_{A2}-y_{A1}}{L}$$

$$y_A(z) = y_{A1} + \frac{y_{A2}-y_{A1}}{L}(z-z_1)$$



Exercises:

1- Consider a binary mixture composed of particles A and B in motion such that:

xA = 1/6; V* = 12 cm/s; VA - V* = 3 cm/s; MA = 5MB. Calculate:

VB; VB - V*; V; VA - V; VB - V