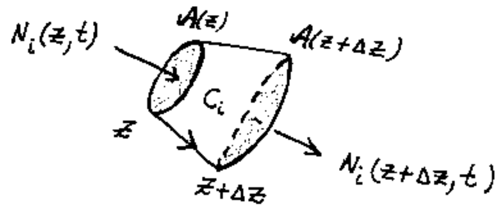
Diffusion Theory { 1-D and Quasi 1-D flux in Binary Systems

Typical Element



Geometry	z var.	$A(z)$	N_i
Linear	z	Constant	$N_{i,z}$
Cylindrical	r + Const	$\propto r$	$N_{i,r}$
Spherical	r + Const.	$\propto r^2$	$N_{i,r}$

Mass Balance on Element, Species i :

$$\frac{\partial}{\partial t}\left[C_i A \Delta z\right] = \left[N_i A\right]_z - \left[N_i A\right]_{z+\Delta z} + \left[r_i A \Delta z\right]$$

Accumulation = In. - Out. + Gen.

Let $\Delta z \to 0$

General 1-dim. balance(s)

$$\boxed{\frac{\partial C_i}{\partial t} = -\frac{1}{A}\frac{\partial}{\partial z}\left(A N_i\right) + r_i} \qquad i = 1, 2, \ldots$$

+ Rate Laws $\begin{cases} r_i(C_1, C_2, \ldots), \text{ and} \\ N_i = B_i + J_i \\ J_i = J_i\left(\frac{dC_1}{dz}, \frac{dC_2}{dz}, \ldots\right) \end{cases}$ Diffusion flux.

+ B.C.'s

2. Fick's Law - Binary Mixtures (or for "dilute" Systems)

$$N_A = B_A + J_A$$

$$B_A = x_A N \equiv x_A (N_A + N_B)$$

$$J_A = -\mathcal{D}_{AB}\, C \frac{d x_A}{dz}$$

or

$$\boxed{N_A = x_A N - \mathcal{D}_{AB}\, C \frac{d x_A}{dz}.}$$

Also

$$\boxed{N_B = x_B N - \mathcal{D}_{BA}\, C \frac{d x_B}{dz}}, \ldots$$

$$(\mathcal{D}_{AB} = \mathcal{D}_{BA})$$

2. Inert Systems ($r_i \equiv 0$)

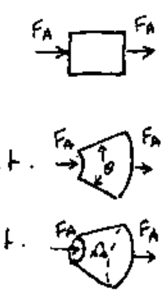
2.1 Steady-State Diffusion (in Binary Systems)

Mass Balance

$$\frac{\partial c_A}{\partial t}\nearrow^{0} = -\frac{1}{A}\frac{\partial (A N_A)}{\partial z} + r_A \nearrow^{0} \quad \text{, etc.}$$

$$\therefore \quad \boxed{A N_A(z) = \text{Constant} = F_A \text{, say}}$$

Geometry	Flux Relation
Linear	$N_A(z) = F_A / A = \text{Const.}$
Cylindrical	$N_A(r) = F_A / \theta r \ell = \text{Const.}$
Spherical	$N_A(r) = F_A / \Omega r^2 = \text{Const.}$



θ = Sector of Cylinder
Ω = Solid angle of Sphere
ℓ = Length of cylinder ($\perp$ to figure)

(Similarly $\begin{cases} A N_i = F_i \\ A N = F \end{cases}$)

Combination with Fick's Law gives

$$N_A = x_A N - \mathcal{D} C \frac{d x_A}{dz} = F_A / A(z)$$

(where $N = F / A(z)$ & F, F_A are constan

For constant $\mathcal{D}C$ (e.g. ideal gases, cons (or for given $\mathcal{D}(z)C(z)$) the above equ is a (linear) first-order differenti equation that can be integrated, boundary condition(s) (There are two F, F_A involved).

§ Example. Linear Diffusion, F_A/A = Const

Integrating gives:

$$\ln (N x_A - N_A) = \left(\frac{N}{C\mathcal{D}}\right) z + \text{Const}$$

For $x_A = x_{A0}$ at $z = 0$
$x_A = x_{AL}$ at $z = L$

One finds

$$\boxed{N_A = \frac{C\mathcal{D}}{L\chi_M}(x_{A0}-x_{AL}) = \frac{\mathcal{D}}{L\chi_M}(C_{A0}-C_{AL})}$$

where ("film factor")

(Chi) $$\chi_M = \text{Log Mean}\left[(b-1)x_A+1\right]$$

$$\overset{def}{=} \frac{\left[(b-1)x_A+1\right]_0 - \left[(b-1)x_A+1\right]_L}{\ln\left\{\frac{\left[(b-1)x_A+1\right]_0}{\left[(b-1)x_A+1\right]_L}\right\}}$$

and

$$b = -N_B/N_A \quad (\text{Const.})$$ {other data needed for specification

Other Special Cases:

I.) Stagnant gas B, $N_B \equiv 0 \Rightarrow b = 0$

$$\chi_M = \frac{-(x_{A0}-x_{AL})}{\ln\frac{(1-x_A)_0}{(1-x_A)_L}}$$

$$\left(N_A = \frac{\mathcal{D}C}{L}\ln(x_{BL}/x_{B0}) \right)$$

For stagnant film:

$N = N_A \neq 0$

Generally: $N = N_A + N_B = (1-b)N_A$

("Diffusive Convection" - Stefan-N

II.) "Equimolar Counter-diffusion"; $N_B = -N_A$

and $N = 0$

$$\chi_M = 1$$

and $$N_A = \frac{\mathcal{D}C}{L}(x_{A0}-x_{AL}) = \frac{\mathcal{D}}{L}(C_{A0}-C_{AL})$$

- linear in "driving force" or c… gradient.

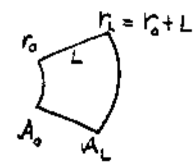
III.) "Dilute" System (in A) or Negligible Convection: x_{A0}, x_{AL} ($N x_A \ll$ …

$$\chi_M \doteq 1$$

~ Same flux relation as abov…

<u>Other Geometries</u> (Derive these!)

Cylindrical :



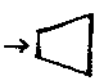
$$F_A = (\mathcal{A} N_A)_L = (\mathcal{A} N_A)_0$$

$$= \frac{\mathcal{A}_M}{\chi_M} \frac{\mathcal{D}(C_{A0} - C_{AL})}{L}$$

$$\mathcal{A}_M = \mathcal{A}_{Log\,mean} \equiv \frac{\mathcal{A}_L - \mathcal{A}_0}{\ln\left(\frac{\mathcal{A}_L}{\mathcal{A}_0}\right)} = \frac{l\theta(r_L - r_0)}{\ln(r_L/r_0)}$$

Spherical : Same as above, with

$$\mathcal{A}_M \equiv \mathcal{A}_{Geo.\,Mean} = \sqrt{\mathcal{A}_0 \mathcal{A}_L} = \Omega r_0 r_L$$

Approximate : (e.g. →  →)

Same, with

$$\mathcal{A}_M = \left[\frac{1}{L} \int_0^L \frac{dz}{\mathcal{A}(z)} \right]^{-1} .$$