Nenad Miljkovic

Mass Transfer

Let's begin with some definitions:

ρ_i = mass concentration of species i $[kg/m^3]$
C_i = molar concentration of i $[kmol/m^3]$

$$\rho = \sum \rho_i \quad , \quad m_i = \frac{\rho_i}{\rho}$$

$$C = \sum C_i \quad , \quad x_i = \frac{C_i}{C}$$

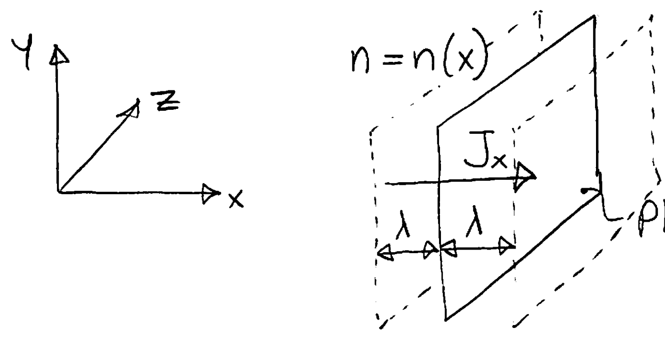
$$C_i = \frac{\rho_i}{M_i} \quad , \quad M = \sum x_i M_i$$

$$C = \frac{\rho}{M} \quad , \quad \frac{1}{M} = \sum \frac{m_i}{M_i}$$

$$\frac{P_i}{P} = X_i \quad , \quad P = \sum P_i$$

m_i = mass fraction of i
ρ = total mass of mixture
x_i = mole fraction of i
P_i = partial pressure of i
P = total pressure

Now lets consider the self-diffusion of a gas.



J_x = mean number of molecules crossing unit area of plane per unit time.

Similar analysis to when we derived viscosity on page 146 of notes.

$$J_x = \frac{1}{6}\bar{v}n_1(x-\lambda) - \frac{1}{6}\bar{v}n_1(x+\lambda)$$

$$= \frac{1}{6}\bar{v}\left(n_1(x-\lambda) - n_1(x+\lambda)\right] = \frac{1}{6}\bar{v}\left(-2\frac{\partial n_1}{\partial x}\lambda\right)$$

$$\boxed{J_x = -D\frac{\partial n_1}{\partial x}} \quad \text{and} \quad \boxed{D = \frac{1}{3}\bar{v}\lambda} \Rightarrow \text{Coefficient of self diffusion. } [m^2/s]$$

↳ Fick's Law

Nenad Miljkovic

Note Fick's Law doesn't only apply to self-diffusion. As long as the molecules are similar (ie. N_2 & O_2), it still works.

Other ways of writing it are:

$$j_{m,x} = -D_{i,m}\frac{\partial \rho_i}{\partial x} = -D_{i,m}\rho\frac{\partial m_i}{\partial x} \Rightarrow D_{i,m} = \text{diffusion coefficient of } i \text{ in } m.$$

$$\boxed{\vec{j}_{m,i} = -D_{i,m}\rho\nabla m_i}$$

$$J_{m,x} = -D_{i,m}\frac{\partial C_i}{\partial x} = -D_{i,m}\cdot C\cdot\frac{\partial x_i}{\partial x}$$

$$\boxed{\vec{J}_{m,i} = -D_{im}\cdot C\cdot\nabla x_i}$$

For a Lagrangian system:

$$\boxed{\frac{DC_i}{Dt} = D_{i,m}\nabla^2 C_i} \iff \boxed{\frac{DT}{Dt} = \alpha\nabla^2 T}$$

Mass Transfer Heat Transfer

Our governing equation is:

$$\boxed{\frac{DC_i}{Dt} = \frac{\partial C_i}{\partial t} + \vec{v}\cdot\nabla C_i = D_{i,m}\nabla^2 C_i}$$

At steady state and $\vec{v} = 0$

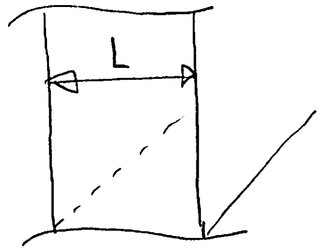
$$\nabla^2 C_i = 0, \quad \nabla^2 x_i = 0, \quad \nabla^2 \rho_i = 0, \quad \nabla^2 m_i = 0$$

If we have a 1-D problem and steady, with $\vec{v} = 0$

$$N_i = \frac{\Delta C_i}{R_m} \longleftrightarrow \text{Mass transfer resistance}$$

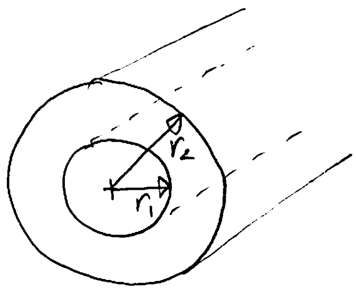
So our mass transfer resistances are:

Slab:



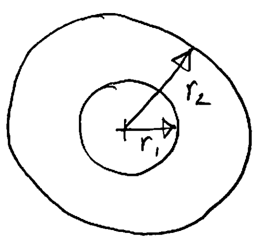
$$\boxed{R_m = \frac{L}{D_{1,2} A}}$$

Cylinder:



$$\boxed{R_m = \frac{\ln\left(r_2/r_1\right)}{2\pi L D_{1,2}}}$$

Sphere:



$$\boxed{R_m = \frac{1}{2\pi D_{1,2}}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)}$$

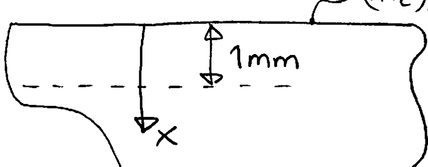
Example | Case hardening of mild steel.

Mild steel 0.2% or carbon (mass fraction). $m_c = 0.002$

$$\left.\begin{aligned} t = 0,\ x = 0 \quad (m_c)_{x=0} &= 0.015 \\ t = ?,\ x = 1\text{mm} \quad (m_c)_{x=1\text{mm}} &= 0.008 \end{aligned}\right\} \quad D_{c,s} = 5.6\times10^{-10}\ m^2/s$$

At what time, t, will this happen $(m_c)_{x=1mm} = 0.008$?
To solve, we first need to model the problem. We can use the semi-infinite body approach.

$(m_c)_{x=0,t=0} = 0.015$



$$\frac{(m_c)_{x=1mm} - (m_c)_\infty}{(m_c)_{x=0mm} - (m_c)_\infty} = \mathrm{erfc}\left(\frac{x}{2\sqrt{D_{c,s}t}}\right)$$

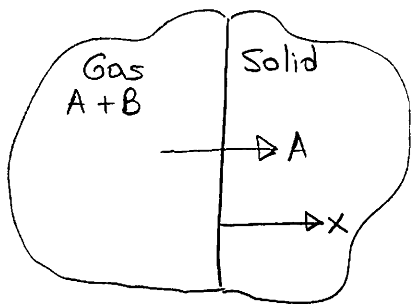
$$\frac{6}{13} = 0.4615 = \operatorname{erfc}(\beta) \Rightarrow \text{Look in Mills pg. 924} \quad \beta = 0.52$$

So our solution becomes:

$$0.52 = \frac{10^{-3}\,m}{2\sqrt{Dt}} \Rightarrow \boxed{t = 1650\,s = 28\text{ minutes}}$$

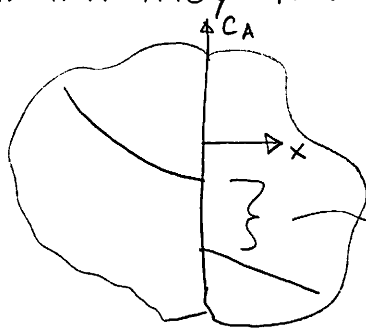
Where heat and mass transfer begin to differ is the fact that mass transfer allows for equilibrium to be reached with a concentration difference.

For example:



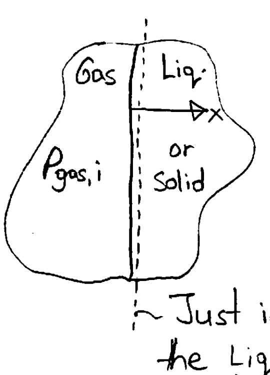
$$-CD_{AB}\frac{\partial x_A}{\partial x}\bigg|_{x=0} = J_{A,s}\bigg|_{x=0}$$

So our concentration may look like:



Discontinuity (Can't happen with temperature!)

To deal with this, we can use Henry's Law to solve for mole fraction just inside:



Just inside the Liquid or solid.

$$\boxed{P_{gas,i} = X_{i,u} \cdot H} \; ; \; H = \text{Henry's constant}$$

H (1 atm (10^5 Pa)) ⇒ in Water

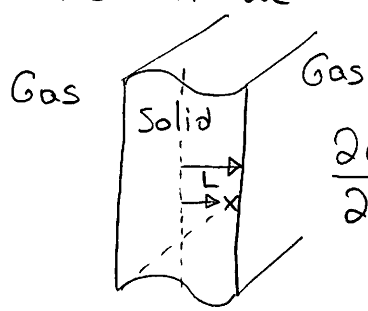
	290K	300K	320K	330K	340K
O_2	38 000	45 000	52 000	57 000	65 000
CO_2	1 280	1710	2170	3 220	4500
Air	62 000	74 000	92 000	99 000	

Nenad Miljkovic

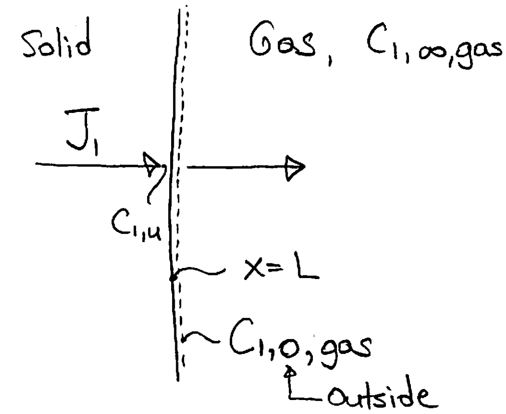
If we treat the gas and solid as a solution, we can say:

$$\boxed{C_{i,u} = S\,P_{gas,i}} \quad , \qquad \begin{aligned} P_{gas,i} &= \text{partial pressure of gas } i \text{ next to the interface} \\ C_{i,u} &= \text{kilomoles of gas } i \text{ per cubic meter of solid } \left[\tfrac{kmol}{m^3}\right] \\ S &= \text{solubility} \end{aligned}$$

So now if we look at a slab problem again:



$$\frac{\partial C_i}{\partial t} = D_{1,2}\nabla^2 C_1 \quad \Longleftrightarrow$$



Our boundary condition becomes:

$$\underbrace{-D_{1,2}\left(\frac{\partial C_1}{\partial x}\right)\Bigg|_{x=L}}_{\text{Inside the solid}} = J_1 = \underbrace{h_m\left(C_{1,0,gas} - C_{1,\infty,gas}\right)}_{\text{Outside, in the gas}} \quad (1)$$

h_m = mass transfer coeff. $\left[\frac{m}{s}\right]$

Now we can solve our problem.

Multiplying (1) by S/S $\quad (X_{1,u} = X_{1,gas}\cdot S)$

$$-D_{1,2}\left(\frac{\partial C_1}{\partial x}\right) = \frac{h_m}{S}\left[\left(C_{1,0} - C_{1,\infty}\right)_{gas}\cdot S\right] \quad (2)$$

Non-dimensionalizing equation (2)

$$\bar{x} = \frac{x}{L} \quad , \qquad \phi = \frac{C_1 - C_{1,u,\infty}}{C_{1,u,0} - C_{1,u,\infty}}$$

$$d\bar{x} = \frac{dx}{L} \quad , \qquad d\phi = \frac{dC_1}{C_{1,u,0} - C_{1,u,\infty}}$$

$C_1 = C(x=L,t)$ inside solid

$C_{1,u,\infty} = C(t\to\infty)$ inside

$C_{1,u,0} = C(t\to 0)$ inside

$C_{1,0,gas}$ = C at interface outside in gas

$C_{1\infty,gas} = C(x\to\infty)$ outside

Nenad Miljkovic

$$-D_{1,2}\frac{1}{L}\frac{\partial\phi}{\partial\bar{x}}\left(C_{1,u,0}-C_{1,u,\infty}\right)=\frac{h_m}{S}\left[\left(C_{1,0}-C_{1,\infty}\right)_{gas}\cdot S\right]$$

But note that $C_{1,0,gas}\cdot S=C_1$ and $C_{1,\infty,gas}\cdot S=C_{1,u,\infty}$

$$-D_{1,2}\frac{1}{L}\frac{\partial\phi}{\partial\bar{x}}\left(C_{1,u,0}-C_{1,u,\infty}\right)=\frac{h_m}{S}\left(C_1-C_{1,u,\infty}\right)$$

$$-D_{1,2}\frac{1}{L}\frac{\partial\phi}{\partial\bar{x}}=\frac{h_m}{S}\underbrace{\left(\frac{C_1-C_{1,u,\infty}}{C_{1,u,0}-C_{1,u,\infty}}\right)}_{\phi}$$

$$-D_{1,2}\frac{1}{L}\frac{\partial\phi}{\partial\bar{x}}=\frac{h_m\phi}{S}$$

$$\boxed{-\frac{\partial\phi}{\partial\bar{x}}=\underbrace{\left(\frac{h_mL}{D_{1,2}S}\right)}_{Bi_m}\phi}$$

$\Rightarrow$ Similar to heat transfer solution. Just added factor S.

Bi_m = mass transfer Biot number

$$=\frac{\text{internal diffusion resistance}}{\text{external convection resistance}}$$

If we look back at our heat transfer analogy