Flux relative to a stationary coordinate, N_A

For a binary system:

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

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

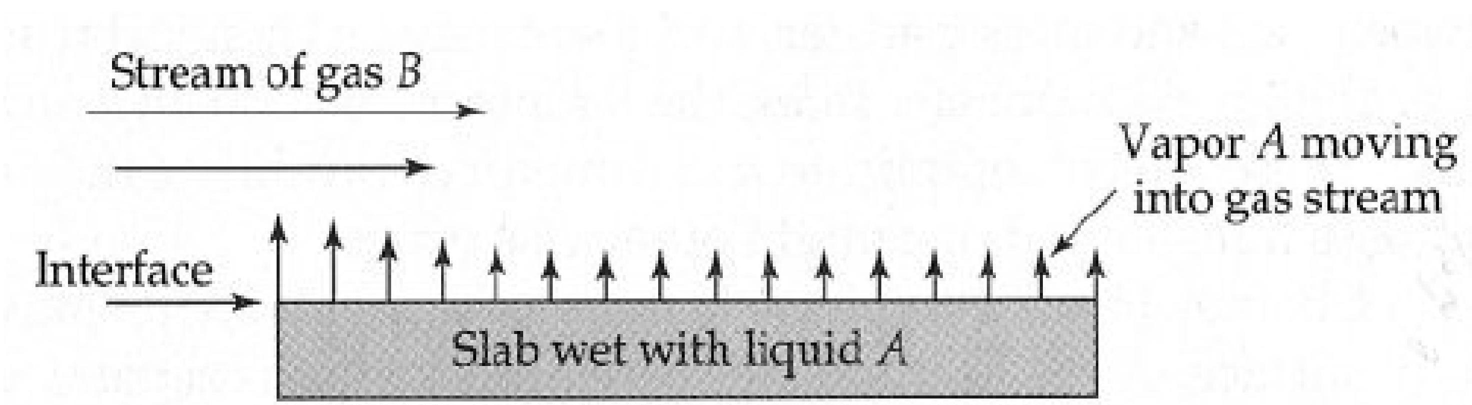
Total flux of A relative to a stationary point

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

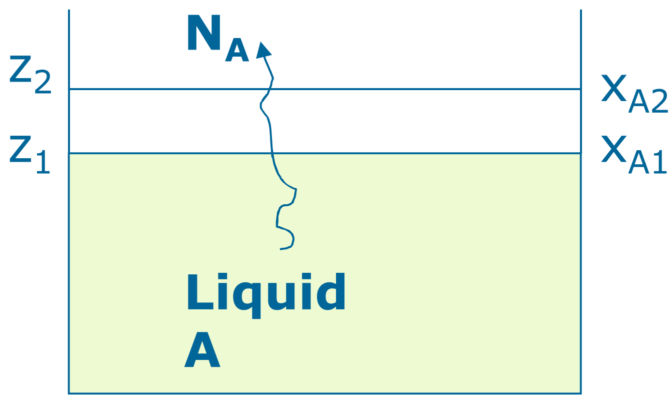
- Mass transfer across a plane boundary, drying of a saturated slab



Diffusion Cases

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

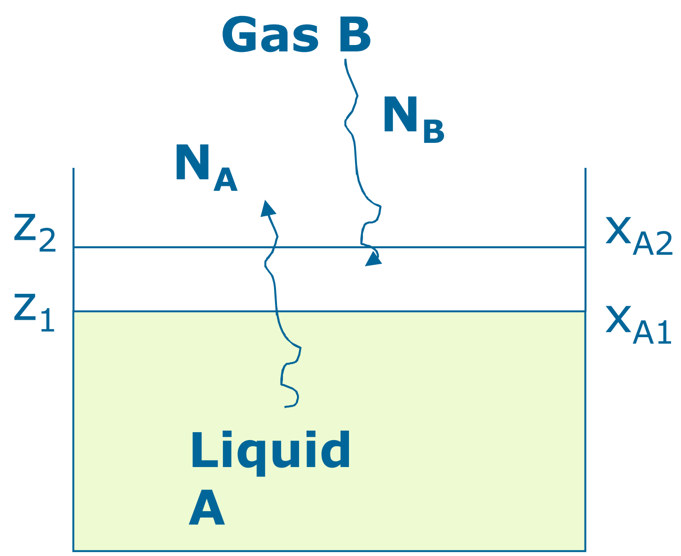
Gas B (stagnant, non-diffusing) $N_B = 0$



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

Diffusion Cases

Equimolar counter diffusion



$$N_A = -N_B$$

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

$$N_A = -\frac{CD_{AB}}{\Delta z}(x_{A_2} - x_{A_1}) \qquad N_B = +\frac{CD_{BA}}{\Delta z}(x_{B_2} - x_{B_1})$$

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

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

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: $N_{Kn} \leq \frac{1}{100}$ **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 $\alpha = 1 + \frac{N_A}{N_B}$

Example :

Calculate the binary diffusion coefficients of water vapor in air at 298.15 K and 1 atm.

Solution

The following parameters are given in standard references:

Air: $M_{Air} = 28.97$, $\sigma_{Air} = 3.62$ Å, $(\varepsilon_{Air}/k) = 97$ K

Water vapor: $M_{water} = 18.02$, $\sigma_{water} = 2.65$ Å, $(\varepsilon_{water}/k) = 356$ K

$$\sigma_{AB} = (3.62 + 2.65)/2 = 3.14$$

$$\varepsilon_{AB}/k = \sqrt{(97)(356)} = 185.8$$

$$T_D^* = (298.15)/(185.8) = 1.604$$

$$D_{AB} = \frac{1.858 \times 10^{-7}\, T^{3/2} \left(1/M_A + 1/M_B\right)^{1/2}}{(P/101325)\, \sigma_{AB}^2\, \Omega\,(T_D^*)} \quad [\mathrm{m^2\, s^{-1}}]$$

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2$$

$$k/\varepsilon_{AB} = \sqrt{(k/\varepsilon_A)(k/\varepsilon_B)}$$

$$T_D^* = kT/\varepsilon_{AB}$$

$$D_{AB} = \frac{1.858 \times 10^{-7}(298.15)^{1.5}\sqrt{1/(28.97) + 1/(18.02)}}{(101325/101325)(3.14)^2(1.167)} = 2.50 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$$

Mass Transfer Coefficients

(Rate of mass transfer) = (Mass transfer coefficient)(Concentration driving force)