CHAPTER 2: Stationary and quasi-stationary one-dimensional scattering

1. Introduction

The study of the transport of matter in any medium requires the understanding of the mechanisms allowing the description of matter transfer. Writing the material balance is the first step in this understanding. The resolution of differential equations from the material balance firstly allow the calculation of equipment.

2. Material balance-Continuity equation

In the previous chapter, we gave several definitions of mass flow. For simplicity, we will use the molar flux relative to a fixed reference Ni for a binary mixture. We will take the Z direction as a reference, thus:

$$N_{AZ} = -CD_{AB}\frac{dx_A}{dz} + y_A(N_{AZ} + N_{BZ})$$

Combined flow = Molecular flow + convective flow

This equation describes the diffusion of element A governed by the diffusion molecular and convective and can be solved by reasoning methods physical or chemical.

3. Reminders on gradient operators and divergence of a vector

We give the following expressions for the mathematical operators gradient and divergence in scalar coordinates in three-dimensional space. All these operators are constructed from the fundamental operator Nabla: $\vec{\nabla}$

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Gradient : $\vec{\nabla} f = \begin{bmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{bmatrix}$

The divergence operator is a linear differential operator of degree 1.

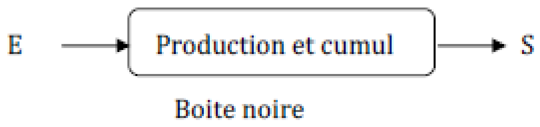
In Cartesian coordinates, the divergence of a vector field $\vec{A} = \begin{bmatrix} A_x \\ A_y \\ A_z \end{bmatrix}$

for expression:

$$\text{Divergence : } \vec{\nabla} A = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}$$

4. Balance of the total mass on an element of fixed volume

Consider a black box which represents industrial chemistry equipment. THE total mass balance on a volume element of this equipment considers that the mass total mass entering is equal to the total mass exiting this volume element. Given that chemical equipment involves chemical reactions that are responsible of the production or consumption of a chemical species in the volume considered but also from an accumulation of the latter in the same volume element, we have the material balance following total:



Output = Input – Cumulative + Production

From the moment the material balance has been established, it can be developed to obtain a continuity equation which reflects the principle of conservation of mass.

The continuity equation can be presented in several forms, the most commonly used is of the following form:

$$(\nabla \rho v) + \frac{\partial \rho}{\partial t} = 0$$

5. Balance of the mass of a constituent i on an element of fixed volume

Consider an elementary volume of dimensions Δx, Δy, Δz, figure 3.1. In applying the material balance for constituent A we can define the mass flow rates entering and leaving this volume element through its different faces:

Mass flow of A in the x direction:

- position x (input): (nAx)x Δy Δz, which corresponds to: MA (NAx)x Δy Δz.

- position x + Δx (output): (nAx)x+Δx Δy Δz, which corresponds to: MA (NAx) x+Δx Δy Δz.

With MA the molecular mass of element A and (NAx) is the flow in the x direction and (NAx)x

its value at point x.

Mass flow of A in the y direction:

- position y (input): (nAy)y Δx Δz, which corresponds to: MA (NAy)y Δx Δz.

- position y + Δy (output): (nAy)y+Δy Δx Δz, which corresponds to: MA (NAy) y+Δy Δx Δz.

Mass flow rate of A in z direction:

- position z (input): (nAz)z Δx Δy, which corresponds to: MA (NAz)z Δx Δy.

- position z + Δz (output): (nAz)z+Δz Δx Δy, which corresponds to: MA (NAz)z+Δz Δx Δy.

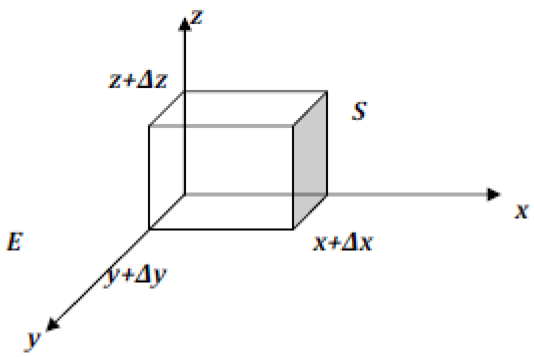


Figure 3.1. Volume element of dimensions Δx, Δy, Δz.

Thus, the mass flow of element A entering the volume element through the three faces is:

(nAx)x Δy Δz + (nAy)y Δx Δz + (nAz)z Δx Δy.

The mass flow of element A exiting the volume element through the three east faces:

(nAx)x+Δx Δy Δz + (nAy)y+Δyz Δx Δz + (nAz)z+Δz Δx Δy.

Given that the total mass of A in this volume is ρA Δx Δy Δz, the expression for

accumulation flow will be written as follows:

$$\frac{\partial \rho_A}{\partial t} \Delta x \, \Delta y \, \Delta z$$

The production of A in the volume element Δx Δy Δz can be done by reaction chemical, this can then take place according to two different mechanisms:

a) Homogeneous reaction where the reaction rate can be written as follows:

$$R_A = K_n(C_A)^n$$

b) Heterogeneous reaction where the speed of the reaction on the surface of the catalyst can be expressed by a relation of the form:

$$N_{AZ\,/\,surface} = K''_n\,(C_A)^n{}_{/\,surface}$$

With in both cases:
RA: reaction rate (moles.cm-3.s-1),
K: reaction constant (s-1, if the reaction is of order 1),
CA: concentration of A (mol.cm-3),
n: exponent indicating the order of the reaction,
NAz: Combined molar flux (moles.cm-2.s-1),
K"n: Reaction constant based on reaction surface.
Let us take the case where A is produced by homogeneous chemical reaction at a rate of
reaction RA then the production rate of A is:

MA RA Δx Δy Δz

The material balance of A in this elementary volume is:

$$[(n_{Ax})_{x+\Delta x}\,\Delta y\,\Delta z - (n_{Ax})_x\,\Delta y\,\Delta z + (n_{Ay})_{y+\Delta yz} - (n_{Ay})_y\,\Delta x\,\Delta z + (n_{Az})_{z+\Delta z}\,\Delta x\,\Delta y - (n_{Az})_z\,\Delta x\,\Delta y] + \frac{\partial \rho_A}{\partial t}\,\Delta x\,\Delta y\,\Delta z = M_A\,R_A\,\Delta x\,\Delta y\,\Delta z$$

By dividing by (Δx Δy Δz) and taking the limit when the three dimensions tend towards zero, we obtain:

$$\left[\frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z}\right] + \frac{\partial \rho_A}{\partial t} = M_A R_A$$

$$(\nabla n_A) + \frac{\partial \rho_A}{\partial t} = M_A R_A$$

Dividing the equation by MA, we find

$$(\nabla N_A) + \frac{\partial C_A}{\partial t} = R_A$$

6. Boundary conditions and initial conditions

In order to solve the continuity equations, surface concentration or flow surface mass must be specified. In this case the boundary conditions can be of one of the following forms:

·NAZ = NA0.
• NAZ / NBZ is given.
• NBZ = 0 (B not diffusing).

7. Diffusive transfer in steady state

In steady state, the concentrations of species A and B do not depend on the time. Thus, the production and accumulation terms are zero. Equation becomes:

$$\left[\frac{\partial n_{Ax}}{\partial x}+\frac{\partial n_{Ay}}{\partial y}+\frac{\partial n_{Az}}{\partial z}\right]=0 \qquad \text{ou} \qquad \nabla n_A = 0$$

And the equation becomes

$$\left[\frac{\partial N_{Ax}}{\partial x}+\frac{\partial N_{Ay}}{\partial y}+\frac{\partial N_{Az}}{\partial z}\right]=0 \qquad \text{ou} \qquad \nabla N_A = 0$$

By replacing with the Fick equation; equation (3.1), assuming that A is a solute which diffuses through B while B is stationary then $N_{Bz} = 0$, we obtain

$$N_{AZ} = -D_{AB}\nabla C_A$$

It is common to assume that the total concentration is constant and that the fraction molar; xA is very small, so the global flux term is eliminated from the Fick equation. For diffusion along a single dimension (unidirectional) the expression of the flow molar as a function of distance, for different geometries, is given as follows:

a) For a plane wall of thickness z2 - z1;

$$N_{AZ} = -D_{AB}\frac{C_{A2}-C_{A1}}{z_2 - z_1}$$

b) For a hollow cylinder of inner radius r1 and outer radius r2 and a length L with a diffusion in the radial direction:

$$N_{Ar} = -2\pi\ LD_{AB}\frac{C_{A2}-C_{A1}}{\ln(r_2/r_1)}$$

c) For a hollow sphere of interior radius r1 and exterior r2 with diffusion in the radial direction;

$$N_{Ar} = -4\pi\ r_1\ r_2 D_{AB}\frac{C_{A2}-C_{A1}}{r_2\ - r_1}$$

For the study of the phenomenon of transport of matter for a binary mixture (A,B) we proceed as follows:

• Specification of the problem,
• Make assumptions and explain mathematical simplifications using in relation to the assumptions made,
• Write the continuity equation,
• Simplify the continuity equation using the assumptions made,
• We therefore obtain the flow of the species in consideration as a function of concentration gradient,
• Replace the flux by the expression (concentration gradient) in the equation of continuity,
• Solve the differential equation,
• Use the boundary conditions for the integration constants,
• Obtain the model representing the variation of the concentration or its distribution in depending on the direction considered.

The two simple problems to study are:
- The diffusion of an element A through another immobile element B,
- Equimolar counter diffusion.

7.1. Diffusion of a gas through a stagnant gas film

In the figure below is described the phenomenon of diffusion of a compound A to through another immobile element B.

In summary, let us be a vertical tube of small diameter which contains a liquid A of which the interface corresponds to the height z = z1. Liquid A begins to evaporate in the portion of the tube in which a gas B is contained. A current of gas B is sent to prevent gas A from moving and therefore displacing gas B outwards. The gas B is therefore kept in the tube all the time and behaves as if it is immobile. On the other hand, the gas B is sent to release A at its exit, consequently the concentration of A at the outlet is zero.

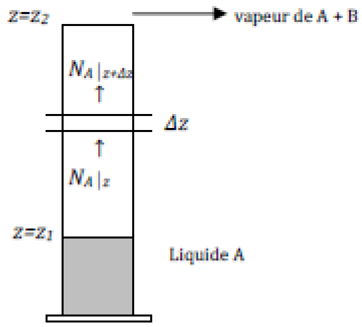


Figure 3.2. Schematic representation of the diffusion of A through immobile B

Assumptions

a) B stationary

b) Steady state CA does not depend on time,

c) A single z direction,

d) No chemical reaction,

e) CA at the tube outlet, that is to say at z = z2 is zero,

f) Element B is not absorbed by the liquid; the mole fraction of B in the liquid is nothing.

g) Concentration of element A at the interface z = z1,

$P_t\, y_A = P'_A\, x_A$, thus $x_A = 1/\, y_A = P'_A / P_t$.

With :

P'_A: vapor pressure of element A.

y_A: mole fraction of A at z = z2.

x_A: mole fraction of A at the interface.

Simplifications

a') B being immobile, therefore $N_{BZ} = 0$.

b') C_A = constant; therefore $\frac{\partial cA}{\partial t} = 0$

c') NAx = NAy = 0 (no flow in the x and y directions).

d') RA = 0; no chemical reaction.

After simplifying the continuity equation we obtain:

$$\frac{\partial N}{\partial Z}=0 \text{ so } N_{AZ}= \text{constant}$$

By appealing to Fick's law; equation

$$N_{A_z} = -CD_{AB}\frac{dy_A}{dz} + y_A(N_{AZ} + N_{BZ})$$

With NBz = 0, we have $N_{A_z} = -CD_{AB}\frac{dy_A}{dz} + y_A N_{AZ}$

We find :

$$N_{A_z} = \frac{-CD_{AB}}{(1-y_A)}\frac{dy_A}{dz}$$

We replace N_{Az} by its value in:

$$\frac{dN_{A_z}}{dz} = 0$$

$$\frac{d}{dz}\left[\frac{-CD_{AB}}{(1-y_A)}\frac{dy_A}{dz}\right] = 0$$

We arrive at a second degree differential equation. The concentration C is constant because the temperature and pressure are constant. We integrate a first once then a second time:

First integration

$$\left[\frac{-CD_{AB}}{(1-y_A)}\frac{dy_A}{dz}\right] = L \Rightarrow \frac{CD_{AB}}{(1-y_A)}\frac{dy_A}{dz} = -L$$

$$\frac{1}{(1-y_A)}\frac{dy_A}{dz} = \frac{-L}{CD_{AB}} = k_1$$

Second integration:

$$-\ln(1-y_A) = k_1 z + k_2$$

Conditions to the limits :

$$\begin{cases} \text{à } z = z_1,\ y_A = P'_A / P_t = y_{A1} \\ \text{à } z = z_2,\ y_A = y_{A2} = 0 \end{cases} \qquad \begin{cases} -\ln(1-y_{A1}) = k_1 z_1 + k_2 & (*) \\ -\ln(1-y_{A2}) = k_1 z_2 + k_2 & (**) \end{cases}$$

It remains to find the value of the constants k1 and k2.

Subtracting equations (*) and (**) gives:

$$\ln(1-y_{A2}) - \ln(1-y_{A1}) = k_1(z_1 - z_2) \qquad \text{ainsi, } \begin{cases} k_1 = \dfrac{1}{(z_1 - z_2)} \ln\left(\dfrac{1-y_{A2}}{1-y_{A1}}\right) \\ k_2 = -\ln(1-y_{A1}) - k_1 z_1 \end{cases}$$

$$k_2 = -\ln(1-y_{A1}) - \frac{z_1}{(z_1 - z_2)} \ln\left(\frac{1-y_{A2}}{1-y_{A1}}\right)$$

$$k_2 = \frac{z_2 \ln(1-y_{A1}) - z_1 \ln(1-y_{A2})}{(z_1 - z_2)}$$

From the equation resulting from the second integration

$$-\ln(1-y_A) = k_1 z + k_2,$$

We replace k1 and k2 by their value and we find after some rearrangements

$$\frac{1-y_A}{1-y_{A1}} = \left(\frac{1-y_{A2}}{1-y_{A1}}\right)^{\frac{z-z_1}{(z_2-z_1)}}$$

7.2. Equimolar diffusion

Or two balloons connected by a tube blocked in the middle by a tap; Figure 3.4. Balloon A contains gas A and balloon B contains gas B. If at any point given, we remove the cap which separates the two gases A and B, there will be a mixture between A and B which, over time, will become uniform. However, if the same number of A's and B's move towards each other, i.e. opposite directions, we conclude that this is the phenomenon of equimolar counter-diffusion. In in other words, the flow of B is equal to that of A in absolute value.

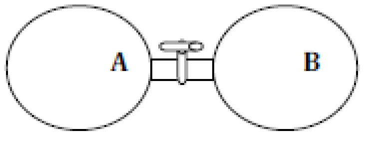


Figure 3.4. Descriptive diagram of equimolar counter diffusion.

Assumptions

a) Against equimolar diffusion.

b) No chemical reaction between A and B.

c) A single direction of diffusion (z).

d) Stable state (i.e. the study is not carried out when the tap is opened).

Simplifications

a') $N_A = - N_B$

b') $R_A = 0$

c') $N_{Ax} = N_{Ay} = 0$

$d')\ \frac{\partial C_A}{\partial t} = 0$

The continuity equation in this case will be simplified as follows:

$$\frac{\partial C_A}{\partial t} + \frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} = R_A$$

$$\frac{\partial N_{Az}}{\partial z} = 0$$

So

N_{AZ} = constant

By appealing to Fick's law;

$$N_{AZ} = -D_{AB} \nabla C_A + y_A (N_{AZ} + N_{Bz})$$

Who becomes

$$N_{AZ} = -D_{AB} \frac{dC_A}{dz} + y_A (N_{AZ} + N_{Bz})$$

Because the diffusion takes place in only one direction. By replacing with the simplification a'), we obtain :

$$N_{AZ} = -N_{BZ} \Rightarrow N_{AZ} + N_{BZ} = 0$$

We obtain:

$$N_{AZ} = -D_{AB} \frac{dC_A}{dz}$$

This is the molar flux of element A as a function of concentration. we replace N_{AZ}

by its value in:

$$\frac{dN_{Az}}{dz} = 0$$

We obtain

$$\frac{d}{dz}\left[-D_{AB}\frac{dC_A}{dz}\right] = 0$$

It is a second degree differential equation of CA that we will have to integrate.

After a first integration:

$$\left[-D_{AB}\frac{dC_A}{dz}\right] = L \Rightarrow \frac{dC_A}{dz} = -\frac{L}{D_{AB}} = cons\tan te = K_1$$

And a second integration we obtain:

$$C_A = K_1 Z + K_2$$

This expression shows that the CA concentration varies linearly with z. We evaluate the integration constants K1 and K2 knowing the boundary conditions:

$$\begin{cases} \text{à } z = z_1 \text{ on a } C_A = C_{A1} \\ \text{à } z = z_2 \text{ on a } C_A = C_{A2} \end{cases}$$

After replacement, we find:

$$C_A = \frac{C_{A1} - C_{A2}}{z_1 - z_2} z + \frac{C_{A2} z_1 - C_{A1} z_2}{(z_1 - z_2)}$$

By rearranging, it results

$$\frac{C_A - C_{A1}}{C_{A1} - C_{A2}} z + \frac{z - z_1}{(z_1 - z_2)}$$