Constitutive Laws (CL)

The mathematical analysis of the diffusion of heat, mass, or momentum is incorporated into *constitutive laws* that relate this diffusion to easily measurable quantities (like temperature, velocity (pressure), and concentration).

- Use a resistor analogy to solve for heat flows [15.5, 17.1]
  - Calculate the thermal resistance and magnitude of conductive heat flow/flux through a planar wall
  - Calculate the thermal resistance and magnitude of conductive heat flow/flux through multiple planar walls
  - Calculate the thermal resistance and magnitude of conductive heat flow/flux through a cylindrical shell
  - Calculate the thermal resistance and magnitude of conductive heat flow/flux through a spherical shell
  - Calculate the resistance and magnitude of heat flow in systems in which multiple modes of heat transfer are present
  - Extend the resistor analogy to non-one-dimensional problems using shape factors [Ch 17.4]
  - Determine the heat flow through these solids from their temperature profiles
  - Use film theory and other correlations to obtain h [19.5]
- Explain and calculate viscous stresses [7.1, 7.2, 7.4]
  - Calculate viscous stresses/forces from velocity distributions
  - Identify Newtonian and non-Newtonian behavior from stress versus strain curves
- Solve diffusive mass flows problems
  - Explain the difference between the total flux and the diffusive flux [24.1]
  - Calculate the magnitude of diffusive mass flow/flux through a planar film in equimolar counter-diffusion [25.4]
  - Calculate the magnitude of diffusive mass flow/flux through a planar *stagnant* film [26.1]
  - Calculate the magnitude of diffusive mass flow/flux for systems with non-zero bulk flow
  - Calculate the magnitude of diffusive mass flow/flux through a cylindrical and spherical shells
  - Use film theory and other correlations to obtain kc [28.6]
  - Use the two-resistance model to perform fluid-fluid mass transfer calculations [29.1-29.3]
  - Calculate mass/molar flows/fluxes from concentration profiles

A *microscopic* or *continuum* description of transport requires that we examine "diffusion" of our conserved quantities at the molecular level.

- Estimate transport properties from molecular calculations
  - Explain the molecular origins of fluid viscosity and shear stresses.
  - Estimate fluid viscosities [7.3]
  - Explain the molecular origins of thermal and mass diffusion/conduction [15.2, 24.2]
  - Estimate thermal and mass diffusivities/conductivities [15.2, 24.2]

OUTCOME:

Calculate the thermal resistance and magnitude of conductive heat flow/flux through a planar wall

EXAMPLE:

Lets look at an example:
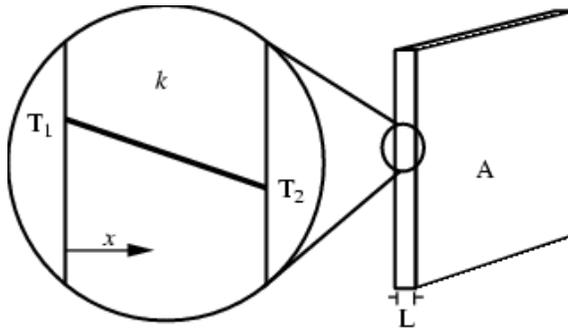
The inner and outer surfaces of a glass window are kept at 12.5 C and -9 C, respectively. What is the rate of heat loss through a window that is 5 mm thick and is 1m by 1.5m on a side? The thermal conductivity of the glass is 1.4 W/mK.

In how many different directions is heat flowing? (i.e., what is the dimensionality of the problem?)

Governing equation:

$$\frac{q}{A} = -k\frac{dT}{dx}$$

We can separate these variables and integrate...

$$\int_0^L q\,dx = \int_{T_1}^{T_2} -kA\,dT$$

We can reason that *q* should not change with *x* (or else we would have accumulation).

If we also assume that *k* (and A) are not functions of *T*, we get:

$$q\int_0^L dx = -kA\int_{T_1}^{T_2} dT$$

which can be integrated to yield:

$$qL = -kA(T_2 - T_1)$$

or

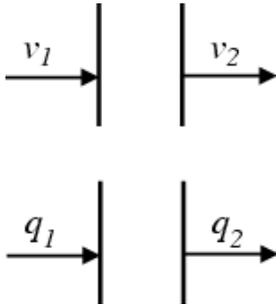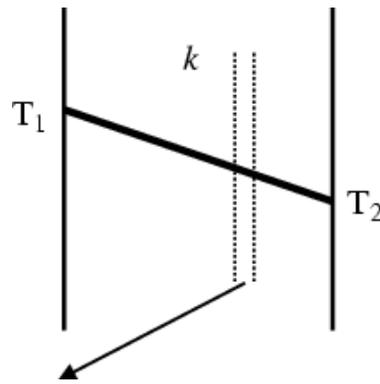$$q = \frac{kA}{L}(T_1 - T_2)$$

Plugging in our numbers...

$$q = \frac{(1.4W/mK)(1m)(1.5m)}{0.005m}(12.5^oC - (-9^oC)) = 9.0kW$$

In order to understand why the heat flow within the planar wall must be constant in x at steady state, let's consider some small segment within the wall:

If you consider a *fluid* flow across this section of our planar wall, it is easy to realize that if v_1 is not equal to v_2 then we have more material flowing *into (out of)* our small region then is flowing *out of (into)* this region. By definition, if IN does not equal OUT, we have *accumulation* (unsteady conditions!).

This idea is very similar to the idea behind the "continuity equation" (conservation of mass) for an incompressible fluid at steady state, which we will see soon:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

Also, the General Thermal Energy Balance Equation will prove this to use, at least mathematically. In any case, it is useful to recognize intuitively that in 1-D, the (heat) **flow** cannot change in the direction that the flow is occurring (at steady state).

Another (more complicated) example:
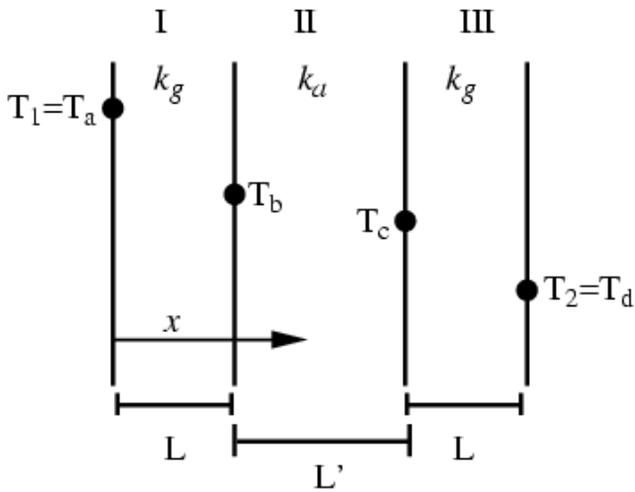
We have now added a second pane of glass (also 5 mm) with an air gap in between (7 mm). The inner and outer **surfaces** are again kept constant at 12.5 C and -9 C, respectively. What is the rate of heat loss through the window (it is still 1m by 1.5m on a side)? The thermal conductivity of the glass is 1.4 W/mK of air is 0.025 W/mK.

Each region (I, II, and III) may be solved *exactly* like our previous example, so our solutions for each (stolen from previous example) are:

$$q_{a \to b} = \frac{k_g A}{L_g}(T_a - T_b)$$

$$q_{b \to c} = \frac{k_{air} A}{L_{air}}(T_b - T_c)$$

$$q_{c \to d} = \frac{k_g A}{L_g}(T_c - T_d)$$

Any of these equations would suffice to tell us what the rate of heat flow is since we are at steady state. However, since we only know T_a and T_b, we cannot solve *any* of them! So...

Rearranging the equations:

$$q_{a \to b}\frac{L_g}{k_g A} = (T_a - T_b)$$

$$q_{b \to c}\frac{L_{air}}{k_{air} A} = (T_b - T_c)$$

$$q_{c \to d}\frac{L_g}{k_g A} = (T_c - T_d)$$

We can now *add* them (we need to note that $q_{ab}=q_{bc}=q_{cd}=q$):

$$q\left(\frac{L_g}{k_gA} + \frac{L_{air}}{k_{air}A} + \frac{L_g}{k_gA}\right) = (T_a - T_b + T_b - T_c + T_c - T_d)$$

which simplifies to:

$$q\left(\frac{L_g}{k_gA} + \frac{L_{air}}{k_{air}A} + \frac{L_g}{k_gA}\right) = (T_1 - T_2)$$

If we now denote (for reasons we will discuss in a minute)

$$R = \left(\frac{L_g}{k_gA} + \frac{L_{air}}{k_{air}A} + \frac{L_g}{k_gA}\right)$$

we can write this solution in a very simple equation:

$$q_{1\rightarrow2} = \frac{(T_1 - T_2)}{R}$$

Plugging in our numbers for R:

$$R = \left(\frac{0.005m}{(1.4W/mK)(1.5m^2)} + \frac{0.007m}{(0.025W/mK)(1.5m^2)} + \frac{0.005m}{(1.4W/mK)(1.5m^2)}\right) = 0.19K/W$$
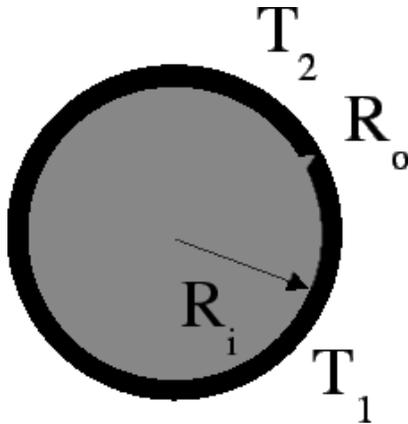
So our heat flow becomes:

$$q_{1\rightarrow2} = \frac{(12.5C - (-9C))}{0.19K/W} = 112W$$

This is *remarkably* smaller than the case of a single pane of glass!

Recall that we have proven to ourselves, at least conceptually (for now), that the heat **flow** may not vary spatially in a steady one dimensional conduction problem.
Let's consider a more difficult example...

A pipe with inside diameter (ID) of 2mm has an outside diameter (OD) of 2.5mm. If the inside wall of the pipe is held at T_i = 300K and the outside is kept at T_o = 350K. What is the rate of heat flow per length of pipe if the thermal conductivity of the pipe is k = 10 W/mK?

We clearly start with Fourier's Law in cylindrical coordinates:

$$\frac{q}{A} = -k\frac{dT}{dr}$$

Our first difference between the slab and the cylinder is that we need to write out the correct area (because it depends on r!):

$$\frac{q}{2\pi rL} = -k\frac{dt}{dr}$$

The second issue is when we write the integrals...what can we pull out of the left hand side?!

$$\frac{q}{2\pi L}\int_{R_i}^{R_o}\frac{dr}{r} = -k\int_{T_1}^{T_2}dT$$

Integration gives:

$$\frac{q}{2\pi L}\ln\left(\frac{R_o}{R_i}\right) = -k(T_2 - T_1)$$

which can be rearranged to:

$$q = \frac{2\pi Lk(T_1 - T_2)}{\ln\left(\frac{R_o}{R_i}\right)}$$

Writing this in terms of a resistor gives

$$q = \frac{\Delta T}{R}$$

where R is given as

$$R_{cyl} = \frac{\ln\left(\frac{R_o}{R_i}\right)}{2\pi kL}$$

OUTCOME:

Calculate the thermal resistance and magnitude of conductive heat flow/flux through a cylindrical shell

CL: Multiple modes of heat transfer

Previously, we introduced heat transfer problems in cylindrical coordinates, and looked at a *very* simple example. As it turns out, problems in cylindrical coordinates are slightly more interesting than they let on. Let's take a look...
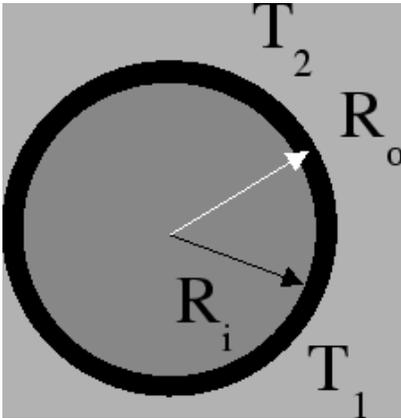
Let's look at our simple pipe again. Where the inside diameter (ID) is 2mm and the outside diameter (OD) is 2.5mm. Let's now include convective heat transfer, so the inside *fluid* is at T_i = 300K and the outside *fluid* at T_o = 350K. What is the rate of heat flow per length of pipe if the thermal conductivity of the pipe is k = 10 *W/mK*, and the inside and outside convective heat transfer coefficients are 35 W/m^sK (inside) and 70 W/m^2K (outside)?

We have already derived the governing equation:

$$q = \frac{\Delta T}{R}$$

Noting that for conduction through a cylinder, q_{cond} was

$$q_{1 \to 2} = \frac{2\pi k L}{\ln(r_2/r_1)}(T_1 - T_2)$$

so that R for conduction is given by

$$R_{cyl} = \frac{\ln(r_2/r_1)}{2\pi k L}$$

Recalling that the resistance due to convection is given by

$$R_{conv} = \frac{1}{hA} = \frac{1}{2\pi r L h}$$

(which r do we use now?!)

For this problem our thermal circuit is simply three resistors in series, so our total resistance, R_T is
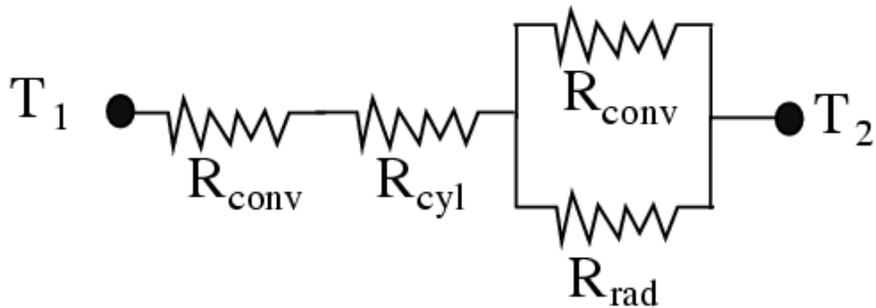
$$R_T = R_{conv(i)} + R_{cyl} + R_{conv(o)}$$

so that

$$R_{tot} = \frac{1}{2\pi r_1 L h} + \frac{\ln(r_2/r_1)}{2\pi k L} + \frac{1}{2\pi r_2 L h}$$

From here it is simply plugging in numbers!

Similarly, if we had both convection and radiation leaving the exterior of the pipe, we would have a thermal circuit that would look like:

and we would simply sum the total resistance as

$$R_T = R_{conv(i)} + R_{cyl} + R_{eff}$$

where

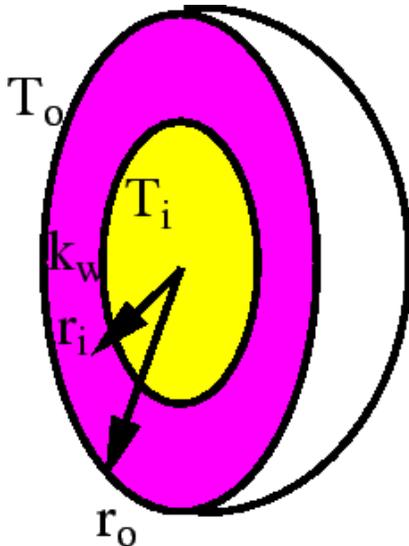$$R_{eff} = \frac{1}{1/R_{rad} + 1/R_{conv}}$$

OUTCOME:

Calculate the resistance and magnitude of heat flow in systems in which multiple modes of heat transfer are present

TEST YOURSELF

What happens if we increase the outer radius of the pipe? (or, equivalently, we add insulation to the exterior of the pipe)

A hollow sphere with inside diameter (ID) of r_o has an outside diameter (OD) of r_o. The inside wall is held at T_i and the outside is kept at T_o (these are our boundary conditions!). We know k. We would like to determine what the rate of heat flow is.

Again, we start with Fourier's Law only now in spherical coordinates:

$$\frac{q}{A} = -k\frac{dT}{dr}$$

Writing the surface area in spherical coordinates (recall that the surface area is our area perpendicular to the heat flow) gives us

$$\frac{q}{4\pi r^2} = -k\frac{dT}{dr}$$

Rearranging so that we can integrate,

$$\frac{q}{4\pi}\int_{r_i}^{r_o}\frac{dr}{r^2} = -k\int_{T_i}^{T_o}dT$$

Integrating and rearranging again gives:

$$q = \frac{4\pi k}{\frac{1}{r_i} - \frac{1}{r_o}}(T_i - T_o)$$

Writing this in terms of a resistor gives

$$q = \frac{\Delta T}{R}$$

where R is given as

$$R_{sph} = \frac{\frac{1}{r_i} - \frac{1}{r_o}}{4\pi k}$$

OUTCOME:

Calculate the thermal resistance and magnitude of conductive heat flow/flux through a spherical shell

How can we use the same $\Delta T/R$ approach to multi-dimensional problems?!
Using shape factors!

DEFINITION:

*A **shape factor** is a constant or an expression that is typically dimensionless (but sometimes has units of length) and accounts for the curvature of heat flows lines in a specific geometry such that we can use a linear relationship (i.e., $\Delta T/R$) to solve for heat flows in multi-dimensional problems.*

NOTE:

In the notes below, we use a dimensionless shape factor like your text. For shape factors that have units of length, simply omit the L (the "depth").

$q = kSL\,\Delta T$

it is useful to recast this equation into our familiar notation:

$$\frac{\Delta T}{R_{shape}} = kSL\,\Delta T$$

to yield a new resistor,

$$R_{shape} = \frac{1}{kSL}$$

In this way, we extend the use of shape factors to two very useful classes of problems:

- very complex shapes that are only possible to attain through the use of multiple shape factors in parallel
- complex problems that integrate multi-dimensional shapes into "traditional" resistor networks

OUTCOME:

Use shape factors to calculate heat flow in multi-d geometries

EXAMPLE:

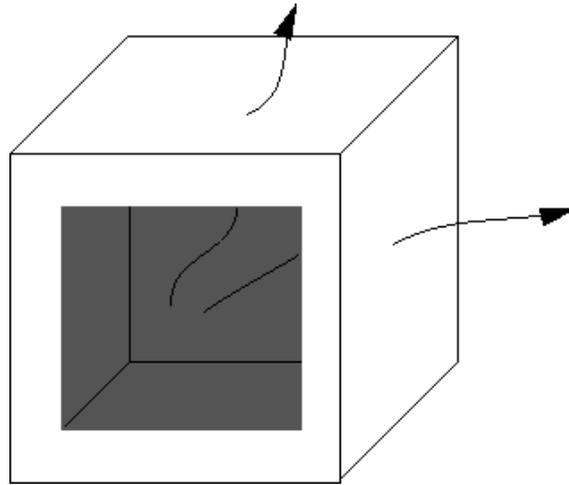*For an example that uses a shape factor with units of length (so that $R_{shape} = 1/(kS)$) ... see below:*

Recall in this case that:

$q = kS\,\Delta T$

so that

$$R_{shape} = \frac{1}{kS}$$

We want to figure out the heat loss through our new fridge (in order to calculate how expensive it will be to run). The fridge is a square, with side lengths of W and wall thickness of L. The inside temperature is given by T_{cold} and the outside (surface) temperature is given by $T_{surface}$. We know the thermal conductivity k and it is constant with respect to T.

Since we only want the heat flow, and we have a relatively complex geometry, we want to use shape factors.

The best way to approach this problem is to break it up...
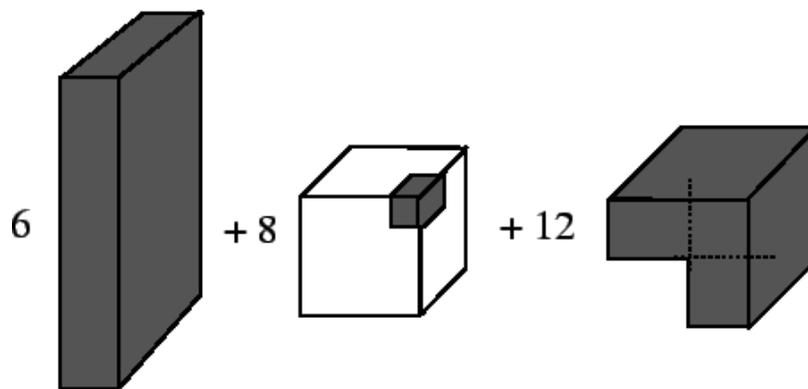
We can break our problem into it flat walls, edges, and corners (6 plane walls, 8 corners, and 12 edges). Since heat flows through each of these components *in parallel* we simply add each contribution to obtain the total heat flow.

Doing this, our heat flow is given by

$q = 6k\,S_{wall}\,(T_{cold}-T_{surface}) + 8k\,S_{corner}\,(T_{cold}-T_{surface}) +$

$12k\,S_{edge}\,(T_{cold}-T_{surface})$

or

$q = k\,(6S_{wall} + 8S_{corner} + 12S_{edge})\,(T_{cold}-T_{surface})$

we can actually figure out S_{wall} ourselves since we know the answer for heat flow through a plane wall...

$q_{wall} = kS_{wall}\,\Delta T = \dfrac{kA}{L}\,\Delta T$

so,

$$S_{wall} = \frac{A}{L}$$

we look up the answer for corners and edges...

$$S_{corner} = 0.15L$$

$$S_{edge} = 0.54W$$

Our final answer is given by

$$q = k\left(6\frac{A}{L} + 8(0.15L) + 12(0.54W)\right)(T_{cold} - T_{surface})$$

or, since $A=W^2$

$$q = k\ (6W^2/L + 8(0.15L) + 12(0.54W))\ (T_{cold}-T_{surface})$$

$$=k\ (6W^2/L + 1.2L + 6.48W)\ (T_{cold}-T_{surface})$$

As we progress further in our knowledge of transport, we will actually calculate the full temperature fields within heat transfer problems.

An alternative way to determine the heat flow is to use the temperature profile in conjuction with Fourier's Law; *this is particularly useful (in fact, **necessary**) for problems where the heat flow varies with position!*

Suppose a given problem yields a temperature profile of the following:

$$T = T_2 + \beta(1 - r^2) + \gamma \ln(r)$$

We could plug this into Fourier's Law in cylindrical (or spherical) corrdinates:

$$\frac{q}{A} = -k\frac{dT}{dr}$$

where dt/dr is given as

$$\frac{dT}{dr} = -2\beta r + \frac{\gamma}{r}$$

Combining these equations yields a flux of

$$\frac{q}{A} = k\left(2\beta r - \frac{\gamma}{r}\right)$$
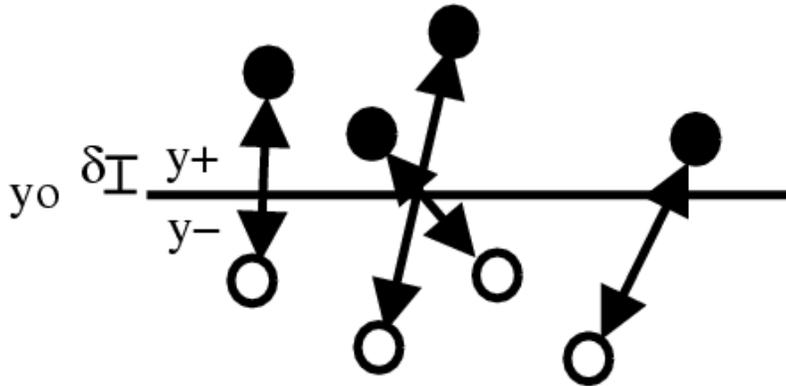
or (in cyliundrical coordinates), a flow of

$$q = 2\pi k L(2\beta r^2 - \gamma)$$

where q is clearly now a function of position.

OUTCOME:

Determine the heat flow through these solids from their temperature profiles

Returning to our molecular picture, we can think of a heat flux as being related to the movement (swapping) of molecules across a plane. These molecules each have their own value of thermal energy (given as $\rho c T$) so that their motion represents a flux (or a flow per unit area). We might write this flux (for Z molecules that moved) as:

$$\frac{q_y}{A} = \sum_{n=1}^{Z} m_n c_p \left(T|_{y-} - T|_{y+} \right)$$

Again, the $|_{y-}$ refers to the value of the temperature at the location *just below* our plane. We can relate this temperature (and the + variety) to a local value of the slope of the temperature (i.e., a derivative of the temperature with respect to position) by:

$$T|_{y-} = T|_{y_0} - \left(\frac{dT}{dy} \right)_{y_o} \delta$$

$$T|_{y+} = T|_{y_0} + \left(\frac{dT}{dy} \right)_{y_o} \delta$$

we can then combine these equations to give

$$\frac{q_y}{A} = -2 \sum_{n=1}^{Z} m_n c_p \frac{dT}{dy}|_{y_o} \delta$$

Again, relating δ to the *mean free path* using $\delta = (2/3)\lambda$ gives (for molecules of the same mass):

$$\frac{q_y}{A} = -\frac{4}{3} \lambda Z m c_p \frac{dT}{dy}|_{y_o}$$

The proportionality constant between the heat flux and the temperature gradient, which we will call the conductivity, can then be written as

$$k = \frac{4}{3} m Z c_p \lambda$$

Z can be related to the molecular concentration N and the average random molecular velocity C as Z = NC/4. Using this and the statistical mechanics expressions for the hard-sphere mean free path and average velocity:

$$\lambda = \frac{1}{\sqrt{2}\,\pi N d^2}$$

$$C = \sqrt{\frac{8\kappa T}{\pi m}}$$

where d is the molecular diameter. Finally, we can write an expression for the heat capacity of the material using the Boltzmann constant κ (which also showed up in the average velocity) to give:
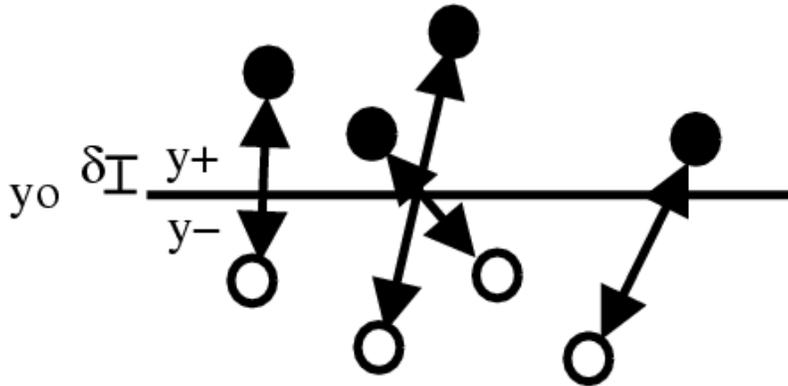
$$c_p = \frac{4}{3}\frac{\kappa}{N}$$

Combining these expressions gives the conductivity as:

$$k = \frac{1}{\pi^{3/2}d^2}\sqrt{\frac{\kappa^3 T}{m}}$$

OUTCOME:

Explain the molecular origins of thermal and mass diffusion/ conduction

Returning to our molecular picture of shear stresses, we can think of the momentum flux (shear stress) as being related to the movement (swapping) of molecules across a plane. We might write this flux (for Z molecules that moved) as:

$$\tau = -\sum_{n=1}^{Z} m_n \left(v_x|_{y-} - v_x|_{y+} \right)$$

where the $|_{y-}$ refers to the value at the location *just below* our plane. If we relate this value (and the + variety) to our slope of the velocity (shear rate or rate of strain) by:

$$v_x|_{y-} = v_x|_{y_0} - \left(\frac{dv_x}{dy} \right)_{y_o} \delta$$

$$v_x|_{y+} = v_x|_{y_0} + \left(\frac{dv_x}{dy} \right)_{y_o} \delta$$

we can then combine these equations to give

$$\tau = 2 \sum_{n=1}^{Z} m_n \frac{dv_x}{dy}|_{y_o} \delta$$

Here, we can think of δ as the average distance between molecular collisions. This can be related to a statistical mechanics quantity, the *mean free path* as $\delta = (2/3)\lambda$ so that our sum becomes (for molecules of the same mass):

$$\tau = \frac{4}{3} \lambda Z m \frac{dv_x}{dy}|_{y_o}$$

which we can show gives us

$$\mu = \frac{4}{3} \lambda Z m$$

Z can be related to the molecular concentration N and the average random molecular velocity C as Z = NC/4. Using this and the statistical mechanics expressions for the hard-sphere mean free path and average velocity:

$$\lambda = \frac{1}{\sqrt{2}\,\pi N d^2}$$

$$C = \sqrt{\frac{8\kappa T}{\pi m}}$$

where d is the molecular diameter. Combining these expressions gives the hard sphere viscosity:

$$\mu = \frac{2}{3\pi^{3/2}} \frac{\sqrt{m\kappa T}}{d^2}$$
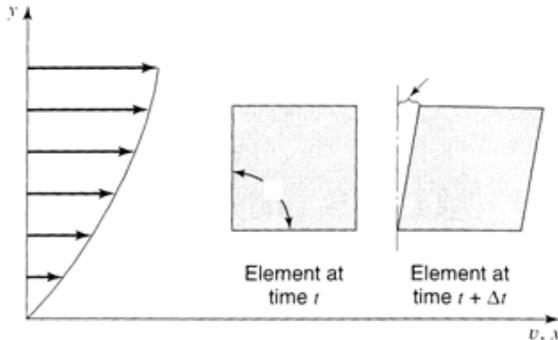
Recall that viscous stresses (sometimes called "frictional stresses") arise from adjacent fluid elements *moving relative to one another*. As the pieces of fluid "slide" past each other they exert a friction-like force from layer to layer.
The viscous stresses therefore are the forces per unit are acting on fluid elements, due to friction.

It should not be surprising, therefore, that the *velocities* of these fluid elements must actually be different from each other (or else they would not be moving relative to each other). The simplest case of this are shear stresses arising from fluid deformation.

DEFINITION:

*The **rate of strain (or shear rate)** is the rate at which a fluid element is deformed. this can be shown to be related to the slope (gradient) of the velocity.*

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{dv_x}{dy}$$

DEFINITION:

*We can actually define a **fluid** as a material whose rate of strain (or shear rate) is proportional to the imposed shear stress, whereas a solid is a material whose total strain is proportional to the shear stress.*

A special case of a fluid (but the only thype of fluid that we will spend any real time studying) is one whose relationship between shear rate and stress is linear.

DEFINITION:

*A **Newtonian fluid** is one whose rate of strain (or shear rate) is linearly proportional to the imposed shear stress, according to the following expression:*

$$\tau = \mu\dot{\gamma} = \mu\frac{dv_x}{dy}$$

NOTE:

*This expression is often called **Newton's law of viscosity** and the constant of proportionality is called the viscosity.*

As we will see in future fluid studies, the ratio of the viscosity to the fluid density often appears in equation and is thus given a name: the kinematic viscosity.

$$v = \frac{\mu}{\rho}$$

OUTCOME:

Calculate viscous shear stresses (momentum fluxes!) directly from velocity profiles

NOTE:

*We do this in the **exact** same fashion as getting a heat flow/flux from a temperature profile!*

There are a number of types of fluid that do not obey Newton's Law of viscosity. Identifying these is simplest by plotting the rate of strain (shear rate) as a function of the applied shear stress:
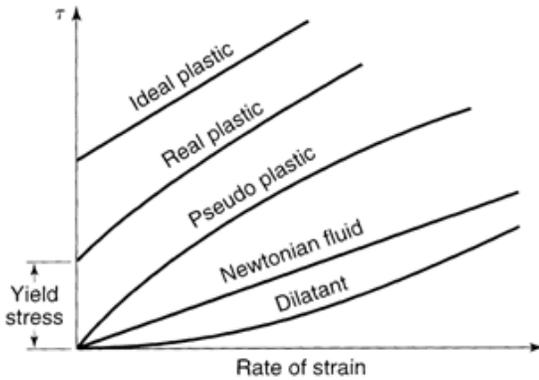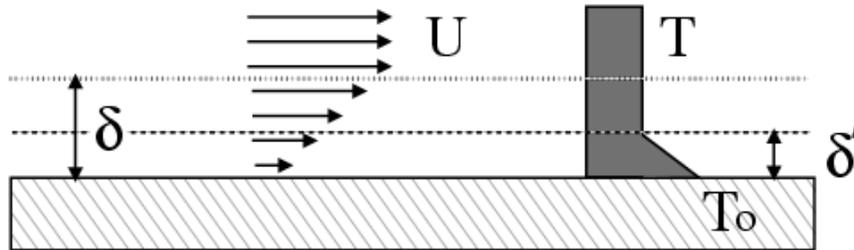

OUTCOME:

Identify Newtonian and non-Newtonian behavior from stress versus strain curves

Near a solid boundary it is often assumed that there is a "film" of fluid that is slower than the bulk flow where we might further assume that the velocity varies linearly with position:

For reasons that will be discussed in the next section, this means that the shear stresses on the solid are constant and may be written as:

$$\tau = \frac{F_s}{A} = \mu \frac{U}{\delta}$$

which can be rearranged to give:

$$\delta = \mu \frac{U}{\tau}$$

Recalling that the definition of the friction factor was:

$$f = \frac{\tau}{\frac{1}{2}\rho U^2}$$

means that we can write the film thickness, scaled by some length, L, as:

$$\frac{\delta}{L} = \frac{2}{f Re}$$

As discussed previously, we can write the heat flux due to convection as a product of the heat transfer coefficient and the driving force. For reasons that will be discussed in the next section, if we assume a linear temperture profile within a *thermal film* (see picture) we can write:

$$\frac{q}{A} = k \frac{\Delta T}{\delta'} = h \Delta T$$

This shows that the "film coefficient" name for the heat transfer coefficient comes from the fact that, using film theory, it can be related to the thermal film thickness and fluid properties by:

$$h = \frac{q/A}{\Delta T}$$

Making an analogy to the friction factor, we can define a dimensionless heat flux as:

$$Nu = \frac{q/A}{k(\Delta T / L)}$$

which can be combined with Newton's law of cooling to give:

$$Nu = \frac{h \Delta T}{k(\Delta T / L)} = \frac{hL}{k}$$

Using the film theory definition of h, we can get:

$$Nu = \frac{L}{\delta'} = \frac{L}{\delta}\left(\frac{\delta}{\delta'}\right) = \frac{f Re}{2}\left(\frac{\delta}{\delta'}\right)$$

As we will see later in the course, the ratio of film thicknesses can be related to the material properties for heat transfer, through the Prandtl number, Pr, to give:

$$Nu = \frac{f\,Re}{2}\left(\frac{v}{\alpha}\right)^{1/3} = \frac{f}{2}RePr^{1/3}$$

where the factor of 1/3 will be explained later in the course.

This expression is a useful generic formula for the convective heat transfer coefficient that can be used when no better correlation is available (provided you have a decent correlation for f). One further aid to correlations was devised by Colburn, where a "j-factor" has been defined as:

$$j_H = \frac{Nu}{RePr^{1/3}}$$

so that a direct relation to the friction factor is given as:

$$j_H = \frac{f}{2}$$

NOTE:

Using the above analysis, one can use correlations for Nu directly, j-factor correlation directly, or film theory along with correlations for f to yield h values!

OUTCOME:

Use film theory and other correlations to obtain h

Recall that in terms of mass transfer we are interested in either **N**$_i$ (called the *molar flux*) or **n**$_i$ (*mass flux*) so that we are interesting in the rate at which *mass* traveles through a certain *area* in a given *time*. While we have written this as a flow dived by an area:

$$n = \frac{\dot{m}}{A},$$

we might instead (for something like a pipe flow) write that the mass flow rate is given by:

$$\dot{m} = \rho v A$$

where ρ is the mass concentration (density), v is the (average) velocity in the pipe, and A is the cross section of the pipe so that we can then write the mass flux as:

$$n = \frac{\dot{m}}{A} = \frac{\rho v A}{A} = \rho v$$

These simple arguments, in fact, can be applied to *any* mass flow to determine the total mass flux, so that, in general, the mass flux of component i is given by:

$$n_i = \rho_i v_i$$

Similar arguments can give us an expression for the molar flux

$$N_i = c_i v_i$$

where c_i is the molar concentration of component i.

Unfortunately, the velocity in these expressions v_i is not trivial to calculate (or measure!) without some further consideration. (Think, for example, of measuring the velocity of *oxygen* in the cool breeze on a summer afternoon instead of measuring the velocity of the *air*! Clearly, measuring the air velocity would be simple, but distinguishing the velocity of the *oxygen* from all the other gases that make up air would be quite troublesome.) So, let's think in more detail about the *bulk* velocity (like the air velocity).

Let's assume for a minute that we do actually know the velocities of each the individual gases that make up air. How might we calculate the bulk or average velocity?

Well, for our purposes there are essentially two methods: averaging by mass, or averaging by mole. If we wanted to calculate the bulk velocity of the air by mass we would add up all of the velocities of the individual gases, weighted by the mass of that particular gas and then divide the total by the mass of the air. In other words, we would calculate a weighted average (by mass) like this:

$$v = \frac{\sum_i \rho_i v_i}{\sum_i \rho_i}$$

We could do the exact same thing using moles

$$V = \frac{\sum_i c_i v_i}{\sum_i c_i}$$

where c_i is the molar concentration of component i.

Now that we know how the actual velocity of each component in a mixture is related to the average (bulk) velocity (which we can measure). We can try to determine how to go in the other direction (in other words, how to calculate the actual component velocity from the bulk velocity.)
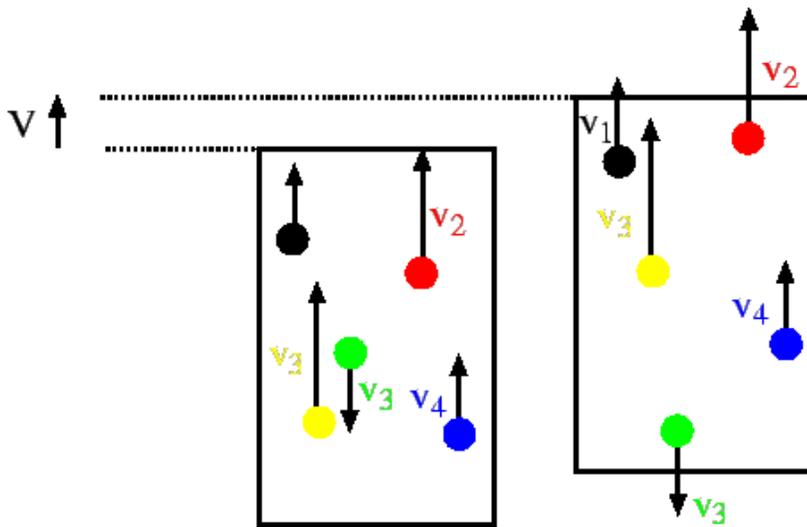
If we think of a crowd of people walking down the hallway, it is certainly possible that the *individuals* within the crowd are walking at different speeds. If we draw a box (centered) around the individuals at one time, and then again a little while later, it is clear that the crowd as a whole is moving at some average velocity, *V* (which is not necessarily equal to the velocity of *any* of the individuals). If we take the difference between the individual's velocity and the bulk velocity we get a quantitative measure of the individual's deviation (diffusion!) velocity.

$v_{diff_i} = v_i - v$ or $v_{diff_i} = v_i - V$

In exactly the same way that we defined a total mass (mole) flux using the component's total (actual) velocity, we can then define a component's *diffusive* flux j_i (mass) or J_i (molar) to be:

$j_i = \rho_i v_{diff_i} = \rho_i(v_i - v)$

or

$J_i = c_i v_{diff_i} = c_i(v_i - C)$

We discussed earlier in the course that the *actual* origin of diffusive motion is the random fluctuations of molecules "swapping" their way down a concentration gradient. This explanation clearly has much in common with heat flow (down a temperature gradient) and thus it is not surprising that Fick's Law (proposed for binary mixtures) looks much like Fourier's Law

$J_i = -D\nabla c_i$

for the diffusive flux, where *D* is the binary diffusivity of component *i* in the system (species *j*. This expression shows that (just like temperature) concentration "flows downhill" (until there isn't a hill!) A more general equation to account for possible changes in overall concentration, c_{total} (in non isobaric, isothermal systems), is

$J_i = -c_{total}D\nabla y_i$

where y_i is the mole fraction.

NOTE:

While Fick's Law is formally true for only binary mixtures, it is often used for multi-component systems with a somewhat fudged value of D.

If we then plug this equation into our definition of the diffusive flux

$$J_i = c_i(v_i - V) = -c_{total}D\nabla y_i$$

we can solve for the component's actual velocity v_i

$$v_i = \frac{-c_{total}D\nabla y_i}{c_i} + V$$

We can then plug *this* equation into our expression for the molar flux

$$N_i = c_i v_i = c_i\left(\frac{-c_{total}D\nabla y_i}{c_i} + V\right) = -c_{total}D\nabla y_i + c_i V$$

which (finally!) gives us the total molar flux in terms of things we can measure easily.

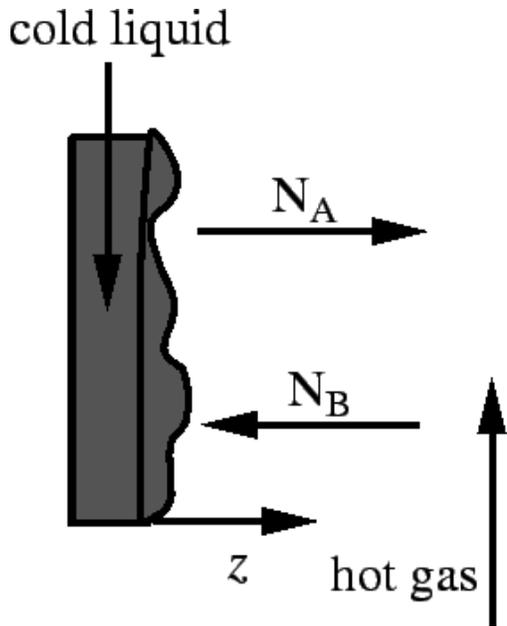Again, deriving the expression based on mass is not any more difficult

$$n_i = -\rho_{total}D\nabla\omega_i + \rho_i v$$

where ω_i is the mass fraction of component *i*.

OUTCOME:

Explain the difference between the total flux and the diffusive flux

cold liquid

N_A

N_B

z hot gas

In a distillation column, there is a temperature gradient as you move from the bottom of the column upwards. Because of this, if we assume that the system is at equilibrium everywhere, then, as (colder) liquid flows downward and (hotter) gas flows upward they must exchange material in order to maintain equilibrium (since the equilibrium is temperature dependent). If we think about a simple system: a binary mixture, the column is at constant pressure, and the latent heats of vaporization of the two components are similar, we can argue that the flux of A exactly counterbalances the flux of B (i.e., $N_A = -N_B$).

If we are interested in the flux and concentration profile of A, the governing equation is given by (see above for assumptions):

Recall that N_A is given by

$$N_A = -c_{total}D\nabla y_A + c_A V$$

Further recall the definition of the molar-averaged velocity V, so that we can write it for a binary system as

$$V = \frac{c_A v_A + c_B v_B}{c_A + c_B} = \frac{N_A + N_B}{c_{total}}$$

in this particular problem (equimolar counter-diffusion) we have already noted that $N_A = -N_B$, so

$$V = \frac{-N_B + N_B}{c_{total}} = 0$$

this reduces our expression for N_A to

$$N_A = -c_{total}D\nabla y_A$$

For a one dimensional isobaric, isothermal system we may write this as

$$N_A = -D\frac{dc_A}{dz}$$

Assuming that the liquid surface is at the saturation concentration and that the concentration drops to some value C_{A_δ} at some distance δ, we can then solve for the molar flow by rearranging:

$$\dot{M}_A = N_A A = -DA\frac{dc_A}{dz}$$

and integrating (why did $\dot{M}_A$ come out of the integral?!)

$$\dot{M}_A\int_0^\delta = -DA\int_{c_{A_{sat}}}^{c_{A_\delta}} dc_A$$

to get

$$\dot{M}_A\delta = -DA(c_{A_\delta} - c_{A_{sat}})$$

which can be re-written as

$$\dot{M}_{A_{0\to\delta}} = \frac{DA}{\delta}(c_{A_{sat}} - c_{A_\delta})$$

to highlight that it is very similar to our heat transfer solution (for conduction through a rectangular slab) for a variety of reasons:

• The flux is independent of position
• The flux is linearly dependent on the driving force (concentration difference)
• We can write the flow of mass (the flux times the area) as being equal to $\frac{DA}{L}\Delta c$ much like the conduction expression $\frac{kA}{L}\Delta T$

OUTCOME:

Calculate the magnitude of diffusive mass flow/flux through a planar film in equimolar counter-diffusion

Air (species B)

A is evaporating

z

species A
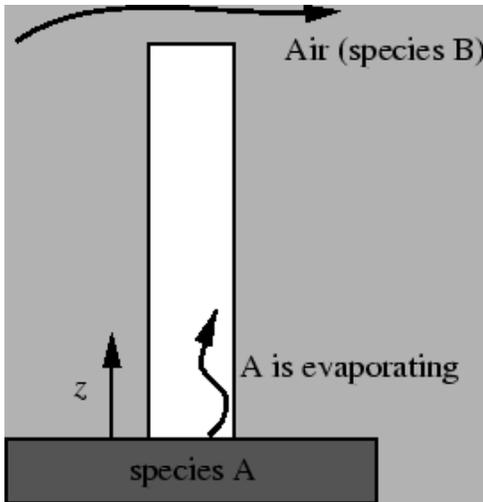
Consider a tank of some volatile liquid, A, which is vented to the atmosphere through a chimney that has a stiff breeze blowing by it. Once we have reached steady state, there will be a mixture of A and air (which we will call B) within the chimney. The A is evaporating and flowing (diffusing) up through the column until it is ultimately blown away by the wind. The B, on the other hand, is completely stagnant (not moving up the chimney nor down the chimney).

This is clear if you consider that, at steady state with no accumulation, any B that moves down the chimney must exit the bottom and that any that moves up the chimney must be *replaced* at the bottom (if either of these is not met, there *will* be accumulation). Also note that this is *not* the case for the A since there is a steady stream of A being supplied by the liquid in the tank. In this case there is no net flux of B ($N_B = 0$), but there *is* a non-zero flux of A ($N_A \neq 0$).

By definition, N_A is given by

$N_A = -c_{total}D\nabla y_A + c_A V$

where the molar-averaged velocity V, we can written for a binary system as

$V = \dfrac{c_A v_A + c_B v_B}{c_A + c_B} = \dfrac{N_A + N_B}{c_{total}}$

In this particular problem (diffusion through a stagnant gas) we have already noted that $N_B = 0$, so

$V = \dfrac{N_A + 0}{c_{total}} = \dfrac{N_A}{c_{total}}$

NOTE:

We can have a non-zero bulk flow even in a "diffusion" problem (as long as the total fluxes do not cancel out). We must determine if there is a flow or not from examining the total mass flux term itself! (This is the most important difference between heat and mass transfer.)

Plugging in our expression for V, we reduces our expression for N_A to

$N_A = -c_{total}D\nabla y_A + y_A N_A$

we can solve this for N_A to give

$$N_A = -\frac{c_{total}D\nabla y_A}{1-y_A}$$

which in one dimension becomes

$$N_A = -\frac{c_{total}D\frac{dy_A}{dz}}{1-y_A}$$

We can then solve for the flux by integrating between $z=0,L$ and note that the corresponding concentrations are $y_A = y_{A_{sat}}$, 0

$$N_A\int_0^L dz = -c_{total}D\int_{y_{A_{sat}}}^0 \frac{dy_A}{1-y_A}$$

(Here we note that $N_A \neq F(z)$ by analogy to our previous example as well as heat transfer...if it *did* change with *z*, we would have accumulation!)

Integrating gives

$$N_AL = c_{total}D(\ln[1-0] - \ln[1-y_{A_{sat}}]) = -c_{total}D\ln[1-y_{A_{sat}}]$$

so that N_A is

$$N_A = -\frac{c_{total}D}{L}\ln[1-y_{A_{sat}}]$$

which we note is not a function of *z*, as we stipulated.

OUTCOME:

Calculate the magnitude of diffusive mass flow/flux through a planar stagnant film

In addition to diffusion through a stagnant gas, there are a variety of other scenarios from which non-equimolar counter diffusion can arise (i.e., where we might obtain a bulk flow). A good example is heterogeneous catalysis problems (i.e. reactions on a surface). Consider the reaction:

$$2A \rightarrow 2B + C$$
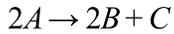
If this reaction occurs between gas molecules on a solid surface:
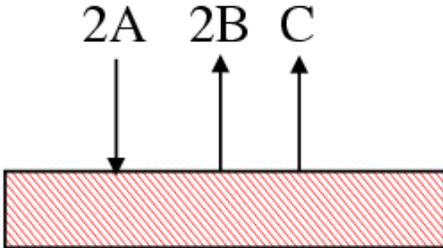
we clearly have a net molar flux away from the surface as two moles/molecules of A is making a total of three moles of product (although our net *mass* flux would still be zero). In solving the problem for the total flux of species A, we again start with the definition of the total flux:

$$N_A = -c_{total}D\nabla y_A + c_A V$$

In this case our *V* is given as

$$V = \frac{c_A v_A + c_B v_B + c_C v_C}{c_{total}} = \frac{N_A + N_B + N_C}{c_{total}}$$

where we can use stoichiometry to relate N_A to the other N's to get:

$$\frac{1}{2}N_A = -\frac{1}{2}N_B = -N_C$$

NOTE:

Be careful not to trick yourself into saying 2N$_A$ = -2N$_B$ = -N$_C$. Since there are already 2 moles of A forming 1 mole of C, this would actually be backward and make our answer really wrong.

Plugging this into N_A we get

$$N_A = -c_{total}D\nabla y_A + y_A\left(N_A - N_A - \frac{1}{2}N_A\right)$$

$$N_A = -c_{total}D\nabla y_A - \frac{y_A}{2}N_A$$

solving for N_A gives

$$N_A = -\frac{c_{total}D\nabla y_A}{1 + \frac{y_A}{2}}$$
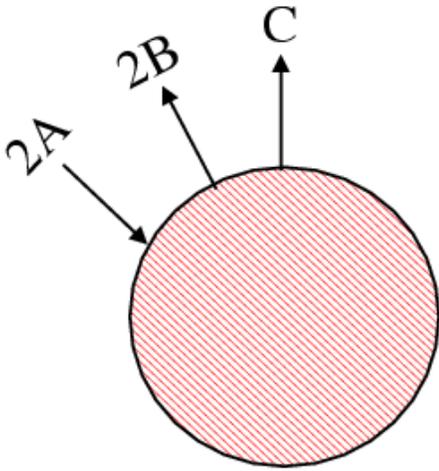
which in one dimension becomes

$$N_A = -\frac{c_{total}D\frac{dy_A}{dz}}{1 + \frac{y_A}{2}}$$

OUTCOME:

Calculate the magnitude of diffusive mass flow/flux for systems with non-zero bulk flow

If we examine the same heterogeneous catalysis problem as before, for reaction,

$$2A \rightarrow 2B + C$$

but now use a spherical catalyst:

our problem changes slightly.

We still have a net molar flux away from the surface, and must still begin with the definition of the total flux (if solving for species A):

$$N_A = -c_{total}D\nabla y_A + c_A V$$

Again, V is given as

$$V = \frac{c_A v_A + c_B v_B + c_C v_C}{c_{total}} = \frac{N_A + N_B + N_C}{c_{total}}$$

where we can use stoichiometry to relate N_A to the other N's to get:

$$\frac{1}{2}N_A = -\frac{1}{2}N_B = -N_C$$

Plugging this into N_A we get

$$N_A = -c_{total}D\nabla y_A + y_A\left(N_A - N_A - \frac{1}{2}N_A\right) = -c_{total}D\nabla y_A - \frac{y_A}{2}N_A$$

solving for N_A gives

$$N_A = -\frac{c_{total}D\nabla y_A}{1 + \frac{y_A}{2}}$$

If our one dimension now is spherical coordinates we get

$$N_A = -\frac{c_{total}D\frac{dy_A}{dr}}{1 + \frac{y_A}{2}}$$

NOTE:

While the flux was constant in a planar system (since the area didn't change with position), only the flow is constant in cylindrical or spherical coordinates! This changes how we integrate this equation.

Writing this in terms of the molar flow, we get

$$\dot{M}_A = -4\pi r^2 c_{total}D\frac{\frac{dy_A}{dr}}{1 + \frac{y_A}{2}}$$

Taking c_{total} to be constant and rearranging, we can integrate between the surface of the catalyst (where $y_A = 0$, if the reaction is very fast) and "far away" from the surface (where we expect to regain the bulk concentration):

$$\dot{M}_A \int_R^{\infty} \frac{dr}{r^2} = -4\pi r^2 c_{total} D \int_0^{y_{A_{bulk}}} \frac{dy_A}{1+\frac{y_A}{2}}$$

whose solution is

$$\dot{M}_A = -8\pi R c_{total} D \ln\left(1+\frac{y_{A_{bulk}}}{2}\right)$$

(Recall that the negative sign means that the flow of A is *toward* the sphere surface.)

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NOTE:

The approach for cylindrical geometries is the same, but a solution for a known concentration at infinity is not possible.

OUTCOME:

Calculate the magnitude of diffusive mass flow/flux through a cylindrical and spherical shells

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Again assuming that their is a "film" near the solid boundary where both velocity and concentration change fromt he bulk value to the surface value, we get something like this:
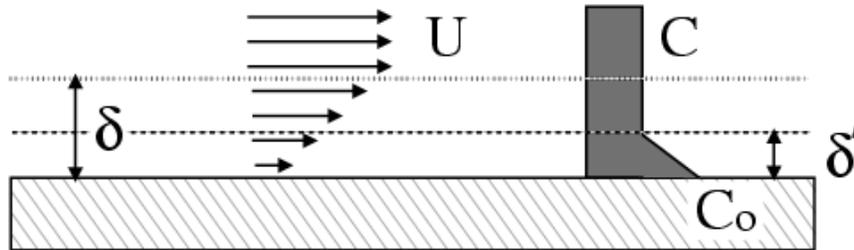
Again, the shear stresses on the solid are constant, so that we might use the friction factor to write the size of the fluid film as:

$$\frac{\delta}{L} = \frac{2}{f\,Re}$$

We can then write the mass flux due to convection as a product of the mass transfer coefficient and the driving force. For reasons that will be discussed in the next section, if we assume a linear concentration profile within a *mass film* (see picture) we can write:

$$N_A = D\frac{\Delta C_A}{\delta'} = k_c\,\Delta C_A$$

Making an analogy to the friction factor and the Nu, we can define a dimensionless mass flux, Sherwood number, as:

$$Sh_L = \frac{N_A}{D(\Delta C_A/L)}$$

which can be combined with our convection expression to give:

$$Sh_L = \frac{k_c L}{D}$$

Using the film theory definition of k_c (i.e., $k_c = D/\delta'$), we can get:

$$Sh_L = \frac{L}{\delta'} = \frac{L}{\delta}\left(\frac{\delta}{\delta'}\right) = \frac{f\,Re_L}{2}\left(\frac{\delta}{\delta'}\right)$$

As we will see later in the course, the ratio of film thicknesses can be related to the material properties for mass transfer, through the Schmidt number, Sc, to give:

$$Sh_L = \frac{f\,Re}{2}\left(\frac{\nu}{D}\right)^{1/3} = \frac{f}{2}Re\,Sc^{1/3}$$

where the factor of 1/3 will also be seen explained later in the course.
This expression is a useful generic formula for the convective mass transfer coefficient that can be used when no better correlation is available (provided you have a decent correlation for f). One further aid to correlations was devised by Chilton and Colburn, where a "j-factor" has been defined as:

$$j_D = \frac{Sh}{Re\,Sc^{1/3}}$$

so that a direct relation to the friction factor is given as:

$$j_D = \frac{f}{2}$$

NOTE:

Using the above analysis, one can use correlations for Sh directly, j-factor correlation directly, or film theory along with correlations for f to yield k_c values!

HIST NOTE:

The precusor of the Chilton-Colburn analogy, the Reynolds analogy, assumed that the two films where the same size, and thus works for Sc=1

OUTCOME:

Use film theory and other correlations to obtain k_c

We have already shown how two heat flows in parallel can be combined using a resistance analogy. Here, we will examine mass transfer across a fluid-fluid boundary using the same logic.
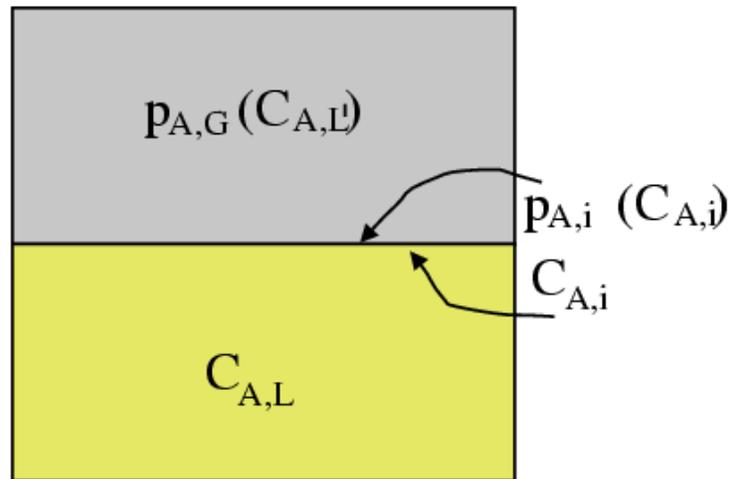
Here we have a convective mass transfer in the liquid phase (from the bulk to the "surface" or interface) given by:

$$N_{A,L} = k_L(C_{A,L} - C_{A,i})$$

Similarly we have convection in the gas phase (or the second liquid phase) which is given by:

$$N_{A,G} = k_G(p_{A,i} - p_{A,G})$$

At steady state, these two fluxes need to be equal (*why?!*(so that we can write the ratio of mass transfer coefficients as:

$$\frac{k_L}{k_G} = \frac{(p_{A,i} - p_{A,G})}{(C_{A,L} - C_{A,i})}$$

Clearly if the transfer in one phase is considerably faster than in the other phase, the driving force in the "fast" phase goes to zero; however, in general, the convection coefficents might be of similar magnitude so that both phases must be considered.

In contrast to the case of combining radiation and convection (or any modes of heat transport, as we will see), combining these two mass transfers using resistances is not as simple (unless it is two liquids, how do we handle that case?). The main difficulty arising from problems combining the driving forces (concentrations versus pressures).

In order to handle this, we define two new variables: p_A^* as the pressure of A in equilibrium with the bulk concentration $C_{A,L}$; and C_A^* as the concentration of A in equilibrium with the gas pressure $p_{A,G}$.

NOTE:

While we know that, at the interphase, an equilibrium expression of the type $p_{A,i} = mC_{A,i}$ can be written (Henry's Law), the "equilibrium" concentrations defined here are fictitious because we are using bulk concentrations!

Using these definitions, we can then write the mass flux across the interface as:

$$N_A = K_G(p_A^* - p_{A,G}) = K_L(C_{A,L} - C_A^*)$$

where K_G and K_L are overall transfer coefficients that combine both phase convection constants, k_G and k_L.

The origin of the relationship between "big" and "little" k's can be shown by rearranging the flux relation:

$$\frac{1}{K_G} = \frac{(p_A^* - p_{A,G})}{N_A} = \frac{(p_A^* - p_{A,i}) + (p_{A,i} - p_{A,G})}{N_A} =$$

$$\frac{m(C_{A,L} - C_{A,i}) + (p_{A,i} - p_{A,G})}{N_A} = \frac{m}{k_L} + \frac{1}{k_G}$$

OUTCOME:

Use the two-resistence model to perform fluid-fluid mass transfer calculations