

CHAPTER 3: Transfer of material to an interface

1. Introduction

In most separation operations, the system consists of a set of two phases, one of which is dispersed in the form of drops, bubbles, solid particles or films. Transfers often take place at an interface: the interface can be chemically reactive (electrode in electrochemistry, catalyst, adsorbent, etc.) or also be physically responsible for a release of material (solubilization, evaporation, etc.) or consumption (absorption, condensation, etc.). In such system, the movement of fluids is extremely complex and we are obliged to have use models to best represent the characteristics of the transfer.

2. Material transfer coefficient

At an interface, the material transfer flow can be written:

$$N_A = k\Delta C_A$$

Where ΔC_A is the concentration difference between the average concentration of constituent A in the phase considered and its concentration at the interface: $\Delta C_A = C_A - C_{Ai}$.

k is the material transfer coefficient (in m/s). The transfer coefficient of matter is thus a simple tool to use to describe the transfer to an interface. THE material transfer coefficient is defined by relating the interfacial flow to a difference in characteristic concentrations:

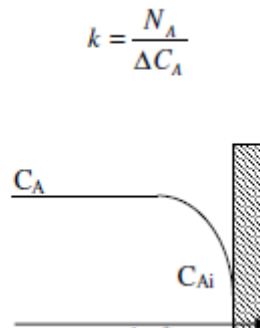


Figure 3.1. Diagram describing the concentration profile at the interface

The transfer coefficient; k is analogous to a conductance in electricity; her inverse is the transfer resistance. With the units chosen for the flux ($\text{mol cm}^{-2} \text{s}^{-1}$) and concentrations (mol cm^{-3}), k has the dimensions of a speed (cm s^{-1}). It may be convenient to use, instead of C_A molar concentrations, the fractions molar x_A or partial pressures p_A and to define the transfer coefficients correspondents:

$$k_x = \frac{N_A}{\Delta x_A} \quad (\text{mol cm}^{-2} \text{s}^{-1})$$

$$k_p = \frac{N_A}{\Delta p_A} \quad (\text{mol cm}^{-2} \text{s}^{-1} \text{atm}^{-1})$$

Table3.1. summarizes the different mass transfer coefficients and their uses.

Table 3.1. Common definitions of mass transfer coefficient

Equation of base Remarks	Unit of k	Remarks
$N_A = K \Delta C_A$	cm/s	Writing is common in old literature; used here for its physical importance
$N_A = k \Delta P_A$	mol/cm ² s Pa	Used in gas adsorption; shapes equivalents arise in problems medical
$N_A = K_x \Delta X_A$	mol/cm ² s	Preferred because of the practical calculations, especially in the gases

In this table, N_A is defined in moles/L²T and C^A in moles/L³. We can find parallel definitions where: N_A is in M/L² T and C_A is in M/L³. These different coefficients are linked together such that:

$$k_x = k C_T$$

C_T being the total molar concentration of the phase considered. In the event that this is a mixture of ideal gases:

$$k_p = \frac{k}{RT}$$

Figure 3.2. represents the shape of the concentration profile. It should be noted the discontinuity of concentrations at the interface.

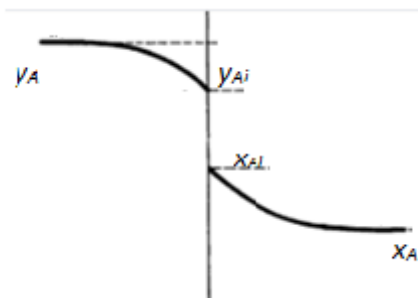


Figure 3.2. Profile of the mole fraction of solute A, according to the z direction of the transfer, in a two-phase system

Figure 3.3. gives the phase diagram with the mole fractions in phase gas and liquid phase in the case of a transfer of matter between a gas and a liquid. Example: the dissolution (absorption) of a gas by a liquid.

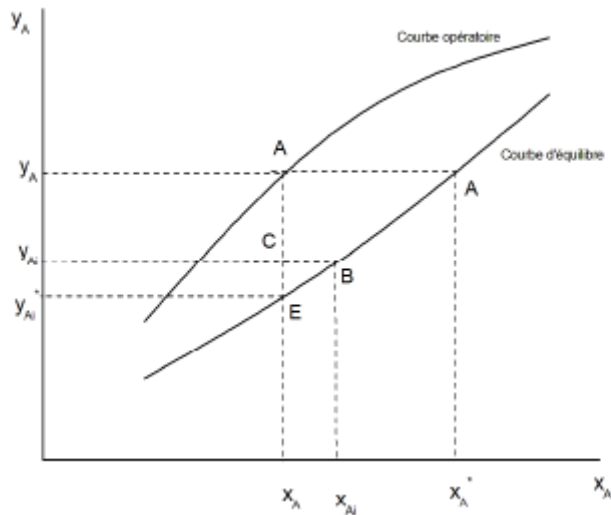


Figure 3.3. Relations between the different mole fractions in the gas phases and liquid.

x_A^* is the mole fraction of A in the liquid phase which would be in equilibrium with the mole fraction of A in the gas phase y_A , according to the gas/liquid equilibrium curve. y_A^* is the mole fraction of A in the gas phase which would be in equilibrium with the mole fraction of A in the liquid phase x_A , according to the gas/liquid equilibrium curve. Thus, we can define four transfer potentials depending on the phase considered:

in the liquid phase

in the gas phase

$$N_A = k_x (x_{Ai} - x_A) \quad (3.1)$$

$$N_A = k_y (y_A - y_{Ai}) \quad (3.2)$$

$$N_A = K_x (x_A^* - x_A) \quad (3.3)$$

$$N_A = K_y (y_A - y_A^*) \quad (3.4)$$

k_x and k_y are the particular transfer coefficients of A respectively in the phase liquid and gas.

K_x and K_y are the global transfer coefficients of A respectively in the phase liquid and gas.

Determination of film transfer coefficients k_x and k_y (depending on the nature and fluid properties, flow characteristics and geometry of interfaces). This determination is an important objective of the research in chemical engineering. However, the direct measurement of these coefficients is not possible because concentrations at the interface are not accessible

By equalizing the equations we obtain the two equations below:

$$N_A = K_x(x_A^* - x_A) = k_x(x_{Ai} - x_A)$$

$$N_A = k_y(y_A - y_{Ai}) = K_y(y_A - y_A^*)$$

From equation we find:

$$\frac{1}{K_y} = \frac{1}{k_y} \frac{(y_A - y_A^*)}{(y_A - y_{Ai})}$$

By adding and subtracting the value y_{Ai} from the numerator, we obtain:

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{(y_{Ai} - y_A^*)}{k_x(x_{Ai} - x_A)}$$

Referring to Figure 3.4, we notice that the ratio $\frac{y_{Ai} - y_A^*}{x_{Ai} - x_A} = m$. It is the tangent of the BE curve.

With :

m is calculated from the knowledge of the equilibrium of A between the two phases (Henry's constant in the case of the dissolution of O₂ in water, for example).

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{m}{k_x}$$

From this equation, the following information can be concluded:

The overall resistance = resistance in the gas film + resistance in the liquid film multiplied by m

In the same way we find:

$$\frac{1}{K_x} = \frac{1}{k_x} + \frac{1}{k_y m}$$

It is easy to see that $K_x = m K_y$

When m is small, component A is very poorly soluble in the gas phase. $m/k_x \sim 0$ and the overall resistance in the gas phase depends only on the resistance some gas.

It is possible to measure the transfer coefficient in a phase determined by an experiment involving a transfer between two phases. The transfer of a compound from the gas phase to the liquid phase depends, on the one hand, the thermodynamic equilibrium between the two phases and, on the other hand, the simultaneous transfers within each of the two phases. The existing conditions at proximity of the interface being very difficult to observe, or to explore experimentally, several theories have emerged to quantify the transfer between the two phases; these theories being based on the fact that the resistance to mass transfer is localized near the interface.

3. Double film theory

The double film theory was suggested by Lewis and Whitman in 1924. It considers that the interface between two fluids is composed of two stagnant films in which the transfer takes place by pure diffusion. (In special cases of transfer of matter, as in the evaporation of a pure liquid in a diffusion cell or the absorption of a pure gas in a stirred container, the transfer of material is unidirectional and we can neglect the convective terms in the diffusion equation).

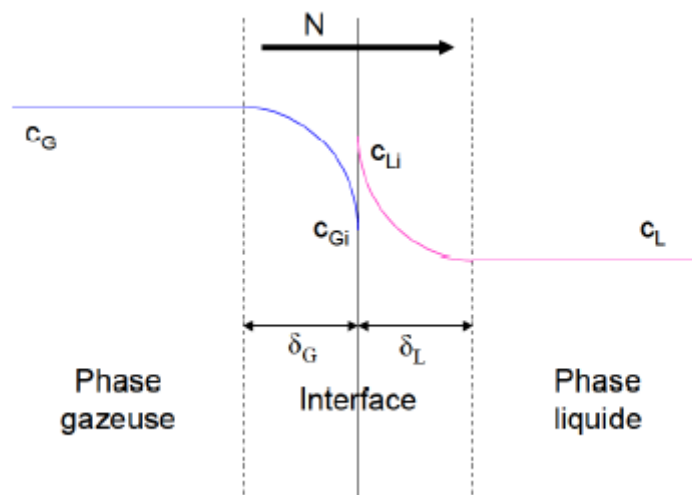


Figure 3.4. Schematization of the double film theory.

In Whitman's double film theory, it is admitted that:

- the resistance to transfer is exclusively located in these films,
- the interface itself does not present any resistance to transfer,
- thermodynamic equilibrium between the two phases is reached at the interface and obeys to the same equilibrium relationships as for the two phases as a whole.

The double film theory leads to expressions for the flow of matter implying that the transfer coefficients in film are proportional to the diffusion coefficients:

$$k_g = \frac{D_g}{\delta_g} \quad \text{et} \quad k_l = \frac{D_l}{\delta_l}$$

With the solute flux equal to equation in the gas film, and to equation in the liquid film:

$$N_A = \frac{D_g}{\delta_g} (C_g - C_{gi})$$

$$N_A = \frac{D_l}{\delta_l} (C_{li} - C_l)$$

With ;

C_g concentration in the gas phase,

C_{gi} concentration in the gas phase at the interface,

C_l concentration in the liquid phase,

C_{li} concentration in the liquid phase at the interface.

Thus, the double layer model provides a proportional transfer coefficient to D.

4. Penetration theory

Higbie's penetration theory (1935) is based on the principle that the interface is made up of a large number of liquid elements, coming from the heart of the liquid, which will stay for a time t_C (contact time) at the interface and thus absorb the solute by diffusion in transient regime. Each element remains the same time the interface (t_C) and absorbs the same quantity of gas per unit of interfacial area, figure 3.5.

In summary, the hypotheses are as follows:

- the heart of the phase to which the model is applied is perfectly agitated,
- the elements from the heart come to the interface, they all stay there for a time identical during which they exchange material with the other phase through unidirectional molecular diffusion mechanisms, before returning to mix with the heart of the phase.
- the balance is achieved at the interface.

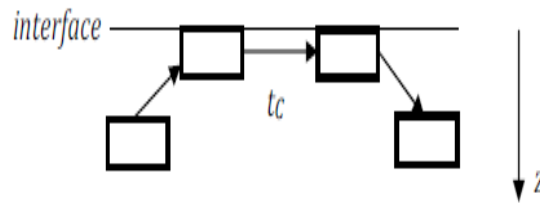


Figure 3.5. Cycle followed by an element, for the penetration model. t_c : time of stay of elements at interface

The transfer is described by Fick's second law:

$$\frac{\partial C(t, z)}{\partial t} = D \frac{\partial^2 C(t, z)}{\partial z^2}$$

Integrating this equation provides the profile of concentrations in an element of fluid which stays for a time t_c at the interface. The calculation of the average flow, expressed according to the relationship $NA = kl(CA_i - CA_0)$, gives for very short contact times:

$$k_l = 2 \sqrt{\frac{D_l}{\pi t_c}}$$

The penetration model provides a transfer coefficient proportional to the square root of the diffusion coefficient ($D^{1/2}$). It is characteristic of systems in which exchanges take place through short-term contacts.

5. Interface renewal theory

This model proposes the same hypotheses as in the penetration model, except that concerning the residence time at the interface. This last hypothesis is replaced by the following: the probability of renewal of the interface is constant (or the probability of replacement of an element participating in the exchange is independent of the duration of stay at the interface).

Which gives the average transfer coefficient:

$$k_R = \sqrt{\frac{D_l}{\theta}}$$

$$N_A = K_R(C_i - C)$$

The relationship between the penetration and renewal models of the interface is obvious, both by the hypotheses on which they are based and by the results to which they allow to succeed. We can therefore group them together to compare them to the double model.

6. π -Buchingham theorem

If an equation with k variables is homogeneous, it can be reduced to one relationship between $(k-r)$ independent dimensionless products, where r is the minimum number of dimensions required to describe the k variables. The application of this theorem is based on the use of a systematic method:

- 1- list the variables of system k ,
- 2- write the equation with the dimensions of each of the k variables, using the table 4.2.
- 3- determine r and therefore $k-r$ the number of dimensionless products characterizing the issue,
- 4- among the k variables, choose a number r which are dimensionally independent (r primary variables),
- 5- form the $k-r$ products P by combining the $k-r$ non-primary variables with the r primaries so as to obtain dimensionless quantities,
- 6- formulate the relationship between the $k-r$ products P found.

Noticed

When reasoning in dimensional analysis, there always remains a dimensionless constant whose numerical value is not known. Despite everything, when the chosen parameters are relevant, it turns out that the remaining numerical constant is very often of an order of magnitude close to unity.

7. Estimation of material transfer coefficients (correlations dimensionless)

Correlations between dimensionless numbers (or correlations dimensionless) make it possible to calculate the Sherwood number according to the

operating conditions, i.e. hydrodynamics, Re , and the properties of the solution, Sc . Obtaining the Sherwood number then makes it possible to estimate the transfer coefficient of material k (or the thickness of the diffusion boundary layer by applying the film model).

8. Conclusion

This fourth chapter focused essentially on the transfer coefficient of material which is a key parameter in any unit operation. The latter allows to estimate the thickness of the diffusion layer by passing, generally by an analysis dimensional and modeling of the system.