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

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:

$$N_A = -D\frac{dC_A}{dy} \qquad \text{(equation 10.4)}$$

$$N_B = -D\frac{dC_B}{dy} = D\frac{dC_A}{dy} \qquad \text{(from equation 10.3)}$$

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:

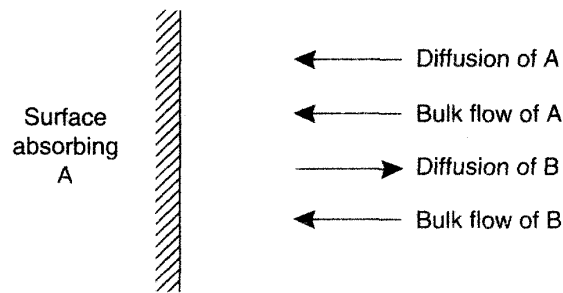$$\text{Bulk flow of } \mathbf{B} = -D\frac{dC_A}{dy} \qquad (10.28)$$

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: $$\text{Bulk flow of } \mathbf{A} = -D\frac{dC_A}{dy}\frac{C_A}{C_B} \qquad (10.29)$$

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

$$N_A' = -D\frac{dC_A}{dy} - D\frac{dC_A}{dy}\frac{C_A}{C_B}$$

$$= -D\frac{dC_A}{dy}\frac{C_T}{C_B} \qquad (10.30)$$

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:

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

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

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

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

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

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

or in terms of partial pressures:

$$N'_A = \left(\frac{D}{RT(y_2 - y_1)}\frac{P}{P_{Bm}}\right)(P_{A_1} - P_{A_2}) \qquad (10.34)$$

Similarly, in terms of mole fractions:

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

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

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

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

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

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

where:
$$k_G = \frac{D}{RT(y_2 - y_1)} \frac{P}{P_{Bm}}$$
(10.40)

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

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

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

$$N_A = -\frac{D}{RTx}(P/P_{BM})(P_{A2} - P_{A1})$$
(equation 10.31)

In this case, $x = 0.001$ m, $D = 1.8 \times 10^{-5}$ m^2/s, $R = 8314$ 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).