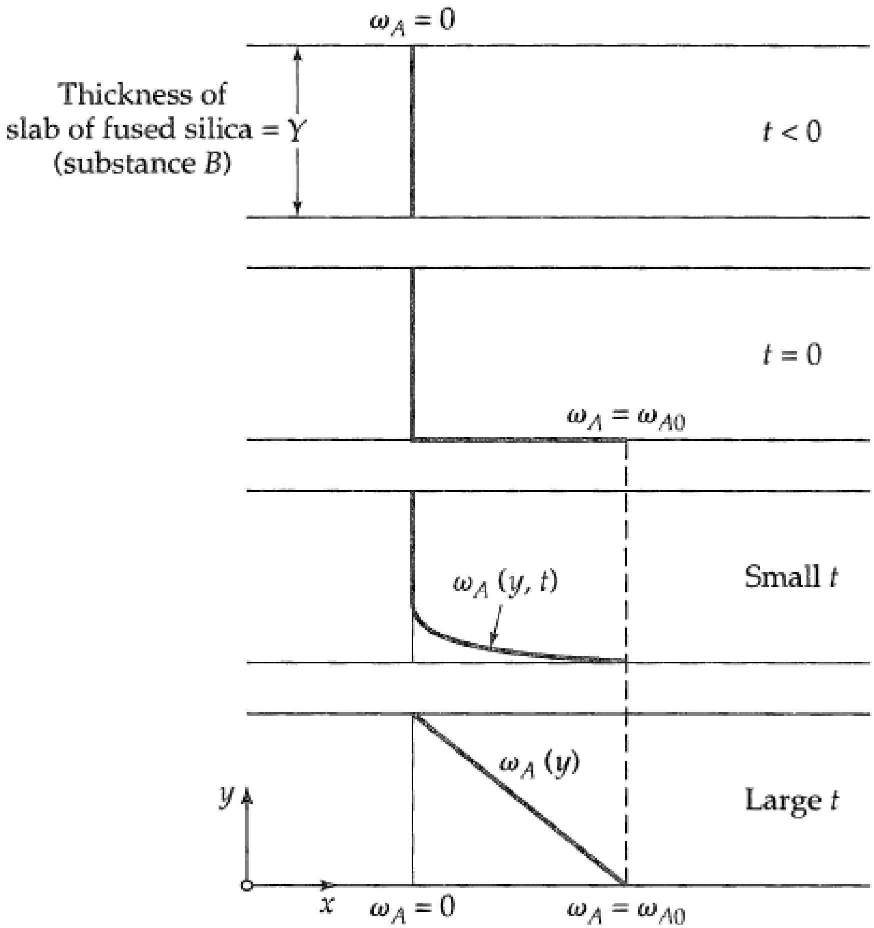
Chapter 17. Diffusivity and the mechanisms of mass transport

- Fick's law of binary diffusion (molecular mass transport)
- Temperature and pressure dependence of diffusivities
- Theory of diffusion in gases at low density, in binary liquids, in colloids suspensions, and polymers
- Mass and molar transport by convection
- Summary of mass and molar fluxes
- The Maxwell-Stefan equations for multicomponent diffusion in gases at low density

Behaviour of polymeric liquids



"Transport Phenomena" 2nd ed.,
R.B. Bird, W.E. Stewart, E.N. Lightfoot

- At steady state

$$\frac{w_{Ay}}{A} = \rho \mathscr{D}_{AB} \frac{\omega_{A0} - 0}{Y}$$

- Fick's law of binary diffusion

$$j_{Ay} = -\rho \mathscr{D}_{AB} \frac{d\omega_A}{dy}$$

Fick's law of binary diffusion

$$j_{Ay} = -\rho \mathscr{D}_{AB} \frac{d\omega_A}{dy}$$

j_{Ay}, the *molecular mass flux*

ω_A, the mass fraction

$\mathscr{D}_{AB}$ the *diffusivity*

ρ is the density

- Mass average velocity for a binary mixture

$$v_y = \omega_A v_{Ay} + \omega_B v_{By}$$

- Mass flux

$$j_{Ay} = \rho \omega_A (v_{Ay} - v_y)$$

Dimensionless numbers

mass diffusivity $\mathcal{D}_{AB}$

thermal diffusivity $\alpha = k/\rho\hat{C}_p$

momentum diffusivity $\nu = \mu/\rho$

The Prandtl number: $\Pr = \dfrac{\nu}{\alpha} = \dfrac{\hat{C}_p\mu}{k}$

The Schmidt number:[2] $\mathrm{Sc} = \dfrac{\nu}{\mathcal{D}_{AB}} = \dfrac{\mu}{\rho\mathcal{D}_{AB}}$

The Lewis number:[2] $\mathrm{Le} = \dfrac{\alpha}{\mathcal{D}_{AB}} = \dfrac{k}{\rho\hat{C}_p\mathcal{D}_{AB}}$

17.2 Temperature and pressure dependence of Diffusivities

- For gas mixtures at low pressure (kinetic theory)

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

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

17.3 Theory of diffusion in gases at low density

- Self diffusivity

$$\mathscr{D}_{AA^*} = \frac{2}{3}\frac{\sqrt{\kappa T/\pi m_A}}{\pi d_A^2}\frac{1}{n} = \frac{2}{3\pi}\frac{\sqrt{\pi m_A \kappa T}}{\pi d_A^2}\frac{1}{\rho}$$

- For binary mixtures

$$\mathscr{D}_{AB} = \frac{2}{3}\sqrt{\frac{\kappa T}{\pi}}\sqrt{\frac{1}{2}\left(\frac{1}{m_A}+\frac{1}{m_B}\right)}\frac{1}{\pi(\frac{1}{2}(d_A+d_B))^2}\frac{1}{n}$$

- Chapman-Enskog kinetic theory

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

collision integral

17.7 Mass and molar transport by convection

- Mass and molar concentrations
  - Mass average and molar average velocities
  - Molecular mass and molar fluxes
  - Convective mass and molar fluxes

Mass and molar concentrations

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

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

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

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

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

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

Mass and molar concentrations

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Algebraic relations:

$$c_\alpha = \rho_\alpha / M_\alpha \quad \text{(H)}$$

$$\rho_\alpha = c_\alpha M_\alpha \quad \text{(I)}$$

$$\sum_{\alpha=1}^{N} x_\alpha = 1 \quad \text{(J)}$$

$$\sum_{\alpha=1}^{N} \omega_\alpha = 1 \quad \text{(K)}$$

$$\sum_{\alpha=1}^{N} x_\alpha M_\alpha = M \quad \text{(L)}$$

$$\sum_{\alpha=1}^{N} \omega_\alpha / M_\alpha = 1/M \quad \text{(M)}$$

$$x_\alpha = \frac{\omega_\alpha / M_\alpha}{\sum_{\beta=1}^{N} (\omega_\beta / M_\beta)} \quad \text{(N)}$$

$$\omega_\alpha = \frac{x_\alpha M_\alpha}{\sum_{\beta=1}^{N} (x_\beta M_\beta)} \quad \text{(O)}$$

Differential relations:

$$\nabla x_\alpha = -\frac{M^2}{M_\alpha} \sum_{\substack{\gamma=1 \\ \gamma\neq\alpha}}^{N} \left[\frac{1}{M} + \omega_\alpha\left(\frac{1}{M_\gamma} - \frac{1}{M_\alpha}\right)\right] \nabla\omega_\gamma \quad \text{(P)}^a$$

$$\nabla \omega_\alpha = -\frac{M_\alpha}{M^2} \sum_{\substack{\gamma=1 \\ \gamma\neq\alpha}}^{N} [M + x_\alpha(M_\gamma - M_\alpha)] \nabla x_\gamma \quad \text{(Q)}^a$$

[a]Equations (P) and (Q), simplified for binary ystems, are

$$\nabla x_A = \frac{\dfrac{1}{M_A M_B} \nabla\omega_A}{\left(\dfrac{\omega_A}{M_A} + \dfrac{\omega_B}{M_B}\right)^2} \quad \text{(P')}$$

$$\nabla\omega_A = \frac{M_A M_B \nabla x_A}{(x_A M_A + x_B M_B)^2} \quad \text{(Q')}$$

Mass average and molar averages velocity

- Mass average velocity

$$\mathbf{v} = \frac{\sum_{\alpha=1}^{N} \rho_\alpha \mathbf{v}_\alpha}{\sum_{\alpha=1}^{N} \rho_\alpha} = \frac{\sum_{\alpha=1}^{N} \rho_\alpha \mathbf{v}_\alpha}{\rho} = \sum_{\alpha=1}^{N} \omega_\alpha \mathbf{v}_\alpha$$

- Molar average velocity

$$\mathbf{v}^* = \frac{\sum_{\alpha=1}^{N} c_\alpha \mathbf{v}_\alpha}{\sum_{\alpha=1}^{N} c_\alpha} = \frac{\sum_{\alpha=1}^{N} c_\alpha \mathbf{v}_\alpha}{c} = \sum_{\alpha=1}^{N} x_\alpha \mathbf{v}_\alpha$$

17.8 Summary of mass and molar fluxes

- Equivalent forms of Fick's law of binary diffusion

Table 17.8-2 Equivalent Forms of Fick's (First) Law of Binary Diffusion

Flux	Gradient	Form of Fick's Law
$\mathbf{j}_A$	$\nabla \omega_A$	$\mathbf{j}_A = -\rho \mathscr{D}_{AB} \nabla \omega_A$
$\mathbf{J}_A^*$	∇x_A	$\mathbf{J}_A^* = -c \mathscr{D}_{AB} \nabla x_A$
$\mathbf{n}_A$	$\nabla \omega_A$	$\mathbf{n}_A = \omega_A(\mathbf{n}_A + \mathbf{n}_B) - \rho \mathscr{D}_{AB} \nabla \omega_A = \rho_A \mathbf{v} - \rho \mathscr{D}_{AB} \nabla \omega_A$
$\mathbf{N}_A$	∇x_A	$\mathbf{N}_A = x_A(\mathbf{N}_A + \mathbf{N}_B) - c \mathscr{D}_{AB} \nabla x_A = c_A \mathbf{v}^* - c \mathscr{D}_{AB} \nabla x_A$

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Molecular mass and molar fluxes

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Table 17.8-1 Notation for Mass and Molar Fluxes*

Quantity	With respect to stationary axes		With respect to mass average velocity $\mathbf{v}$		With respect to molar average velocity $\mathbf{v}^*$	
Velocity of species α (cm/s)	$\mathbf{v}_\alpha$	(A)	$\mathbf{v}_\alpha - \mathbf{v}$	(B)	$\mathbf{v}_\alpha - \mathbf{v}^*$	(C)
Mass flux of species α (g/cm^2 s)	$\mathbf{n}_\alpha = \rho_\alpha \mathbf{v}_\alpha$	(D)	$\mathbf{j}_\alpha = \rho_\alpha(\mathbf{v}_\alpha - \mathbf{v})$	(E)	$\mathbf{j}^*_\alpha = \rho_\alpha(\mathbf{v}_\alpha - \mathbf{v}^*)$	(F)
Molar flux of species α (g-moles/cm^2 s)	$\mathbf{N}_\alpha = c_\alpha \mathbf{v}_\alpha$	(G)	$\mathbf{J}_\alpha = c_\alpha(\mathbf{v}_\alpha - \mathbf{v})$	(H)	$\mathbf{J}^*_\alpha = c_\alpha(\mathbf{v}_\alpha - \mathbf{v}^*)$	(I)
Sums of mass fluxes	$\sum_{\alpha=1}^{N} \mathbf{n}_\alpha = \rho \mathbf{v}$	(J)	$\sum_{\alpha=1}^{N} \mathbf{j}_\alpha = 0$	(K)	$\sum_{\alpha=1}^{N} \mathbf{j}^*_\alpha = \rho(\mathbf{v} - \mathbf{v}^*)$	(L)
Sums of molar fluxes	$\sum_{\alpha=1}^{N} \mathbf{N}_\alpha = c\mathbf{v}^*$	(M)	$\sum_{\alpha=1}^{N} \mathbf{J}_\alpha = c(\mathbf{v}^* - \mathbf{v})$	(N)	$\sum_{\alpha=1}^{N} \mathbf{J}^*_\alpha = 0$	(O)
Relations between mass and molar fluxes	$\mathbf{n}_\alpha = M_\alpha \mathbf{N}_\alpha$	(P)	$\mathbf{j}_\alpha = M_\alpha \mathbf{J}_\alpha$	(Q)	$\mathbf{j}^*_\alpha = M_\alpha \mathbf{J}^*_\alpha$	(R)
Interrelations among mass fluxes	$\mathbf{n}_\alpha = \mathbf{j}_\alpha + \rho_\alpha \mathbf{v}$	(S)	$\mathbf{j}_\alpha = \mathbf{n}_\alpha - \omega_\alpha \sum_{\beta=1}^{N} \mathbf{n}_\beta$	(T)	$\mathbf{j}^*_\alpha = \mathbf{n}_\alpha - x_\alpha \sum_{\beta=1}^{N} \frac{M_\alpha}{M_\beta} \mathbf{n}_\beta$	(U)
Interrelations among molar fluxes	$\mathbf{N}_\alpha = \mathbf{J}^*_\alpha + c_\alpha \mathbf{v}^*$	(V)	$\mathbf{J}_\alpha = \mathbf{N}_\alpha - \omega_\alpha \sum_{\beta=1}^{N} \frac{M_\beta}{M_\alpha} \mathbf{N}_\beta$	(W)	$\mathbf{J}^*_\alpha = \mathbf{N}_\alpha - x_\alpha \sum_{\beta=1}^{N} \mathbf{N}_\beta$	(X)

Maxwell-Stefan equations for multicomponent diffusion in gases at low pressure

- Maxwell-Stefan equations

$$\nabla x_\alpha = -\sum_{\beta=1}^{N} \frac{x_\alpha x_\beta}{\mathscr{D}_{\alpha\beta}} (\mathbf{v}_\alpha - \mathbf{v}_\beta) = -\sum_{\beta=1}^{N} \frac{1}{c\mathscr{D}_{\alpha\beta}} (x_\beta \mathbf{N}_\alpha - x_\alpha \mathbf{N}_\beta) \qquad \alpha = 1, 2, 3, \ldots, N$$

- Other cases in multicomponent diffusion
  - Reverse diffusion, a species move against its own gradient
  - Osmotic diffusion, a species diffuses though its concentration gradient is zero
  - Diffusion barrier, a species does not diffuse through its concentration gradient is nonzero