Relations Between Diffusivities, D_{AB}, D_{BA}

➢ is easily determined by ideal gases, since the molar density does not depend on the composition:

$$c_A + c_B = \rho_M = \frac{P}{RT} \qquad \text{.....(8)}$$

For diffusion of A and B in a gas at constant temperature and pressure,

$$dc_A + dc_B = d\rho_M = 0 \qquad \text{.....(9)}$$

Choosing the reference plane for which there is zero volume flow, we can set the sum of the molar diffusion fluxes of A and B to zero, since the molar volumes are the same:

$$J_A + J_B = 0 \qquad \text{.....(10)}$$

$$-D_{AB}\frac{dc_A}{dz} - D_{BA}\frac{dc_B}{dz} = 0 \qquad \text{.....(11)}$$

Since $dC_A = -dC_B$, the diffusivities must be equal, that is,

$$D_{AB} = D_{BA} \qquad \text{.....(12)}$$

➢ **If we are dealing with liquids, the same results is found if all mixtures of *A* and *B* have the same mass density**

$$c_A M_A + c_B M_B = \rho \qquad \text{.....(13)}$$

$$M_A dc_A + M_B dc_B = 0 \qquad \text{.....(14)}$$

For no volume flow across the reference plane, the sum of the volumetric flows due to diffusion is zero. The volumetric flow is the molar flow times the molar volume M/ρ and

$$-D_{AB}\frac{dc_A}{dz}\left(\frac{M_A}{\rho}\right) - D_{BA}\frac{dc_B}{dz}\left(\frac{M_B}{\rho}\right) = 0 \qquad \text{.....(15)}$$

Since $M_A dc_A = -M_B dc_B$, again the diffusivities must be equal, thus,

$$D_{AB} = D_{BA} \qquad \text{.....(16)}$$

General Case for Diffusion of Gases A and B Plus Convection

➢ **Up to now we have considered Fick's law for diffusion in a stationary fluid; that is, there has been no net movement or convective flow of the entire phases of the binary mixture *A* and *B*.**

➢ **The diffusion flux J_A occurred because of the concentration gradient.**

➢ **The rate at which moles *A* passed a fixed point to the right, which will be taken as positive flux, is J_A kg mol A/s·m² .**

➢ **This flux can be converted to a velocity of diffusion of *A* to the right by**

$$\mathrm{J}_A\,(kg\ mole\ A/m^2 \cdot s) = \upsilon_{Ad}\,c_A \left(\frac{m}{s}\ \frac{kg\ mole\ A}{m^3} \right) \qquad \text{.....(17)}$$

where υ_{Ad} is the diffusion velocity of *A* in m/s.

➢ **Now let us consider what happens when the whole fluid is moving in bulk or convective flow to the right. The molar average velocity of the whole fluid relative to a stationary point is υ_M m/s.**

➢ **Component *A* is still diffusing to the right, but now its velocity υ_{Ad} is measured relative to the moving fluid.**

➢ **To a stationary observer, *A* is moving faster than the bulk of the phase, since its diffusion velocity υ_{Ad} is added to that of the bulk phase υ_M .**

$$\upsilon_A$$

$$\upsilon_{Ad} \qquad \upsilon_M$$
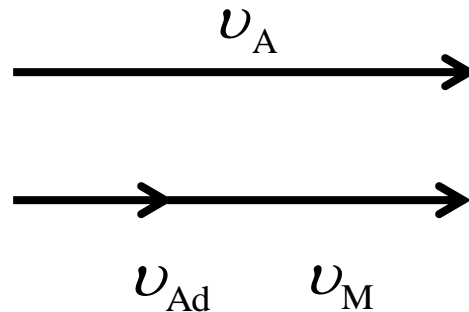
➢ **Expressed mathematically, the velocity of *A* relative to the stationary point is the sum of the diffusion velocity and the average or convective velocity**

$$\upsilon_A = \upsilon_{Ad} + \upsilon_M \qquad \text{.....(18)}$$

Multiplying the above equation by c_A.

$$c_A \upsilon_A = c_A \upsilon_{Ad} + c_A \upsilon_M \qquad \text{.....(19)}$$

➤ **Each of the three terms represents a flux.**

➤ **The first term, $c_A \upsilon_A$ can be represented by the flux N_A (kg mol A/m^2.s).**

➤ **The second term is J_A, the diffusion flux relative to the moving fluid.**

➤ **The third term is the convective flux of *A* relative to the stationary point. Hence**

$$N_A = J_A + c_A \upsilon_M \qquad \text{.....(20)}$$

- Let *N* be the total convective flux of the whole stream relative to the stationary point. Then

$$N = c\,\upsilon_{\mathrm{M}} = N_A + N_B \qquad \text{.....(21)}$$

Or, solving for υ_{M}

$$\upsilon_{\mathrm{M}} = \frac{N_A + N_B}{c} \qquad \text{.....(22)}$$

Thus, substitute Eq. (22) into Eq. (20)

$$N_{\mathrm{A}} = J_A + \frac{c_A}{c}\left(N_A + N_B\right) \qquad \text{.....(23)}$$

Since J_A is the Fick's law, then

$$N_{\mathrm{A}} = -cD_{AB}\frac{\mathrm{d}x_A}{\mathrm{d}z} + \frac{c_A}{c}\left(N_A + N_B\right) \qquad \text{.....(24)}$$

➢ **Equation above is the final general equation for diffusion plus convection to use when the flux N_A is used, which is relative to a stationary point.**

➢ **A similar equation can be written for N_B.**

$$N_B = -cD_{BA}\frac{dx_B}{dz} + \frac{c_B}{c}\left(N_A + N_B\right) \quad \text{.....(25)}$$

➢ **To solve the above two equations, the relation between the flux N_A and N_B must be known. The equations hold for diffusion in a gas, liquid or solid.**

➢ **For equimolar counterdiffusion, $N_A = -N_B$ and the convective term become zero. Then**

$$N_A = J_A = -N_B = -J_B \quad \text{.....(26)}$$

The above equations can also be used in different forms. For example, since $N = cv_M$ and $cx_A = c_A$, $(cx_B = c_B)$ thus from Eq. (20):

$$N_A = c_A v_M - D_{AB} \frac{dc_A}{dz} \qquad \text{.....(27)}$$

$$N_B = c_B v_M - D_{BA} \frac{dc_B}{dz} \qquad \text{.....(28)}$$

Therefore, the appropriate equation used to solve a problem would entirely depends on the information given in the problem.

Those equations are the basic equations for mass transfer in a non-turbulent fluid phase. It accounts for the amount of component *A* carried by the convective bulk flow of the fluid and the amount of *A* being transferred by molecular diffusion.

There are two types of situation will be discussed in the syllabus:

1) Equimolar counterdiffusion

2) Unimolecular diffusion (diffusion of a single component through stationary second component).

Equimolar Counterdiffusion

In equimolar counterdiffusion, the molar fluxes of *A* and *B* are equal, **but in opposite direction** or the net volumetric and molar flows are zero.

A typical example of this case is the diffusion of *A* and *B* in the vapor phase for distillation that have constant molar overflow.
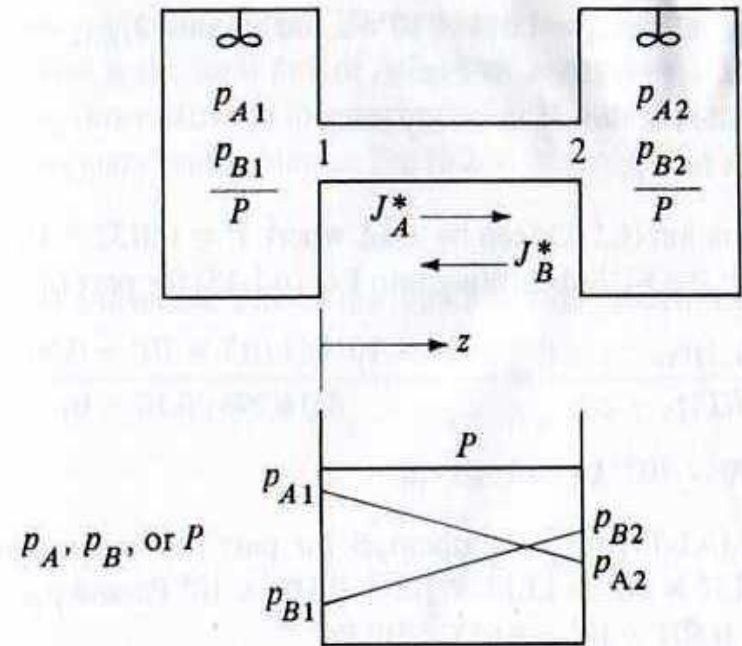

Figure 11   *Equimolar counterdiffusion of gases A and B.*

$$p_{A1} > p_{A2};$$
$$P_{B2} > P_{B1}$$

➢ **Since the net volumetric and molar flows are zero, thus Eq. (24) can be used with the convective term is set to zero, as shown below:**

$$J_A = -cD_{AB}\frac{dx_A}{dz} \qquad\qquad .....(29)$$

➢ **Eq. (29) is then integrated over a film thickness of z_T, assuming a constant flux, J_A:**

$$-D_{AB}c\int_{x_{Ai}}^{x_A} dx_A = J_A\int_0^{z_T} dz \qquad .....(30)$$

➢ **Integrating Eq. (30) and rearranging gives:**

$$J_A = \frac{D_{AB}c}{z_T}(x_{Ai} - x_A) \quad \text{or} \quad J_A = \frac{D_{AB}}{z_T}(c_{Ai} - c_A) \quad \text{.....(31)}$$

➢ **The concentration gradient for *A* is linear in the film, and the gradient for *B* has the <u>same magnitude</u> but the <u>opposite sign</u>.**

- ➢ **Molecular of *A* diffuse to the right and *B* to the left.**

- ➢ **Since the total pressure *P* is constant throughout, the net moles of *A* diffusing to the right must equal the net moles of *B* to the left.**

- ➢ **If this is not so, the total pressure would not remain constant. This means that**

$$J_A = -J_B \qquad \text{.....(32)}$$

- ➢ **Writing Fick's law for *B* for constant c,**

$$J_B = -D_{BA}\frac{dc_B}{dz} \qquad \text{.....(33)}$$

Now since $P = p_A + p_B$ = constant, then

$$c = c_A + c_B \qquad \text{.....(34)}$$

Differentiating both sides,

$$dc_A = -dc_B \qquad \text{.....(35)}$$

Thus,

$$J_A = -D_{AB}\frac{dc_A}{dz} = -cD_{AB}\frac{dx_A}{dz} = -J_B = -(-)D_{BA}\frac{dc_B}{dz} = -(-)cD_{BA}\frac{dx_B}{dz} \quad \text{.....(36)}$$

Substituting and canceling like terms,

$$D_{AB} = D_{BA} \qquad \text{.....(37)}$$

➢ **For a binary gas mixture of *A* and *B*, the diffusivity coefficient D_{AB} for *A* diffusing into *B* is the same as D_{BA} for *B* diffusing into *A*.**

Example :

Ammonia gas (*A*) is diffusing through a uniform tube 0.10 m long containing N_2 gas (*B*) at 1.0132×10^5 Pa pressure and 298 K. At a point 1, $p_{A1} = 1.013 \times 10^4$ Pa and at a point 2, $p_{A2} = 0.507 \times 10^4$ Pa. The diffusivity $D_{AB} = 0.230 \times 10^{-4}$ m²/s. Calculate the flux J_A at steady state and repeat for J_B.

Solution:

Given: $P = 1.0132 \times 10^5$ Pa $T = 298$ K

$z_2 - z_1 = 0.10$ m

Substitute known values into the following equation:

$$J_A = \frac{D_{AB}(p_{A1} - p_{A2})}{RT(z_2 - z_1)}$$

$$J_A = \frac{D_{AB}(p_{A1} - p_{A2})}{RT(z_2 - z_1)} = \frac{(0.23 \times 10^{-4})\left(\dfrac{\text{m}^2}{\text{s}}\right)(1.013 \times 10^4 - 0.507 \times 10^4)(\text{Pa})}{8314\left(\dfrac{\text{m}^3 \cdot \text{Pa}}{\text{kg mol} \cdot \text{K}}\right)(298)(\text{K})(0.10 - 0)(\text{m})}$$

$$= 4.70 \times 10^{-7} \left(\frac{\text{kg mol A}}{\text{s} \cdot \text{m}^2}\right)$$

For component B:

$p_{B1} = P - p_{A1} = 1.0132 \times 10^5 - 1.013 \times 10^4 = 9.119 \times 10^4$ Pa

$p_{B2} = P - p_{A2} = 1.0132 \times 10^5 - 0.507 \times 10^4 = 9.625 \times 10^4$ Pa

Hence,

$$J_B = \frac{D_{BA}(p_{B1} - p_{B2})}{RT(z_2 - z_1)} = \frac{(0.23 \times 10^{-4})\left(\dfrac{\mathrm{m}^2}{\mathrm{s}}\right)(9.119 \times 10^4 - 9.625 \times 10^4)(\mathrm{Pa})}{8314\left(\dfrac{\mathrm{m}^3 \cdot \mathrm{Pa}}{\mathrm{kg\,mol} \cdot \mathrm{K}}\right)(298)(\mathrm{K})(0.10 - 0)(\mathrm{m})}$$

$$= -4.70 \times 10^{-7}\left(\frac{\mathrm{kg\,mol\,B}}{\mathrm{s} \cdot \mathrm{m}^2}\right)$$

➢ **The negative value for J_B means the flux goes from point 2 to point 1.**

Unimolecular Diffusion

In unimolecular diffusion, mass transfer of component A occurs through stagnant component B, $N_B = 0$.

Therefore, the total flux to or away from the interface, N is the same as N_A.

Special Case for A Diffusing Through Stagnant, Nondiffusing B

➢ In this case one boundary at the end of the diffusion path is impermeable to component B, so it cannot pass through.