

Chapter 1

Fundamentals of Mass Transfer

When a single phase system contains two or more species whose concentrations are not uniform, mass is transferred to minimize the concentration differences within the system. In a multi-phase system mass is transferred due to the chemical potential differences between the species. In a single phase system where temperature and pressure are uniform, the difference in chemical potential is due to the variation in concentration of each species. Mass transfer is the basis for many chemical and biological processes such as the removal of sulfur dioxide from the flue gas, a chemical process, or the design of an artificial kidney, a biological process.

1.1 Molecular Mass Transfer

For a binary mixture of A and B, the molar flux, $N_{A,z}$, of species A relative to the z axis is

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z}) \quad (1.1)$$

In this equation, c is the total molar concentration, D_{AB} is the diffusivity of A in B, y_A is the mole fraction of A, and $N_{B,z}$ is the molar flux of B. For a binary mixture $D_{AB} = D_{BA}$. The term $-cD_{AB} \frac{dy_A}{dz}$ is the molar flux, J_A , resulting from the concentration gradient and the term $y_A(N_{A,z} + N_{B,z})$ is the molar flux resulting from the bulk flow of the fluid.

In a multi-component mixture, the concentration of a particular species can be expressed in mass or molar concentration. For species A, the mass concentration, ρ_A , is defined as the mass of A per unit volume of the mixture. The total mass concentration is the density of the mixture which is the total mass of the mixture per unit volume. The total mass concentration is related to the species mass concentration by

$$\rho = \sum_{i=1}^n \rho_i \quad (1.2)$$

In this equation, n is the number of species in the mixture. The mass fraction, ω_A , is the mass concentration of species A divided by the total mass density,

$$\omega_A = \frac{\rho_A}{\rho} \quad (1.3)$$

The mass concentration and the molar concentration are related by

$$c_A = \frac{\rho_A}{M_A} \quad (1.4)$$

For a binary mixture of A and B, the mass flux, $n_{A,z}$, of species A relative to the z axis is

$$n_{A,z} = -\rho D_{AB} \frac{d\omega_A}{dz} + \omega_A(n_{A,z} + n_{B,z}) \quad (1.5)$$

The molar flux of species i can be expressed as

$$N_i = c_i \mathbf{v}_i \quad (1.6)$$

In this equation, \mathbf{v}_i is the absolute velocity of species i relative to the stationary coordinate axis. Similarly, the mass flux of species i is given by

$$n_i = \rho_i \mathbf{v}_i \quad (1.7)$$

The total molar flux is the sum of the species molar flux

$$N_i = c \mathbf{V} \quad (1.8)$$

In this equation \mathbf{V} is the molar average velocity defined by

$$\mathbf{V} = \frac{\sum_{i=1}^n c_i \mathbf{v}_i}{\sum_{i=1}^n c_i} = \sum_{i=1}^n x_i \mathbf{v}_i \quad (1.9)$$

Similarly, the total mass flux is the sum of the species mass flux

$$N_i = c \mathbf{v} \quad (1.10)$$

In this equation \mathbf{v} is the mass average velocity defined by

$$\mathbf{v} = \frac{\sum_{i=1}^n \rho_i \mathbf{v}_i}{\sum_{i=1}^n \rho_i} = \sum_{i=1}^n \omega_i \mathbf{v}_i \quad (1.11)$$

Example 1.1-1 -----

A mixture of oxygen and nitrogen gas is contained in a pipe at 298 K and 1 atm total pressure which is constant throughout. At one end of the pipe the partial pressure p_{A1} of oxygen is 0.70 atm and at the other end 0.8 m, $p_{A2} = 0.2$ atm. Calculate the molar and mass flux of oxygen at steady state if D_{AB} of the mixture is $0.206 \text{ cm}^2/\text{s}$.

Solution -----

Since the temperature and pressure is constant throughout the pipe, the total concentration is a constant.

$$c = \frac{P}{RT} = \frac{1}{82.057 \times 298} = 4.09 \times 10^{-5} \text{ mol/cm}^3$$

Note: $R = 82.057 \text{ cm}^3 \cdot \text{atm/mol} \cdot \text{K}$

The total concentration is a constant therefore $N_{A,z} = -N_{B,z}$. This condition is known as equimolar counterdiffusion. The molar flux of A is

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z}) = -cD_{AB} \frac{dy_A}{dz}$$

For steady state and constant area of mass transfer $N_{A,z} = \text{constant}$. Separating the variable and integrating

$$N_{A,z} \int_0^L dz = -cD_{AB} \int_{y_{A1}}^{y_{A2}} dy_A$$

$$N_{A,z} = \frac{cD_{AB}(y_{A1} - y_{A2})}{L} = \frac{(4.09 \times 10^{-5})(0.206)(0.7 - 0.2)}{80}$$

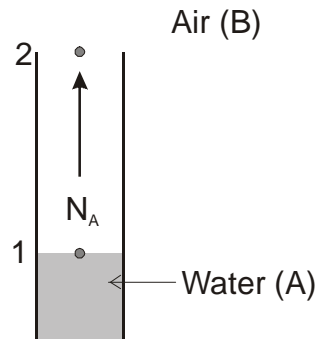
$$N_{A,z} = 5.27 \times 10^{-8} \text{ mol/cm}^2 \cdot \text{s}$$

The mass flux of O_2 is

$$n_{A,z} = M_A N_{A,z} = (32)(5.27 \times 10^{-8}) = 1.69 \times 10^{-6} \text{ g/cm}^2 \cdot \text{s}$$

Example 1.1-2

Water in the bottom of a narrow metal tube is held at a constant temperature of 298 K. The dry ambient air outside the tube is at 1 atm (101.3 kPa) and 298 K. Water evaporates and diffuses through the air in the tube, and the diffusion path $z_2 - z_1$ is 50 cm long. Calculate the rate of evaporation at steady state in $\text{mol/s} \cdot \text{cm}^2$. The diffusivity of water vapor (A) in air (B) at 1 atm and 298 K is $0.250 \text{ cm}^2/\text{s}$. Assume that air is insoluble in water.



Solution

The molar flux of A (water vapor) is

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

Since air is insoluble in water, it is stagnant (or nondiffusing) and $N_{B,z} = 0$. Solving for $N_{A,z}$ give

$$N_{A,z}(1 - y_A) = -cD_{AB} \frac{dy_A}{dz} \Rightarrow N_{A,z}dz = -\frac{cD_{AB}}{1 - y_A} dy_A$$

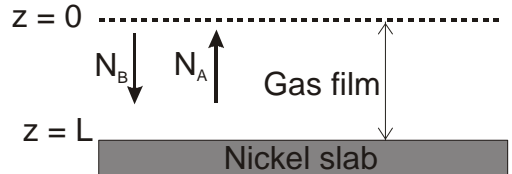
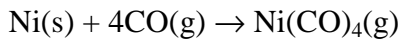
$$N_{A,z} \int_0^L dz = -cD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1 - y_A} \Rightarrow N_{A,z}L = cD_{AB} \ln \frac{1 - y_{A2}}{1 - y_{A1}}$$

The ambient air is dry so $y_{A2} = 0$. Vapor pressure of water at 298 K is 3.17 kPa, therefore $y_{A1} = 3.17/101.3 = 0.0313$.

$$N_{A,z} = \frac{cD_{AB}}{L} \ln \frac{1 - y_{A2}}{1 - y_{A1}} = \frac{0.250}{82.057 \times 298 \times 50} \ln \frac{1 - 0}{1 - 0.313} = 6.5 \times 10^{-9} \text{ mol/cm}^2 \cdot \text{s}$$

Example 1.1-3 ¹-----

Nickel carbonyl (A) is produced by passing carbon monoxide (B) at 323 K and 1 atm over a nickel slab. The following reaction takes place at the solid surface:



The reaction is very rapid, so that the partial pressure of CO at the metal surface is essentially zero. The gases diffuse through a film with a thickness $L = 0.625$ mm. Estimate the rate of production of nickel carbonyl, in mole/s·cm² of solid surface at steady state. The composition of the bulk gas phase ($z = 0$) is 50 mol% CO. The binary diffusivity is $D_{AB} = 20.0$ mm²/s.

Solution -----

The molar flux of A (nickel carbonyl) is

$$N_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

From the stoichiometry of the reaction $N_{B,z} = -4N_{A,z}$. Therefore $N_{A,z} + N_{B,z} = -3N_{A,z}$

$$N_{A,z}(1 + 3y_A) = -cD_{AB} \frac{dy_A}{dz} \Rightarrow N_{A,z}dz = -\frac{cD_{AB}}{1 + 3y_A} dy_A$$

$$N_{A,z} \int_0^L dz = -cD_{AB} \int_{y_{A,0}}^{y_{A,L}} \frac{dy_A}{1 + 3y_A} \Rightarrow N_{A,z}L = \frac{cD_{AB}}{3} \ln \frac{1 + 3y_{A,L}}{1 + 3y_{A,0}}$$

Since $y_{A,0} = 0.5$ and $y_{A,L} = 1.0$, we have

¹ Benitez, J. Principle and Modern Applications of Mass Transfer Operations, Wiley, 2009, p. 44

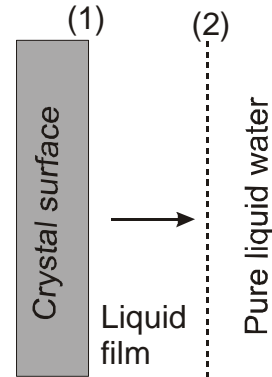
$$N_{A,z} = \frac{cD_{AB}}{3L} \ln \frac{1+3}{1+1.5} = \frac{1 \times 0.20}{3 \times 82.057 \times 323 \times 0.0625} \ln \frac{4}{2.5} = 1.89 \times 10^{-5} \text{ mol/cm}^2 \cdot \text{s}$$

Example 1.1-4² -----

A crystal of chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) dissolves in a large tank of pure water according to the following equation:



Estimate the rate at which the crystal dissolves by calculating the flux of CuSO_4 from the crystal surface to the bulk solution. Assume that molecular diffusion occurs through a liquid film uniformly 0.01 mm thick surrounding the crystal. At the inner side of the film adjacent to the crystal surface the solution is saturated with CuSO_4 while at the outer side of the film the solution is virtually pure water.



The solubility of chalcantite in water at 275 K is 24.3 g of crystal/100 g of water, and the density of the corresponding saturated solution is 1140 kg/m^3 . The diffusivity of CuSO_4 in dilute aqueous solution at 275 K can be estimated as $3.6 \times 10^{-10} \text{ m}^2/\text{s}$.

Solution -----

For each mole of chalcantite (molecular weight 249.71) that dissolves, 1 mole of CuSO_4 (molecular weight 159.63) and 5 mole of hydration water diffuse through the liquid film from the surface of the crystal to the bulk of the liquid phase. Let $A = \text{CuSO}_4$ and $B = \text{H}_2\text{O}$ then,

$$N_B = 5N_A$$

The molar flux of A is

$$N_{A,z} = -cD_{AB} \frac{dx_A}{dz} + x_A(N_{A,z} + N_{B,z}) = -cD_{AB} \frac{dx_A}{dz} + 6x_A N_{A,z}$$

$$N_{A,z} dz = -cD_{AB} \frac{dx_A}{1 - 6x_A}$$

Using an average value for the total concentration c_a , the above equation can be integrated over the thickness of the liquid film, L .

$$N_{A,z} \int_0^L dz = -c_a D_{AB} \int_{x_{A1}}^{x_{A2}} \frac{dx_A}{1 - 6x_A}$$

² Benitez, J. Principle and Modern Applications of Mass Transfer Operations, Wiley, 2009, p. 54

$$N_{A,z} = \frac{c_a D_{AB}}{6L} \ln \frac{1 - 6x_{A2}}{1 - 6x_{A1}}$$

We need the mole fraction of component A at the inner side of the film (x_{A1}), a saturated solution of chalcantite in water at 275 K. The solubility of the salt under these conditions is 24.3 g/100 g H₂O. For a basis of 100 g of H₂O, we have 24.3 g of CuSO₄·5H₂O. The mass of CuSO₄ in 24.3 of of the crystal is

$$24.3 \times 159.63 / 249.71 = 15.53 \text{ g}$$

The mass of hydration water in the crystal is 24.3 – 15.53 = 8.77. The total mass of water is then 100 + 8.77 = 108.77 g. Therefore,

$$x_{A1} = \frac{\frac{15.53}{159.63}}{\frac{15.53}{159.63} + \frac{108.77}{18}} = 0.0158$$

The other end of the film is virtually pure water; therefore $x_{A2} = 0$. Next, we calculate the film average molar concentration c_a . At location 1, the average molecular weight is

$$M_1 = (0.0158)(159.63) + (1 - 0.0158)(18) = 20.24 \text{ kg/kmol.}$$

The corresponding molar concentration is $c_1 = 1140/20.24 = 56.32 \text{ kmol/m}^3$. At location 2, the molar concentration is $c_2 = 1000/18 = 55.55 \text{ kmol/m}^3$. Then

$$c_a = 0.5(c_1 + c_2) = 0.5(56.32 + 55.55) = 55.93 \text{ kmol/m}^3$$

$$N_{A,z} = \frac{c_a D_{AB}}{6L} \ln \frac{1 - 6x_{A2}}{1 - 6x_{A1}}$$

$$N_{A,z} = \frac{55.93 \times 3.6 \times 10^{-10}}{6 \times 10^{-5}} \ln \frac{1}{1 - 6 \times 0.0158} = 3.35 \times 10^{-5} \text{ kmol/s} \cdot \text{m}^2$$

1.2 Gas diffusivities

One of the most common method to estimate the binary gas diffusivity D_{AB} in low pressure system was proposed by Wilke and Lee³:

$$D_{AB} = \frac{\left[3.03 - \left(\frac{0.98}{M_{AB}^{1/2}} \right) \right] (10^{-3}) T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^2 \Omega_D} \quad (1.2-1)$$

In this equation: $M_{AB} = 2 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{-1}$

D_{AB} = diffusion coefficient, cm^2/s

M_A, M_B = molecular weights of A and B, respectively

T = temperature, K

P = pressure, bar

σ_{AB} = "collision diameter," a Lennard-Jones parameter, angstrom

Ω_D = diffusion collision integral, dimensionless

The collision integral, Ω_D , is a function of temperature and intermolecular potential field for one molecule of A and one molecule of B. It can be approximated by the following expression⁴:

$$\Omega_D = \frac{a}{(T^*)^b} + \frac{c}{\exp(dT^*)} + \frac{e}{\exp(fT^*)} + \frac{g}{\exp(hT^*)} \quad (1.2-2)$$

The parameters in this equation are listed in the following table

$T^* = \kappa T / \epsilon_{AB}$	$a = 1.06036$	$b = 0.15610$
$c = 0.19300$	$d = 0.47635$	$e = 1.03587$
$f = 1.52996$	$g = 1.76474$	$h = 3.89411$

For a binary system of nonpolar molecular pair, the Lennard-Jones parameters can be obtained from the pure components by the following expression:

$$\sigma_{AB} = 0.5(\sigma_A + \sigma_B); \quad \epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2} \quad (1.2-3)$$

Lennard-Jones parameters for pure components may be estimated from the following correlations:

$$\sigma = 1.18(V_b)^{1/3} \quad \epsilon_A / \kappa = 1.15T_b \quad (1.2-3)$$

$$V_b = 0.285(V_c)^{1.048}$$

³ Wilke, C. R., and C. Y. Lee, Ind. Eng. Chem., 47, 1253 (1955)

⁴ Neufield, P. D., A. R. Jansen, and R. A. Aziz, J. Chem. Phys., 57, 1100 (1972)

Example 1.2-1⁵ -----

Estimate the diffusivity of carbon disulfide vapor in air at 273 K and 1 bar using the Wilke-Lee equation

$$D_{AB} = \frac{\left[3.03 - \left(\frac{0.98}{M_{AB}^{1/2}} \right) \right] (10^{-3}) T^{3/2}}{PM_{AB}^{1/2} \sigma_{AB}^2 \Omega_D}$$

Data:	$\sigma, \text{ \AA}$	$\epsilon/\kappa, \text{ K}$	Mw
CS ₂	4.483	467	76
Air	3.620	97	29

Solution -----

$$\sigma_{AB} = 0.5(\sigma_A + \sigma_B) = 0.5(4.483 + 3.620) = 4.052 \text{ \AA}$$

$$\frac{\epsilon_{AB}}{\kappa} = \left(\frac{\epsilon_A}{\kappa} \frac{\epsilon_B}{\kappa} \right)^{1/2} = (467 \times 97)^{1/2} = 212.8 \text{ K}$$

$$T^* = \frac{\kappa T}{\epsilon_{AB}} = \frac{273}{212.8} = 1.283$$

$$\Omega_D = \frac{a}{(T^*)^b} + \frac{c}{\exp(dT^*)} + \frac{e}{\exp(fT^*)} + \frac{g}{\exp(hT^*)}$$

The parameters in this equation are listed in the following table

$T^* = \kappa T / \epsilon_{AB}$	$a = 1.06036$	$b = 0.15610$
$c = 0.19300$	$d = 0.47635$	$e = 1.03587$
$f = 1.52996$	$g = 1.76474$	$h = 3.89411$

$$\Omega_D = 1.282$$

$$M_{AB} = 2 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{-1} = 2 \left(\frac{1}{76} + \frac{1}{29} \right)^{-1} = 41.981$$

Substituting these values into the Wilke-Lee equation yields

$$D_{AB} = \frac{\left[3.03 - \left(\frac{0.98}{41.981^{1/2}} \right) \right] (10^{-3}) (273)^{3/2}}{(1)(41.981)^{1/2} (4.052)^2 (1.282)} = \mathbf{0.0952 \text{ cm}^2/\text{s}}$$

⁵ Benitez, J. Principle and Modern Applications of Mass Transfer Operations, Wiley, 2009, p. 21