

Mass Transfer

10.1. INTRODUCTION

The term mass transfer is used to denote the transference of a component in a mixture from a region where its concentration is high to a region where the concentration is lower. Mass transfer process can take place in a gas or vapour or in a liquid, and it can result from the random velocities of the molecules (*molecular diffusion*) or from the circulating or eddy currents present in a turbulent fluid (*eddy diffusion*).

In processing, it is frequently necessary to separate a mixture into its components and, in a physical process, differences in a particular property are exploited as the basis for the separation process. Thus, *fractional distillation* depends on differences in volatility, *gas absorption* on differences in solubility of the gases in a selective absorbent and, similarly, *liquid-liquid extraction* is based on the selectivity of an immiscible liquid solvent for one of the constituents. The rate at which the process takes place is dependent both on the *driving force* (concentration difference) and on the *mass transfer resistance*. In most of these applications, mass transfer takes place across a *phase boundary* where the concentrations on either side of the interface are related by the phase equilibrium relationship. Where a chemical reaction takes place during the course of the mass transfer process, the overall transfer rate depends on both the chemical kinetics of the reaction and on the mass transfer resistance, and it is important to understand the relative significance of these two factors in any practical application.

In this chapter, consideration will be given to the basic principles underlying mass transfer both with and without chemical reaction, and to the models which have been proposed to enable the rates of transfer to be calculated. The applications of mass transfer to the design and operation of separation processes are discussed in Volume 2, and the design of reactors is dealt with in Volume 3.

A simple example of a mass transfer process is that occurring in a box consisting of two compartments, each containing a different gas, initially separated by an impermeable partition. When the partition is removed the gases start to mix and the mixing process continues at a constantly decreasing rate until eventually (theoretically after the elapse of an infinite time) the whole system acquires a uniform composition. The process is one of molecular diffusion in which the mixing is attributable solely to the random motion of the molecules. The rate of diffusion is governed by Fick's Law, first proposed by FICK⁽¹⁾ in 1855 which expresses the mass transfer rate as a linear function of the molar concentration gradient. In a mixture of two gases A and B, assumed ideal, Fick's Law for steady state diffusion may be written as:

$$N_A = -D_{AB} \frac{dC_A}{dy} \quad (10.1)$$

where N_A is the molar flux of **A** (moles per unit area per unit time),
 C_A is the concentration of **A** (moles of **A** per unit volume),
 D_{AB} is known as the diffusivity or diffusion coefficient for **A** in **B**, and
 y is distance in the direction of transfer.

An equation of exactly the same form may be written for **B**:

$$N_B = -D_{BA} \frac{dC_B}{dy} \quad (10.2)$$

where D_{BA} is the diffusivity of **B** in **A**.

As indicated in the next section, for an ideal gas mixture, at constant pressure ($C_A + C_B$), is constant (equation 10.9) and hence:

$$\frac{dC_A}{dy} = -\frac{dC_B}{dy} \quad (10.3)$$

The condition for the pressure or molar concentration to remain constant in such a system is that there should be no net transference of molecules. The process is then referred to as one of *equimolecular counterdiffusion*, and:

$$N_A + N_B = 0$$

This relation is satisfied only if $D_{BA} = D_{AB}$ and therefore the suffixes may be omitted and equation 10.1 becomes:

$$N_A = -D \frac{dC_A}{dy} \quad (10.4)$$

Equation 10.4, which describes the mass transfer rate arising solely from the random movement of molecules, is applicable to a stationary medium or a fluid in streamline flow. If circulating currents or eddies are present, then the molecular mechanism will be reinforced and the total mass transfer rate may be written as:

$$N_A = -(D + E_D) \frac{dC_A}{dy} \quad (10.5)$$

Whereas D is a physical property of the system and a function only of its composition, pressure and temperature, E_D , which is known as the *eddy diffusivity*, is dependent on the flow pattern and varies with position. The estimation of E_D presents some difficulty, and this problem is considered in Chapter 12.

The molecular diffusivity D may be expressed in terms of the molecular velocity u_m and the mean free path of the molecules λ_m . In Chapter 12 it is shown that for conditions where the kinetic theory of gases is applicable, the molecular diffusivity is proportional to the product $u_m \lambda_m$. Thus, the higher the velocity of the molecules, the greater is the distance they travel before colliding with other molecules, and the higher is the diffusivity D .

Because molecular velocities increase with rise of temperature T , so also does the diffusivity which, for a gas, is approximately proportional to T raised to the power of 1.5. As the pressure P increases, the molecules become closer together and the mean free path is shorter and consequently the diffusivity is reduced, with D for a gas becoming approximately inversely proportional to the pressure.

Thus:
$$D \propto T^{1.5}/P \quad (10.6)$$

A method of calculating D in a binary mixture of gases is given later (equation 10.43). For *liquids*, the molecular structure is far more complex and no such simple relationship exists, although various semi-empirical predictive methods, such as equation 10.96, are useful.

In the discussion so far, the fluid has been considered to be a continuum, and distances on the molecular scale have, in effect, been regarded as small compared with the dimensions of the containing vessel, and thus only a small proportion of the molecules collides directly with the walls. As the pressure of a gas is reduced, however, the mean free path may increase to such an extent that it becomes comparable with the dimensions of the vessel, and a significant proportion of the molecules may then collide directly with the walls rather than with other molecules. Similarly, if the linear dimensions of the system are reduced, as for instance when diffusion is occurring in the small pores of a catalyst particle (Section 10.7), the effects of collision with the walls of the pores may be important even at moderate pressures. Where the main resistance to diffusion arises from collisions of molecules with the walls, the process is referred to *Knudsen diffusion*, with a Knudsen diffusivity D_{Kn} which is proportional to the product $u_m l$, where l is a linear dimension of the containing vessel.

Since, from the *kinetic theory*⁽²⁾, $u_m \propto (RT/M)^{0.5}$:

$$D_{Kn} \propto l(RT/M)^{0.5} \quad (10.7)$$

Each resistance to mass transfer is proportional to the reciprocal of the appropriate diffusivity and thus, when both molecular and Knudsen diffusion must be considered together, the effective diffusivity D_e is obtained by summing the resistances as:

$$1/D_e = 1/D + 1/D_{Kn} \quad (10.8)$$

In *liquids*, the effective mean path of the molecules is so small that the effects of Knudsen-type diffusion need not be considered.

10.2. DIFFUSION IN BINARY GAS MIXTURES

10.2.1. Properties of binary mixtures

If **A** and **B** are ideal gases in a mixture, the ideal gas law, equation 2.15, may be applied to each gas separately and to the mixture:

$$P_A V = n_A RT \quad (10.9a)$$

$$P_B V = n_B RT \quad (10.9b)$$

$$PV = n RT \quad (10.9c)$$

where n_A and n_B are the number of moles of **A** and **B** and n is the total number of moles in a volume V , and P_A , P_B and P are the respective partial pressures and the total pressure.

Thus:
$$P_A = \frac{n_A}{V} RT = C_A RT = \frac{c_A}{M_A} RT \quad (10.10a)$$

$$P_B = \frac{n_B}{V} RT = C_B RT = \frac{c_B}{M_B} RT \quad (10.10b)$$

and:
$$P = \frac{n}{V} RT = C_T RT \quad (10.10c)$$

where c_A and c_B are mass concentrations and M_A and M_B molecular weights, and C_A , C_B , C_T are, the molar concentrations of **A** and **B** respectively, and the total molar concentration of the mixture.

From Dalton's Law of partial pressures:

$$P = P_A + P_B = \mathbf{RT}(C_A + C_B) = \mathbf{RT} \left(\frac{c_A}{M_A} + \frac{c_B}{M_B} \right) \quad (10.11)$$

Thus: $C_T = C_A + C_B \quad (10.12)$

and: $1 = x_A + x_B \quad (10.13)$

where x_A and x_B are the mole fractions of **A** and **B**.

Thus for a system at constant pressure P and constant molar concentration C_T :

$$\frac{dP_A}{dy} = -\frac{dP_B}{dy} \quad (10.14)$$

$$\frac{dC_A}{dy} = -\frac{dC_B}{dy} \quad (10.15)$$

$$\frac{dc_A}{dy} = -\frac{dc_B}{dy} \frac{M_A}{M_B} \quad (10.16)$$

and: $\frac{dx_A}{dy} = -\frac{dx_B}{dy} \quad (10.17)$

By substituting from equations 10.7a and 10.7b into equation 10.4, the mass transfer rates N_A and N_B can be expressed in terms of partial pressure gradients rather than concentration gradients. Furthermore, N_A and N_B can be expressed in terms of gradients of mole fraction.

Thus: $N_A = -\frac{D}{\mathbf{RT}} \frac{dP_A}{dy} \quad (10.18)$

or $N_A = -DC_T \frac{dx_A}{dy} \quad (10.19)$

Similarly: $N_B = -\frac{D}{\mathbf{RT}} \frac{dP_B}{dy} = +\frac{D}{\mathbf{RT}} \frac{dP_A}{dy}$ (from equation 10.14) (10.20)

or $N_B = -DC_T \frac{dx_B}{dy} = +DC_T \frac{dx_A}{dy}$ (from equation 10.17) (10.21)

10.2.2. Equimolecular counterdiffusion

When the mass transfer rates of the two components are equal and opposite the process is said to be one of *equimolecular counterdiffusion*. Such a process occurs in the case of the box with a movable partition, referred to in Section 10.1. It occurs also in a distillation column when the molar latent heats of the two components are the same. At any point in the column a falling stream of liquid is brought into contact with a rising stream of vapour with which it is *not* in equilibrium. The less volatile component is transferred from

the vapour to the liquid and the more volatile component is transferred in the opposite direction. If the molar latent heats of the components are equal, the condensation of a given amount of less volatile component releases exactly the amount of latent heat required to volatilise the same molar quantity of the more volatile component. Thus at the interface, and consequently throughout the liquid and vapour phases, equimolecular counterdiffusion is taking place.

Under these conditions, the differential forms of equation for N_A (10.4, 10.18 and 10.19) may be simply integrated, for constant temperature and pressure, to give respectively:

$$N_A = -D \frac{C_{A_2} - C_{A_1}}{y_2 - y_1} = \frac{D}{y_2 - y_1} (C_{A_1} - C_{A_2}) \quad (10.22)$$

$$N_A = -\frac{D}{RT} \frac{P_{A_2} - P_{A_1}}{y_2 - y_1} = \frac{D}{RT(y_2 - y_1)} (P_{A_1} - P_{A_2}) \quad (10.23)$$

$$N_A = -DC_T \frac{x_{A_2} - x_{A_1}}{y_2 - y_1} = \frac{DC_T}{y_2 - y_1} (x_{A_1} - x_{A_2}) \quad (10.24)$$

Similar equations apply to N_B which is equal to $-N_A$, and suffixes 1 and 2 represent the values of quantities at positions y_1 and y_2 respectively.

Equation 10.22 may be written as:

$$N_A = h_D (C_{A_1} - C_{A_2}) \quad (10.25)$$

where $h_D = D/(y_2 - y_1)$ is a *mass transfer coefficient* with the driving force expressed as a *difference in molar concentration*; its dimensions are those of velocity (LT^{-1}).

Similarly, equation 10.23 may be written as:

$$N_A = k'_G (P_{A_1} - P_{A_2}) \quad (10.26)$$

where $k'_G = D/[RT(y_2 - y_1)]$ is a *mass transfer coefficient* with the driving force expressed as a *difference in partial pressure*. It should be noted that its dimensions here, $\text{NM}^{-1}\text{L}^{-1}\text{T}$, are different from those of h_D . It is always important to use the form of mass transfer coefficient corresponding to the appropriate driving force.

In a similar way, equation 10.24 may be written as:

$$N_A = k_x (x_{A_1} - x_{A_2}) \quad (10.27)$$

where $k_x = DC_T/(y_2 - y_1)$ is a *mass transfer coefficient* with the driving force in the form of a *difference in mole fraction*. The dimensions here are $\text{NL}^{-2}\text{T}^{-1}$.

10.2.3. Mass transfer through a stationary second component

In several important processes, one component in a gaseous mixture will be transported relative to a fixed plane, such as a liquid interface, for example, and the other will undergo no net movement. In gas absorption a soluble gas **A** is transferred to the liquid surface where it dissolves, whereas the insoluble gas **B** undergoes no net movement with respect to the interface. Similarly, in evaporation from a free surface, the vapour moves away from the surface but the air has no net movement. The mass transfer process therefore differs from that described in Section 10.2.2.