

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 $(\text{kmol}/\text{m}^2\text{s})/(\text{kmol}/\text{m}^3) = \text{m/s}$.

For diffusion according to Fick's Law:

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

and:

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

Since $N_B = -N_A$, then:

$$u_{DB} = -u_{DA} \frac{C_A}{C_B} = -u_{DA} \frac{x_A}{x_B} \quad (10.45)$$

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

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:

$$\text{Total transfer} = \text{Transfer by diffusion} + \text{Transfer by bulk flow.}$$

For component **A**:

$$\text{Total transfer (moles/area time)} = N'_A$$

$$\text{Diffusional transfer according to Fick's Law} = N_A = -D \frac{dC_A}{dy}$$

$$\text{Transfer by bulk flow} = u_F C_A$$

$$\text{Thus for A:} \quad N'_A = N_A + u_F C_A \quad (10.46a)$$

$$\text{and for B:} \quad N'_B = N_B + u_F C_B \quad (10.46b)$$

$$\begin{aligned} \text{The bulk flow velocity } u_F &= \frac{\text{Total moles transferred/area time}}{\text{Total molar concentration}} \\ &= \frac{(N'_A + N'_B)}{C_T} \end{aligned} \quad (10.47)$$

Substituting:

$$\begin{aligned} N'_A &= N_A + \frac{C_A}{C_T} (N'_A + N'_B) \\ N'_A &= -D \frac{dC_A}{dy} + x_A (N'_A + N'_B) \\ N'_A &= -DC_T \frac{dx_A}{dy} + x_A (N'_A + N'_B) \end{aligned} \quad (10.48)$$

$$\text{Similarly for B:} \quad N'_B = DC_T \frac{dx_A}{dy} + (1 - x_A) (N'_A + N'_B) \quad (10.49)$$

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.

$$\text{For the general case:} \quad f N'_A = -N'_B \quad (10.50)$$

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:

$$N'_A = -DC_T \frac{dx_A}{dy} + x_A(N'_A - fN'_A) \quad (10.51)$$

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

If x_A changes from x_{A1} to x_{A2} as y goes from y_1 to y_2 , then:

$$N'_A \int_{y_1}^{y_2} dy = -DC_T \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{1 - x_A(1 - f)}$$

Thus: $N'_A(y_2 - y_1) = -DC_T \frac{1}{1 - f} \left[\ln \frac{1}{(1 - f)^{-1} - x_A} \right]_{x_{A1}}^{x_{A2}}$

or: $N'_A = \frac{DC_T}{y_2 - y_1} \frac{1}{1 - f} \ln \frac{1 - x_{A2}(1 - f)}{1 - x_{A1}(1 - f)} \quad (10.52)$

10.2.7. Diffusion as a mass flux

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

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

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:

$$J_A = -D \frac{dc_A}{dy} = -DM_A \frac{dC_A}{dy} = -DC_T M_A \frac{dx_A}{dy} \quad (10.53)$$

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

Similarly, for component **B**:

$$J_B = -D \frac{dc_B}{dy} \quad (10.54)$$

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 dc_A/dy and dc_B/dy are not equal and opposite,

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

or: $\frac{1}{M_A} \frac{dc_A}{dy} + \frac{1}{M_B} \frac{dc_B}{dy} = 0$

and:
$$\frac{dc_B}{dy} = -\frac{M_B}{M_A} \frac{dc_A}{dy} \quad (10.56)$$

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⁾:

$$(N_A)_{Th} = -D_{Th} \frac{1}{T} \frac{dT}{dy} \quad (10.57)$$

where $(N_A)_{Th}$ is the molar flux of **A** (kmol/m² 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:

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

N_A is given by Fick's Law as:

$$N_A = -D \frac{dC_A}{dy} = -DC_T \frac{dx_A}{dy} \quad (\text{equation 10.53})$$

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:

$$-D_{Th} \frac{1}{T} \frac{dT}{dy} - DC_T \frac{dx_A}{dy} = 0 \quad (10.59)$$

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*.