Mass Transfer: Diffusion

Fick's First Law

Fluxes

$$ {}_{v}J_{AZ} = -D_{AB}\frac{dC_A}{dz} $$

Flux relative to the volume average velocity

$$ {}_{M}J_{AZ} = -CD_{AB}\frac{dx_A}{dz} $$

Flux relative to the molar average velocity

$$ {}_{m}J_{AZ} = -\rho D_{AB}\frac{d\omega_A}{dz} $$

Flux relative to the mass average velocity

Mass and molar concentrations

$$\rho_\alpha = \text{mass concentration of species } \alpha$$

$$\rho = \sum_{\alpha=1}^{N} \rho_a = \text{mass density of solution}$$

$$\omega_\alpha = \rho_\alpha / \rho = \text{mass fraction of species } \alpha$$

$$c_\alpha = \text{molar concentration of species } \alpha$$

$$c = \sum_{\alpha=1}^{N} c_a = \text{molar density of solution}$$

$$x_\alpha = c_\alpha / c = \text{molar fraction of species } \alpha$$

Fick's First Law

Mass average velocity

$$v_m = \frac{\sum_{i=1}^{n} \rho_i v_i}{\sum_{i=1}^{n} \rho_i}$$

Molar average velocity

$$v_M = \frac{\sum_{i=1}^{n} c_i v_i}{\sum_{i=1}^{n} c_i}$$

Volume average velocity

$$v_v = \sum_{i=1}^{n} \rho_i v_i \left(\frac{\overline{v}_i}{M_i}\right)$$

v_i =velocity of the *ith* species wrt a stationary coordinate

Mass average and molar averages velocity

- Mass average velocity

$$v = \frac{\sum_{a=1}^{N} \rho_a v_a}{\sum_{a=1}^{N} \rho_a} = \frac{\sum_{a=1}^{N} \rho_a v_a}{\rho} = \sum_{a=1}^{N} \omega_a v_a$$

- Molar average velocity

$$v^* = \frac{\sum_{a=1}^{N} c_a v_a}{\sum_{a=1}^{N} c_a} = \frac{\sum_{a=1}^{N} c_a v_a}{c} = \sum_{a=1}^{N} x_a v_a$$

Molecular mass and molar fluxes

- Molecular mass flux, with respect to
  - stationary axes

$$n_{\alpha} = \rho_{\alpha} v_{\alpha}$$

  - mass average velocity

$$j_{\alpha} = \rho_{\alpha} \left(v_{\alpha} - v \right)$$

  - molar average velocity

$$j_{\alpha}^{*} = \rho_{\alpha} \left(v_{\alpha} - v^{*} \right)$$

Molecular mass and molar fluxes

- Molecular molar flux, with respect to
  - stationary axes

$$N_\alpha = c_\alpha v_\alpha$$

  - mass average velocity

$$J_\alpha = c_\alpha \left(v_\alpha - v\right)$$

  - molar average velocity

$$J_\alpha^* = c_\alpha \left(v_\alpha - v^*\right)$$

Summary of mass and molar fluxes

- Equivalent forms of Fick's law of binary diffusion

$$j_A = -\rho D_{AB} \nabla \omega_A$$

$$J_A^* = -c D_{AB} \nabla x_A$$

$$n_A = \omega_A (n_A + n_B) - \rho D_{AB} \nabla \omega_A = \rho_A v - \rho D_{AB} \nabla \omega_A$$

$$N_A = x_A (N_A + N_B) - c D_{AB} \nabla x_A = c_A v^* - c D_{AB} \nabla x_A$$

Flux relative to a stationary coordinate, N_A

For a binary system:

$$N_A = {}_M J_{AZ} + x_A (N_A + N_B)$$

$$N_A = -CD_{AB} \frac{dx_A}{dz} + x_A (N_A + N_B)$$

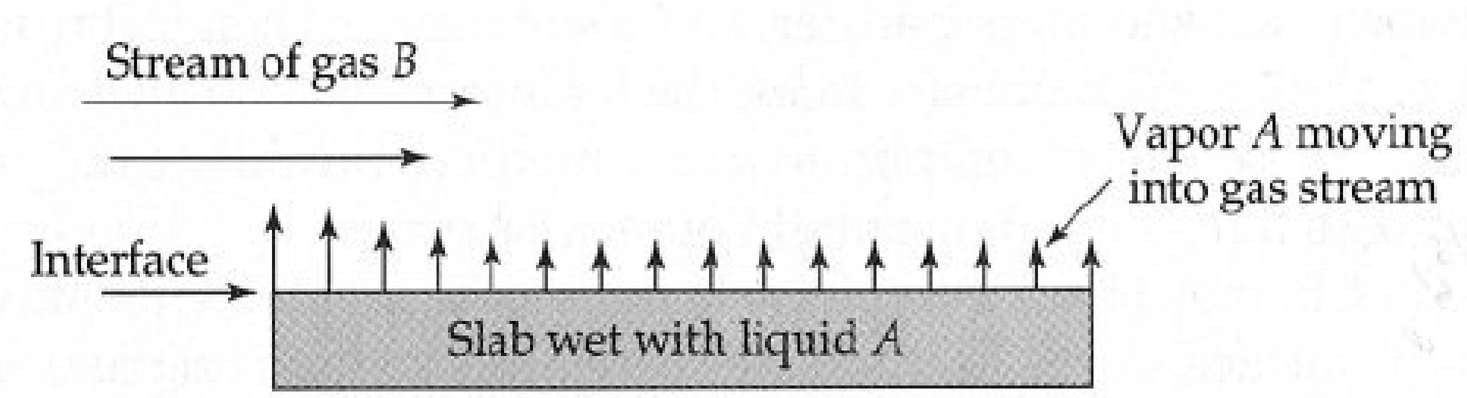
Total flux of A relative to a stationary point

Diffusion flux of A relative to the moving fluid

Convective flux of A relative to a stationary point

Definition of transfer coefficients in one phase. Some examples

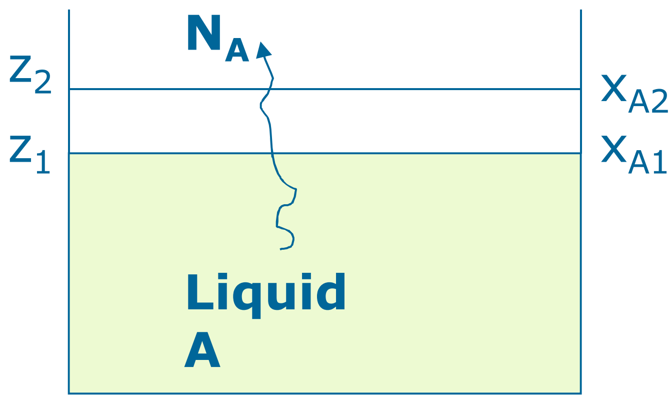
- Mass transfer across a plane boundary, drying of a saturated slab



Diffusion Cases

Unimolar diffusion (Diffusion of A through stagnant , non-diffusing B)

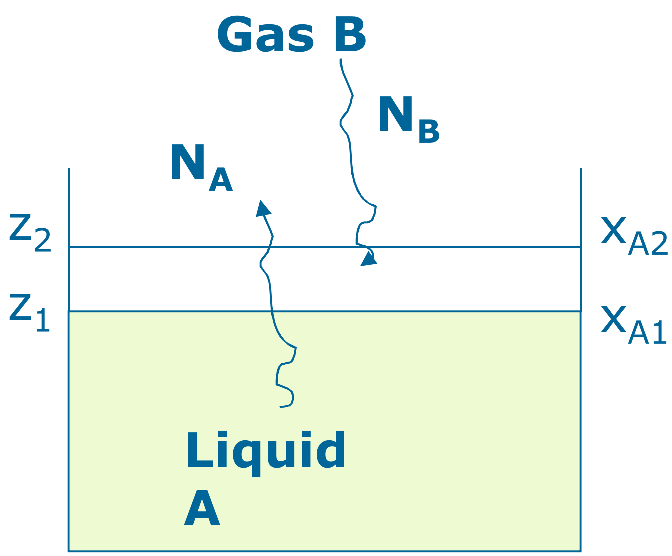
Gas B (stagnant, non-diffusing) $N_B = 0$



$$N_A = \frac{C D_{AB}}{\Delta z} \ln \frac{1 - x_{A_2}}{1 - x_{A_1}}$$

Diffusion Cases

Equimolar counter diffusion



$$N_A = -N_B$$

$$D_{AB} = D_{BA}$$

$$N_A = -\frac{CD_{AB}}{\Delta z}(x_{A_2} - x_{A_1})$$

$$N_B = +\frac{CD_{BA}}{\Delta z}(x_{B_2} - x_{B_1})$$

Diffusion Cases

Steady-state diffusion

$$N_A \neq N_B \neq 0$$

$$N_A = \frac{CD_{AB}}{\Delta z} \frac{N_A}{N_A + N_B} \ln \frac{\dfrac{N_A}{N_A + N_B} - x_{A_2}}{\dfrac{N_A}{N_A + N_B} - x_{A_1}}$$

Diffusion IN Gases

Case I: Unimolar diffusion

$$N_A = \frac{CD_{AB}}{\Delta z} \ln \frac{1 - x_{A_2}}{1 - x_{A_1}}$$

But **$C = P_T/RT$**

$$N_A = \frac{P_T D_{AB}}{RT\Delta z} \ln \frac{1 - x_{A_2}}{1 - x_{A_1}}$$

Diffusion IN Gases

Case II: Equimolar counter diffusion

$$N_A = -\frac{CD_{AB}}{\Delta z}\left(x_{A_2} - x_{A_1}\right)$$

But **C = P_T/RT**

$$N_A = -\frac{P_T D_{AB}}{RT\Delta z}\left(x_{A_2} - x_{A_1}\right)$$

Diffusion Coefficients of A IN Gas (B)

I. Experimental diffusivity data

Table 6.2-1 (Geankoplis)

II. Prediction using correlation

Correction of D_{AB}

$$\frac{D'_{AB}P'}{T'^{1.75}} = \frac{D''_{AB}P''}{T''^{1.75}}$$

Diffusion Coefficients of A IN Gas (B)

Fuller-Schettler-Giddings Correlation

$$D_{AB} = \frac{0.001T^{1.75}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P\left[\left(\sum v_A\right)^{1/3} + \left(\sum v_B\right)^{1/3}\right]^2}$$

Σv_A = sum of structural volume increments (Table 6.2-2)

M_A, M_B = molecular weights of A and B

D_{AB} [=] cm^2/s

# of Diffusivities

- For gas mixtures at low pressure (kinetic theory)

$$\frac{pD_{AB}}{(p_{cA}p_{cB})^{1/3}(T_{cA}T_{cB})^{5/12}(1/M_A+1/M_B)^{1/2}} = a\left(\frac{T}{\sqrt{T_{cA}T_{cB}}}\right)^b$$

- Diffusivities
  - are inversely proportional to the pressure
  - increases with increasing temperature
  - almost independent of composition

Theory of diffusion in gases at low density

- Self diffusivity

$$D_{AA^*} = \frac{2}{3\pi}\frac{\sqrt{\pi m_A \kappa T}}{\pi d_A^2}\frac{1}{\rho}$$

- For binary mixtures

$$D_{AB} = \frac{2}{3}\sqrt{\frac{\kappa T}{\pi}}\sqrt{\frac{1}{2}\left(\frac{1}{m_A}+\frac{1}{m_B}\right)}\cdot\frac{1}{\pi[0.5(d_A + d_B)]^2}\cdot\frac{1}{n}$$

Chapman-Enskog

$$cD_{AB} = \frac{3}{16}\sqrt{\frac{2RT}{\pi}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\cdot\frac{1}{\tilde{N}\sigma_{AB}^{2}\Omega_{D,AB}}$$

Homework

1. Evaluate the diffusion coefficient of CO_2 in air at 20 °C and atmospheric pressure. Compare the value with the reported experimental data.

2. An open circular tank 8 m in diameter contains benzene at 22°C exposed to the atmosphere in such a manner that the liquid is covered with stagnant air film estimated to be 5 mm thick. The concentration of benzene beyond the stagnant film is negligible. The vapor pressure of benzene at 22 °C is 100 mmHg. How much benzene is lost from this tank per day?

Diffusion in Liquids

Case I: Unimolar diffusion

$$N_A = \frac{C_{AV} D_{AB}}{\Delta z} \ln \frac{1 - x_{A_2}}{1 - x_{A_1}}$$

Case II: Equimolar counter diffusion

$$N_A = -\frac{C_{AV} D_{AB}}{\Delta z} \left(x_{A_2} - x_{A_1} \right)$$

where

$$C_{AV} = \left(\frac{\rho}{M} \right)_{AV} = \frac{\frac{\rho_1}{M_1} + \frac{\rho_2}{M_2}}{2}$$

Diffusion Coefficients of A in Liquids

I. Experimental diffusivity data

Table 6.3-1 (Geankoplis)

II. Prediction using correlation

Correction of D_{AB}

$$\frac{D'_{AB}\mu'}{T'} = \frac{D''\mu''}{T''}$$

Diffusion Coefficients of A in Liquids

Wilke-Chang Correlation

$$D_{AB} = 1.173x10^{-16}(\varphi\, M_B)^{1/2}\frac{T}{\mu_B V_A^{0.6}}$$

φ = association parameter

M_B = molecular weights of solvent B

D_{AB} [=] m^2/s

V_A = solute molar volume at the boiling point (Table 6.3-2)

μ_B = viscosity of B [=] Pa-s or kg/m-s

Diffusion in Solids

Case I: Fickian Diffusion

(No network f pore openings is present for the solid to travel)

Assumption: bulk flow term is small

General equation for gas/liquid diffusing in solid

$$N_A = -D_{AB} \frac{C_{A2} - C_{A1}}{\Delta z}$$

Diffusion in Solids

For Gases in Solids:

$$N_A = -\frac{D_{AB}S}{22.414\,\Delta z}(P_{A2} - P_{A1})$$

In terms of permeability : $P_M = D_{AB}\,S$

$$N_A = -\frac{P_M}{22.414\,\Delta Z}(P_{A2} - P_{A1})$$

Diffusion in Solids

Case II: Non-Fickian Diffusion

(Porous solids that have pores or interconnected voids in the solid)

General equation for gas/liquid diffusing in solid

$$N_A = -\frac{\varepsilon D_{AB}}{\tau \Delta z}(C_{A2} - C_{A1})$$

τ **= tortuosity (actual path length)**

ε **= porosity (open void fraction)**

$D_{Aeff} = \varepsilon D_{AB} / \tau$ **[=] m^2/s**

Diffusion in Solids

Case III: Knudsen Diffusion

(Diffusion in small pores , mean free path,λ, > diameter)

λ= average distance traveled by 2 molecules before collision

$$\lambda = \frac{3.2\mu}{P}\sqrt{\frac{RT}{2\pi M}}$$

Knudsen number:

$$N_{Kn} = \frac{\lambda}{2\bar{r}}$$

Average pore radius

Diffusion in Solids

Case 1: $N_{Kn} \leq \dfrac{1}{100}$ **Fickian (Fick's Law)**

Case 2: $N_{Kn} \geq 10$ **Knudsen diffusion**

Knudsen diffusivity

$$D_{KA} = 97.0\bar{r}\left(\frac{T}{M_A}\right)^{1/2}$$

$$N_A = -D_{KA}\frac{dC_A}{dz}$$

Diffusion in Solids

Case 3: $\frac{1}{100} < N_{Kn} < 10$ **Transition region (both Fickian and Knudsen)**

$$N_A = \frac{D_{AB} P_T}{\alpha\, RT\, \Delta z} \ln \frac{1 - \alpha\, x_{A2} + \dfrac{D_{AB}}{D_{KA}}}{1 - \alpha\, x_{A1} + \dfrac{D_{AB}}{D_{KA}}}$$

where $\alpha = 1 + \frac{N_A}{N_B}$