Part 9

Mass Transfer

Define basic quantities:

Mass units:

ρ_A = mass concentration (mass/volume)

$\rho = \sum_i \rho_i$ = mass density of fluid

$\omega_A = \rho_A/\rho$ = mass fraction ($\sum \omega_i = 1$)

Molar units:

C_A = molar concentration

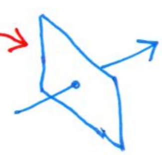
$C = \sum C_i$ = total molar concentration

$x_A = C_A/C$ = mole fraction ($\sum x_i = 1$)

Velocities:

v_A = species velocity (velocity of species)

fixed plane



$$\frac{N_A}{C_A} = \frac{n_A}{\rho_A} = v_A$$

$$v = \frac{\sum \rho_i v_i}{\rho} = \sum \omega_i v_i$$

= mass average velocity

ρv = total mass flux with respect to a fixed plane

$$v^* = \frac{\sum C_i v_i}{C} = \sum x_i v_i$$ = mole average velocity

$C v^*$ = total molar flux with respect to a fixed plane

BSL → ■

Volume fraction

$$v^{V} = \sum_i \bar{V}_i c_i v_i = \sum \phi_i v_i$$

note that $\sum \phi_i = 1$

Fluxes:

$n_i = \rho_i v_i$ = mass flux w/r to fixed plane

$N_i = c_i v_i$ = molar flux w/r to fixed plane

$j_i = \rho_i (v_i - v)$ = mass flux w/r to mass average velocity

$J_i^* = c_i (v_i - v^*)$ = molar flux w/r to mole average velocity

$J_i^V = c_i (v_i - v^V)$ = molar flux w/r to volume average velocity

$j_i^V = \rho_i (v_i - v^V)$ = mass flux w/r to volume average velocity

Relations between fluxes:

$$\sum_i j_i = \sum_i \rho_i (v_i - v) = \sum_i \rho_i v_i - v \sum_i \rho_i$$

$$= \sum_i \rho_i v_i - \underbrace{\frac{\sum \rho_i v_i}{\cancel{\sum \rho_i}}}_{v} \cancel{\sum \rho_i} = 0$$

Similarly $\sum_i J_i^* = 0$

But $\sum_i J_i^V \neq 0$

Flux carried by the average velocity (also termed the "convective" flux):

$$N_i - J_i^* = c_i v_i - c_i(v_i - v^*) = c_i v^*$$

But $\quad v^* = \dfrac{\sum_i c_i v_i}{c} = \dfrac{\sum_i N_i}{c}$

So $\quad N_i - J_i^* = c_i \sum_i N_i / c = x_i \sum_i N_i$

Similarly $\quad n_i - j_i = \omega_i \sum_i n_i$
$\qquad\qquad\qquad\quad = \rho_i v$

Most common forms of Ficks law for binary system of components A and B:

$$j_A = -\rho \mathcal{D}'_{AB} \nabla \omega_A$$

$$J_A^* = -c \mathcal{D}''_{AB} \nabla x_A$$

$$J_A^V = -\mathcal{D}'''_{AB} \nabla c_A$$

$$j_A^V = -\mathcal{D}''''_{AB} \nabla \rho_A$$

It can be shown that $\mathcal{D}'_{AB} = \mathcal{D}''_{AB} = \mathcal{D}'''_{AB} = \mathcal{D}''''_{AB}$

Prediction of diffusion coefficients:

Gases:

Kinetic theory leads to:

molecular weight

$$\mathcal{D}_{AB} = \frac{2}{3}\left(\frac{k^3}{\pi^3}\right)^{1/2}\left(\frac{1}{2m_A} + \frac{1}{2m_B}\right)^{1/2} \frac{T^{3/2}}{P\left(\frac{d_A + d_B}{2}\right)^2}$$

Chapman Enskog theory (using Leonard Jones 6-12 potential)

Molecular weight

$$\mathcal{D}_{AB} = 0.001858 \frac{\sqrt{T^3\left(\frac{1}{M_A} + \frac{1}{M_B}\right)}}{P\,\sigma_{AB}^2\,\Omega_{\mathcal{D}AB}}$$

$f\left(\frac{KT}{\epsilon_{AB}}\right)$

Assume $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$; $\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$

Liquids:

Nernst Einstein Equation:

$$\mathcal{D}_{AB} = kT \frac{u_A}{F_A}$$

velocity

Force

Boltzman constant

$\frac{u_A}{F_A}$ = "mobility"

For a sphere (Stokes law)

$$\frac{u_A}{F_A} = \frac{1}{6\pi\mu R_A}$$

Radius of molecule "A"

Substitution yields "Stokes Einstein" equation:

$$\mathcal{D}_{AB} = \frac{kT}{6\pi\mu R_A} \quad \text{or} \quad \frac{\mathcal{D}_{AB}\mu}{T} = \frac{k}{6\pi R_A}$$

Works well for large molecules (e.g., Proteins) in solution (solute much larger than solute).

Modifications for small solutes

The "Wilke - Chang" equation

A = solute
B = solvent

Molecular weight of solvent

OK

$$\mathcal{D}_{AB} = 7.4 \times 10^{-8} \frac{(\psi_B M_B)^{1/2} \, T}{\mu \, \tilde{V}_A^{0.6}}$$

Viscosity of solvent in centipoise

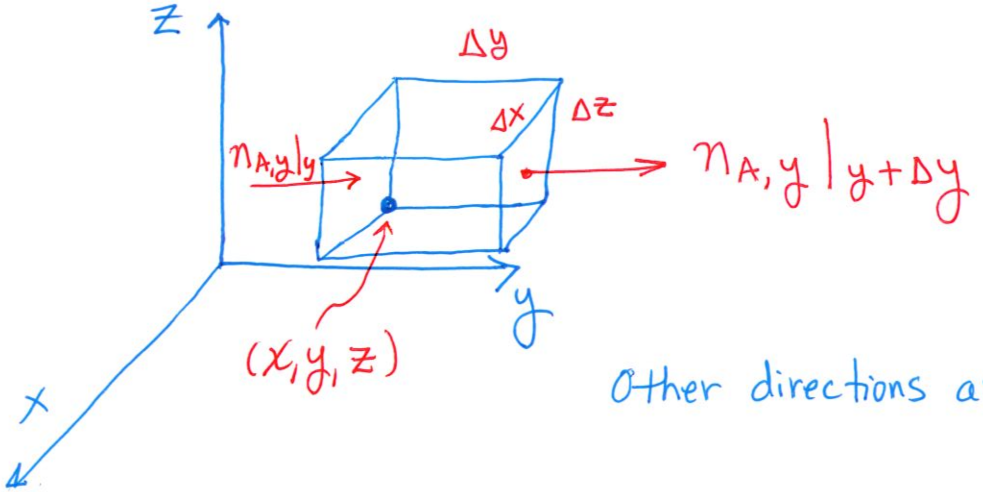
Molar volume of solute at normal boiling point

ψ_B = "association" constant

~ 2.6 for water

~ 1.0 for nonpolar solvent

Equation of continuity for a binary mixture of A and B



Other directions are analogous

Mass balance:

from chemical reaction

Accumulation = inflow − outflow + production

In units of mass per unit time:

$$\frac{\partial \rho_A}{\partial t}\Delta x\,\Delta y\,\Delta z = n_{A,x}|_x\,\Delta y\,\Delta z - n_{A,x}|_{x+\Delta x}\,\Delta y\,\Delta z$$

$$n_{A,y}|_y\,\Delta x\,\Delta z - n_{A,y}|_{y+\Delta y}\,\Delta x\,\Delta z$$

$$n_{A,z}|_z\,\Delta y\,\Delta x - n_{A,z}|_{z+\Delta z}\,\Delta y\,\Delta x$$

$$+\, r_A\,\Delta x\,\Delta y\,\Delta z$$

rate of reaction

Divide by $\Delta x\,\Delta y\,\Delta z$

Species continuity equation

$$\frac{\partial \rho_A}{\partial t} + \frac{\partial n_{A,x}}{\partial x} + \frac{\partial n_{A,y}}{\partial y} + \frac{\partial n_{A,z}}{\partial z} = r_A$$

or $$\partial \rho_A/\partial t + \underbrace{\vec{\nabla}\cdot\vec{n}_A}_{\text{net efflux per unit volume}} = r_A$$

$\vec{n}_A = \vec{i}\,n_{A,x} + \vec{j}\,n_{A,y} + \vec{k}\,n_{A,z}$

flux of A

Similarly for B:

$$\frac{\partial \rho_B}{\partial t} + \vec{\nabla} \cdot \vec{n}_B = r_B$$

Add equations for A and B together:

$$\underbrace{\frac{\partial \rho}{\partial t}}_{\rho = \rho_A + \rho_B} + \vec{\nabla} \cdot \underbrace{(\vec{n}_A + \vec{n}_B)}_{\rho \vec{v}} = 0$$

Note that $\vec{n}_A = \vec{j}_A + \rho_A \vec{v}$

where $\vec{j}_A = -\rho \mathcal{D}_{AB} \vec{\nabla} \omega_A$

Substitute and restrict to constant ρ and $\mathcal{D}_{AB}$ and let $r_A = 0$ (applies to unreactive liquids where solute "A" is dilute):

$$\frac{\partial \rho_A}{\partial t} + \vec{v} \cdot \vec{\nabla} \rho_A = \mathcal{D}_{AB} \nabla^2 \rho_A$$

Alternatively, for constant c and $\mathcal{D}_{AB}$ and where $r_A = 0$, a similar development leads to:

$$\frac{\partial c_A}{\partial t} + \vec{v}^* \cdot \vec{\nabla} c_A = \mathcal{D}_{AB} \nabla^2 c_A$$

See BSL for equations when $r_A, r_B \neq 0$