CHAPTER 10

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 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:

$$N_A = -D_{AB}\frac{dC_A}{dy} \tag{10.1}$$

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**:

$$N_B = -D_{BA}\frac{dC_B}{dy} \tag{10.2}$$

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:

$$\frac{dC_A}{dy} = -\frac{dC_B}{dy} \tag{10.3}$$

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:

$$N_A = -D\frac{dC_A}{dy} \tag{10.4}$$

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:

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

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:

$$D \propto T^{1.5}/P \tag{10.6}$$

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*$^{(2)}$, $u_m \propto (\mathbf{R}T/M)^{0.5}$:

$$D_{Kn} \propto l(\mathbf{R}T/M)^{0.5} \tag{10.7}$$

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:

$$1/D_e = 1/D + 1/D_{Kn} \tag{10.8}$$

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:

$$P_A V = n_A \mathbf{R}T \tag{10.9a}$$

$$P_B V = n_B \mathbf{R}T \tag{10.9b}$$

$$PV = n\mathbf{R}T \tag{10.9c}$$

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:

$$P_A = \frac{n_A}{V}\mathbf{R}T = C_A\mathbf{R}T = \frac{c_A}{M_A}\mathbf{R}T \tag{10.10a}$$

$$P_B = \frac{n_B}{V}\mathbf{R}T = C_B\mathbf{R}T = \frac{c_B}{M_B}\mathbf{R}T \tag{10.10b}$$

and:

$$P = \frac{n}{V}\mathbf{R}T = C_T\mathbf{R}T \tag{10.10c}$$

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:

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

Thus:

$$C_T = C_A + C_B \tag{10.12}$$

and:

$$1 = x_A + x_B \tag{10.13}$$

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:

$$\frac{\mathrm{d}P_A}{\mathrm{d}y} = -\frac{\mathrm{d}P_B}{\mathrm{d}y} \tag{10.14}$$

$$\frac{\mathrm{d}C_A}{\mathrm{d}y} = -\frac{\mathrm{d}C_B}{\mathrm{d}y} \tag{10.15}$$

$$\frac{\mathrm{d}c_A}{\mathrm{d}y} = -\frac{\mathrm{d}c_B}{\mathrm{d}y}\frac{M_A}{M_B} \tag{10.16}$$

and:

$$\frac{\mathrm{d}x_A}{\mathrm{d}y} = -\frac{\mathrm{d}x_B}{\mathrm{d}y} \tag{10.17}$$

By substituting from equations 10.7*a* and 10.7*b* 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:

$$N_A = -\frac{D}{\mathbf{R}T}\frac{\mathrm{d}P_A}{\mathrm{d}y} \tag{10.18}$$

or

$$N_A = -DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} \tag{10.19}$$

Similarly:

$$N_B = -\frac{D}{\mathbf{R}T}\frac{\mathrm{d}P_B}{\mathrm{d}y} = +\frac{D}{\mathbf{R}T}\frac{\mathrm{d}P_A}{\mathrm{d}y} \quad \text{(from equation 10.14)} \tag{10.20}$$

or

$$N_B = -DC_T\frac{\mathrm{d}x_B}{\mathrm{d}y} = +DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} \quad \text{(from equation 10.17)} \tag{10.21}$$

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:

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

$$N_A = -\frac{D}{\mathbf{R}T}\frac{P_{A_2} - P_{A_1}}{y_2 - y_1} = \frac{D}{\mathbf{R}T(y_2 - y_1)}(P_{A_1} - P_{A_2}) \tag{10.23}$$

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

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:

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

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 ($\mathbf{LT}^{-1}$).

Similarly, equation 10.23 may be written as:

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

where $k'_G = D/[\mathbf{R}T(y_2 - y_1)]$ is a *mass transfer coefficient* with the driving force expressed as a *difference in partial pressure*. It should be noted that its dimensions here, $\mathbf{NM}^{-1}\mathbf{L}^{-1}\mathbf{T}$, 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:

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

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 $\mathbf{NL}^{-2}\mathbf{T}^{-1}$.

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.

The concept of a stationary component may be envisaged by considering the effect of moving the box, discussed in Section 10.1, in the opposite direction to that in which **B** is diffusing, at a velocity equal to its diffusion velocity, so that to the external observer **B** appears to be stationary. The total velocity at which **A** is transferred will then be increased to its diffusion velocity plus the velocity of the box.

For the absorption of a soluble gas **A** from a mixture with an insoluble gas **B**, the respective diffusion rates are given by:

$$N_A = -D\frac{\mathrm{d}C_A}{\mathrm{d}y} \qquad \text{(equation 10.4)}$$

$$N_B = -D\frac{\mathrm{d}C_B}{\mathrm{d}y} = D\frac{\mathrm{d}C_A}{\mathrm{d}y} \qquad \text{(from equation 10.3)}$$

Since the total mass transfer rate of **B** is zero, there must be a "bulk flow" of the system towards the liquid surface exactly to counterbalance the diffusional flux away from the surface, as shown in Figure 10.1, where:

$$\text{Bulk flow of } \mathbf{B} = -D\frac{\mathrm{d}C_A}{\mathrm{d}y} \tag{10.28}$$

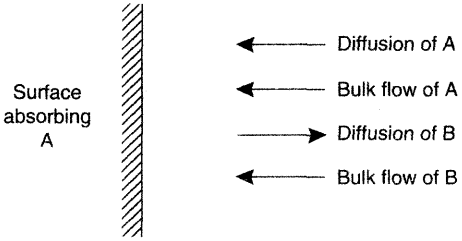

Figure 10.1. Mass transfer through a stationary gas **B**

The corresponding bulk flow of **A** must be C_A/C_B times that of **B**, since bulk flow implies that the gas moves *en masse*.

Thus:

$$\text{Bulk flow of } \mathbf{A} = -D\frac{\mathrm{d}C_A}{\mathrm{d}y}\frac{C_A}{C_B} \tag{10.29}$$

Therefore the total flux of **A**, N'_A, is given by:

$$N'_A = -D\frac{\mathrm{d}C_A}{\mathrm{d}y} - D\frac{\mathrm{d}C_A}{\mathrm{d}y}\frac{C_A}{C_B}$$

$$= -D\frac{\mathrm{d}C_A}{\mathrm{d}y}\frac{C_T}{C_B} \tag{10.30}$$

Equation 10.30 is known as Stefan's Law$^{(3)}$. Thus the bulk flow enhances the mass transfer rate by a factor C_T/C_B, known as the *drift factor*. The fluxes of the components are given in Table 10.1.

Table 10.1. Fluxes of components of a gas mixture

	Component **A**	Component **B**	**A** + **B**
Diffusion	$-D\dfrac{dC_A}{dy}$	$+D\dfrac{dC_A}{dy}$	0
Bulk flow	$-D\dfrac{dC_A}{dy}\cdot\dfrac{C_A}{C_B}$	$-D\dfrac{dC_A}{dy}$	$-D\dfrac{dC_A}{dy}\cdot\dfrac{C_A+C_B}{C_B}$
Total	$-D\dfrac{dC_A}{dy}\cdot\dfrac{C_A+C_B}{C_B}$	0	$-D\dfrac{dC_A}{dy}\cdot\dfrac{C_A+C_B}{C_B}$
	$=-D\dfrac{dC_A}{dy}\cdot\dfrac{C_T}{C_B}$		$=-D\dfrac{dC_A}{dy}\cdot\dfrac{C_T}{C_B}$

Writing equation 10.30 as:

$$N'_A = D\frac{C_T}{C_B}\frac{dC_B}{dy} \qquad \text{(from equation 10.3)}$$

On integration:

$$N'_A = \frac{DC_T}{y_2 - y_1}\ln\frac{C_{B_2}}{C_{B_1}} \tag{10.31}$$

By definition, C_{Bm}, the logarithmic mean of C_{B_1} and C_{B_2}, is given by:

$$C_{Bm} = \frac{C_{B_2} - C_{B_1}}{\ln(C_{B_2}/C_{B_1})} \tag{10.32}$$

Thus, substituting for ln (C_{B_2}/C_{B_1}) in equation 10.31:

$$N'_A = \left(\frac{DC_T}{y_2 - y_1}\right)\frac{C_{B_2} - C_{B_1}}{C_{Bm}}$$

$$= \left(\frac{D}{y_2 - y_1}\frac{C_T}{C_{Bm}}\right)(C_{A_1} - C_{A_2}) \tag{10.33}$$

or in terms of partial pressures:

$$N'_A = \left(\frac{D}{\mathbf{R}T(y_2 - y_1)}\frac{P}{P_{Bm}}\right)(P_{A_1} - P_{A_2}) \tag{10.34}$$

Similarly, in terms of mole fractions:

$$N'_A = \left(\frac{DC_T}{y_2 - y_1}\frac{1}{x_{Bm}}\right)(x_{A_1} - x_{A_2}) \tag{10.35}$$

Equation 10.31 can be simplified when the concentration of the diffusing component **A** is small. Under these conditions C_A is small compared with C_T, and equation 10.31 becomes:

$$N'_A = \frac{DC_T}{y_2 - y_1}\ln\left[1 - \left(\frac{C_{A_2} - C_{A_1}}{C_T - C_{A_1}}\right)\right]$$

$$= \frac{DC_T}{y_2 - y_1}\left[-\left(\frac{C_{A_2} - C_{A_1}}{C_T - C_{A_1}}\right) - \frac{1}{2}\left(\frac{C_{A_2} - C_{A_1}}{C_T - C_{A_1}}\right)^2 - \cdots\right]$$

For small values of C_A, $C_T - C_{A_1} \approx C_T$ and only the first term in the series is significant.

Thus:
$$N'_A \approx \frac{D}{y_2 - y_1}(C_{A_1} - C_{A_2}) \tag{10.36}$$

Equation 10.36 is identical to equation 10.22 for equimolecular counterdiffusion. Thus, the effects of bulk flow can be neglected at low concentrations.

Equation 10.33 can be written in terms of a mass transfer coefficient h_D to give:

$$N'_A = h_D(C_{A_1} - C_{A_2}) \tag{10.37}$$

where:
$$h_D = \frac{D}{y_2 - y_1}\frac{C_T}{C_{Bm}} \tag{10.38}$$

Similarly, working in terms of partial pressure difference as the driving force, equation 10.34 can be written:

$$N'_A = k_G(P_{A_1} - P_{A_2}) \tag{10.39}$$

where:
$$k_G = \frac{D}{\mathbf{R}T(y_2 - y_1)}\frac{P}{P_{Bm}} \tag{10.40}$$

Using mole fractions as the driving force, equation 10.35 becomes:

$$N'_A = k_x(x_{A_1} - x_{A_2}) \tag{10.41}$$

where:
$$k_x = \frac{DC_T}{y_2 - y_1}\frac{C_T}{C_{Bm}} = \frac{DC_T}{(y_2 - y_1)x_{Bm}} \tag{10.42}$$

It may be noted that all the transfer coefficients here are greater than those for equimolecular counterdiffusion by the factor $(C_T/C_{Bm})(= P/P_{Bm})$, which is an integrated form of the drift factor.

When the concentration C_A of the gas being transferred is low, C_T/C_{Bm} then approaches unity and the two sets of coefficients become identical.

Example 10.1

Ammonia gas is diffusing at a constant rate through a layer of stagnant air 1 mm thick. Conditions are such that the gas contains 50 per cent by volume ammonia at one boundary of the stagnant layer. The ammonia diffusing to the other boundary is quickly absorbed and the concentration is negligible at that plane. The temperature is 295 K and the pressure atmospheric, and under these conditions the diffusivity of ammonia in air is 1.8×10^{-5} m^2/s. Estimate the rate of diffusion of ammonia through the layer.

Solution

If the subscripts 1 and 2 refer to the two sides of the stagnant layer and the subscripts A and B refer to ammonia and air respectively, then the rate of diffusion through a stagnant layer is given by:

$$N_A = -\frac{D}{\mathbf{R}Tx}(P/P_{BM})(P_{A2} - P_{A1}) \qquad \text{(equation 10.31)}$$

In this case, $x = 0.001$ m, $D = 1.8 \times 10^{-5}$ m^2/s, $\mathbf{R} = 8314$ J/kmol K, $T = 295$ K and $P = 101.3$ kN/m^2 and hence:

$$P_{A1} = (0.50 \times 101.3) = 50.65 \text{ kN/m}^2$$

$$P_{A2} = 0$$

$$P_{B1} = (101.3 - 50.65) = 50.65\ \text{kN/m}^2 = 5.065 \times 10^4\ \text{N/m}^2$$

$$P_{B2} = (101.3 - 0) = 101.3\ \text{kN/m}^2 = 1.013 \times 10^5\ \text{N/m}^2$$

Thus: $$P_{BM} = (101.3 - 50.65)/\ln(101.3/50.65) = 73.07\ \text{kN/m}^2 = 7.307 \times 10^4\ \text{N/m}^2$$

and: $$P/P_{BM} = (101.3/73.07) = 1.386.$$

Thus, substituting in equation 10.31 gives:

$$N_A = -[1.8 \times 10^{-5}/(8314 \times 295 \times 0.001)]1.386(0 - 5.065 \times 10^4)$$
$$= \underline{\underline{5.15 \times 10^{-4}\ \text{kmol/m}^2\text{s}}}$$

10.2.4. Diffusivities of gases and vapours

Experimental values of diffusivities are given in Table 10.2 for a number of gases and vapours in air at 298K and atmospheric pressure. The table also includes values of the Schmidt number *Sc*, the ratio of the kinematic viscosity (μ/ρ) to the diffusivity (D) for very low concentrations of the diffusing gas or vapour. The importance of the Schmidt number in problems involving mass transfer is discussed in Chapter 12.

Experimental determination of diffusivities

Diffusivities of vapours are most conveniently determined by the method developed by WINKELMANN$^{(5)}$ in which liquid is allowed to evaporate in a vertical glass tube over the top of which a stream of vapour-free gas is passed, at a rate such that the vapour

Table 10.2. Diffusivities (diffusion coefficients) of gases and vapours in air at 298 K and atmospheric pressure$^{(4)}$

Substance	D ($\text{m}^2/\text{s} \times 10^6$)	$\mu/\rho D$	Substance	D ($\text{m}^2/\text{s} \times 10^6$)	$\mu/\rho D$
Ammonia	28.0	0.55	Valeric acid	6.7	2.31
Carbon dioxide	16.4	0.94	i-Caproic acid	6.0	2.58
Hydrogen	71.0	0.22	Diethyl amine	10.5	1.47
Oxygen	20.6	0.75	Butyl amine	10.1	1.53
Water	25.6	0.60	Aniline	7.2	2.14
Carbon disulphide	10.7	1.45	Chlorobenzene	7.3	2.12
Ethyl ether	9.3	1.66	Chlorotoluene	6.5	2.38
Methanol	15.9	0.97	Propyl bromide	10.5	1.47
Ethanol	11.9	1.30	Propyl iodide	9.6	1.61
Propanol	10.0	1.55	Benzene	8.8	1.76
Butanol	9.0	1.72	Toluene	8.4	1.84
Pentanol	7.0	2.21	Xylene	7.1	2.18
Hexanol	5.9	2.60	Ethyl benzene	7.7	2.01
Formic acid	15.9	0.97	Propyl benzene	5.9	2.62
Acetic acid	13.3	1.16	Diphenyl	6.8	2.28
Propionic acid	9.9	1.56	n-Octane	6.0	2.58
i-Butyric acid	8.1	1.91	Mesitylene	6.7	2.31

Note: the group $(\mu/\rho D)$ in the above table is evaluated for mixtures composed largely of air.

In this table, the figures taken from PERRY and GREEN$^{(4)}$ are based on data in *International Critical Tables* **5** (1928) and Landolt-Börnstein, *Physikalische-Chemische Tabellen* (1935).

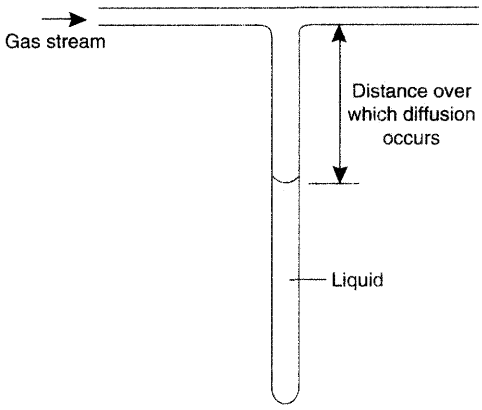

Figure 10.2. Determination of diffusivities of vapours

pressure is maintained almost at zero (Figure 10.2). If the apparatus is maintained at a steady temperature, there will be no eddy currents in the vertical tube and mass transfer will take place from the surface by molecular diffusion alone. The rate of evaporation can be followed by the rate of fall of the liquid surface, and since the concentration gradient is known, the diffusivity can then be calculated.

Example 10.2

The diffusivity of the vapour of a volatile liquid in air can be conveniently determined by Winkelmann's method in which liquid is contained in a narrow diameter vertical tube, maintained at a constant temperature, and an air stream is passed over the top of the tube sufficiently rapidly to ensure that the partial pressure of the vapour there remains approximately zero. On the assumption that the vapour is transferred from the surface of the liquid to the air stream by molecular diffusion alone, calculate the diffusivity of carbon tetrachloride vapour in air at 321 K and atmospheric pressure from the experimental data given in Table 10.3.

Table 10.3. Experimental data for diffusivity calculation

Time from commencement of experiment (h	min)	(ks)	Liquid level (mm)	Time from commencement of experiment (h	min)	(ks)	Liquid level (mm)
0	0	0.0	0.0	32	38	117.5	54.7
0	26	1.6	2.5	46	50	168.6	67.0
3	5	11.1	12.9	55	25	199.7	73.8
7	36	27.4	23.2	80	22	289.3	90.3
22	16	80.2	43.9	106	25	383.1	104.8

The vapour pressure of carbon tetrachloride at 321 K is 37.6 kN/m^2 and the density of the liquid is 1540 kg/m^3. The kilogram molecular volume may be taken as 22.4 m^3.

Solution

From equation 10.33 the rate of mass transfer is given by:

$$N'_A = D\frac{C_A}{L}\frac{C_T}{C_{Bm}}$$

where C_A is the saturation concentration at the interface and L is the effective distance through which mass transfer is taking place. Considering the evaporation of the liquid:

$$N'_A = \frac{\rho_L}{M}\frac{dL}{dt}$$

where ρ_L is the density of the liquid.

Hence:
$$\frac{\rho_L}{M}\frac{dL}{dt} = D\frac{C_A}{L}\frac{C_T}{C_{Bm}}$$

Integrating and putting $L = L_0$ at $t = 0$:

$$L^2 - L_0^2 = \frac{2MD}{\rho_L}\frac{C_A C_T}{C_{Bm}}t$$

L_0 will not be measured accurately nor is the effective distance for diffusion, L, at time t.

Accurate values of $(L - L_0)$ are available, however, and hence:

$$(L - L_0)(L - L_0 + 2L_0) = \frac{2MD}{\rho_L}\frac{C_A C_T}{C_{Bm}}t$$

or:
$$\frac{t}{L - L_0} = \frac{\rho_L}{2MD}\frac{C_{Bm}}{C_A C_T}(L - L_0) + \frac{\rho_L C_{Bm}}{MDC_A C_T}L_0$$

If s is the slope of a plot of $t/(L - L_0)$ against $(L - L_0)$, then:

$$s = \frac{\rho_L C_{Bm}}{2MDC_A C_T} \quad \text{or} \quad D = \frac{\rho_L C_{Bm}}{2MC_A C_T s}$$

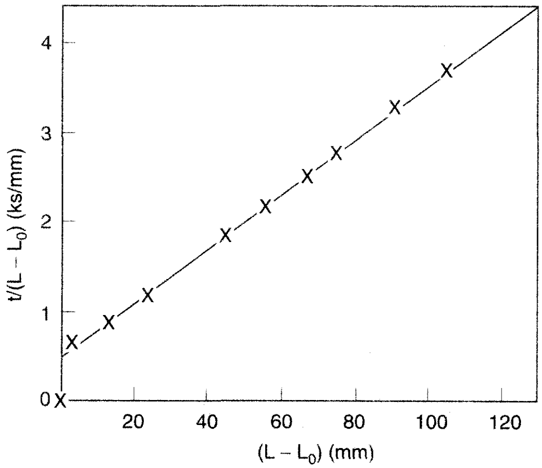

Figure 10.3. Plot of $t/(L - L_0)$ versus $(L - L_0)$ for Example 10.1

From a plot of $t/(L - L_0)$ against $(L - L_0)$ as shown in Figure 10.3:

$$s = 0.0310 \text{ ks/mm}^2 \quad \text{or} \quad 3.1 \times 10^7 \text{ s/m}^2$$

and:
$$C_T = \left(\frac{1}{22.4}\right)\left(\frac{273}{321}\right) = 0.0380 \text{ kmol/m}^3$$

$$M = 154 \text{ kg/kmol}$$

$$C_A = \left(\frac{37.6}{101.3}\right) 0.0380 = 0.0141 \text{ kmol/m}^3$$

$$\rho_L = 1540 \text{ kg/m}^3$$

$$C_{B1} = 0.0380 \text{ kmol/m}^3, \quad C_{B2} = \left(\frac{101.3 - 37.6}{101.3}\right) 0.0380 = 0.0238 \text{ kmol/m}^3$$

Thus:

$$C_{Bm} = \frac{(0.0380 - 0.0238)}{\ln(0.0380/0.0238)} = 0.0303 \text{ kmol/m}^3$$

and:

$$D = \frac{1540 \times 0.0303}{2 \times 154 \times 0.0141 \times 0.0380 \times 3.1 \times 10^7}$$

$$= \underline{\underline{9.12 \times 10^{-6} \text{ m}^2/\text{s}}}$$

Prediction of diffusivities

Where, the diffusivity D for the transfer of one gas in another is not known and experimental determination is not practicable, it is necessary to use one of the many predictive procedures. A commonly used method due to GILLILAND$^{(6)}$ is based on the "Stefan–Maxwell" hard sphere model and this takes the form:

$$D = \frac{4.3 \times 10^{-4} T^{1.5} \sqrt{(1/M_A) + (1/M_B)}}{P\left(\mathbf{V}_A^{1/3} + \mathbf{V}_B^{1/3}\right)^2} \tag{10.43}$$

where D is the diffusivity in m^2/s, T is the absolute temperature (K), M_A, M_B are the molecular masses of **A** and **B**, P is the total pressure in N/m^2, and $\mathbf{V}_A$, $\mathbf{V}_B$ are the molecular volumes of **A** and **B**. The molecular volume is the volume in m^3 of one kmol of the material in the form of liquid at its boiling point, and is a measure of the volume occupied by the molecules themselves. It may not always be known, although an approximate value can be obtained, for all but simple molecules, by application of *Kopp's law* of additive volumes. Kopp has presented a particular value for the equivalent atomic volume of each element$^{(7)}$, as given in Table 10.4, such that when the atomic volumes of the elements of the molecule in question are added in the appropriate proportions, an approximate value the equivalent molecular volume is obtained . There are certain exceptions to this rule, and corrections have to be made if the elements are combined in particular ways.

It will be noted from equation 10.43 that the diffusivity of a vapour is inversely proportional to the pressure and varies with the absolute temperature raised to the power of 1.5, although it has been suggested that this underestimates the temperature dependence.

A method, proposed more recently by FULLER, SCHETTLER and GIDDINGS$^{(8)}$, is claimed to give an improved correlation. In this approach the values of the "diffusion volume" have been "modified" to give a better correspondence with experimental values, and have then been adjusted arbitrarily to make the coefficient in the equation equal to unity. The method does contain some anomalies, however, particularly in relation to the values of $\mathbf{V}$ for nitrogen, oxygen and air. Details of this method are given in Volume 6.

Table 10.4. Atomic and structural diffusion volume increments (m^3/kmol)(7)

Antimony	0.0242	Oxygen, double-bonded	0.0074
Arsenic	0.0305	Coupled to two other elements:	
Bismuth	0.0480	in aldehydes and ketones	0.0074
Bromine	0.0270	in methyl esters	0.0091
Carbon	0.0148	in ethyl esters	0.0099
Chlorine, terminal, as in R—Cl	0.0216	in higher esters and ethers	0.0110
medial, as in R—CHCl—R′	0.0246	in acids	0.0120
Chromium	0.0274	in union with S, P, N	0.0083
Fluorine	0.0087	Phosphorus	0.0270
Germanium	0.0345	Silicon	0.0320
Hydrogen	0.0037	Sulphur	0.0256
Nitrogen, double-bonded	0.0156	Tin	0.0423
in primary amines	0.0105	Titanium	0.0357
in secondary amines	0.0120	Vanadium	0.0320
		Zinc	0.0204

For a three-membered ring, as in ethylene oxide,	deduct 0.0060.
For a four-membered ring, as in cyclobutane,	deduct 0.0085.
For a five-membered ring, as in furane,	deduct 0.0115.
For a six-membered ring, as in benzene, pyridine,	deduct 0.0150.
For an anthracene ring formation,	deduct 0.0475.
For naphthalene	deduct 0.0300.

Diffusion volumes of simple molecules (m^3/kmol)

H_2	0.0143	CO_2	0.0340	NH_3	0.0258
O_2	0.0256	H_2O	0.0189	H_2S	0.0329
N_2	0.0312	SO_2	0.0448	Cl_2	0.0484
Air	0.0299	NO	0.0236	Br_2	0.0532
CO	0.0307	N_2O	0.0364	I_2	0.0715

Example 10.3

Ammonia is absorbed in water from a mixture with air using a column operating at 1 bar and 295 K. The resistance to transfer may be regarded as lying entirely within the gas phase. At a point in the column, the partial pressure of the ammonia is 7.0 kN/m^2. The back pressure at the water interface is negligible and the resistance to transfer may be regarded as lying in a stationary gas film 1 mm thick. If the diffusivity of ammonia in air is 2.36×10^{-5} m^2/s, what is the transfer rate per unit area at that point in the column? How would the rate of transfer be affected if the ammonia air mixture were compressed to double the pressure?

Solution

Concentration of ammonia in the gas

$$= \left(\frac{1}{22.4}\right)\left(\frac{101.3}{101.3}\right)\left(\frac{273}{295}\right)\left(\frac{7.0}{101.3}\right) = 0.00285 \text{ kmol/m}^3$$

Thus:
$$\frac{C_T}{C_{Bm}} = \frac{101.3\ln(101.3/94.3)}{101.3 - 94.3} = 1.036$$

From equation 10.33:

$$N'_A = \frac{D}{y_2 - y_1}\frac{C_T}{C_{Bm}}(C_{A1} - C_{A2})$$

$$= \left(\frac{2.36 \times 10^{-5}}{1 \times 10^{-3}}\right)(1.036 \times 0.00285)$$

$$= \underline{\underline{6.97 \times 10^{-5} \text{ kmol/m}^2\text{s}}}$$

If the pressure is doubled, the driving force is doubled, C_T/C_{Bm} is essentially unaltered, and the diffusivity, being inversely proportional to the pressure (equation 10.43) is halved. The mass transfer rate therefore remains the same.

10.2.5. Mass transfer velocities

It is convenient to express mass transfer rates in terms of velocities for the species under consideration where:

$$\text{Velocity} = \frac{\text{Flux}}{\text{Concentration}},$$

which, in the S.I system, has the units $(\text{kmol/m}^2\text{s})/(\text{kmol/m}^3) = \text{m/s}$.

For diffusion according to Fick's Law:

$$u_{DA} = \frac{N_A}{C_A} = -\frac{D}{C_A}\frac{\mathrm{d}C_A}{\mathrm{d}y} \tag{10.44a}$$

and:

$$u_{DB} = \frac{N_B}{C_B} = -\frac{D}{C_B}\frac{\mathrm{d}C_B}{\mathrm{d}y} = \frac{D}{C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y} \tag{10.44b}$$

Since $N_B = -N_A$, then:

$$u_{DB} = -u_{DA}\frac{C_A}{C_B} = -u_{DA}\frac{x_A}{x_B} \tag{10.45}$$

As a result of the diffusional process, there is no net overall molecular flux arising from diffusion in a binary mixture, the two components being transferred at equal and opposite rates. In the process of equimolecular counterdiffusion which occurs, for example, in a distillation column when the two components have equal molar latent heats, the diffusional velocities are the same as the velocities of the molecular species relative to the walls of the equipment or the phase boundary.

If the physical constraints placed upon the system result in a bulk flow, the velocities of the molecular species relative to one another remain the same, but in order to obtain the velocity relative to a fixed point in the equipment, it is necessary to add the bulk flow velocity. An example of a system in which there is a bulk flow velocity is that in which one of the components is transferred through a second component which is undergoing no net transfer, as for example in the absorption of a soluble gas **A** from a mixture with an insoluble gas **B**. (See Section 10.2.3). In this case, because there is no set flow of **B**, the sum of its diffusional velocity and the bulk flow velocity must be zero.

In this case:

Component	**A**	**B**
Diffusional velocity	$u_{DA} = -\frac{D}{C_A}\frac{\mathrm{d}C_A}{\mathrm{d}y}$	$u_{DB} = +\frac{D}{C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y}$
Bulk flow velocity	$u_F = -\frac{D}{C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y}$	$u_F = -\frac{D}{C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y}$
Total velocity	$u_A = -D\frac{C_T}{C_A C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y}$	$u_B = 0$
Flux	$N'_A = u_A C_A = -D\frac{C_T}{C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y}$	$N'_B = 0$

The flux of **A** has been given as Stefan's Law (equation 10.30).

10.2.6. General case for gas-phase mass transfer in a binary mixture

Whatever the physical constraints placed on the system, the diffusional process causes the two components to be transferred at equal and opposite rates and the values of the diffusional velocities u_{DA} and u_{DB} given in Section 10.2.5 are always applicable. It is the bulk flow velocity u_F which changes with imposed conditions and which gives rise to differences in overall mass transfer rates. In equimolecular counterdiffusion, u_F is zero. In the absorption of a soluble gas **A** from a mixture the bulk velocity must be equal and opposite to the diffusional velocity of **B** as this latter component undergoes no net transfer.

In general, for any component:

Total transfer = Transfer by diffusion + Transfer by bulk flow.

For component **A:**

Total transfer (moles/area time) $= N'_A$

Diffusional transfer according to Fick's Law $= N_A = -D\dfrac{\mathrm{d}C_A}{\mathrm{d}y}$

Transfer by bulk flow $= u_F C_A$

Thus for **A**:
$$N'_A = N_A + u_F C_A \tag{10.46a}$$

and for **B**:
$$N'_B = N_B + u_F C_B \tag{10.46b}$$

$$\text{The bulk flow velocity } u_F = \frac{\text{Total moles transferred/area time}}{\text{Total molar concentration}}$$

$$= \frac{(N'_A + N'_B)}{C_T} \tag{10.47}$$

Substituting:

$$N'_A = N_A + \frac{C_A}{C_T}(N'_A + N'_B)$$

$$N'_A = -D\frac{\mathrm{d}C_A}{\mathrm{d}y} + x_A(N'_A + N'_B)$$

$$N'_A = -DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} + x_A(N'_A + N'_B) \tag{10.48}$$

Similarly for **B:**
$$N'_B = DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} + (1 - x_A)(N'_A + N'_B) \tag{10.49}$$

For equimolecular counterdiffusion $N'_A = -N'_B$ and equation 10.48 reduces to Fick's Law. For a system in which **B** undergoes no net transfer, $N'_B = 0$ and equation 10.48 is identical to Stefan's Law.

For the general case:
$$fN'_A = -N'_B \tag{10.50}$$

If in a distillation column, for example the molar latent heat of **A** is f times that of **B,** the condensation of 1 mole of **A** (taken as the less volatile component) will result in the vaporisation of f moles of **B** and the mass transfer rate of **B** will be f times that of **A** in the opposite direction.

Substituting into equation 10.48:

$$N'_A = -DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} + x_A(N'_A - fN'_A) \tag{10.51}$$

Thus: $$[1 - x_A(1 - f)]N'_A = -DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y}$$

If x_A changes from x_{A_1} to x_{A_2} as y goes from y_1 to y_2, then:

$$N'_A\int_{y_1}^{y_2}\mathrm{d}y = -DC_T\int_{x_{A_1}}^{x_{A_2}}\frac{\mathrm{d}x_A}{1 - x_A(1 - f)}$$

Thus: $$N'_A(y_2 - y_1) = -DC_T\frac{1}{1 - f}\left[\ln\frac{1}{(1 - f)^{-1} - x_A}\right]_{x_{A_1}}^{x_{A_2}}$$

or: $$N'_A = \frac{DC_T}{y_2 - y_1}\frac{1}{1 - f}\ln\frac{1 - x_{A_2}(1 - f)}{1 - x_{A_1}(1 - f)} \tag{10.52}$$

10.2.7. Diffusion as a mass flux

Fick's Law of diffusion is normally expressed in *molar* units or:

$$N_A = -D\frac{\mathrm{d}C_A}{\mathrm{d}y} = -DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} \qquad \text{(equation 10.4)}$$

where x_A is the mole fraction of component **A.**

The corresponding equation for component **B** indicates that there is an equal and opposite molar flux of that component. If each side of equation 10.4 is multiplied by the molecular weight of **A**, M_A, then:

$$J_A = -D\frac{\mathrm{d}c_A}{\mathrm{d}y} = -DM_A\frac{\mathrm{d}C_A}{\mathrm{d}y} = -DC_TM_A\frac{\mathrm{d}x_A}{\mathrm{d}y} \tag{10.53}$$

where J_A is a flux in mass per unit area and unit time (kg/m^2 s in S.I units), and c_A is a concentration in mass terms, (kg/m^3 in S.I units).

Similarly, for component **B:**

$$J_B = -D\frac{\mathrm{d}c_B}{\mathrm{d}y} \tag{10.54}$$

Although the sum of the molar concentrations is constant in an ideal gas at constant pressure, the sum of the mass concentrations is not constant, and $\mathrm{d}c_A/\mathrm{d}y$ and $\mathrm{d}c_B/\mathrm{d}y$ are not equal and opposite,

Thus: $$C_A + C_B = C_T = \frac{c_A}{M_A} + \frac{c_B}{M_B} = \text{constant} \tag{10.55}$$

or: $$\frac{1}{M_A}\frac{\mathrm{d}c_A}{\mathrm{d}y} + \frac{1}{M_B}\frac{\mathrm{d}c_B}{\mathrm{d}y} = 0$$

and:

$$\frac{\mathrm{d}c_B}{\mathrm{d}y} = -\frac{M_B}{M_A}\frac{\mathrm{d}c_A}{\mathrm{d}y} \tag{10.56}$$

Thus, the diffusional process does not give rise to equal and opposite mass fluxes.

10.2.8. Thermal diffusion

If a temperature gradient is maintained in a binary gaseous mixture, a concentration gradient is established with the light component collecting preferentially at the hot end and the heavier one at the cold end. This phenomenon, known as the *Soret effect*, may be used as the basis of a separation technique of commercial significance in the separation of isotopes.

Conversely, when mass transfer is occurring as a result of a constant concentration gradient, a temperature gradient may be generated; this is known as the *Dufour effect*.

In a binary mixture consisting of two gaseous components **A** and **B** subject to a temperature gradient, the flux due to thermal diffusion is given by GREW and IBBS$^{(9)}$:

$$(N_A)_{Th} = -D_{Th}\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}y} \tag{10.57}$$

where $(N_A)_{Th}$ is the molar flux of **A** (kmol/m^2 s) in the Y-direction, and D_{Th} is the diffusion coefficient for thermal diffusion (kmol/m s).

Equation 10.57, with a positive value of D_{Th}, applies to the component which travels preferentially to the *low* temperature end of the system. For the component which moves to the high temperature end, D_{Th} is negative. In a binary mixture, the gas of higher molecular weight has the positive value of D_{Th} and this therefore tends towards the lower temperature end of the system.

If two vessels each containing completely mixed gas, one at temperature T_1 and the other at a temperature T_2, are connected by a lagged non-conducting pipe in which there are no turbulent eddies (such as a capillary tube), then under steady state conditions, the rate of transfer of **A** by thermal diffusion and molecular diffusion must be equal and opposite, or:

$$(N_A)_{Th} + N_A = 0 \tag{10.58}$$

N_A is given by Fick's Law as:

$$N_A = -D\frac{\mathrm{d}C_A}{\mathrm{d}y} = -DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} \qquad \text{(equation 10.53)}$$

where x_A is the mole fraction of **A**, and C_T is the total molar concentration at y and will not be quite constant because the temperature is varying.

Substituting equations 10.53 and 10.57 into equation 10.58 gives:

$$-D_{Th}\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}y} - DC_T\frac{\mathrm{d}x_A}{\mathrm{d}y} = 0 \tag{10.59}$$

The relative magnitudes of the thermal diffusion and diffusion effects are represented by the dimensionless ratio:

$$\frac{D_{Th}}{DC_T} = K_{ABT}$$

where K_{ABT} is known as the *thermal diffusion ratio*.

Thus:

$$-K_{ABT}\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}y} = \frac{\mathrm{d}x_A}{\mathrm{d}y} \tag{10.60}$$

If temperature gradients are small, C_T may be regarded as effectively constant. Furthermore, K_{ABT} is a function of composition, being approximately proportional to the product $x_A x_B$. It is therefore useful to work in terms of the *thermal diffusion factor* α, where:

$$\alpha = \frac{K_{ABT}}{x_A(1 - x_A)}$$

Substituting for α, assumed constant, in equation 10.60 and integrating, gives:

$$\alpha \ln \frac{T_1}{T_2} = \ln \left(\frac{x_{A_2}}{1 - x_{A_2}} \frac{1 - x_{A_1}}{x_{A_1}} \right)$$

Thus:

$$\frac{x_{A_2} x_{B_1}}{x_{A_1} x_{B_2}} = \left(\frac{T_1}{T_2} \right)^{\alpha} \tag{10.61}$$

Equation 10.61 gives the mole fraction of the two components **A** and **B** as a function of the absolute temperatures and the thermal diffusion factor.

Values of α taken from data in GREW and IBBS$^{(9)}$ and HIRSCHFELDER, CURTISS and BIRD$^{(10)}$ are given in Table 10.5.

Table 10.5. Values of thermal diffusion factor (α) for binary gas mixtures (**A** is the heavier component, which moves towards the cooler end)

Systems A	Systems B	Temperature (K)	Mole fraction of **A** x_A	α
D_2	H_2	288–373	0.48	0.17
He	H_2	273–760	0.50	0.15
N_2	H_2	288–373	0.50	0.34
Ar	H_2	258	0.53	0.26
O_2	H_2	90–294	0.50	0.19
CO	H_2	288–373	0.50	0.33
CO_2	H_2	288–456	0.50	0.28
C_3H_8	H_2	230–520	0.50	0.30
N_2	He	287–373	0.50	0.36
		260	0.655	0.37
Ar	He	330	0.90	0.28
		330	0.70	0.31
		330	0.50	0.37
Ne	He	205	0.46	0.31
		330	0.46	0.315
		365	0.46	0.315
O_2	N_2	293	0.50	0.018

10.2.9. Unsteady-state mass transfer

In many practical mass transfer processes, unsteady state conditions prevail. Thus, in the example given in Section 10.1, a box is divided into two compartments each containing a different gas and the partition is removed. Molecular diffusion of the gases takes place and concentrations, and concentration gradients, change with time. If a bowl of liquid evaporates into an enclosed space, the partial pressure in the gas phase progressively increases, and the concentrations and the rate of evaporation are both time-dependent.

Considering an element of gas of cross-sectional area A and of thickness δy in the direction of mass transfer in which the concentrations C_A and C_B of the components **A** and **B** are a function of both position y and time t (Figure 10.4), then if the mass transfer flux is composed of two components, one attributable to diffusion according to Fick's Law and the other to a bulk flow velocity u_F, the fluxes of **A** and **B** at a distance y from the origin may be taken as N'_A and N'_B, respectively. These will increase to $N'_A + (\partial N'_A/\partial y)\delta y$ and $N'_B + (\partial N'_B/\partial y)\delta y$ at a distance $y + \delta y$ from the origin.

At position y, the fluxes N'_A and N'_B will be as given in Table 10.6. At a distance $y + \delta y$ from the origin, that is at the further boundary of the element, these fluxes will increase by the amounts shown in the lower part of Table 10.6.

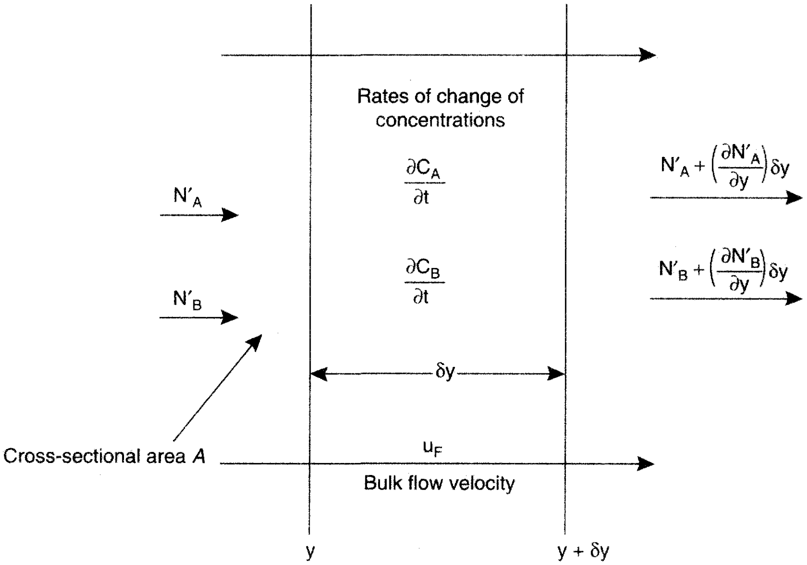

Figure 10.4. Unsteady state mass transfer

Thus, for **A**:

$$\underset{\text{(at } y)}{\text{moles IN/unit time}} \quad - \quad \underset{\text{(at } y+\partial y)}{\text{moles OUT/unit time}} \quad = \underset{\times\ \text{element volume}}{\text{rate of change of concn.}}$$

$$\left\{-D\frac{\partial C_A}{\partial y} + u_F c_A\right\}A - \left\{-D\frac{\partial C_A}{\partial y} + u_F c_A + \frac{\partial}{\partial y}\left[-D\frac{\partial C_A}{\partial y} + u_F C_A\right]\delta y\right\}A = \frac{\partial C_A}{\partial t}(\delta y.A)$$

Simplifying:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial y^2} - \frac{\partial (u_F C_A)}{\partial y} \tag{10.64a}$$

For component **B**:

$$\frac{\partial C_B}{\partial t} = D\frac{\partial^2 C_B}{\partial y^2} - \frac{\partial (u_F C_B)}{\partial y} \tag{10.64b}$$

and adding:

$$\frac{\partial (C_A + C_B)}{\partial t} = D\frac{\partial^2 (C_A + C_B)}{\partial y^2} - \frac{\partial}{\partial y}[(C_A + C_B)u_F]$$

Table 10.6. Fluxes of a gas mixture

	Diffusional flux	Flux due to bulk flow	Total flux	
A	$-D\frac{\partial C_A}{\partial y}$	$u_F C_A$	$N'_A = -D\frac{\partial C_A}{\partial y} + u_F C_A$	(10.62)
B	$-D\frac{\partial C_B}{\partial y}$	$u_F C_B$	$N'_B = -D\frac{\partial C_B}{\partial y} + u_F C_B$	(10.63)
Changes in fluxes over distance δy:				
A	$-D\left(\frac{\partial^2 C_A}{\partial y^2}\right)\delta y$	$\frac{\partial(u_F C_A)}{\partial y}\delta y$	$\left\{-D\frac{\partial^2 C_A}{\partial y^2} + \frac{\partial(u_F C_A)}{\partial y}\right\}\delta y$	
B	$-D\left(\frac{\partial^2 C_B}{\partial y^2}\right)\delta y$	$\frac{\partial(u_F C_B)}{\partial y}\delta y$	$\left\{-D\frac{\partial^2 C_B}{\partial y^2} + \frac{\partial(u_F C_B)}{\partial y}\right\}\delta y$	

Since, for an ideal gas, $C_A + C_B = C_T =$ constant (equation 10.9):

$$0 = 0 - \frac{\partial}{\partial y}(u_F C_T)$$

and:

$$\frac{\partial u_F}{\partial y} = 0$$

where u_F is therefore independent of y.

Thus equation 10.64*a* can be written:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial y^2} - u_F\frac{\partial C_A}{\partial y} \tag{10.65}$$

Equimolecular counterdiffusion

For equimolecular counterdiffusion, $u_F = 0$ and equation 10.65 simplifies to:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial y^2} \tag{10.66}$$

Equation 10.66 is referred to as Fick's Second Law. This also applies when u_F is small, corresponding to conditions where C_A is always low. This equation can be solved for a number of important boundary conditions, and it should be compared with the corresponding equation for unsteady state heat transfer (equation 9.29).

For the more general three-dimensional case where concentration gradients are changing in the x, y and z directions, these changes must be added to give:

$$\frac{\partial C_A}{\partial t} = D\left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right] \tag{10.67}$$

(c/f equation 9.28)

Gas absorption

In general, it is necessary to specify the physical constraints operating on the system in order to evaluate the bulk flow velocity u_F. In gas absorption, there will be no overall flux of the insoluble component **B** at the liquid interface ($y = 0$, say). In an unsteady state process, however, where, by definition, concentrations will be changing with time throughout the system, the flux of **B** will be zero only at $y = 0$. At the interface ($y = 0$), total flux of **B** (from equation 10.43*b*) is given by:

$$N'_B = -D\left(\frac{\partial C_B}{\partial y}\right)_{y=0} + u_F(C_B)_{y=0} = 0$$

or:

$$u_F = \frac{D\left(\dfrac{\partial C_B}{\partial y}\right)_{y=0}}{(C_B)_{y=0}} = \frac{-D}{(C_T - C_A)_{y=0}}\left(\frac{\partial C_A}{\partial y}\right)_{y=0} \tag{10.68}$$

Substituting in equation 10.65:

$$\frac{\partial C_A}{\partial t} = D\left[\frac{\partial^2 C_A}{\partial y^2} + \frac{1}{(C_T - C_A)_{y=0}}\left(\frac{\partial C_A}{\partial y}\right)_{y=0}\frac{\partial C_A}{\partial y}\right] \tag{10.69}$$

Thus at the interface ($y = 0$):

$$\left(\frac{\partial C_A}{\partial t}\right)_{y=0} = D\left[\left(\frac{\partial^2 C_A}{\partial y^2}\right)_{y=0} + \frac{1}{(C_T - C_A)_{y=0}}\left(\frac{\partial C_A}{\partial y}\right)^2_{y=0}\right] \tag{10.70}$$

This equation which is not capable of an exact analytical solution has been discussed by ARNOLD$^{(11)}$ in relation to evaporation from a free surface.

Substituting into equation 10.62 for N'_A:

$$\begin{aligned} N'_A &= -D\frac{\partial C_A}{\partial y} - \frac{DC_A}{(C_T - C_A)_{y=0}}\left(\frac{\partial C_A}{\partial y}\right)_{y=0} \\ &= -D\left[\frac{\partial C_A}{\partial y} + \frac{C_A}{(C_T - C_A)_{y=0}}\left(\frac{\partial C_A}{\partial y}\right)_{y=0}\right] \end{aligned} \tag{10.71}$$

10.3. MULTICOMPONENT GAS-PHASE SYSTEMS

10.3.1. Molar flux in terms of effective diffusivity

For a multicomponent system, the bulk flow velocity u_F is given by:

$$u_F = \frac{1}{C_T}(N'_A + N'_B + N'_C + \cdots) \tag{10.72}$$

or:

$$u_F = x_A u_A + x_B u_B + x_C u_C + \cdots \tag{10.73}$$

or:

$$u_F = \sum x_A u_A = \frac{1}{C_T}\sum N'_A \tag{10.74}$$

Since $N'_A = N_A + u_F C_A$ (equation 10.46*a*), then:

$$N'_A = -D'\frac{dC_A}{dy} + \left[\frac{1}{C_T}\Sigma N'_A\right] C_A$$

$$= -D'C_T\frac{dx_A}{dy} + x_A \Sigma N'_A \qquad (10.75)$$

where D' is the effective diffusivity for transfer of **A** in a mixture of **B**, **C**, **D**, and so on.

For the particular case, where N'_B, N'_C, and so on, are all zero:

$$N'_A = -D'C_T\frac{dx_A}{dy} + x_A N'_A$$

or:

$$N'_A = -D'\frac{C_T}{1 - x_A}\frac{dx_A}{dy} \qquad (10.76)$$

A method of calculating the effective diffusivity D' in terms of each of the binary diffusivities is presented in Section 10.3.2.

10.3.2. Maxwell's law of diffusion

Maxwell's law for a binary system

MAXWELL$^{(12)}$ postulated that the partial pressure gradient in the direction of diffusion for a constituent of a two-component gaseous mixture was proportional to:

(a) the relative velocity of the molecules in the direction of diffusion, and
(b) the product of the molar concentrations of the components.

Thus:

$$-\frac{dP_A}{dy} = FC_A C_B(u_A - u_B) \qquad (10.77)$$

where u_A and u_B are the mean molecular velocities of **A** and **B** respectively in the direction of mass transfer and F is a coefficient.

Noting that:

$$u_A = \frac{N'_A}{C_A} \qquad (10.78)$$

and:

$$u_B = \frac{N'_B}{C_B} \qquad (10.79)$$

and using: $P_A = C_A \mathbf{R}T$ (for an ideal gas) (equation 10.10*a*)

on substitution into equation 10.77 gives:

$$-\frac{dC_A}{dy} = \frac{F}{\mathbf{R}T}(N_A C_B - N_B C_A) \qquad (10.80)$$

Equimolecular counterdiffusion

By definition: $N'_A = -N'_B = N_A$

Substituting in equation 10.80:

$$-\frac{\mathrm{d}C_A}{\mathrm{d}y} = \frac{FN_A}{\mathbf{R}T}(C_B + C_A) \tag{10.81}$$

or:

$$N_A = -\frac{\mathbf{R}T}{FC_T}\frac{\mathrm{d}C_A}{\mathrm{d}y} \tag{10.82}$$

Then, by comparison with Fick's Law (equation 10.4):

$$D = \frac{\mathbf{R}T}{FC_T} \tag{10.83}$$

or:

$$F = \frac{\mathbf{R}T}{DC_T} \tag{10.84}$$

Transfer of A through stationary B

By definition: $N'_B = 0$

Thus: $$-\frac{\mathrm{d}C_A}{\mathrm{d}y} = \frac{F}{\mathbf{R}T}N'_A C_B \qquad \text{(from equation 10.80)}$$

or:

$$N'_A = -\frac{\mathbf{R}T}{FC_T}\frac{C_T}{C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y} \tag{10.85}$$

Substituting from equation 10.83:

$$N'_A = -D\frac{C_T}{C_B}\frac{\mathrm{d}C_A}{\mathrm{d}y} \tag{10.86}$$

It may be noted that equation 10.86 is identical to equation 10.30. (Stefan's Law) and, Stefan's law can therefore also be derived from Maxwell's Law of Diffusion.

Maxwell's Law for multicomponent mass transfer

This argument can be applied to the diffusion of a constituent of a multi-component gas. Considering the transfer of component **A** through a stationary gas consisting of components **B**, **C**, ... if the total partial pressure gradient can be regarded as being made up of a series of terms each representing the contribution of the individual component gases, then from equation 10.80:

$$-\frac{\mathrm{d}C_A}{\mathrm{d}y} = \frac{F_{AB}N'_A C_B}{\mathbf{R}T} + \frac{F_{AC}N'_A C_C}{\mathbf{R}T} + \cdots$$

or:

$$-\frac{\mathrm{d}C_A}{\mathrm{d}y} = \frac{N'_A}{\mathbf{R}T}(F_{AB}C_B + F_{AC}C_C + \cdots) \tag{10.87}$$

From equation 10.84, writing:

$$F_{AB} = \frac{\mathbf{R}T}{D_{AB}C_T}, \quad \text{and so on.}$$

where D_{AB} is the diffusivity of **A** in **B**, and so on.:

$$-\frac{dC_A}{dy} = \frac{N'_A}{C_T}\left(\frac{C_B}{D_{AB}} + \frac{C_C}{D_{AC}} + \cdots\right) \tag{10.88}$$

$$\therefore \quad N'_A = -\frac{C_T}{\dfrac{C_B}{D_{AB}} + \dfrac{C_C}{D_{AC}} + \cdots}\frac{dC_A}{dy}$$

$$= -\frac{1}{\dfrac{C_B}{C_T - C_A}\dfrac{1}{D_{AB}} + \dfrac{C_C}{C_T - C_A}\dfrac{1}{D_{AC}} + \cdots}\frac{C_T}{C_T - C_A}\frac{dC_A}{dy}$$

$$= -\frac{1}{\dfrac{y'_B}{D_{AB}} + \dfrac{y'_C}{D_{AC}} + \cdots}\frac{C_T}{C_T - C_A}\frac{dC_A}{dy} \tag{10.89}$$

where y'_B is the mole fraction of **B** and so on in the stationary components of the gas.

By comparing equation 10.89 with Stefan's Law (equation 10.30) the effective diffusivity of **A** in the mixture (D') is given by:

$$\frac{1}{D'} = \frac{y'_B}{D_{AB}} + \frac{y'_C}{D_{AC}} + \cdots \tag{10.90}$$

Multicomponent mass transfer is discussed in more detail by TAYLOR and KRISHNA(13), CUSSLER(14) and ZIELINSKI and HANLEY(15)

10.4. DIFFUSION IN LIQUIDS

Whilst the diffusion of solution in a liquid is governed by the same equations as for the gas phase, the diffusion coefficient D is about two orders of magnitude smaller for a liquid than for a gas. Furthermore, the diffusion coefficient is a much more complex function of the molecular properties.

For an ideal gas, the total molar concentration C_T is constant at a given total pressure P and temperature T. This approximation holds quite well for real gases and vapours, except at high pressures. For a liquid however, C_T may show considerable variations as the concentrations of the components change and, in practice, the total mass concentration (density ρ of the mixture) is much more nearly constant. Thus for a mixture of ethanol and water for example, the mass density will range from about 790 to 1000 kg/m^3 whereas the molar density will range from about 17 to 56 kmol/m^3. For this reason the diffusion equations are frequently written in the form of a mass flux J_A (mass/area × time) and the concentration gradients in terms of mass concentrations, such as c_A.

Thus, for component **A**, the mass flux is given by:

$$J_A = -D\frac{dc_A}{dy} \tag{10.91}$$

$$= -D\rho\frac{\mathrm{d}\omega_A}{\mathrm{d}y} \tag{10.92}$$

where ρ is mass density (now taken as constant), and ω_A is the mass fraction of **A** in the liquid.

For component **B**:

$$J_B = -D\rho\frac{\mathrm{d}\omega_B}{\mathrm{d}y} \tag{10.93}$$

$$= D\rho\frac{\mathrm{d}\omega_A}{\mathrm{d}y} \quad (\text{since } \omega_A + \omega_B = 1). \tag{10.94}$$

Thus, the diffusional process in a liquid gives rise to a situation where the components are being transferred at approximately equal and opposite mass (rather than molar) rates.

Liquid phase diffusivities are strongly dependent on the concentration of the diffusing component which is in strong contrast to gas phase diffusivities which are substantially independent of concentration. Values of liquid phase diffusivities which are normally quoted apply to very dilute concentrations of the diffusing component, the only condition under which analytical solutions can be produced for the diffusion equations. For this reason, only dilute solutions are considered here, and in these circumstances no serious error is involved in using Fick's first and second laws expressed in molar units.

The molar flux is given by:

$$N_A = -D\frac{\mathrm{d}C_A}{\mathrm{d}y} \tag*{(equation 10.4)}$$

and:

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial y^2} \tag*{(equation 10.66)}$$

where D is now the liquid phase diffusivity and C_A is the molar concentration in the liquid phase.

On integration, equation 10.4 becomes:

$$N_A = -D\frac{C_{A_2} - C_{A_1}}{y_2 - y_1} = \frac{D}{y_2 - y_1}(C_{A_1} - C_{A_2}) \tag{10.95}$$

and $D/(y_2 - y_1)$ is the liquid phase mass transfer coefficient.

An example of the integration of equation 10.66 is given in Section 10.5.3.

10.4.1. Liquid phase diffusivities

Values of the diffusivities of various materials in water are given in Table 10.7. Where experimental values are not available, it is necessary to use one of the predictive methods which are available.

A useful equation for the calculation of liquid phase diffusivities of dilute solutions of non-electrolytes has been given by WILKE and CHANG[(16)]. This is not dimensionally consistent and therefore the value of the coefficient depends on the units employed. Using SI units:

$$D = \frac{1.173 \times 10^{-16}\phi_B^{1/2}M_B^{1/2}T}{\mu \mathbf{V}_A^{0.6}} \tag{10.96}$$

Table 10.7. Diffusivities (diffusion coefficients) and Schmidt numbers, in liquids at 293 K[4]

Solute	Solvent	D ($m^2/s \times 10^9$)	Sc ($\mu/\rho D$)*
O_2	Water	1.80	558
CO_2	Water	1.50	670
N_2O	Water	1.51	665
NH_3	Water	1.76	570
Cl_2	Water	1.22	824
Br_2	Water	1.2	840
H_2	Water	5.13	196
N_2	Water	1.64	613
HCl	Water	2.64	381
H_2S	Water	1.41	712
H_2SO_4	Water	1.73	580
HNO_3	Water	2.6	390
Acetylene	Water	1.56	645
Acetic acid	Water	0.88	1140
Methanol	Water	1.28	785
Ethanol	Water	1.00	1005
Propanol	Water	0.87	1150
Butanol	Water	0.77	1310
Allyl alcohol	Water	0.93	1080
Phenol	Water	0.84	1200
Glycerol	Water	0.72	1400
Pyrogallol	Water	0.70	1440
Hydroquinone	Water	0.77	1300
Urea	Water	1.06	946
Resorcinol	Water	0.80	1260
Urethane	Water	0.92	1090
Lactose	Water	0.43	2340
Maltose	Water	0.43	2340
Glucose	Water	0.60	1680
Mannitol	Water	0.58	1730
Raffinose	Water	0.37	2720
Sucrose	Water	0.45	2230
Sodium chloride	Water	1.35	745
Sodium hydroxide	Water	1.51	665
CO_2	Ethanol	3.4	445
Phenol	Ethanol	0.8	1900
Chloroform	Ethanol	1.23	1230
Phenol	Benzene	1.54	479
Chloroform	Benzene	2.11	350
Acetic acid	Benzene	1.92	384
Ethylene dichloride	Benzene	2.45	301

*Based on $\mu/\rho = 1.005 \times 10^{-6} m^2/s$ for water, 7.37×10^{-7} for benzene, and 1.511×10^{-6} for ethanol, all at 293 K. The data apply only for dilute solutions.

The values are based mainly on *International Critical Tables* **5** (1928).

where D is the diffusivity of solute **A** in solvent **B** (m^2/s),

ϕ_B is the association factor for the solvent (2.26 for water, 1.9 for methanol, 1.5 for ethanol and 1.0 for unassociated solvents such as hydrocarbons and ethers),

M_B is the molecular weight of the solvent,

μ is the viscosity of the solution ($N\,s/m^2$),

T is temperature (K), and

$\mathbf{V}_A$ is the molecular volume of the solute (m^3/kmol). Values for simple molecules are given in Table 10.4. For more complex molecules, $\mathbf{V}_A$ is calculated by summation of the atomic volume and other contributions given in Table 10.4.

It may be noted that for water a value of 0.0756 m^3/kmol should be used.

Equation 10.96 does not apply to either electrolytes or to concentrated solutions. REID, PRAUSNITZ and SHERWOOD$^{(17)}$ discuss diffusion in electrolytes. Little information is available on diffusivities in concentrated solutions although it appears that, for ideal mixtures, the product μD is a linear function of the molar concentration.

The calculation of liquid phase diffusivities is discussed further in Volume 6.

10.5. MASS TRANSFER ACROSS A PHASE BOUNDARY

The theoretical treatment which has been developed in Sections 10.2–10.4 relates to mass transfer within a single phase in which no discontinuities exist. In many important applications of mass transfer, however, material is transferred across a phase boundary. Thus, in distillation a vapour and liquid are brought into contact in the fractionating column and the more volatile material is transferred from the liquid to the vapour while the less volatile constituent is transferred in the opposite direction; this is an example of equimolecular counterdiffusion. In gas absorption, the soluble gas diffuses to the surface, dissolves in the liquid, and then passes into the bulk of the liquid, and the carrier gas is not transferred. In both of these examples, one phase is a liquid and the other a gas. In liquid–liquid extraction however, a solute is transferred from one liquid solvent to another across a phase boundary, and in the dissolution of a crystal the solute is transferred from a solid to a liquid.

Each of these processes is characterised by a transference of material across an interface. Because no material accumulates there, the rate of transfer on each side of the interface must be the same, and therefore the concentration gradients automatically adjust themselves so that they are proportional to the resistance to transfer in the particular phase. In addition, if there is no resistance to transfer at the interface, the concentrations on each side will be related to each other by the phase equilibrium relationship. Whilst the existence or otherwise of a resistance to transfer at the phase boundary is the subject of conflicting views$^{(18)}$, it appears likely that any resistance is not high, except in the case of crystallisation, and in the following discussion equilibrium between the phases will be assumed to exist at the interface. Interfacial resistance may occur, however, if a surfactant is present as it may accumulate at the interface (Section 10.5.5).

The mass transfer rate between two fluid phases will depend on the physical properties of the two phases, the concentration difference, the interfacial area, and the degree of turbulence. Mass transfer equipment is therefore designed to give a large area of contact between the phases and to promote turbulence in each of the fluids. In the majority of plants, the two phases flow continuously in a countercurrent manner. In a steady state process, therefore, although the composition of each element of fluid is changing as it passes through the equipment, conditions at any given point do not change with time. In most industrial equipment, the flow pattern is so complex that it is not capable of expression in mathematical terms, and the interfacial area is not known precisely.