

Chapter #2 Problems

1. A fluid has the following velocity profile in three dimensions:

$$\begin{aligned} v_r &= v_o \left(r^2 \theta + \theta^2 z - r^2 z \right) & v_\theta &= v_o \left(\theta^2 z - \theta^2 r + \theta^3 \right) \\ v_z &= v_o \left(zr^2 - z^2 \theta \right) \end{aligned}$$

- What are the 9 stresses for this fluid?
- Is the fluid incompressible?

It is easiest to answer part (b) first. We need to calculate the divergence of \mathbf{v} ,

$$(\nabla \cdot \mathbf{v}) = \frac{1}{r} \frac{\partial}{\partial r} (r v_r) + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z}.$$

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r) = v_o \left(3r\theta + \frac{\theta^2 z}{r} - 3rz \right)$$

$$\frac{1}{r} \frac{\partial v_\theta}{\partial \theta} = \frac{v_o}{r} (2\theta z - 2r\theta + 3\theta^2)$$

$$\frac{\partial v_z}{\partial z} = v_o (r^2 - 2\theta z)$$

$$(\nabla \cdot \mathbf{v}) = \frac{v_o}{r} (3r^2(\theta - z) + \theta^2(z + 3) - 2r\theta + r^3 + 2\theta z - 2r\theta z)$$

Since $(\nabla \cdot \mathbf{v}) \neq 0$ the fluid is compressible. This is so even though there may be some values of r, θ, z for which $\nabla \cdot \mathbf{v} = 0$. To be incompressible, the divergence must be zero everywhere.

The 9 stresses can be calculated by referring to Table 2.4. Dealing with the shear stresses first:

$$\tau_{r\theta} = \tau_{\theta r} = -\mu \left(r \frac{\partial}{\partial \theta} \left(\frac{v_\theta}{r} \right) + \frac{1}{r} \frac{\partial v_r}{\partial \theta} \right)$$

$$= -\mu v_o \left(2\theta z - 2r\theta + 3\theta^2 + r + \frac{2\theta z}{r} \right)$$

$$\tau_{z\theta} = \tau_{\theta z} = -\mu \left(\frac{\partial v_\theta}{\partial z} + \frac{1}{r} \frac{\partial v_z}{\partial \theta} \right) = -\mu v_o \left(\theta^2 + \frac{z^2}{r} \right)$$

$$\tau_{rz} = \tau_{zr} = -\mu \left(\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right) = -\mu v_o (\theta^2 - r^2 + 2zr)$$

The normal stresses are:

$$\begin{aligned} \tau_{rr} &= - \left(2\mu \frac{\partial v_r}{\partial r} - \left(\frac{2}{3}\mu - \kappa \right) (\nabla \bullet \mathbf{v}) \right) \\ &= -4\mu v_o r (\theta - z) - \left(\frac{2}{3}\mu - \kappa \right) v_o \left(\frac{\theta^2 z}{r} + 3\theta^2 + r\theta + r - 3rz \right) \end{aligned}$$

$$\begin{aligned} \tau_{\theta\theta} &= - \left(2\mu \left(\frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right) - \left(\frac{2}{3}\mu - \kappa \right) (\nabla \bullet \mathbf{v}) \right) \\ &= -2\mu v_o \left(\frac{2\theta z}{r} - 2\theta + \frac{3\theta^2}{r} + r\theta + \frac{\theta^2 z}{r} - rz \right) \\ &\quad - \left(\frac{2}{3}\mu - \kappa \right) v_o \left(\frac{\theta^2 z}{r} + 3\theta^2 + r\theta + r - 3rz \right) \end{aligned}$$

$$\begin{aligned} \tau_{zz} &= - \left(2\mu \frac{\partial v_z}{\partial z} - \left(\frac{2}{3}\mu - \kappa \right) (\nabla \bullet \mathbf{v}) \right) \\ &= -2\mu v_o (2zr - 2\theta z) - \left(\frac{2}{3}\mu - \kappa \right) v_o \left(\frac{\theta^2 z}{r} + 3\theta^2 + r\theta + r^2 - 3rz \right) \end{aligned}$$

2. In 1856 H. Darcy published a paper where he described experiments showing that the flow of fluid through a porous medium was linearly related to the pressure drop across the medium.

$$\vec{v} = -\frac{k}{\mu} \vec{\nabla} P \quad \text{Darcy's Law}$$

where k is the permeability of the porous medium. In three dimensions Darcy's Law can be written as:

$$v_x = -\frac{k}{\mu} \left(\frac{\partial P}{\partial x} \right) \quad v_y = -\frac{k}{\mu} \left(\frac{\partial P}{\partial y} \right) \quad v_z = -\frac{k}{\mu} \left(\frac{\partial P}{\partial z} \right)$$

Show, that if the fluid is incompressible, the pressure must obey Laplace's Equation ($\nabla^2 P = 0$).

If the fluid is incompressible then $\nabla \cdot \vec{v} = 0$. If we plug in for \vec{v} using Darcy's Law we have:

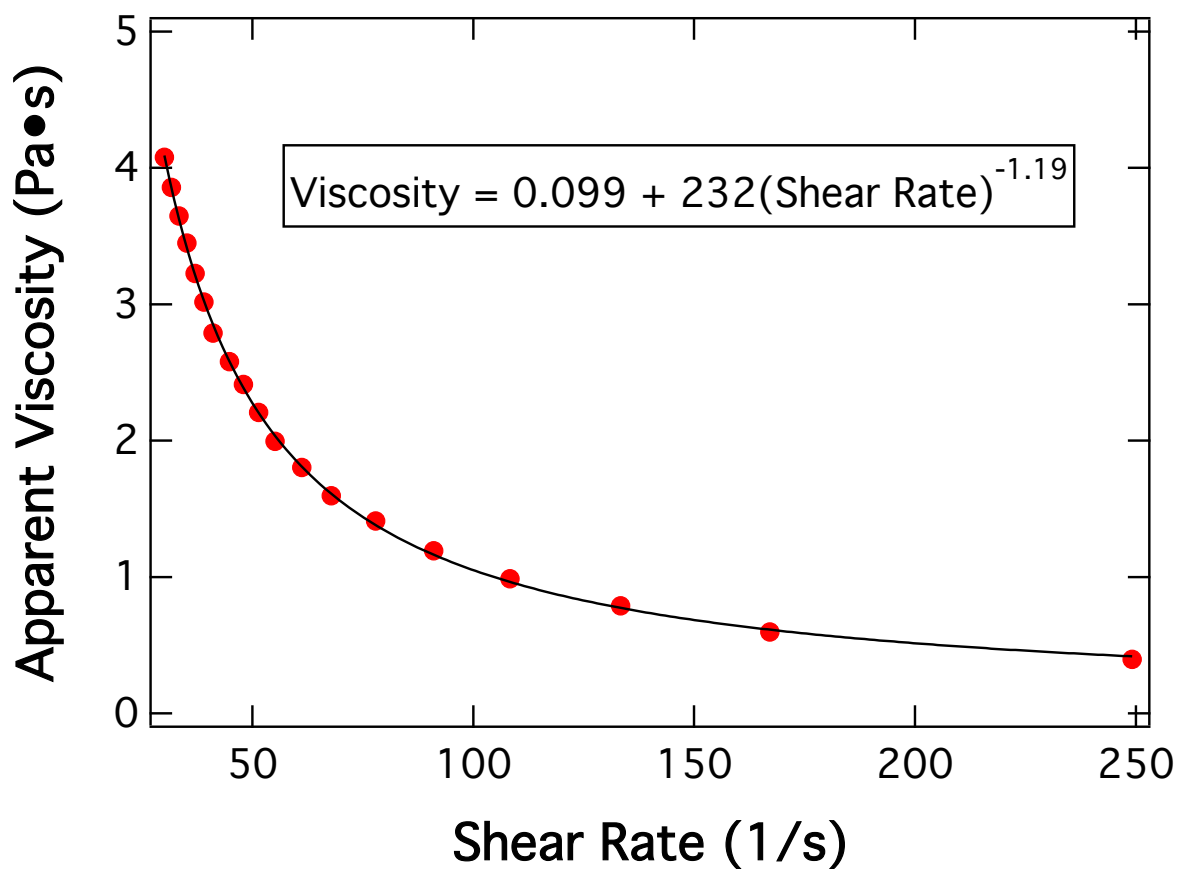
$$-\frac{k}{\mu} \vec{\nabla} \cdot \vec{\nabla} P = 0 = -\frac{k}{\mu} \nabla^2 P$$

and Laplace's equation is satisfied. Of course you can do it brute force by expanding the gradient operator, taking the dot product with the velocity, and then plugging in for the pressure components but that is a lot of work. It is easier to just look up the vector identity.

3. Many fluids are non-Newtonian. A classic non-Newtonian material is low-fat Mayonnaise. The reason behind this is the modified starches and xanthan gum used to stabilize the water and oil emulsion. The following data set is representative of one brand of mayonnaise.
- Plot the data and discuss whether mayonnaise is a shear-thinning or shear-thickening fluid?
 - If you fit the data to a power law expression, what is the exponent you determine?

Apparent Viscosity (Pa•s)	Shear Rate (1/s)	Apparent Viscosity (Pa•s)	Shear Rate (1/s)
0.396	249.096	2.207	51.413
0.598	167.090	2.413	47.971
0.790	133.307	2.580	44.767
0.988	108.264	2.790	41.064
1.194	91.034	3.017	38.983
1.412	77.892	3.227	37.010
1.596	67.828	3.450	35.138
1.805	61.132	3.649	33.363
1.996	55.107	3.859	31.678
2.207	51.413	4.080	30.078

Data: Donatella Peressini, Alessandro Sensidoni, Bruno de Cindio, Journal of Food Engineering 35, 409–417, (1998).

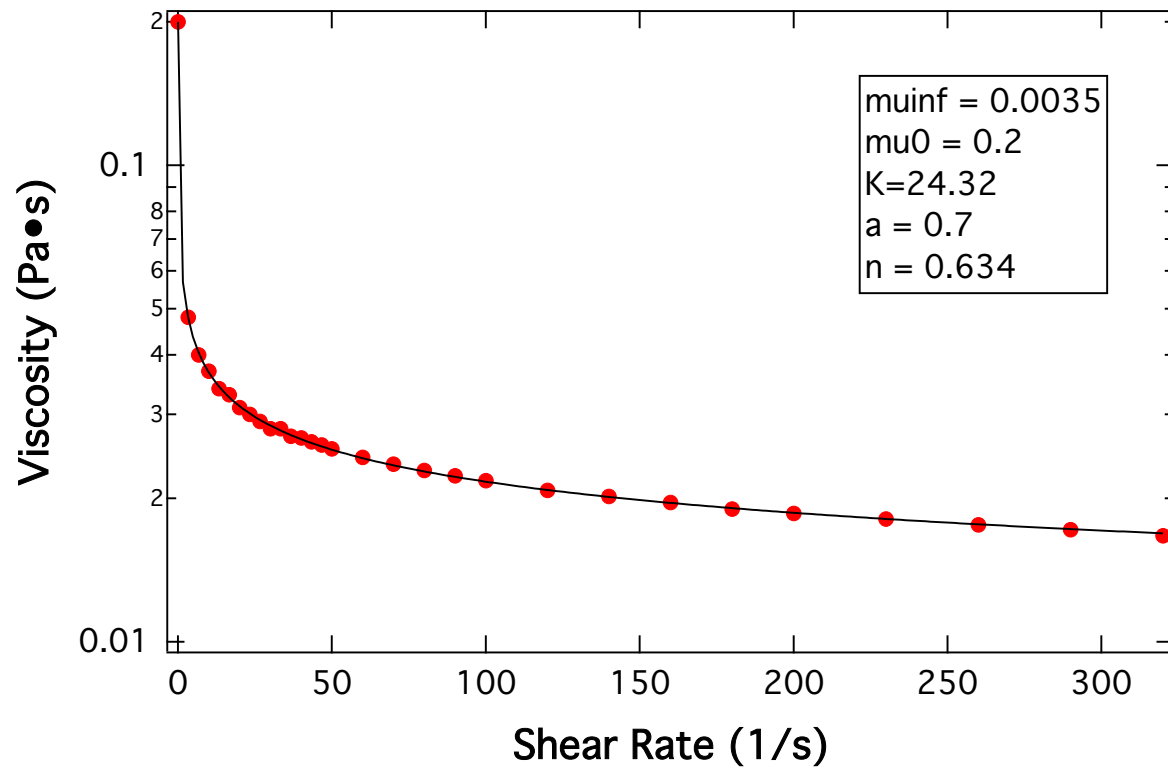


4. The Carreau-Yasuda model is a popular formulation for representing non-Newtonian fluid behavior. The model is:

$$\mu = \left[\mu_{\infty} + (\mu_0 - \mu_{\infty}) \left(1 + (K|\dot{\gamma}|)^a \right)^{\frac{n-1}{a}} \right]$$

where $\dot{\gamma}$ is the shear rate, μ_0 is the viscosity at zero shear rate and μ_{∞} is the viscosity at infinite shear rate. One of the composite materials that the Carreau-Yasuda model has been used for is to determine the rheology of blood. Given the data below, fit the Carreau-Yasuda model and determine the values of the parameters.

Viscosity (Ns/m ²)	Shear Rate (1/s)	Viscosity (Ns/m ²)	Shear Rate (1/s)
0.2	0	0.0254	50
0.048	3.33333	0.0244	60
0.04	6.66667	0.0236	70
0.037	10	0.0229	80
0.034	13.3333	0.0223	90
0.033	16.6667	0.0218	100
0.031	20	0.0208	120
0.030	23.3333	0.0202	140
0.029	26.6667	0.0196	160
0.028	30	0.0190	180
0.028	33.3333	0.0186	200
0.027	36.6667	0.0181	230
0.0268	40	0.0176	260
0.0263	43.3333	0.0172	290
0.0259	46.6667	0.0167	320



5. Prove that all forms of Fick's Law agree with thermodynamics; that is 'At equilibrium, the concentration of all species throughout the system should be uniform.

Lets look at Fick's Law written in terms of the molar flux relative to stationary coordinates and Fick's Law written in terms of the molar flux relative to a molar average velocity.

$$J_a = -D_{ab} \frac{dc_a}{dy}$$

$$N_a = -D_{ab} \frac{dc_a}{dy} + x_a (N_a + N_b)$$

At equilibrium, the flux must be zero. We cannot see any macroscopic change. Thus J_a , N_a , and N_b are all zero. Fick's Laws reduce to:

$$D_{ab} \frac{dc_a}{dy} = 0$$

for both cases. The only way the derivative of concentration can be zero is if it is equal to a constant. We can extend this in three directions quite easily. In that case we end up with

$$D_{ab} \vec{\nabla} \cdot c_a = 0.$$

which just means that the concentration must be uniform in all directions.

6. Prove that in a binary mixture whose total concentration of species, c_t , remains constant, there is only one diffusion coefficient; $D_{ab} = D_{ba}$.
-

In a binary mixture we have

$$\vec{N}_a = -D_{ab} \vec{\nabla} c_a + x_a (\vec{N}_a + \vec{N}_b)$$

$$\vec{N}_b = -D_{ba} \vec{\nabla} c_b + x_b (\vec{N}_a + \vec{N}_b)$$

Adding the two equations we have:

$$-D_{ab} \vec{\nabla} c_a - D_{ba} \vec{\nabla} c_b = 0$$

since $x_a + x_b = 1$. Now if we have no chemical reaction and no great change in volume, i.e. no partial molar volume effects, $c_a + c_b = c_t$. We can substitute for c_a or c_b and obtain an equation of the form:

$$D_{ab} \vec{\nabla} c_b - D_{ba} \vec{\nabla} c_b = 0$$

which shows that $D_{ab} = D_{ba}$. Notice that if we have a chemical reaction or we have large volume changes on mixing, then we have additional effects (i.e. additional components to the flux) we must account for. This gives rise to a change in the diffusion coefficients for the individual species.

7. A solid containing species "a" has been analyzed and the mole fraction profile has been found to obey the following function of y alone:

$$x_a = a_o \sqrt[3]{y - Ky_o} \quad a_o, y_o, K - \text{constants.}$$

- a) Assuming a constant value for the diffusivity, $D_{ab} = D_{abo}$, and a dilute solution of "a" in "b", has the system reached a steady state, i.e. does it obey the continuity equation in one dimension?
- b) Assuming "a" diffused through stagnant "b" ($N_b \approx 0$) and has reached steady-state, what can you say about how the diffusivity varies as a function of composition?

At steady state and dilute solutions, $N_a = \text{constant} = -c_t D_{ab} \frac{dx_a}{dy}$.

Taking the derivative of the mole fraction profile, we see that

$$N_a = -c_t D_{ab} \left[\frac{1}{3} a_o \left(\frac{1}{y - Ky_o} \right)^{2/3} \right]$$

and so the system is not at steady state.

At steady state and $N_b = 0$, we have for Fick's Law:

$$N_a = -\frac{c_t D_{ab}}{1 - x_a} \frac{dx_a}{dy}$$

Since N_a is a constant, we can plug in for x_a and its derivative to obtain an expression for how the diffusivity varies with mole fraction.

$$D_{ab} = -\frac{1 - x_a}{c_t \frac{dx_a}{dy}} = \frac{1 - x_a}{\frac{c_t a_o^3}{3x_a^2}}$$

8. A new lithium sulfate (Li_2SO_4) electrolyte has been developed for battery applications. Assuming ideal solutions and a stationary coordinate system, what does Fick's Law for the flux (N_{Li} , N_{SO_4}) for both lithium and sulfate species look like?

The fluxes for the ions must obey two masters, Fick's law and local electroneutrality. Thus for every sulfate ion that moves, two lithium ions must also move in the opposite direction. Thus we have:

$$\vec{N}_{\text{Li}} = -c_t D_{\text{Li}} \vec{\nabla} x_{\text{Li}} + x_{\text{Li}} (\vec{N}_{\text{Li}} + \vec{N}_{\text{SO}_4})$$

$$\vec{N}_{\text{SO}_4} = -c_t D_{\text{SO}_4} \vec{\nabla} x_{\text{SO}_4} + x_{\text{SO}_4} (\vec{N}_{\text{Li}} + \vec{N}_{\text{SO}_4})$$

Since $N_{\text{Li}} = -2N_{\text{SO}_4}$:

$$\vec{N}_{\text{Li}} = -\frac{c_t D_{\text{Li}} \vec{\nabla} x_{\text{Li}}}{1 - \frac{1}{2} x_{\text{Li}}}$$

$$\vec{N}_{\text{SO}_4} = -\frac{c_t D_{\text{SO}_4} \vec{\nabla} x_{\text{SO}_4}}{1 + x_{\text{SO}_4}}$$

9. We defined a molar flux relative to the molar average velocity as:

$$\vec{J}_i = -c_t D_{ij} \vec{\nabla} x_i$$

We could just as easily have defined the flux relative to the volume average velocity, v^v .

$$\vec{J}_i^v = c_i (v_i - v^v) = -D_{ij}^v \vec{\nabla} c_i$$

Show that the two diffusivities are equal even if the molar concentration, c_t , is not constant.

The easiest way to show this is to operate on the definitions of average velocity.

$$\vec{J}_i^v = c_i \vec{v}_i + c_i \left[\frac{\vec{v}_i V_i + \vec{v}_j V_j}{V_i + V_j} \right]$$

$$\vec{J}_i = c_i \vec{v}_i + c_i \left[\frac{\vec{v}_i c_i + \vec{v}_j c_j}{c_i + c_j} \right]$$

Operating on \vec{J}_i , we divide the term in brackets by c_t both in the numerator and denominator.

$$\vec{J}_i = c_i \vec{v}_i + c_i \left[\frac{\frac{\vec{v}_i c_i}{c_t} + \frac{\vec{v}_j c_j}{c_t}}{\frac{c_i + c_j}{c_t}} \right] = c_i \vec{v}_i + c_i \left[\frac{\vec{v}_i x_i + \vec{v}_j x_j}{1} \right]$$

Now multiplying by V_t in the same way we have:

$$\vec{J}_i = c_i \vec{v}_i + c_i \left[\frac{\vec{v}_i x_i V_t + \vec{v}_j x_j V_t}{V_t} \right] = c_i \vec{v}_i + c_i \left[\frac{\vec{v}_i V_i + \vec{v}_j V_j}{V_t} \right] = \vec{J}_i^v$$

and have proved the premise where $V_i + V_j = V_t$.

10. The mass flux of a species can be written using the chemical potential as a driving force. Consider the case of simple binary diffusion in an ideal mixture of liquids. If the chemical potential is given by:

$$\mu_i^c = \mu_{io}^c + RT \ln x_i$$

prove the total flux $\mathbf{j}_a + \mathbf{j}_b = 0$. What must hold true if the chemical potentials are given by the equation below and the sum of the fluxes is to be zero?

$$\mu_i^c = \mu_{io}^c + RT \ln(\gamma_i x_i)$$

We'll handle the first part, first. We can write the fluxes as:

$$\vec{\mathbf{j}}_a = D_{ab} x_a \vec{\nabla} \mu_a^c \qquad \vec{\mathbf{j}}_b = D_{ba} x_b \vec{\nabla} \mu_b^c$$

Since $D_{ab} = D_{ba}$ we can substitute in for the chemical potentials to give:

$$\vec{\mathbf{j}}_a = D_{ab} x_a \vec{\nabla} [\mu_{ao}^c + RT \ln x_a] \qquad \vec{\mathbf{j}}_b = D_{ab} x_b \vec{\nabla} [\mu_{bo}^c + RT \ln x_b]$$

$$\vec{\mathbf{j}}_a = D_{ab} x_a \frac{RT}{x_a} \vec{\nabla} x_a = D_{ab} RT \vec{\nabla} x_a \qquad \vec{\mathbf{j}}_b = D_{ab} x_b \frac{RT}{x_b} \vec{\nabla} x_b = D_{ab} RT \vec{\nabla} x_b$$

Since $x_a + x_b = 1$

$$\vec{\mathbf{j}}_a + \vec{\mathbf{j}}_b = D_{ab} RT (\vec{\nabla} x_a + \vec{\nabla} x_b) = D_{ab} RT (\vec{\nabla} x_a + \vec{\nabla} (1 - x_a)) = 0$$

If we repeat the process with the activity coefficients, we have:

$$\vec{\mathbf{j}}_a = D_{ab} x_a \vec{\nabla} [\mu_{ao}^c + RT \ln(\gamma_a x_a)] \qquad \vec{\mathbf{j}}_b = D_{ab} x_b \vec{\nabla} [\mu_{bo}^c + RT \ln(\gamma_b x_b)]$$

$$\vec{\mathbf{j}}_a = D_{ab} x_a \frac{RT}{\gamma_a x_a} \vec{\nabla} (\gamma_a x_a) = D_{ab} \frac{RT}{\gamma_a} \vec{\nabla} (\gamma_a x_a) \qquad \vec{\mathbf{j}}_b = D_{ab} x_b \frac{RT}{\gamma_b x_b} \vec{\nabla} (\gamma_b x_b) = D_{ab} \frac{RT}{\gamma_b} \vec{\nabla} (\gamma_b x_b)$$

$$\vec{\mathbf{j}}_a + \vec{\mathbf{j}}_b = D_{ab} RT \left(\frac{\vec{\nabla} (\gamma_a x_a)}{\gamma_a} + \frac{\vec{\nabla} (\gamma_b x_b)}{\gamma_b} \right) = D_{ab} RT \left(\frac{\vec{\nabla} (\gamma_a x_a)}{\gamma_a} + \frac{\vec{\nabla} [\gamma_b (1 - x_a)]}{\gamma_b} \right)$$

Combining all the terms we find:

$$\vec{\mathbf{j}}_a + \vec{\mathbf{j}}_b = D_{ab}RT \left(\frac{x_a \gamma_b \vec{\nabla} \gamma_a + \gamma_a \vec{\nabla} \gamma_b - x_a \gamma_a \vec{\nabla} \gamma_b}{\gamma_a \gamma_b} \right)$$

$$\vec{\mathbf{j}}_a + \vec{\mathbf{j}}_b = 0 \quad \rightarrow \quad x_a \gamma_b \vec{\nabla} \gamma_a + \gamma_a \vec{\nabla} \gamma_b - x_a \gamma_a \vec{\nabla} \gamma_b = 0$$

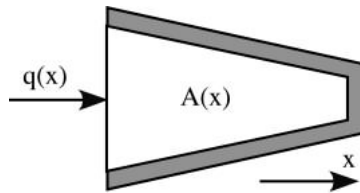
If the activity coefficients are constant the equation is automatically satisfied. If they are a function of \mathbf{x}_a , then we must satisfy the relationship above.

11. Thermocouples attached to a truncated, conical roller bearing show that the temperature profile and heat flow rate are:

$$T(x) = 450(2 - 3x + x^2 - x^3) \quad q = 7500 \text{ W}$$

If the cross sectional area of the bearing is: $A(x) = 0.04\pi(1 - x) \text{ m}^2$

- What is the thermal conductivity as a function of x ?
- What is the heat flux at $x = 0$? $x = 0.2$?
- Where is the heat flux, highest ($0 < x < 0.2$)?



The thermal conductivity is found using Fourier's Law.

$$q = -kA \frac{dT}{dx} \quad k = -\frac{q}{A \frac{dT}{dx}} = -\frac{7500}{0.04\pi(1-x)^2 450(-3+2x-3x^2)}$$

$$k = \frac{132.63}{(1-x)^2(3-2x+3x^2)}$$

The heat flux is also obtained from Fourier's law.

$$q'' = -k \frac{dT}{dx} = -\frac{132.63}{(1-x)^2(3-2x+3x^2)} \{450(-3+2x-3x^2)\} = \frac{59683.5}{(1-x)^2}$$

$$q''(0) = 59683.5 \quad q''(0.2) = 93255.5$$

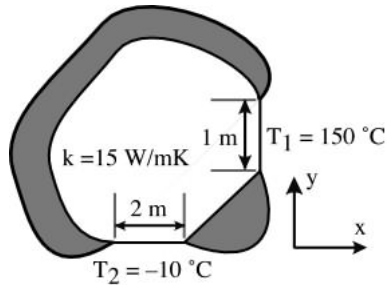
The highest heat flux is at $x = 0.2$ where the area is the smallest.

$$q'' = -k \frac{dT}{dx} = -\frac{132.63}{(1-x)^2(3-2x+3x^2)} \{450(-3+2x-3x^2)\}$$

$$q''(0) = -59,683.5 \frac{\text{W}}{\text{m}^2} \quad q''(0.2) = -93,255.5 \frac{\text{W}}{\text{m}^2}$$

The heat flux is highest at the point where the area is smallest, i.e. at 0.2.

12. The two-dimensional object shown in the figure below is insulated with the exception of two flat portions that are exposed to two different temperatures. The temperature gradient at surface 1 is measured and found to be $\partial T/\partial x = 45 \text{ K/m}$. What are $\partial T/\partial x$ and $\partial T/\partial y$ at surface 2?



At surface II, since the surface is a plate at a constant temperature, $\partial T/\partial x = 0$ there. $\partial T/\partial y$ is found using an energy balance that states whatever heat flows into surface I must flow out of surface II. Using Fourier's law at both surfaces gives:

$$-kA_1 \left. \frac{\partial T}{\partial x} \right|_1 = -kA_2 \left. \frac{\partial T}{\partial y} \right|_2$$

$$\left. \frac{\partial T}{\partial y} \right|_2 = \frac{A_1}{A_2} \left. \frac{\partial T}{\partial x} \right|_1 = 22.5 \text{ K/m}$$

13. A spherical shell of inner radius r_i , outer radius, r_o , and thermal conductivity, k , is being used to dissipate heat. At a particular time, the temperature profile within the shell is measured and found to be:

$$T(r) = \frac{C_1}{r} + C_2$$

- Is the heat transfer at steady-state, i.e. is the rate constant?
- How does the heat flux vary with position?

The heat transfer is at steady-state if the heat flow rate is a constant throughout the device. We can determine this using Fourier's law.

$$q = -kA \frac{dT}{dr} = -k(4\pi r^2) \frac{d}{dr} \left(\frac{C_1}{r} + C_2 \right) = 4\pi k C_1$$

Since the heat flow rate is constant, the system is at steady-state.

The heat flux is again given by Fourier's law.

$$q'' = -k \frac{dT}{dr} = -k \frac{d}{dr} \left(\frac{C_1}{r} + C_2 \right) = \frac{kC_1}{r^2}$$

14. The heat flux, \vec{q}'' , due to a volume source distribution (expressed in spherical coordinates) is given by:

$$D_e = C r^2 \sin(\alpha r) \mathbf{e}_r \quad 0 < r < r_o$$

- What is the temperature gradient for this system?
- If the temperature at $r = 0$ is $T = T_o$, what is the temperature profile?
- At what value of r does the solution become aphysical?

Here, we need to apply the definition for the flux using Fourier's law.

$$q'' = -k \frac{dT}{dr} = Cr^2 \sin(\alpha r)$$

$$\frac{dT}{dr} = -\frac{Cr^2 \sin(\alpha r)}{k}$$

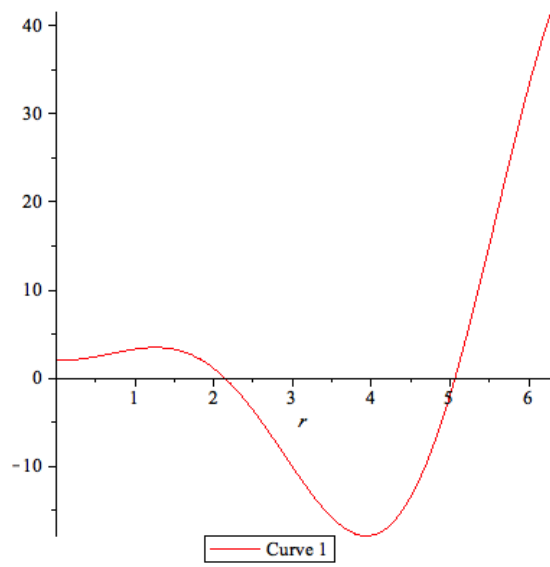
We integrate to get the temperature profile.

$$T = -\frac{C}{\alpha^3 k} \left[2 \cos(\alpha r) + 2\alpha r \sin(\alpha r) - \alpha^2 r^2 \cos(\alpha r) \right] + K$$

$$K = T_o + \frac{2C}{\alpha^3 k}$$

$$T - T_o = \frac{C}{\alpha^3 k} \left[2 - 2 \cos(\alpha r) - 2\alpha r \sin(\alpha r) + \alpha^2 r^2 \cos(\alpha r) \right]$$

The solution becomes aphysical when $T - T_o < 0$. If we assume $\alpha = 1$ for example, we can plot the quantity in brackets as a function of r to get the zeros. The graph is shown below.

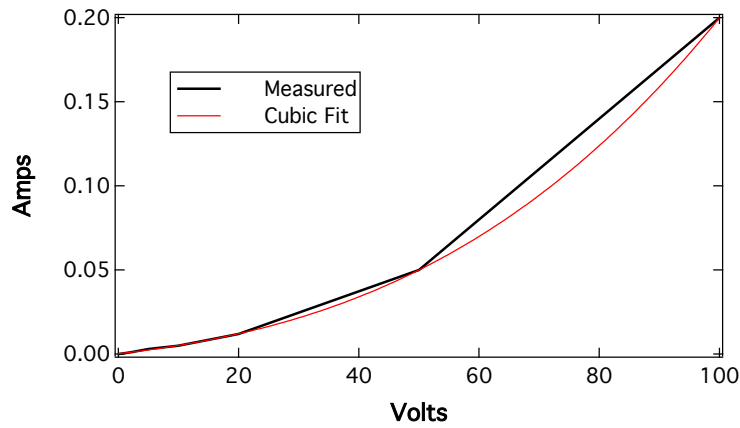


15. The voltage(V) – current(I) behavior for a new material was measured and found to be:

I (amps)	V (volts)
0	0
0.001	2
0.003	5
0.005	10
0.012	20
0.050	50
0.200	100

The material was fashioned into a wire, 1 mm in diameter and 1 m long.

- What is the conductivity of the material?
- What is the conductivity of the material at V = 10 volts?
- What is the diffusivity of the charge carriers at V = 10 volts and T = 298K?
- If the valence of the charge carriers is 1, what is their mobility?



The resistance of a material is related to its resistivity and conductivity by:

$$\mathcal{R}_e = \rho_r \frac{L}{A_c} = \frac{1}{\sigma} \frac{L}{A_c}$$

The conductivity of the material can be determined by:

$$\sigma = \frac{L}{\mathcal{R}_e A_c} = \frac{L}{A_c} \frac{I}{V} = 1.27 \times 10^6 \left(\frac{I}{V} \right)$$

where we have used Ohm's Law to relate the resistance to the voltage and current assuming that it would be valid at every point. The resistance then changes as a function of voltage.

At 10 volts, we find:

$$\sigma = 1.27 \times 10^6 \frac{0.005}{10} = 635 \text{ Siemens/m}$$

The diffusivity of the charge carriers is:

$$D_{\pm} = \left(\frac{RT}{(\mathcal{F}az_e)^2} \right) \sigma = \left(\frac{8.314(298)}{(96500)^2} \right) 636 = 0.169 \times 10^{-3} \text{ m}^2/\text{s}$$

The mobility of the charge carriers is determined using the Einstein relation:

$$\mu_e = \frac{D_{\pm} e z_e}{k_b T} = 6.58 \times 10^{-3} \text{ m}^2/\text{sV}$$

16. We showed that one of the most often used form of Fick's Law for multi-component systems could be written as:

$$\vec{J}_i = - \underbrace{D_{ij}}_{D_{ij}} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln x_i} \right) \vec{\nabla} c_i = c_i (\vec{v}_i - \vec{v}^c)$$

Kinetic theory derivations of the flux equation lead to an expression for the gradient in chemical potential, $\vec{\nabla} \mu_i$, of the form:

$$\vec{\nabla} \mu_i = \frac{RTx_j}{D_{ij}} (\vec{v}_j - \vec{v}_i)$$

Show that these two forms are equivalent representations for the binary case with species "i" and "j". Remember that the chemical potential for species, "i", is given by:

$$\mu_i = \mu_i^o + RT \ln(\gamma_i x_i) \text{ Hint: Use expressions for } J_i \text{ to solve for } v_i \text{ and } v_j.$$

First we divide Fick's laws through by the concentrations

$$\frac{\vec{J}_1}{c_1} = - \frac{D_{12}}{c_1} \vec{\nabla} c_1 = - \frac{D_{12}}{x_1} \vec{\nabla} x_1 = - D_{12} \vec{\nabla} \ln x_1 = \vec{v}_1 - \vec{v}_M$$

$$\frac{\vec{J}_2}{c_2} = - \frac{D_{12}}{c_2} \vec{\nabla} c_2 = - \frac{D_{12}}{x_2} \vec{\nabla} x_2 = - D_{12} \vec{\nabla} \ln x_2 = \vec{v}_2 - \vec{v}_M$$

Subtract J_2 from J_1 :

$$\frac{\vec{J}_1}{c_1} - \frac{\vec{J}_2}{c_2} = - D_{12} \vec{\nabla} \ln x_1 + D_{12} \vec{\nabla} \ln x_2 = D_{12} \vec{\nabla} \ln \frac{x_2}{x_1} = \vec{v}_1 - \vec{v}_2$$

Use definition of chemical potential to get the gradient.

$$\vec{\nabla} \mu_1 = RT \vec{\nabla} \ln x_1 + RT \vec{\nabla} \ln \gamma_1 = \frac{RTx_2}{D_{12o}} (\vec{v}_2 - \vec{v}_1)$$

We plug in for $v_2 - v_1$ from above and use the fact that $x_1 + x_2 = 1$ to show that:

$$\begin{aligned}
\bar{\nabla} \mu_1 &= -\frac{RTx_2}{D_{12o}} D_{12} \bar{\nabla} \ln \frac{x_2}{x_1} = -RTx_2 \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1} \right) \frac{x_1}{x_2} \bar{\nabla} \left(\frac{x_2}{x_1} \right) \\
&= RT \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1} \right) \bar{\nabla} \ln x_1
\end{aligned}$$

17. Activities in solution can often be correlated by the Margules equations.

$$\ln \gamma_1 = x_2^2 \left[A_{12} + 2(A_{21} - A_{12})x_1 \right] \quad \ln \gamma_2 = x_1^2 \left[A_{21} + 2(A_{12} - A_{21})x_2 \right]$$

For 2,4-dimethylpentane (1) and benzene (2), the coefficients A_{12} and A_{21} are 1.96 and 1.48 respectively. Using the relations developed from problem 2.11, plot how D_{ij} will depend upon composition for this binary system.

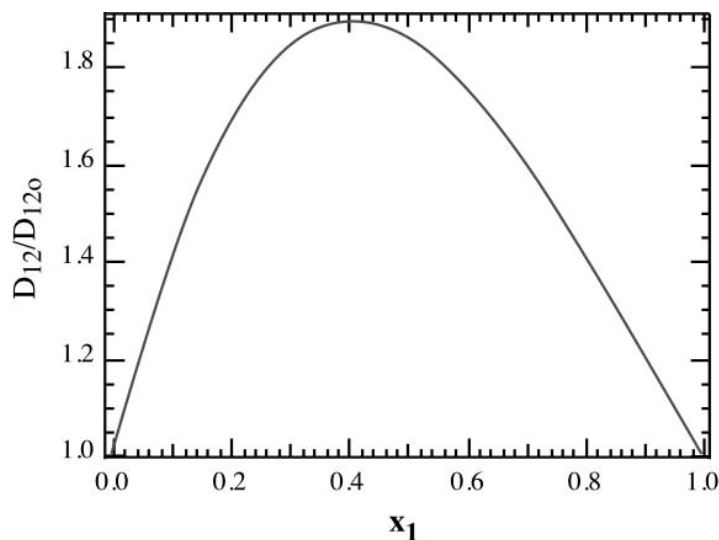
For the binary system, $D_{12} = D_{21}$ so we only need consider one of the terms. Thus:

$$D_{12} = D_{12o} \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1} \right)$$

Now:

$$\begin{aligned} \frac{\partial \ln \gamma_1}{\partial \ln x_1} &= x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_1 (1-x_1)^2 [2(A_{21} - A_{12})] \\ &\quad - 2x_1(1-x_1) [A_{12} + 2(A_{21} - A_{12})x_1] \end{aligned}$$

Now we can plot D_{12}/D_{12o} as a function of x_1 .



18. A student tries to dissolve a congealed mass of NaOH by adding water to the beaker. The concentration profile of NaOH in the water above it was measured and found to be:

$$1 - x_a = (1.143)^{z/L-1}$$

The initial and reference temperature of the water is 0 °C. $c_t = 63055 \text{ mol/m}^3$; $D_{ab} = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$; $L = 5 \text{ cm}$. Assume the water properties are constant at the reference temperature values. Data on the partial molar enthalpies of solution as a function of temperature and hence the partial molar heat capacities can be obtained crudely from the enthalpy concentration diagram (W.L. McCabe, Trans. AIChE 31, 129 (1935)). If the thermal conductivity is taken as that of water, what is the temperature profile?

To solve this problem we need to go back to the example in section 2.10. For a concentration profile like that listed above, the flux of hydroxide and temperature profile are:

$$N_{az} = \frac{c_t D_{ab}}{L} \ln(1.143)$$

$$\frac{\theta}{\theta_o} = \exp\left(\frac{N_{az} \bar{C}_{pa}}{k} z\right)$$

Here we need to assume a temperature between the reference temperature and the highest temperature we would have. Thus this is a trial and error approach. For the concentration range listed, we can consult the enthalpy-concentration diagram and get an estimate of the heat capacity.

$$N_{az} = \frac{c}{L} \frac{D}{ab} \ln(1.143) = \frac{(63055 \text{ mol/m}^3)(1 \times 10^{-9} \text{ m}^2/\text{s})}{0.05 \text{ m}} \ln(1.143)$$

$$= 1.69 \times 10^{-4} \text{ mol} / \text{m}^2 \text{s}$$

$$\bar{C}_{pa} = 2470 \text{ J} / \text{kgK}$$

$$\frac{\theta}{\theta_o} = \exp\left(\frac{N_{az} \bar{C}_{pa}}{k} z\right)$$

$$= \exp\left(\frac{(1.69 \times 10^{-4} \text{ mol} / \text{m}^2 \text{s})(2470 \text{ J} / \text{kgK})(0.04 \text{ kg} / \text{mol})}{0.6 \text{ W} / \text{mK}} z\right)$$

$$= \exp(0.03z)$$

19. A young engineer has the bright idea of trying to separate methanol and water by centrifugation. The target system is an antifreeze consisting of 30 mol % methanol. The partial molar volumes and pure component molar volumes at 25 °C are:

$$\begin{aligned}\bar{V}_m &= 38.632 \text{ cm}^3/\text{mol} & \bar{V}_w &= 17.765 \text{ cm}^3/\text{mol} \\ V_m &= 40.727 \text{ cm}^3/\text{mol} & V_w &= 18.068 \text{ cm}^3/\text{mol}\end{aligned}$$

Assuming a centrifuge like that in Figure P2.19 operates at 20,000 rpm and a temperature of 25 °C, what would be the concentration of m at $r = 0.2$ m? What is the maximum separation ratio there; x_{mL}/x_{wL} ? Assume the pressure gradient, $\partial P/\partial r = 4\pi^2\omega^2\rho r$, where ω is the revolution frequency and ρ is the fluid density.

The pressure gradient in the system is only in the radial direction and is defined by:

$$\frac{\partial P}{\partial r} = 4\pi^2\omega^2\rho r$$

The fluxes for "a" and "b" are as follows:

$$j_m = 0 = -\left(\frac{c_m^2}{\rho}\right) M_{wm} M_{ww} D_{mw} \left[\left(\frac{\partial \ln a_m}{\partial \ln x_m} \right)_{T,P} \bar{\nabla} x_m + \frac{M_{wm} x_m}{RT} \left(\frac{\bar{V}_m}{M_{wm}} - \frac{1}{\rho} \right) \bar{\nabla} P \right]$$

$$j_w = 0 = -\left(\frac{c_w^2}{\rho}\right) M_{wm} M_{ww} D_{mw} \left[\left(\frac{\partial \ln a_w}{\partial \ln x_w} \right)_{T,P} \bar{\nabla} x_w + \frac{M_{ww} x_w}{RT} \left(\frac{\bar{V}_w}{M_{ww}} - \frac{1}{\rho} \right) \bar{\nabla} P \right]$$

Assuming the solution is ($a_m = x_m$) and getting rid of as many constants as possible we find:

$$\frac{dx_m}{dr} + \frac{M_{wm} x_m}{RT} \left(\frac{\bar{V}_m}{M_{wm}} - \frac{1}{\rho} \right) \frac{dP}{dr} = \frac{dx_m}{dr} + \frac{M_{wm} x_m}{RT} \left(\frac{\bar{V}_m}{M_{wm}} - \frac{1}{\rho} \right) 4\pi^2\omega^2\rho r = 0$$

$$\frac{dx_w}{dr} + \frac{M_{ww} x_w}{RT} \left(\frac{\bar{V}_w}{M_{ww}} - \frac{1}{\rho} \right) \frac{dP}{dr} = \frac{dx_w}{dr} + \frac{M_{ww} x_w}{RT} \left(\frac{\bar{V}_w}{M_{ww}} - \frac{1}{\rho} \right) 4\pi^2\omega^2\rho r = 0$$

$$\frac{d \ln x_m}{dr} + \frac{4\pi^2\omega^2}{RT} (\rho \bar{V}_m - M_{wm}) r = 0$$

$$\frac{d \ln x_w}{dr} + \frac{4\pi^2\omega^2}{RT} (\rho \bar{V}_w - M_{ww}) r = 0$$

Now we multiply the equation for species "m" by \bar{V}_w and the equation for species "w" by \bar{V}_m and subtract "m" from "w" to find:

$$\bar{V}_w \frac{dx_m}{x_m} - \bar{V}_m \frac{dx_w}{x_w} = \frac{4\pi^2 \omega^2}{RT} (\bar{V}_w M_{wm} - \bar{V}_m M_{ww}) r dr$$

Assuming the only variables are x_m and x_w we can integrate the equation to give:

$$\left(\frac{x_m}{x_{m0}} \right)^{\bar{V}_w} \left(\frac{x_w}{x_{w0}} \right)^{\bar{V}_m} = \exp \left[\frac{2\pi^2 \omega^2}{RT} (\bar{V}_w M_{wm} - \bar{V}_m M_{ww}) r^2 \right]$$

Here we have used the condition that at $r = 0$ we have $x_m = x_{m0}$ and $x_w = x_{w0}$. Taking the log of both sides and putting in the numbers:

$$\begin{aligned} & 17.765 \left(\frac{cm^3}{mol} \right) \ln \left(\frac{x_m}{0.3} \right) + 38.632 \left(\frac{cm^3}{mol} \right) \ln \left(\frac{0.7}{1 - x_m} \right) \\ &= \left(38.632 \left(\frac{cm^3}{mol} \right) (0.018 kg) - 17.765 \left(\frac{cm^3}{mol} \right) (0.032 kg) \right) \frac{2\pi^2 (20000/60 s^{-1})^2 (0.2m)^2}{\left(8.314 \frac{J}{mol \cdot K} \right) (298K)} \end{aligned}$$

$$x_m = 0.34$$

$$x_{mR}/x_{wR} = 0.52$$

20. Often we have a multi-component mixture of gases and do not want to deal with the diffusion coefficients for every pair of gases. We would like to define a pseudo-binary diffusion coefficient for each species relative to the mixture.

a) Show how using Fick's Law in the form:

$$\vec{N}_i = -c_t \mathcal{D}_{im} \vec{\nabla} x_i + x_i \sum_{j=1}^n \vec{N}_j$$

and the Stefan-Maxwell relations, equation (2.77) we can define such a coefficient based on individual binary diffusion coefficients for each pair of gases. \mathcal{D}_{im} is the pseudo-binary diffusion coefficient.

b) Show in the limit where $x_1 \approx x_2 \approx 0$ that:

$$\mathcal{D}_{3m} = \frac{D_{31}D_{32}}{D_{31} + D_{32}} \quad \mathcal{D}_{2m} = D_{23} \quad \mathcal{D}_{1m} = D_{13}$$

c) Use your result to calculate the pseudo-binary diffusion coefficient for each species in the system H_2O , He , N_2 :

$$\begin{array}{lll} \text{H}_2\text{O} - \text{He} & 0.908 \times 10^{-9} \text{ m}^2/\text{s} & \text{H}_2\text{O} - \text{N}_2 \quad 0.256 \times 10^{-9} \text{ m}^2/\text{s} \\ \text{He} - \text{N}_2 & 0.687 \times 10^{-9} \text{ m}^2/\text{s} & \end{array}$$

d) Can your results be extended to higher order mixtures?

The Stefan-Maxwell relations for the three components are:

$$\vec{\nabla} x_1 = \frac{1}{c_t D_{12}} (x_1 \vec{N}_2 - x_2 \vec{N}_1) + \frac{1}{c_t D_{13}} (x_1 \vec{N}_3 - x_3 \vec{N}_1)$$

$$\vec{\nabla} x_2 = \frac{1}{c_t D_{21}} (x_2 \vec{N}_1 - x_1 \vec{N}_2) + \frac{1}{c_t D_{23}} (x_2 \vec{N}_3 - x_3 \vec{N}_2)$$

$$\vec{\nabla} x_3 = \frac{1}{c_t D_{31}} (x_3 \vec{N}_1 - x_1 \vec{N}_3) + \frac{1}{c_t D_{32}} (x_3 \vec{N}_2 - x_2 \vec{N}_3)$$

Fick's Laws are:

$$\vec{N}_1 = -c_t \mathcal{D}_{1m} \vec{\nabla} x_1 + x_1 (\vec{N}_1 + \vec{N}_2 + \vec{N}_3)$$

$$\vec{N}_2 = -c_t \mathcal{D}_{2m} \vec{\nabla} x_2 + x_2 (\vec{N}_1 + \vec{N}_2 + \vec{N}_3)$$

$$\vec{N}_3 = -c_t \mathcal{D}_{3m} \vec{\nabla} x_3 + x_3 (\vec{N}_1 + \vec{N}_2 + \vec{N}_3)$$

Substituting for the $\vec{\nabla} x_i$ from the Stefan-Maxwell relations and solving for the \mathcal{D}_{im} yields:

$$\mathcal{D}_{1m} = -\frac{D_{12}D_{13}(x_1N_1 + x_1N_2 + x_1N_3 - N_1)}{x_2D_{13}N_1 - x_1D_{13}N_2 + x_3D_{12}N_1 - x_1D_{12}N_3}$$

$$\mathcal{D}_{2m} = \frac{D_{21}D_{23}(x_2N_1 + x_2N_2 + x_2N_3 - N_2)}{x_2D_{23}N_1 - x_1D_{23}N_2 - x_3D_{21}N_2 + x_2D_{21}N_3}$$

$$\mathcal{D}_{3m} = \frac{D_{31}D_{32}(x_3N_1 + x_3N_2 + x_3N_3 - N_3)}{x_3D_{32}N_1 - x_1D_{32}N_3 + x_3D_{31}N_2 - x_2D_{31}N_3}$$

With $x_1 \approx x_2 \approx 0$ we arrive at:

$$\mathcal{D}_{3m} = \frac{D_{31}D_{32}}{D_{31} + D_{32}} \quad \mathcal{D}_{2m} = D_{23} \quad \mathcal{D}_{1m} = D_{13}$$

Notice that since water and helium are extremely dilute, their interaction is inconsequential and so D_{21} never enters into the final solution.

Plugging in the numbers from part (c) with H_2O (1), He (2), and N_2 (3), we have:

$$\mathcal{D}_{3m} = \frac{(0.256 \times 10^{-9} \text{ m}^2/\text{s})(0.687 \times 10^{-9} \text{ m}^2/\text{s})}{(0.256 \times 10^{-9} \text{ m}^2/\text{s}) + (0.687 \times 10^{-9} \text{ m}^2/\text{s})} = 0.187 \times 10^{-9} \text{ m}^2/\text{s}$$

$$\mathcal{D}_{2m} = 0.687 \times 10^{-9} \text{ m}^2/\text{s}$$

$$\mathcal{D}_{1m} = 0.256 \times 10^{-9} \text{ m}^2/\text{s}$$

The results are easily extended to higher order mixtures though the procedures become

quite cumbersome.

21. A mixture of gases, "a" in "b" are to be separated from one another by thermal diffusion. A set of experiments are conducted at various temperatures to measure the thermal diffusion coefficients. Defining the separation ratio as $\frac{k_a^T}{k_b^T}$, what are the best temperature conditions with which to operate the device?

Experimental Data

T_1	T_2	$x_{a2} - x_{a1}$	$x_{b2} - x_{b1}$	k_a^T	k_b^T
25	50	0.05	0.03	-0.072	0.0433
	75	0.08	0.05	-0.073	0.0455
	100	0.10	0.06	-0.072	0.0433
50	75	0.07	0.01	-0.173	0.0247
	100	0.120	0.017	-0.173	0.0245
	150	0.190	0.027	-0.173	0.0246
100	150	0.06	-0.02	-0.148	-0.0493
	200	0.103	-0.034	-0.149	-0.0491
	300	0.163	-0.054	-0.148	-0.0492

To solve this problem we must first calculate the k^T 's. These are shown in the table. Then we must remember that if k^T is positive the substance moves from the hot region to the cool region. If k^T is negative, the substance moves from the cool to the hot region. Thus we want the k^T 's to have opposite sign. With that in mind and the separation ratio defined above, the optimum place to operate the device seems to be $T_2 = 100$, $T_1 = 50$.

22. In sintering of materials, we can have mass flow in the absence of a concentration gradient via *surface diffusion*. In this process, surface molecules redistribute themselves driven by a gradient in surface curvature. This phenomenon causes metals to bead up on surfaces when heated and other materials to redistribute themselves over time. It is of fundamental importance to the semiconductor industry. If we express the mass flux as:

$$\vec{N}_a = -\vec{\nabla}(\gamma\kappa) \quad \kappa = \frac{\pm \frac{d^2y}{dx^2}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}}$$

where γ is a surface energy parameter and κ is the curvature, what are the two possible equilibrium surface shapes?

At equilibrium, the mass or molar flux will be equal to zero. Thus:

$$-\vec{\nabla}(\gamma\kappa) = 0$$

$$\gamma\kappa = C$$

There are two possible shapes where the curvature would be a constant. One is flat since the curvature is identically zero and the other is spherical where the curvature is the inverse of the radius of the sphere.

23. Let's put some numbers to our well example from the text. Fracking for natural gas promises to be a clean technology because we are probing so deeply for the gas. Such deep wells mean there might be a considerable difference in gas composition from the bottom to the top. The well contains methane and propane and is 2000 m deep. You may assume the mixture behaves ideally, but as the well gets deeper, the temperature rises, 20°C for every kilometer in depth. At the surface, the composition is 80% methane, 20% propane, and the surface temperature is 25 °C. What is the composition at the bottom of the well?

We can start with the equation from our example.

$$\frac{g}{RT} (M_{wb} \bar{V}_a - M_{wa} \bar{V}_b) dy = \bar{V}_b \frac{dx_a}{x_a} - \bar{V}_a \frac{dx_b}{x_b}$$

For an ideal gas, $\bar{V}_a = x_a V$ $\bar{V}_b = x_b V$ and so substituting into the above gives:

$$\frac{g}{RT} (M_{wb} x_a - M_{wa} x_b) dy = \frac{x_b}{x_a} dx_a - \frac{x_a}{x_b} dx_b$$

$$x_b = 1 - x_a \quad dx_b = -dx_a$$

$$\frac{g}{RT} dy = \frac{1 - 2x_a}{x_a (1 - x_a) [(M_{wa} + M_{wb}) x_a - M_{wa}]} dx_a$$

The temperature obeys: $T = T_0 + \Delta T y$. Substituting and integrating using the boundary condition that $y=0$, $x_a = x_{a0}$ gives:

$$\frac{g}{RT} \ln \left[\frac{T_0 + \Delta T y}{T_0} \right] = \frac{1}{M_{wb}} \ln \left[\frac{x_a - 1}{x_{a0} - 1} \right] + \frac{1}{M_{wa}} \ln \left[\frac{x_{a0}}{x_a} \right] +$$

$$\ln \left[\frac{(M_{wa} + M_{wb}) x_a - M_{wa}}{(M_{wa} + M_{wb}) x_{a0} - M_{wa}} \right] \left[\frac{1}{M_{wa}} - \frac{1}{M_{wb}} \right]$$

Now for methane ($M_{wa} = 16$; $M_{wb} = 44$; $T_0 = 298$; $\Delta T = 0.02$; $x_{a0} = 0.8$) we find:

$$y=2000 \quad x_a = 0.724.$$

24. Our electrophoresis sample needs some numbers to make sense of the concentration that can be achieved. Let's assume that we are operating at room temperature, 298 K. We have adjusted the pH of the solution so that the protein we are trying to separate has a valence charge now of -5.

- If the initial protein concentration is 10 mmol and we apply a voltage of +100 volts at the anode and ground (0V) the cathode, plot the concentration profile.
- What is the maximum concentration that can be achieved?

$$\beta_e = \frac{z_{ea} \mathcal{F}_a}{RT} = \frac{-5 \left(96485 \frac{C}{mol} \right)}{\left(8.314 \frac{J}{molK} \right) (298K)} = -194.7 \frac{C}{J}$$

$$\begin{aligned} \frac{c_a}{c_{ao}} &= \left(\frac{\beta_e (\Phi^+ - \Phi^-)}{\exp[-\beta_e \Phi^-] - \exp[-\beta_e \Phi^+]} \right) \exp[-\beta_e \Phi] \\ &= \left(\frac{-194.7(100 - 0)}{\exp[194.7(0)] - \exp[194.7(100)]} \right) \exp[194.7\Phi] \end{aligned}$$

The plot is basically an exponential decay but one that is shaped like an “L”. The maximum concentration one can achieve is easily seen from the equation. At the point where $\Phi = 100$ we achieve a 194700x increase in concentration over the bulk.