Nenad Miljkovic

Mass Conservation

Applying mass conservation on an elemental control volume for a constituent i:

$$\underbrace{\frac{\partial \rho_i}{\partial t}}_{\text{Accumulation}} + \underbrace{\frac{\partial}{\partial x}(\rho_i u_i) + \frac{\partial}{\partial y}(\rho_i v_i)}_{\text{Net mass flux}} = \underbrace{m_i'''}_{\text{Mass Generation } \left[\frac{kg}{m^3 \cdot s}\right]}$$

Note, we get all of our old results back if summing over all constituents and let $m_i''' = 0$.

$$\boxed{\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}\sum \rho_i u_i + \frac{\partial}{\partial y}\sum \rho_i v_i = 0}$$

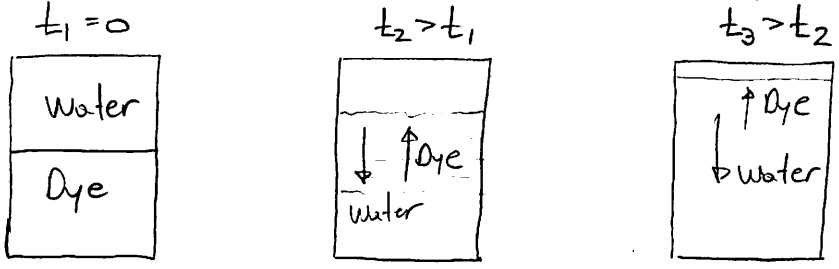
$\Updownarrow$ Has to be true for an equilibrium mixture

$$\boxed{\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) + \frac{\partial}{\partial y}(\rho v) = 0} \Rightarrow \text{Derived in 1'st part of class.}$$

So from this, we can say:

$$\boxed{u = \frac{1}{\rho}\sum \rho_i u_i} \; ; \; \boxed{v = \frac{1}{\rho}\sum \rho_i v_i} \equiv \text{Mass averaged velocity}$$

Note, $u \neq u_i$ or $v \neq v_i$. Think of dye diffusing in water



$V_{Dye} = V_1 > 0$

$V_{water} = V_2 < 0$

$V = 0$

While the mass averaged velocity (V) is zero, the velocity of the constituents is not.

Nenad Miljkovic

$(u_i - u) \equiv$ Diffusion Velocity in x-direction
$\rho_i (u_i - u) \equiv$ Flow rate per unit area of i in x-direction relative to the bulk motion of the mixture.

$$\boxed{\begin{array}{l} j_{x,i} = \rho_i (u_i - u) \\ \hline j_{y,i} = \rho_i (v_i - v) \end{array}} \equiv \text{Diffusive Flux}$$

Back substituting into our initial constituent mass conservation

$$\frac{\partial \rho_i}{\partial t} + \frac{\partial}{\partial x}(\rho_i u) + \frac{\partial}{\partial y}(\rho_i v) = -\frac{\partial j_{x,i}}{\partial x} - \frac{\partial j_{y,i}}{\partial y} + m_i'''$$

Noting that $C_i = \rho_i$ and $\rho =$ constant (incompressible)

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial x} + v\frac{\partial C_i}{\partial y} = -\frac{\partial j_{x,i}}{\partial x} - \frac{\partial j_{y,i}}{\partial y} + m_i'''$$

or

$$\boxed{\frac{DC_i}{Dt} = -\nabla \cdot j_i + m_i'''} \Rightarrow \text{Looks Familiar?}$$

The diffusion flux vector j_i is driven by ∇C_i, same as the heat flux vector q'' is driven by ∇T.

In 1855, Fick noticed this and mass transfer was born:
For a 2 component mixture: (dilute approximation, $\rho_{TOT} =$ const.)

$$\boxed{j_1 = -D_{12}\nabla C_1} \; ; \; D_{12} = D_{21} = \underset{[m^2/s]}{D} \equiv \text{Mass Diffusivity of component 1 into component 2.}$$

Back substituting j_1 into mass conservation above:

$$\boxed{\frac{DC}{Dt} = D\nabla^2 C + \dot{m}'''} \equiv \text{Dropped the subscript } i$$

↳ Just like heat transfer

Nenad Miljkovic

Note, in heat transfer we had:

$$\frac{DT}{Dt} = \alpha \nabla^2 T + \frac{q'''}{\rho c_p} \equiv \text{Energy Equation}$$

$$q'' = -k \nabla T$$

$$\boxed{C \rightleftharpoons T} \quad , \quad \boxed{D \rightleftharpoons \alpha}$$

So we can solve everything through analogy.

For <u>cartesian</u>

$$\boxed{\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} + w\frac{\partial C}{\partial z} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) + \dot{m}'''}$$

For <u>mass fraction</u>:

$$\boxed{\frac{D\phi}{Dt} = D\nabla^2\phi + \frac{\dot{m}'''}{\rho}}$$

$$\boxed{j = -\rho D \nabla \phi}$$

For <u>mole fraction</u>:

$$\boxed{\frac{Dx}{Dt} = D\nabla^2 x + \frac{M}{M_1}\frac{\dot{m}'''}{\rho}}$$

$$\boxed{j = -\rho \frac{M_i}{M} D \nabla x}$$

$\Rightarrow$ M_1 is molar mass of constituent of interest, whose mole fraction is x.

<u>Mass Diffusivities</u> (Binary Mixtures)

See Table 11.1 of pg. 498 in Bejan for $D_{12} = D_{21} = D$ at T_0, P_0

$$\boxed{\frac{D(T,P)}{D(T_0,P_0)} \cong \left(\frac{T}{T_0}\right)^{1.75} \frac{P_0}{P}}$$

*Note, D for liquid mixtures is 10^4 to 10^5 smaller than for gases

Table 11.1 Mass diffusivities of binary gaseous mixtures at atmospheric pressure

Gaseous Mixture	D (m^2/s)	T (K)
Air-acetone	1.09×10^{-5}	273
Air-ammonia	2.80×10^{-5}	298
Air-benzene	0.77×10^{-5}	273
Air-carbon dioxide	1.42×10^{-5}	276
	1.77×10^{-5}	317
Air-ethanol	1.45×10^{-5}	313
Air-helium	7.65×10^{-5}	317
Air-*n*-hexane	0.80×10^{-5}	294
Air-methanol	1.32×10^{-5}	273
Air-naphthalene	5.13×10^{-6}	273
Air-water vapor	2.60×10^{-5}	298
	2.88×10^{-5}	313
Ammonia-hydrogen	5.70×10^{-5}	263
	1.10×10^{-4}	358
Argon-carbon dioxide	1.33×10^{-5}	276
Argon-hydrogen	8.29×10^{-5}	295
Benzene-hydrogen	4.04×10^{-5}	311
Benzene-nitrogen	1.02×10^{-5}	311
Carbon dioxide-nitrogen	1.67×10^{-5}	298
Carbon dioxide-oxygen	1.53×10^{-5}	293
Carbon dioxide-water vapor	1.98×10^{-5}	307
Cyclohexane-nitrogen	0.73×10^{-5}	288
Helium-methane	6.76×10^{-5}	298
Hydrogen-nitrogen	7.84×10^{-5}	298
Hydrogen-water vapor	9.15×10^{-5}	307
Methane-water vapor	3.56×10^{-5}	352
Nitrogen-water vapor	3.59×10^{-5}	352
Oxygen-water vapor	3.52×10^{-5}	352

***Table adapted from Bejan, Convection Heat Transfer, 4th Edition, pp. 498**

Table 11.2 Mass diffusivities of gases and organic solutes at low concentrations in water (dilute aqueous solutions)

Solute	Solvent	D (m^2/s)	T (K)
Acetone	Water	1.16×10^{-9}	293
Air	Water	2.5×10^{-9}	293
Aniline	Water	0.92×10^{-9}	293
Benzene	Water	1.02×10^{-9}	293
Carbon dioxide	Water	1.92×10^{-9}	298
Chlorine	Water	1.25×10^{-9}	298
Ethanol	Water	0.84×10^{-9}	298
Ethylene glycol	Water	1.04×10^{-9}	293
Glycerol	Water	0.72×10^{-9}	288
Hydrogen	Water	4.5×10^{-9}	298
Nitrogen	Water	2.6×10^{-9}	293
Oxygen	Water	2.1×10^{-9}	298
Propane	Water	0.97×10^{-9}	293
Urea	Water	1.2×10^{-9}	293
Vinyl chloride	Water	1.34×10^{-9}	298

***Table adapted from Bejan, Convection Heat Transfer, 4th Edition, pp. 499**

Table 11.3 Henry's constant H for several gases in water at moderate pressures

	H (bar)					
T (K)	Air	N_2	O_2	H_2	CO_2	CO
290	6.2×10^4	7.6×10^4	3.8×10^4	6.7×10^4	1.3×10^3	5.1×10^4
300	7.4×10^4	8.9×10^4	4.5×10^4	7.2×10^4	1.7×10^3	6×10^4
320	9.2×10^4	1.1×10^5	5.7×10^4	7.6×10^4	2.7×10^3	7.4×10^4
340	1.04×10^5	1.24×10^5	6.5×10^4	7.6×10^4	3.7×10^3	8.4×10^4

***Table adapted from Bejan, Convection Heat Transfer, 4th Edition, pp. 501**

Nenad Miljkovic

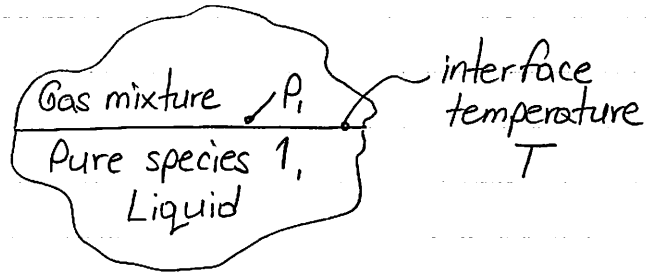
Boundary Conditions

For mass transfer problems, B.C.'s are always applied on the inner side of boundaries facing the domain of mass transfer.

Unlike T, C (concentration) does not vary continuously across an interface

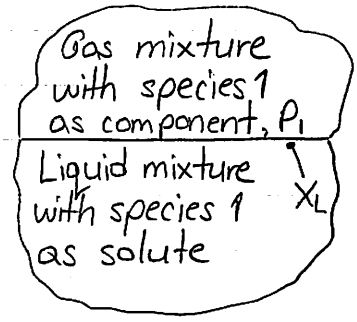
We can have 3 separate cases to consider:

Case 1: Ideal gas mixture and liquid phase of one component



$$\Rightarrow \boxed{P_1 = P_{1,SAT}(T)}$$

Case 2: Interface between a liquid mixture and gas mixture



X_L ≡ mole fraction of species 1 on liquid side

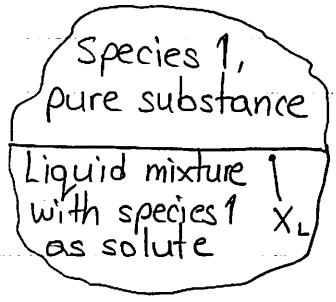
$$\boxed{X_L = \frac{P_1}{H}}$$

P_1 ≡ partial Pressure of 1.
≡ Henry's Law
H ≡ Henry's constant

Look up H in Table 11.3 on pg. 188 of notes
Valid for dilute solutions only.

Henry's law also only valid at low pressures ($P_1 < 1$ atm). At higher pressures, $H = f(P_1)$.

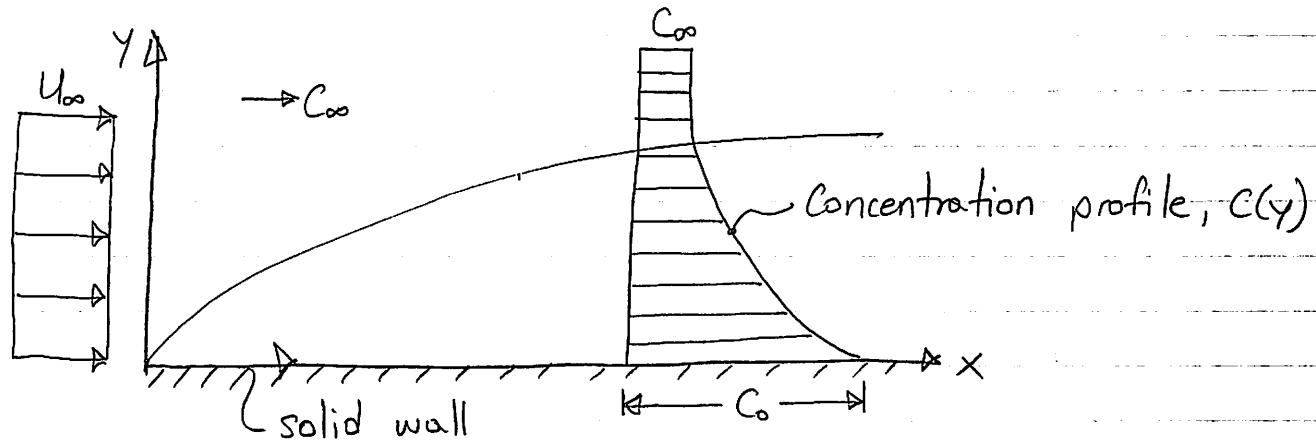
Case 3: Interface between a liquid mixture and a pure species 1 (liquid, solid)



⇒ X_L determined by assuming thermodynamic equilibrium at the interface and looking up the solubility of species 1 in the solvent.

Nenad Miljkovic

Laminar Forced Convection Mass Transfer



Assuming we have a wet wall with humid air at C_∞ flowing past it. Assuming a slender b.l. with $\frac{\partial P_\infty}{\partial x} = 0$ and T = uniform everywhere.

$$j_o = -D\left(\frac{\partial C}{\partial y}\right)\Big|_{y=0}$$

$$u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = D\frac{\partial^2 C}{\partial y^2} \quad (1)$$

$$\text{B.C.'s}: \left.\begin{array}{l} C = C_o \text{ at } y=0 \\ C \rightarrow C_\infty \text{ at } y \rightarrow \infty \end{array}\right\} (2)$$

We know (u,v) from the <u>Blasius solution</u> (flow over a flat plate). The mass transfer problem (eq. (1) & (2)) is analogous to the <u>Pohlhausen solution</u> for heat transfer.

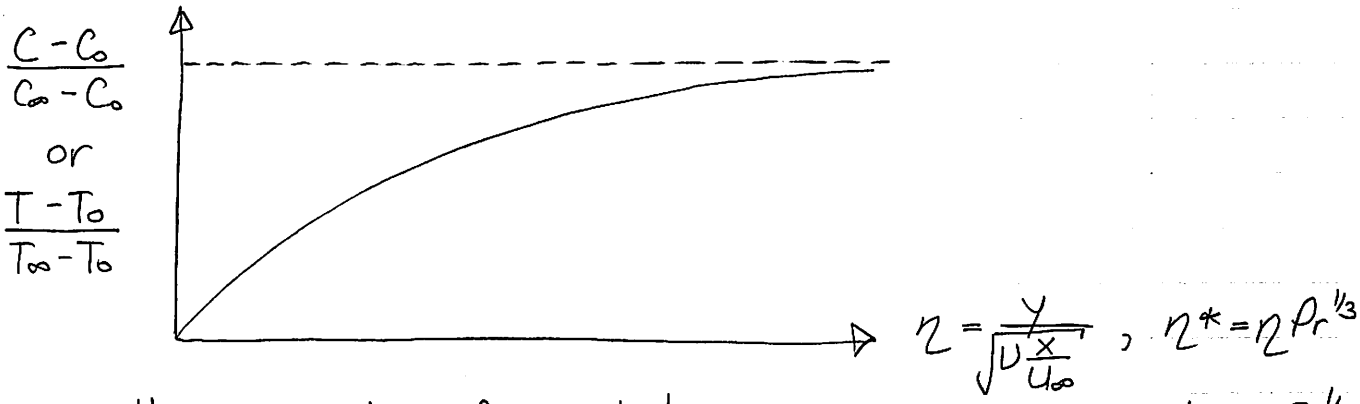
Noting that: $T \rightarrow C$ and $\alpha \rightarrow D$:

$$\boxed{\frac{\partial C}{\partial y}\Big|_{y=0} = (C_\infty - C_o)\left(\frac{U_\infty}{\nu x}\right)^{1/2}\left\{\int_0^\infty \exp\left[-\frac{\nu D}{2}\int_0^\gamma f(\beta)\,d\beta\right]d\gamma\right\}^{-1}}$$

↳ See page 55 of notes to see how we got this.

Graphically, we can draw this.

Nenad Miljkovic



For the mass transfer solution:

$$\eta^*_m = \eta Sc^{1/3} \quad \text{where} \quad \boxed{Sc = \frac{\nu}{D}} \equiv \text{Schmidt \#}$$

ν = mixture viscosity

For the thermal solution, we had $\eta^* = \eta Pr^{1/3}$, so $Sc \leftrightarrow Pr$.
Everything else is <u>analogous</u>!

$$\boxed{h_m = \frac{\hat{j}_0}{C_0 - C_\infty}} \equiv \text{mass transfer coefficient}$$

All we need to do is replace Pr with Sc, & h with h_m:

$$\left.\begin{aligned} Nu &= \frac{hx}{k} = 0.332\, Re_x^{1/2} Pr^{1/3} \\ \overline{Nu_L} &= \frac{\bar{h}L}{k} = 0.664\, Re_L^{1/2} Pr^{1/3} \end{aligned}\right\} \text{Heat Transfer}$$

$\Downarrow$ Mass Transfer

$$\left.\begin{aligned} Sh &= \frac{h_m x}{D} = 0.332\, Re_x^{1/2} Sc^{1/3} \\ \overline{Sh_L} &= \frac{\bar{h}_m L}{D} = 0.664\, Re_x^{1/2} Sc^{1/3} \end{aligned}\right\} \text{Mass Transfer } Sc > 0.5$$

$Sh \equiv$ Sherwood # (Analogous to Nusselt #)

$Nu \to Sh$; $Pr \to Sc$; $Re_x \to Re_x$; $h \to h_m$,

Nenad Miljkovic

Lastly, we want the mass transfer rate, $\dot{m}'$ (kg of species per second per meted depth):

$$\boxed{\dot{m}' = \bar{h}_m L (C_0 - C_\infty)} \quad ; \quad \boxed{\bar{h}_m = \frac{1}{L}\int_0^L h_m \, dx}$$

$$\boxed{\dot{m} = \bar{h}_m A (C_0 - C_\infty)}$$

<u>Impermeable Surface Model</u>

Note, our previous solution relies on the Blasius model where we assumed $v|_{y=0} = 0$. For mass transfer problems, this may not be the case.

Let's try some scaling arguments:

$$j_0 \sim (C_0 - C_\infty)\frac{D}{x} Re_x^{1/2} Sc^n \quad ; \quad n = \frac{1}{3} \text{ if } Sc > 0.5$$
$$n = \frac{1}{2} \text{ if } Sc < 0.5$$

So the velocity scale v associated with the mass flux is:

$$v_0 \sim \frac{j_0}{\rho} \quad (1)$$

For our laminar boundary layer, the vertical (transverse) velocity leaving the boundary layer is:

$$v_\infty \sim U_\infty Re_x^{-1/2} \quad \text{(see page 48 of notes)}$$

$$\frac{v}{U_\infty} = \frac{1}{2} Re_x^{-1/2}(\eta f' - f)$$
$$\eta = \frac{y}{\delta(x)} = 1 \text{ (at boundary)}$$
$$f' = \frac{u}{U_\infty} = 1 \text{ (at boundary)}$$
$$f \sim \frac{\eta^2}{2}$$

We can say that the solution is valid if $v_0 < v_\infty$

Back substituting:

$$\frac{v_0}{v_\infty} \sim \frac{(C_0 - C_\infty)\frac{D}{x\rho} Re_x^{1/2} Sc^n}{U_\infty Re_x^{-1/2}} \sim \left(\frac{C_0 - C_\infty}{\rho}\right)\frac{D}{U_\infty x} \cdot Re_x \cdot \left(\frac{\nu}{D}\right)^n$$

$$\sim \left(\frac{C_0 - C_\infty}{\rho}\right)\frac{D^{1/2}}{\nu^{1/2}} \cdot \overbrace{\frac{\nu}{U_\infty x}}^{Re_x^{-1}} \cdot \cancel{Re_x} \sim \left(\frac{C_0 - C_\infty}{\rho}\right) \cdot Sc^{-1/2} < 1$$

$$\boxed{\left(\frac{C_0 - C_\infty}{\rho}\right) < Sc^{1/2} < 1} \Rightarrow \text{Valid for small concentration differences.}$$