$$P_{A2} = 0$$

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

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

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 (m^2/s $\times 10^6$)	$\mu/\rho D$	Substance	D (m^2/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).
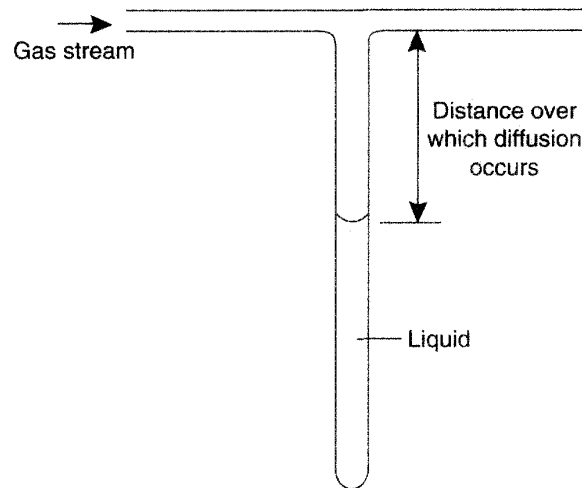
Figure 10.2. Determination of diffusivities of vapours

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		Liquid level (mm)	Time from commencement of experiment		Liquid level (mm)
(h | min)	(ks)		(h | min)	(ks)	
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:

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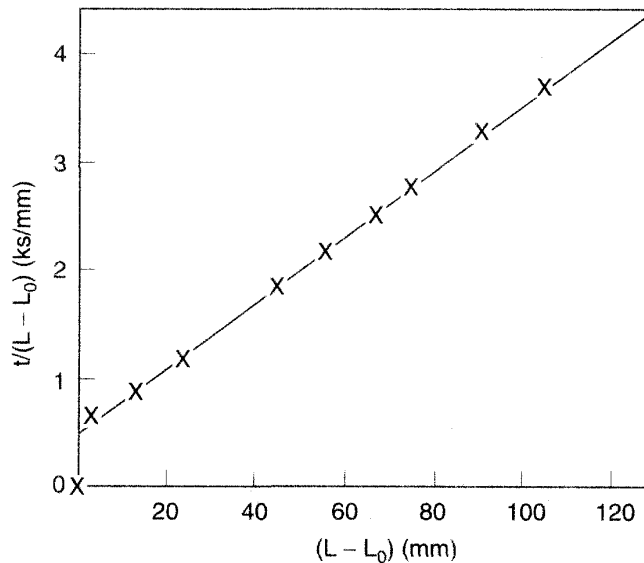

Figure 10.3.   Plot of $t/(L - L_0)$ versus $(L - L_0)$ for Example 10.1

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:

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

where D is the diffusivity in m²/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/m², and $\mathbf{V}_A, \mathbf{V}_B$ are the molecular volumes of A and B. The molecular volume is the volume in m³ 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:

$$u_{DA} = \frac{N_A}{C_A} = -\frac{D}{C_A}\frac{dC_A}{dy} \tag{10.44a}$$

and:

$$u_{DB} = \frac{N_B}{C_B} = -\frac{D}{C_B}\frac{dC_B}{dy} = \frac{D}{C_B}\frac{dC_A}{dy} \tag{10.44b}$$

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	$u_{DA} = -\dfrac{D}{C_A}\dfrac{dC_A}{dy}$	$u_{DB} = +\dfrac{D}{C_B}\dfrac{dC_A}{dy}$
Bulk flow velocity	$u_F = -\dfrac{D}{C_B}\dfrac{dC_A}{dy}$	$u_F = -\dfrac{D}{C_B}\dfrac{dC_A}{dy}$
Total velocity	$u_A = -D\dfrac{C_T}{C_A C_B}\dfrac{dC_A}{dy}$	$u_B = 0$
Flux	$N'_A = u_A C_A = -D\dfrac{C_T}{C_B}\dfrac{dC_A}{dy}$	$N'_B = 0$

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