CHAPTER 1: Matter transfer mechanism

1.Introduction

In an immobile, homogeneous and balanced system the concentration of the different constituents is the same in every respect. The same is true of temperature and pressure. If one of these factors is varied, the system is no longer in balance and it produces within the system a phenomenon called transfer which tends to reestablish the balance.

2. Diffusive transfer

If there is a difference in concentration in space, for example between two compartments separated by a permeable membrane (allowing the solvent and the solute); there will be, over time, a movement of matter, of the compartment concentrated towards the least concentrated, figure 1.1. This transfer takes place until balance in concentration is achieved. This spontaneous phenomenon is called diffusion.

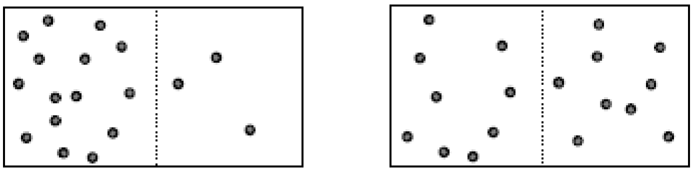


Figure 1.1. Diffusion from the most concentrated medium to the least concentrated medium

If we consider a plane normal to the direction of the concentration gradient of a any reactant A, or any other plane, there exists a flow of molecules A through this plan.

The movement of the chemical element, from the region of high concentration towards the low concentration region, can be observed by putting a piece of KMnO4 (potassium permanganate) in water. The KMnO4 begins to dissolve in water and near the crystal we see a dark blue color which becomes light as we move away from the crystal.

2.1. Fick's law

If you place a small amount of a volatile liquid at the bottom of a test tube and leaves in contact with a current of dry air, as illustrated in figure 1.2, a profile of Linear concentration is established in the test tube at steady state when time tends towards infinity and a continuous evaporation of the liquid will take place. This phenomenon, according to which, a transfer of matter is caused by a non-uniform distribution of the concentration is called diffusion.

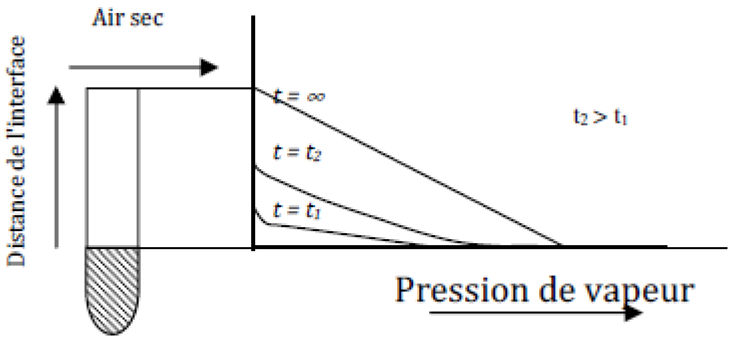


Figure 1.2. Diffusion of a vapor in a gas

Diffusion can be described by the following empirical law

$$J_{Ay} = -CD_{AB}\frac{dx_A}{dy} \qquad J_{Ay} = -D_{AB}\frac{dC_A}{dy} \qquad (1.1)$$

The index A designates the chemical species which diffuses while y indicates the direction in which the transport takes place. In this case, JAy is defined as the molar flux of species A relative to average speed, DAB; the diffusion coefficient, C; there total concentration, xA; the mole fraction of species A, CA; the molar concentration of A. This equation can be expressed either using the mole fraction or the fraction mass as follows:

$$j_{Ay} = -\rho D_{AB}\frac{d\omega_A}{dy} \qquad j_{Ay} = -D_{AB}\frac{d\rho_A}{dy} \qquad (1.2)$$

jAy is defined as the mass flow relative to the average speed, r; there total mass concentration, ωA and rA; mass fraction and mass concentration of species A, respectively.

This is **the first Fick's law of diffusion** (1855) in one dimension. It is valid for any solid, liquid or gas mixture.

2.2. Definition of molecular diffusion

Molecular diffusion is so called because it results from the thermal agitation of molecules and is carried out at the molecular scale. The kinetics of the phenomenon is quantified by diffusivity which is also called the diffusion coefficient D.

Consider a fairly thin glass plate of surface area S and thickness Y. Suppose that initially (for t<0), the two horizontal faces of the plate are in contact with air, which is assumed to be completely insoluble in glass. At time (t = 0), the air below the plate is suddenly replaced by pure helium, which on the other hand is very soluble in glass. The helium gently penetrates the glass by virtue of its molecular movement and ultimately appears on the other side above the plate of glass. This transport of a molecule relative to another substance is diffusion molecular. Since the air above is quickly replaced, there will be no accumulation of helium molecules on this face, Figure 1.3.

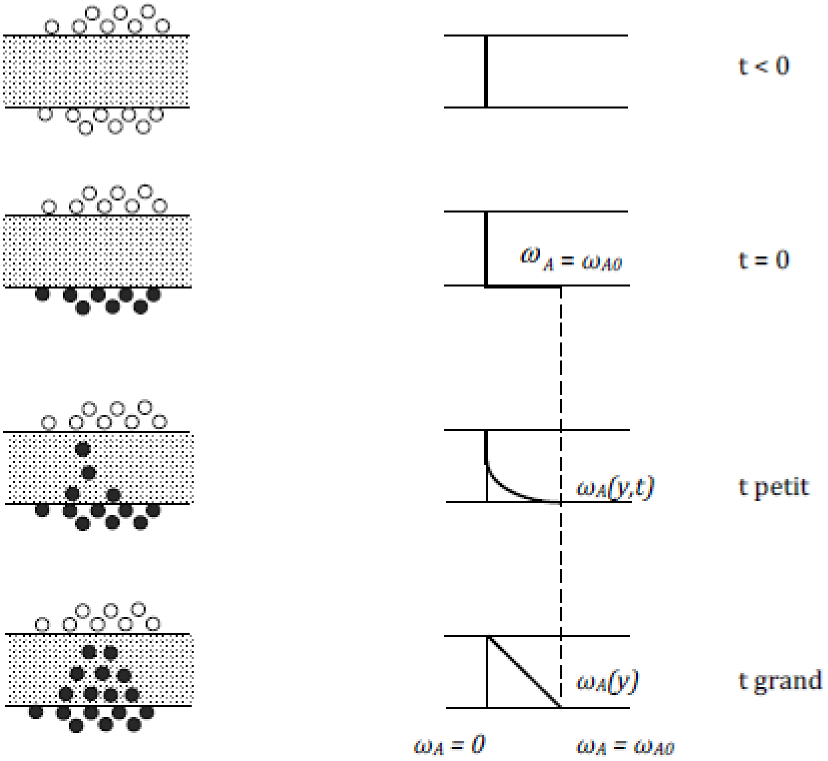


Figure 1.3. Progression of helium diffusion (A) through glass (B) and profile of Concentration

In this system, helium will be called species A and glass species B. The concentrations will be given by the mass fractions ωA and ωB. We say that there is a concentration gradient of helium in the y direction.

For a time t < 0, ωA is everywhere equal to zero.

For a time t > 0, at the level of the lower face, y = 0, the mass fraction of

helium is equal to ωA0.

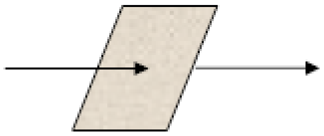
As time progresses, the mass fraction profile develops with ωA0

at the lower level of the plate and ωA = 0 at the upper level thereof. As shown in Figure 1.3, the concentration profile tends towards a straight line when the weather gets big.

2.3. Concepts of material flow density

The transport of matter is quantified by a flow of matter (or more precisely a

matter flux density), J, which represents the mass (or number of moles) that passes to across a unit area (perpendicular to the direction of transport) per unit of time. Its unit is (kg.m-2.s-1 or mol.m-2.s-1), figure 1.4.



J : densité de flux de matière (nombre de kg ou mol transféré à travers la surface par unité de temps et de surface)

Figure 1.4. Descriptive diagram of the diffusion flow through a plane.

2.4. Definition of molar and mass average velocities

a) The average mass speed

In a diffusion mixture the elements are moving at speeds

different. Assuming that vi is the speed of element i relative to a fixed reference. We

defines **the average mass velocity** v for a mixture of n constituents as follows:

$$v = \sum_i (\rho_i v_i) / \sum_i \rho_i \qquad (1.3)$$

$$v = \frac{1}{\rho} \sum_i (\rho_i v_i) \qquad (1.4)$$

ρv is the mass flow rate that passes through a unit area placed perpendicular to the speed v.

b) The average molar speed

Similarly, we could define the average molar speed as follows

$$v^* = \sum_i (c_i v_i) / \sum_i c_i \qquad (1.5)$$

cv is the flow rate of moles passing through a unit area perpendicular to the speed v*.

c) Flows

The mass flux (molar) of element i represents the mass (number of moles) of

the element i which passes for a unit of time through a surface perpendicular to the

broadcast direction).

Noticed

When it comes to material transport, three types of flow rates are defined:

Volumetric flow rate is volume per unit time; [L s-1].

Molar flow rate is the number of moles per unit time; [mol s-1].

Mass flow rate is the number of grams per unit time; [kg s-1].

3. Convective transfer

In addition to transport by molecular motion, matter can also be transported by the mass movement of the fluid.

A typical example of the contribution of convection in the transfer of matter in process engineering is the case of distillation. In the binary distillation operation, for example, condensation of vapor mixtures and evaporation of solutions volatiles is always accompanied by an interfacial speed, due to the condensation of vapors or evaporation of liquids. Although the transfer of matter in such cases is considerably affected by the convective mass flow, this effect has long been neglected by engineers.

4. Combined transfer: diffusion + convection

Consider a binary mixture where the molecules move by molecular diffusion: it results, for each constituent, a mass flux, i.e. NA and NB (mole/cm² s). If cA and cB are the molar concentrations (mole/cm3) of A and B, respectively, we can define for each constituent a speed v such that:

In addition to the transport of matter by virtue of the movement of molecules, matter can also be transported by the movement of the fluid. Consider a binary mixture where the molecules move by molecular diffusion: it results, for each constituent, a mass flux, i.e. NA and NB (mole/cm² s). If cA and cB are the molar concentrations (mole/cm3) of A and B, respectively, we can define for each constituent a speed such that:

$$N_A = c_A v_A \qquad N_B = c_B v_B \tag{1.6}$$

Diffusion is accompanied by movement of the fluid even in the absence of anything pressure/concentration gradient. The average molar speed can be written for a binary system:

$$v_* = x_A v_A + x_B v_B = 1/C\,(N_A + N_B) \tag{1.7}$$

xA and xB are the mole fractions of A and B. C is the total molar concentration

$$C = c_A + c_B \tag{1.8}$$

We know that if a solution whose concentration of its constituents is everywhere uniform, no change takes place, but as long as there is no uniformity, the solution is spontaneously brought back to uniformity by diffusion.

Thus the rate of movement of the solute from one point to another must depend on the concentration gradient over this distance.

Since

$$J_A^* = c_A(v_A - v^*) \tag{1.9}$$

$$J_A^* = c_A v_A - c_A\left(\frac{c_A v_A + c_B v_B}{c}\right) \tag{1.10}$$

$$J_A^* = N_A - x_A(N_A + N_B) \tag{1.11}$$

$$N_A = J_A^* + x_A(N_A + N_B) \tag{1.12}$$

$$N_A = -D_{AB}\nabla C_A + x_A(N_A + N_B) \tag{1.13}$$

This equation shows that the flow NA, relative to a fixed reference, is the result of two vectors:

For element B we have:

$$N_B = -D_{BA}\nabla C_B + x_B(N_A + N_B) \tag{1.14}$$

The sum NA and NB gives:

$$-D_{AB}\nabla C_A - D_{BA}\nabla C_B = 0 \tag{1.15}$$

$$J_A^* + J_B^* = 0 \tag{1.16}$$

5. Conclusion

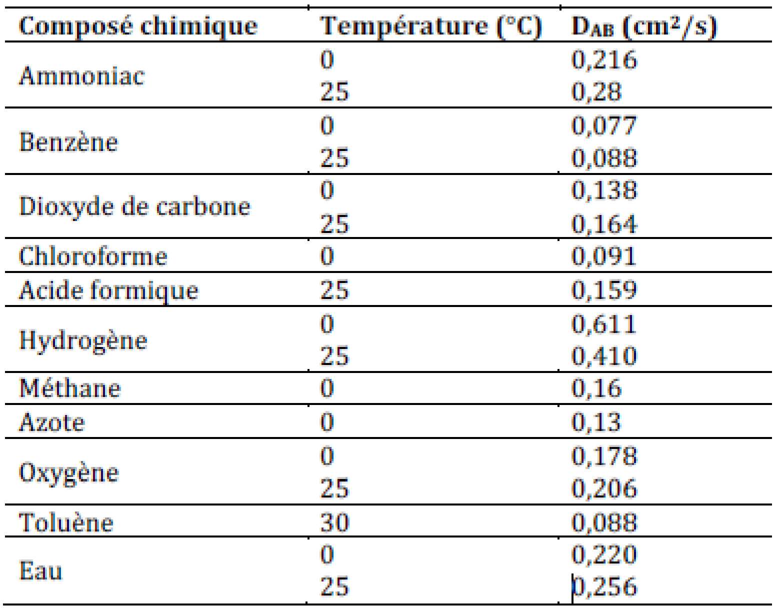
Fick's law is the main equation that is related to the transport of matter from one environment to another. It can be written in several forms.

6. Estimation of diffusion coefficients

The diffusion coefficient can be determined using equipment more or less sophisticated. For more details, consult the book in reference [4].

The DAB diffusion coefficient is a property of the system depending on the temperature, pressure and the nature of the constituents. The diffusion coefficient gases at low density is practically independent of concentration, it increases with temperature and is inversely proportional to the total pressure. However for liquids and solids, the diffusion coefficient depends strongly on the concentration. A non-exhaustive list of diffusion coefficients for mixtures binary is given as an example in the table below.

Table.6.1. Air diffusion coefficient of some chemical compounds



Composé chimique	Température (°C)	D_{AB} (cm²/s)
Ammoniac	0 25	0,216 0,28
Benzène	0 25	0,077 0,088
Dioxyde de carbone	0 25	0,138 0,164
Chloroforme	0	0,091
Acide formique	25	0,159
Hydrogène	0 25	0,611 0,410
Méthane	0	0,16
Azote	0	0,13
Oxygène	0 25	0,178 0,206
Toluène	30	0,088
Eau	0 25	0,220 0,256

7. Diffusion coefficients (gas phase, liquid phase)

The values of the diffusion coefficients tabulated in the different references are limited because they generally give the value of the diffusion coefficient at 25 °C of a chemical compound compared to air. Very little data is available on the diffusion coefficient of other gas pairs under other pressure and temperature conditions. Based on this observation, researchers have, for several decades, attempted to estimate the diffusion coefficient from the properties physicochemical studies of compounds in diffusion.

7.1. Gas phase diffusion coefficients

Several methods have been proposed for the estimation of DAB at low pressure for a gaseous binary system. These are generally of the form of equation (2.1) which arise from the kinetic theory of gases.

7.1.1. Chapman-Enskog relationship (1952)

The expression for the diffusion coefficient, also in this case, arises from the kinetic theory of gases. It is given by the Chapman Enskog equation:

$$CD_{AB} = 2{,}2646.10^{-5}\frac{\left(T\left(\frac{1}{M_A}+\frac{1}{M_B}\right)\right)^{0.5}}{\sigma_{AB}^{2}\Omega_{DAB}}$$

With :

D_{AB} [cm² s-1],

M_A, M_B: molar masses [g/mol] of A and B, respectively,

T: thermodynamic temperature [K],

K: Boltzmann constant 1.38 10-23 J K-1,

C: Total concentration of the mixture [mol/cm3],

σ_{AB}: The effective collision diameter (Å) is a factor depending on the structure of the molecule. It is given by the relation below.

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

Ω_{DAB}: It is a dimensionless value which arises from the integral function of collision, it is tabulated as a function of KT/εAB. This value can be obtained from table.A.1.

The value of Ω_{DAB} can also be calculated by approximations analytical such as the relationship of Neufeld et al. (1972):

$$\Omega_{DAB} = \frac{1{,}06036}{(T^*)^{0{,}1561}} + \frac{0{,}193}{\exp(0{,}47635T^*)} + \frac{1{,}03587}{\exp(1{,}52996T^*)} + \frac{1{,}76474}{\exp(3{,}89411T^*)}$$

Where: T* = KT/εAB, with K the Boltzmann constant

$$\varepsilon_{AB} = (\varepsilon_A \varepsilon_B)^{0.5}$$

The Lennard-Jones parameters σAB and εAB can be estimated for the non-polar elements and for molecules which do not react after collision from of table.A.2.

For ideal gases we have: C = P/RT, with R=82.05 cm3.atm/mol.K, and P: pressure total gas [atm]. Equation (2.1) will become:

$$D_{AB} = 0{,}0018583 \frac{\left(T^{3/2}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{0.5}\right)}{P\sigma_{AB}^2 \Omega_{DAB}}$$

This equation is developed for mixtures of diluted gases consisting of non-polar, spherical and monatomic molecules. This equation gives good results over a wide temperature range and predicts approximate values very useful ATMs.

The DAB values estimated from the Chapman equation are, in general, in agreement with the experimental with only 5 to 10% difference. In very few cases, this deviation can be up to 20%.

7.1.2. Relationship of Wilke and Lee (1955)

This relationship is also deduced from the kinetic theory of gases. It is written as following :

$$D_{AB} = \frac{\left[3{,}03 - \left(0{,}98 / M_{AB}^{1/2}\right)\right] 10^{-3} T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^{2} \Omega_{DAB}}$$

The parameter σ_{AB} is given by equation (2.7) where for each component we used :

$$\sigma = 1{,}18\ (V_b)^{1/3}$$

With V_b the molar volume of the liquid at the normal boiling temperature

$$M_{AB} = 2 \frac{M_A M_B}{M_A + M_B}$$

Ω_{DAB} is determined from the equation of Neufeld et al. with;

$$\varepsilon / K = 1{,}15\ T_b$$

T_b is the normal boiling temperature.

This equation cannot be used for helium and hydrogen.

7.1.3. Slattery equation (1958)

At low pressure, an equation is developed to estimate the coefficient of

D_{AB} broadcast, it is denoted Slattery equation.

$$\frac{P D_{AB}}{(P_{CA} P_{CB})^{1/3} (T_{CA} T_{CB})^{5/12} \left(1/M_A + 1/M_B \right)^{1/2}} = a \left[\frac{T}{(T_{CA} T_{CB})^{1/2}} \right]^{b}$$

For non-polar gas pairs a = 2.745.10-4 and b= 1.823. (This equation does not cannot be used for the case of helium and hydrogen).

This equation applies if one of the constituents is water and the other is a non-gas

polar with a =3.64 .10-4 and b= 2.334.

The Slattery equation is in agreement with the experimental results at pressure

atmospheric with an average deviation from experimental data of approximately 8%.

7.1.4. Gilliland equation (1934)

Gilliland developed an empirical equation assuming that the diameters of

collision are proportional to the cubic root of the molar volumes at the temperature

normal boiling.

$$D_{AB} = 0{,}0043\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}\frac{T^{3/2}}{P\left[V_A^{1/3}+V_B^{1/3}\right]^2}$$

With, D_{AB} [m². s-1], P: [atm], T: [K], V: molecular molar volume [m3. mol-1], M_A and M_B: [kg. mol-1].

From this equation we can deduce an approximate equation for the

calculation of the diffusion coefficient at T2 and P2 if the latter is known at T1 and P1:

$$(D_{AB})_{T_2,P_2} = (D_{AB})_{T_1,P_1}\left(\frac{T_2}{T_1}\right)^{3/2}\frac{P_1}{P_2}$$

With: P: [atm], T: [K].

7.1.5. Relationship of Fuller, Schettler and Giddings, known as FSG (1966)

Another empirical approach for estimating the gas diffusion coefficient

in air is called the FSG method. It will be used for pressures up to

10 atm (and even more). It is given by the relationship of Fuller, Schettler and Giddings.

$$D_{AB} = \frac{10^{-3}T^{1{,}75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}}{P\left[V_A^{1/3}+V_B^{1/3}\right]^2}$$

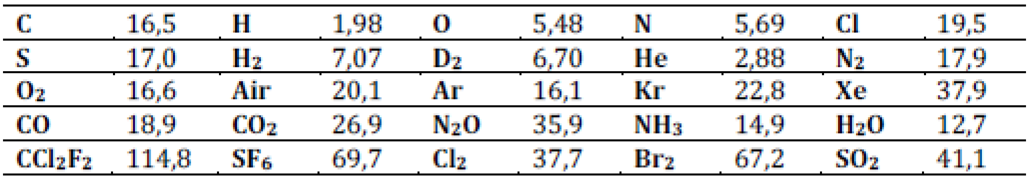
With: D_{AB} [cm². s-1], P: [atm], T: [K].

MA and MB are the molar masses of gas and air, respectively [g.mol-1]. There

molar mass of air being equal to 28.97 g.mol-1. The values of VA and VB are the molar volumes of gas and air (in cm3.mol-1), respectively.

Estimating the molar volume of specific gases would require data on the atomic structure. The following table gives the values of the atomic volumes allowing the molar volume of many organic compounds to be calculated by the sum of the atomic diffusion volumes.

Table.7.2. Atomic diffusion volume and molecular diffusion volume of some compounds



C	16,5	**H**	1,98	**O**	5,48	**N**	5,69	**Cl**	19,5
S	17,0	**H_2**	7,07	**D_2**	6,70	**He**	2,88	**N_2**	17,9
O_2	16,6	**Air**	20,1	**Ar**	16,1	**Kr**	22,8	**Xe**	37,9
CO	18,9	**CO_2**	26,9	**N_2O**	35,9	**NH_3**	14,9	**H_2O**	12,7
CCl_2F_2	114,8	**SF_6**	69,7	**Cl_2**	37,7	**Br_2**	67,2	**SO_2**	41,1

The FSG equation gives a good estimate of the diffusion coefficient and has been developed by minimizing the error between the predicted diffusion coefficient and the measured one for a large number of gases.

This method is more suitable for non-polar gases at low temperatures up to moderate temperatures. In addition, it gives an estimate of the coefficient of diffusion very close to that which is measured with an error of ± 5% for alkanes, ketones and aromatic compounds.

7.1.6. Estimation of the diffusion coefficient of gases at high pressure

At high pressure, DAB no longer varies with the inverse of the pressure, and little

Much information is available about the relationship between DAB and pressure.

However, Takahashi et al. (1974) proposed the following method which is satisfactory

given the limited data available. Its correlation is:

$$\frac{PD_{AB}}{(PD_{AB})_0} = f(P_r, T_r)$$

In other words, the ordinate is the ratio of the product (pressure diffusion) at pressure P and temperature T, by the product (pressure diffusion) at the same temperature but at low pressure. This report is plotted according to of the reduced pressure Pr = P/Pc and the reduced temperature Tr = T/Tc.

In the absence of any other information, it is suggested to estimate DAB to use the figure A.3 if Pc and Tc are known. For a binary mixture, these values are replaced by pseudocritical values

$$P'_c = \sum (x_i P_{ci})$$

$$T'_c = \sum (x_i T_{ci})$$

7.2 Liquid phase diffusion coefficients

The unit of diffusion coefficient in liquids is the same as that of diffusion coefficient in gases. However, the diffusion coefficient in liquids varies appreciably with concentration and its estimation is not as precise as those of gases. The two equations which follow will be used when we have deal with diluted solutions.

7.2.1. Wilke and Chang equation

For dilute solutions, we recommend the Wilke and Chang correlation which is the most used formula:

$$D_{AB} = 7{,}4.10^{-8} \frac{T(\Phi M_B)^{0.5}}{\mu V_A^{0.6}}$$

Where: DAB: diffusion coefficient [cm². s-1], T: [K], MB: molar mass of the solvent [g/mol], V_A: molar volume of the solute at the normal boiling point [mol/cm3], μ: viscosity of the solvent in CPoise (10-3 kg m-1 s-1).

Φ: solvent association factor (unitless).

Wilke and Chang proposed that Φ is 2.6 for water as the solvent; 1.9 for the methanol; 1.5 for ethanol and 1.0 for non-associated solvents such as benzene, ether, heptane.

7.2.2. Stokes–Einstein equation

The theoretical basis for estimating the diffusion coefficient in water is the Stokes –Einstein equation, it is of the following form:

$$D_{AB} = \frac{KT}{6\pi\mu r} \text{ ou } \frac{KT}{f}$$

Where: K: Boltzmann constant (1.38 10-23 kg m² s-2 K-1 or 1.38 10-16 g cm² s-2 K-1),

μ: dynamic viscosity (kg m-1 s-1), r: molecular radius (m), f: Coefficient of friction.

This equation applies well to the diffusion phenomenon in the case of a large number of spherical molecules in small molecular weight solvents. She is also applicable inthe case of suspended molecules. This equation, like that of Wilke and Chang, is limited to solutions infinitely diluted.

Furthermore, the Stokes-Einstein equation is limited to the case where the size of the solute ismuch larger than that of the solvent, the Wilke and Chang correlation is applicable in the case where the solvent and solute have similar sizes.

7.2.3. Diffusion coefficient in concentrated solutions

Correlations were found for the calculation of the diffusion coefficients in the concentrated solutions, they are of the form:

$$D_{AB} = \alpha\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln c_A}\right)$$

Vines Equation:

$$D_{AB} = \left(\left(D_{AB}{}^{0}\right)^{x_A}\left(D_{BA}{}^{0}\right)^{x_B}\right)\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln c_A}\right)$$

With :

xA: mole fraction of A in the mixture (A,B).

xB: mole fraction of B in the mixture (A,B).

$D_{AB}{}^{0}$: diffusion coefficient of A in B at infinite dilution.

$D_{BA}{}^{0}$: diffusion coefficient of B in A at infinite dilution.

γ: activity coefficient.

$(D_{AB}{}^{0})^{x_A}$ and $(D_{BA})^{x_B}$ bis the geometric mean of the diffusion coefficients at dilution infinite.

$D_{AB}{}^{0}$ and $D_{BA}{}^{0}$ can be calculated using the Wilke and Chang equation or the of Stokes-Einstein, for example.

- Darken, Hartley and Crank equation

Another variation of the Vignes equation will use the arithmetic mean of diffusion coefficients instead of the geometric mean at infinite dilution.

$$D_{AB} = \left(x_A\left(D_{AB}{}^{0}\right) + x_B\left(D_{BA}{}^{0}\right)\right)\left(1 + \frac{\partial \ln \gamma}{\partial \ln C_A}\right)$$

7.3. Diffusion coefficients for multicomponent gas systems (Equation by Stefan Maxwell)

There is an important difference between diffusion in a binary mixture and in a multi-component mixture. In a binary mixture, the movement of species A is always proportional (in absolute value) to the concentration gradient of the species A. When it comes to a diffusion where several components intervene in a mixture, other interesting situations can emerge:

(i) reverse diffusion, in which a species diffuses in the opposite direction of its own concentration gradient,

(ii) osmotic diffusion, in which a species diffuses even if its gradient concentration is zero,

(iii) diffusion barrier, when a species does not diffuse even if its gradient of concentration is non-zero.

For diffusion in a multicomponent gas mixture at low density, it has been demonstrated with a very good approximation that:

$$\nabla x_i = -\sum_{=1}^{n} \frac{x_i x_j}{D_{ij}}\left(v_i - v_j\right) = -\sum_{j=1}^{n} \frac{1}{CD_{ij}}\left(x_j N_i - x_i N_j\right) \; avec \quad i = 1,2,..n$$

This equation is known by the Maxwell-Stefan equation, because it is Maxwell who suggested it from a binary system based on the kinetic theory of gases (1868) and Stefan (1872) generalized it to describe diffusion in a mixture of gases with n components. For dense gases, liquids and polymers, it has been shown that the equation of Stefan-Maxwell remains valid.

8. Order of magnitude of the diffusion coefficients in the different media (gas, liquids, solids)

Generally, diffusivity increases with temperature. However, while the gas diffusion coefficient is practically independent of the composition but varies with pressure, it is essentially dependent on concentration in the case liquids and solids

9. Diffusion coefficients in porous solids

A porous medium, figure 2.1, is characterized by the pore volume εT which is different from the total volume but also by the tortuosity of the pores τ.

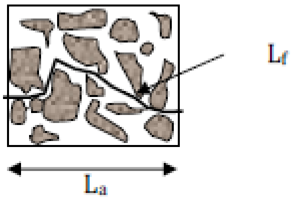


Figure 2.1. Sectional view of a porous medium.

10. Concept of effective diffusion coefficients

Diffusion in the porous medium brings into play a new notion which is that of the effective diffusion coefficient which takes into account the specificities of this environment.

$$D_{eff} = fD = \frac{D\varepsilon_T}{\tau}$$

With :

D: diffusion coefficient in gases or liquids filling the pores [m²s-1].

f: factor which reflects the hindrance to molecular movement in the porous medium. He is called impedance factor and depends on the viscosity of the fluid but especially on the geometry of the pore space by tortuosity.

ε_T: total porosity available for transport (pore volume/volume of medium 'dimensional').

τ: 'adimensional' tortuosity is a function of the ratio between the length of the real diffusion path (Lf) and the length of the apparent diffusion path (La):

$$\tau = \left(\frac{L_f}{L_a}\right)^n$$

It is common to consider that tortuosity is simply given by the L_f/L_a ratio or by its square. Several values of the exponent n have been proposed (n=2, 3/2, 4/3).

11. Conclusion

This chapter allows us to estimate the diffusion coefficient in different environments. with, in most cases, a good approximation.