

SOLUTIONS MANUAL FOR
**TRANSPORT
PHENOMENA
FUNDAMENTALS**
THIRD EDITION

_____ by _____

Joel Plawsky

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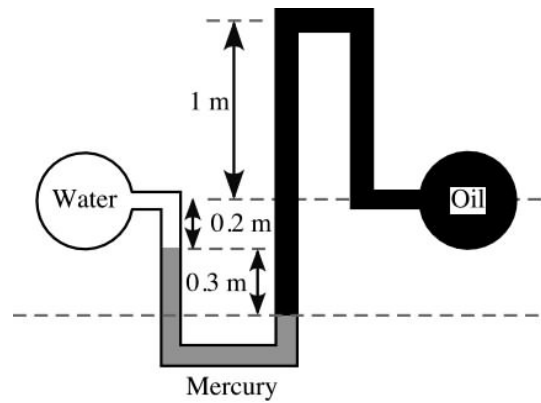
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Chapter #1 Problems

1. Determine the pressure difference between water in the left-hand bulb and the oil in the right-hand bulb.



The dashed lines represent lines of equal pressure. Thus looking at the lower line we see the pressure in the two arms of the manometer must be:

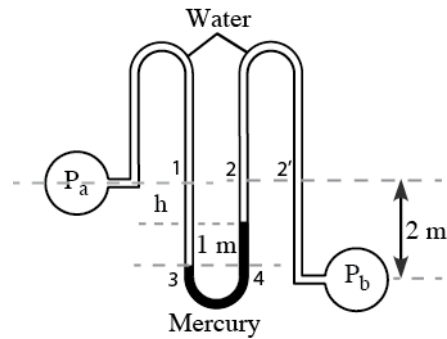
$$P_{oil} + g\rho_{oil}h_{oil} = P_w + g(\rho_w h_w + \rho_{hg} h_{hg})$$

$$P_{oil} - P_w = g(\rho_w h_w + \rho_{hg} h_{hg} - \rho_{oil} h_{oil})$$

$$= 9.8(1000(0.2) + 13600(0.3) - 760(0.5))$$

$$= 38220 \text{ N / m}^2$$

2. Determine the pressure difference between the two fluids in bulbs "a" and "b". The system is shown in P1.2.



Pressures are the same at points P_a and 1, 2 and 2', and at points 3 and 4. Thus we have:

$$P_3 = P_a + \rho_w (1+h)g$$

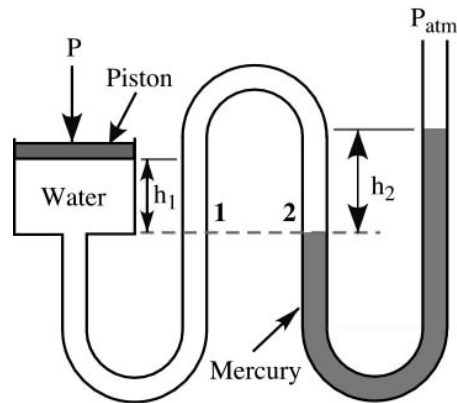
$$P_4 = P_2 + \rho_w gh + \rho_{hg}g(1) = P_b - \rho_w g(2) + \rho_w gh + \rho_{hg}g(1)$$

$$P_3 = P_4$$

$$P_a + \rho_w (1+h)g = P_b - \rho_w g(2) + \rho_{hg}g(1) + \rho_w gh$$

$$P_a - P_b = \rho_{hg}g(1) - \rho_w 3g$$

3. A piston of area 0.1 m^2 sits atop a container filled with water. A U-tube manometer is connected to the container at one end. The other end is open to the atmosphere. If $h_1 = 50 \text{ mm}$ and $h_2 = 120 \text{ mm}$, what is the force, P , acting on the piston? The weight of the piston is 1 kg .



The pressures on both sides of the dashed line are equal.

$$P_1 = P + \frac{mg}{A} + \rho_w gh_1$$

$$P_1 = P_2$$

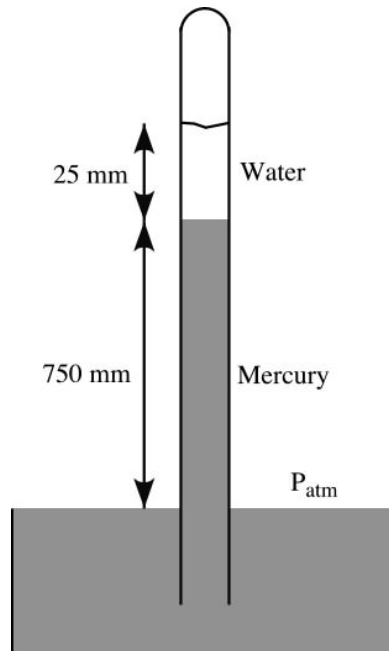
$$P_2 = P_{atm} + \rho_{Hg} gh_2$$

$$P = P_{atm} + \rho_{Hg} gh_2 - \frac{mg}{A} - \rho_w gh_1 = 101,325 + (13600)(9.8)0.12 - \frac{1(9.8)}{0.1} - (1000)(9.8)0.05$$

$$= 116,731 \text{ N/m}^2$$

$$\text{Force} = P * A = 11,637 \text{ N}$$

4. A barometer is contaminated with water. 25 mm of water sits atop the mercury of the barometer. If the height of the mercury is 750 mm, what is the atmospheric pressure?

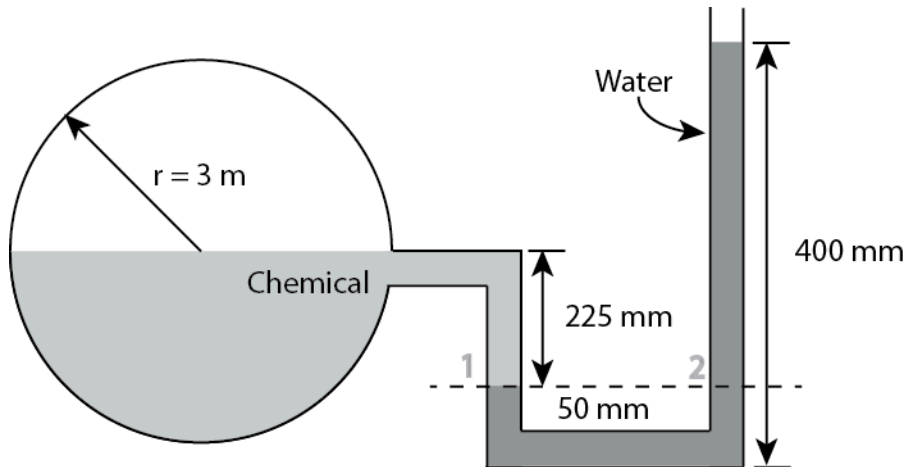


In the barometer, the pressure at the level of the surface of the mercury is the same. Thus:

$$P_{atm} = P_o + \rho_w g h_w + \rho_{Hg} g h_{Hg}$$

$$= 0 + 1000(9.8)(0.025) + 13600(9.8)(0.75) = 100,205 \text{ N/m}^2$$

5. An open water manometer is used to measure the pressure in a spherical tank. The tank is half-filled with 20,000 kg of a chemical that is immiscible with water. The manometer tube is partially filled with the chemical. What is the pressure in the tank if the situation is shown in Figure P1.5?



Tank Volume

$$V_{\text{tank}} = \frac{4}{3}\pi r_{\text{tank}}^3 = \frac{4}{3}\pi(3)^3 = 113.1\text{ m}^3$$

Fluid Density

$$\rho_{\text{fluid}} = \frac{\text{liquid mass}}{\text{tank volume}} = \frac{50000}{113.1/2} = 884 \frac{\text{kg}}{\text{m}^3}$$

Tank Pressure

$$P_{\text{tank}} + \rho_{\text{fluid}}gh_{\text{fluid}} = P_{\text{atm}} + \rho_{\text{water}}gh_{\text{water}}$$

$$P_{\text{tank}} - P_{\text{atm}} = \rho_{\text{water}}gh_{\text{water}} - \rho_{\text{fluid}}gh_{\text{fluid}}$$

$$= \left(1000 \frac{\text{kg}}{\text{m}^3}\right) \left(9.8 \frac{\text{m}}{\text{s}^2}\right) (0.4 - 0.05\text{ m}) - \left(884 \frac{\text{kg}}{\text{m}^3}\right) \left(9.8 \frac{\text{m}}{\text{s}^2}\right) (0.225\text{ m})$$

$$= 1481\text{ Pa}$$

6. The U2 spy plane was designed to fly at altitudes of up to 21,000 m. Its wing span was so large that special wheels were incorporated within the wings to keep them from scraping the runway when taking off, landing, or being parked. If the air temperature at sea level is 25 °C, drops off at a rate of 5.0×10^{-3} K/m and the pressure at sea level is 1.03×10^5 N/m², what is the temperature and pressure at the airplane's height? The molecular weight of air is 29 kg/kg-mole.

We can use our equation (1.45) to help answer this question. The temperature at 21,000 m is found from:

$$T = T_o - \left(\frac{\Delta T}{\Delta H} \right) z = (25 + 273) - 5 \times 10^{-3} (21000) = 193 \text{ K}$$

Now at this temperature, the pressure is:

$$\frac{P}{P_o} = \left[\frac{T_o - (\Delta T/h)z}{T_o} \right]^{\frac{M_w g}{(\Delta T/h)R}} = \left[\frac{193}{298} \right]^{\frac{29(9.8)}{(5 \times 10^{-3})8314}}$$

$$P = 5285 \text{ Pa}$$

7. An atmospheric inversion has taken place such that the temperature at the surface is 5 °C while the temperature at 4,000 m is a balmy 20 °C. Assuming a linear temperature drop over that distance and a barometric pressure of 750 mm Hg at the surface, what is the pressure at 4,000 m?
-

Here, we need to alter the equation in the text because the temperature profile is in the opposite direction. If the temperature increases with height we have:

$$\frac{P}{P_o} = \left[\frac{T_o + (\Delta T / h)z}{T_o} \right]^{\frac{M_w g}{(\Delta T / h)R}}$$

For this problem, $\Delta T/h = 0.00375$ °C/m. Plugging in gives:

$$\frac{P}{100000} = \left[\frac{278 + (0.00375)(4000)}{278} \right]^{\frac{29(9.8)}{(0.00375)8314}}$$

$$P = 6.194 \times 10^4 \text{ Pa}$$

8. The atmosphere on Venus can be considered to behave as an ideal gas with a mean molecular weight of 44. The temperature varies little with depth but hovers at an incredible 350 °C. The density of the atmosphere at the planet's surface is 2 kg/m³ and the acceleration due to gravity is the same as the Earth's. Calculate how the density of the atmosphere varies as a function of height above the surface.
-

We start with the equation:

$$\frac{dP}{dz} = -\rho g$$

Using the ideal gas law, $P = \frac{nRT}{V} = \frac{\rho RT}{M_w}$ we have:

$$\frac{RT}{M_w} \frac{d\rho}{dz} = -\rho g$$

$$\frac{d\rho}{\rho} = -\frac{M_w g}{RT} dz$$

$$\ln \left[\frac{\rho}{\rho_o} \right] = -\frac{M_w g}{RT} z \quad \ln \left[\frac{\rho}{2} \right] = -[8.3 \times 10^{-5}] z$$

9. Water boils at 100 °C at atmospheric pressure, i.e. at sea level. The boiling point is defined as the temperature at which the vapor pressure of water is equal to the atmospheric pressure. This has consequences for cooking in places like Denver and Santa Fe where it takes quite a bit longer to make a hard boiled egg than it would in New York. If the vapor pressure of water obeys the Antoine equation (below), and the albumen in an egg needs to reach 90 °C for the protein to coagulate, at what height would it be impossible to hard boil an egg?

$$\text{Antoine Equation} \quad \ln P_{\text{vap}} \text{ (kPa)} = 16.262 - \frac{3799.89}{T \text{ (}^\circ\text{C)} + 226.35}$$

The key here is to realize that we cannot exceed the boiling point of liquid water when we try to cook an egg. Thus, if the boiling point of water is below 90 °C, we will not be able to hard boil an egg. The solution to the problem involves first finding out what the vapor pressure of water is at 90 °C and then coupling that to our equation for atmospheric pressure as a function of height.

$$\ln P_{\text{vap}} \text{ (kPa)} = 16.262 - \frac{3799.89}{90 + 226.35} = 70.13 \text{ kPa}$$

$$\frac{dP}{dz} = -\rho g = -\left(\frac{M_w g}{RT}\right)P$$

$$\frac{dP}{P} = -\left(\frac{M_w g}{RT}\right)dz$$

If we assume that the temperature does not change with z, we can integrate and get a height. We are looking for the pressure of air to be 38.57 kPa and we assume standard temperature of 25 °C.

$$\ln \frac{P}{P_o} = -\left(\frac{M_w g}{RT}\right)z$$

$$\begin{aligned} z &= -\left(\frac{RT}{M_w g}\right) \ln\left(\frac{P}{P_o}\right) = -\left(\frac{8314(298)}{29(9.8)}\right) \ln\left(\frac{70.13}{101.3}\right) \\ &= 3206 \text{ m} \end{aligned}$$

The real value is quite a bit less since the air temperature will decrease with height. For this problem, if we assume $\Delta T/h = -0.00375$ °C/m, the temperature at 3200 m is about 286K. Using an average temperature, the height would drop by a few hundred meters.

10. The successor to Alvin, the submersible that was used to locate the Titanic, among its other research tools, is being built. The goal is to be able to reach the deepest depths in the Atlantic and Pacific oceans, about 11,000 m. Assuming water density is unchanged with depth,
- What is the pressure at the 11,000 m mark?
 - If the submersible is to be nominally 3 m in diameter, what force does the water exert on the craft?
 - How thick would the hull of the submersible have to be? The design equation for thick-walled spherical shells can be expressed as:

$$t_h \cong r_i \left[\left(\frac{2S_d + 2P}{2S_d - P} \right)^{1/3} - 1 \right]$$

where t_h is the wall thickness, r_i is the inner radius of the shell (3 m), S_d is the design stress for the wall material, and P is the pressure the vessel is exposed to. For this example, the hull material is a titanium-molybdenum alloy whose design stress is approximately 275 MPa.

- a) **Here we use the manometer equation assuming water is essentially incompressible and that we maintain the same temperature throughout, 20 or 25 °C. The reference height, $z = 0$ is on the water's surface.**

$$\frac{dP}{dz} = -\rho g$$

$$\begin{aligned} P &= P_o - \rho g(z - z_o) = 101,300 - 1000(9.8)(-11000 - 0) \\ &= 107901300 \text{ Pa} = 107.9 \text{ MPa} = 1065 \text{ atm} \end{aligned}$$

- b) **Force = Pressure*Area so:**

$$F = PA = 4\pi r^2 P = (107901300)4\pi(1.5)^2 = 3.05 \times 10^9 \text{ N}$$

- c) **The thickness of the shell is:**

$$t_h \cong r_i \left[\left(\frac{2S_d + 2P}{2S_d - P} \right)^{1/3} - 1 \right] = 1.5 \left[\left(\frac{2(275) + 2(107.9)}{2(275) - 107.9} \right)^{1/3} - 1 \right] = 0.3 \text{ m}$$

11. The three-gorges dam spanning the Yangtze River in China will be the largest dam in the world when completed. The dam is designed to be 101 m tall and when filled will contain water to a height of 91 m.

- What would be the pressure at the bottom of the dam?
- Dam design is a very complicated topic, but to simplify it a bit we can just look at the pressure the water exerts at the dam bottom and the pressure the concrete exerts and compare the two numbers. Assuming the dam is 115 meters thick at the bottom and 40 m thick at the top, what is the pressure per unit width at the bottom due to the weight of the concrete? Is that enough to hold back the water?

a) To calculate the pressure at the bottom of the dam, we need to use our manometer equation:

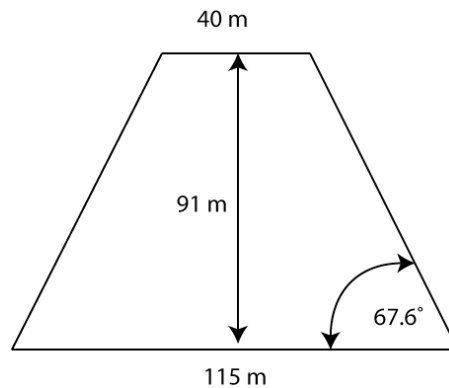
$$\frac{dP}{dz} = -\rho g$$

With the density of water at about 1000 kg/m^3 and the pressure at the surface at $101,300 \text{ Pa}$ we have at the bottom:

$$P - P_0 = -\rho g(z - z_0)$$

$$P = P_0 - \rho g z = 101300 - 1000(9.8)(-91) = 9.93 \times 10^5 \text{ Pa}$$

b) We can calculate the pressure that the concrete exerts at the bottom of the dam in pretty much the same way we did the water. Since the concrete is a solid, we need to determine the weight of the dam per unit length and use the area at the bottom to determine the pressure. Assuming the dam looks like:



we can calculate the area, a , and hence the volume per unit length. Then we can determine the pressure from the weight of the concrete and the footprint of the dam bottom.

$$a = 40(91) + 2\left(\frac{1}{2}\right)(37.5)(91) = 7052.5 \text{ m}^2$$

$$m = a(1)(\text{density}) = 7052.5(1)(2400) = 1.69 \times 10^7 \text{ kg}$$

$$\text{pressure} = mg / a_c = 1.69 \times 10^7 (9.8) / (155)(1) = 1.44 \times 10^6 \text{ Pa}$$

So, it looks like the dam will be able to resist the pressure of the water, though a more accurate calculation and larger safety factor is likely in order.

12. One of the most accurate means of determining the percentage fat content of a person is by measuring the person's specific gravity. The measurement is made by immersing the person in a tank of water and measuring their net weight. Derive an expression for the specific gravity of a person in terms of their weight in air, net weight in water, and specific gravity of the water. Find values for the density of fat and muscle to develop your correlation. Are there any items left out of your analysis that might affect the accuracy of the measurement?
-

The weight of the person in air is given by the product of their mass times gravity. Thus:

$$w_{p,air} = mg = (m_{fat} + m_m)g$$

The net weight of the person in water is equal to their weight in air minus the weight of the volume of water displaced.

$$w_{p,net} = mg - \rho_w gV = (m_{fat} + m_m)g - \rho_w gV$$

The specific gravity of the person is defined by:

$$s.g. = \frac{\text{person density}}{\rho_w} = \frac{(m_m + m_{fat}) / V}{\rho_w}$$

Substituting in for the volume of the person gives:

$$s.g. = \frac{(m_m + m_{fat})g}{w_{p,air} - w_{p,net}} = s.g.(fat) + s.g.(muscle)$$

and with values for the specific gravity of fat and muscle, we can determine the percentage fat content of a person.

13. Icebergs are dangerous because most of the ice lies below the surface of the water. The old rule of thumb is that 90% of the volume of the iceberg lies below the water. Assuming water at $-4\text{ }^{\circ}\text{C}$ in equilibrium with the ice and a spherical iceberg, determine if this rule of thumb is accurate.
-

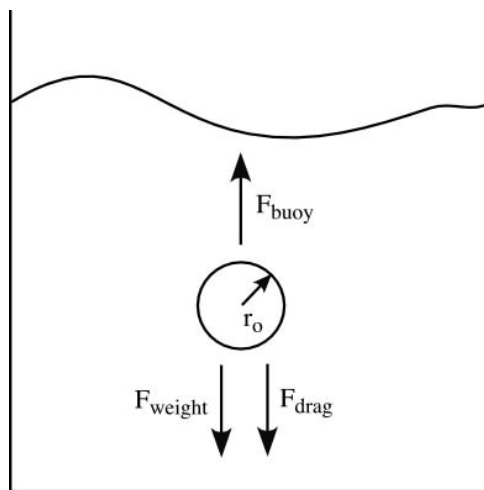
In this problem we are basically interested in determining the specific gravity of the ice. If that is about 0.9, then the rule of thumb will be correct. For water and ice at $-4\text{ }^{\circ}\text{C}$, the densities are: 999 kg/m^3 and 920 kg/m^3 . Based on these values, the rule of thumb is correct.

14. An air bubble rises slowly through maple syrup. Three forces act on the bubble, the weight of the bubble, the buoyant force, and a "drag" force due to fluid friction between the bubble and syrup as the bubble forces the syrup out of the way to rise. The drag force is given by $F_{drag} = 6\pi\mu vr_o$ where v is the velocity of the bubble and μ is the viscosity of the syrup. Assuming a 5 mm bubble and properties of the syrup given by:

$$\mu = 1 \text{ Ns/m}^2 \quad \rho = 1250 \text{ kg/m}^3$$

what is the velocity of the bubble? In which direction does the drag force act?

The free body diagram for the drop is:



The buoyant force opposes the weight of the bubble. The drag force acts to oppose the motion of the bubble through the syrup. The velocity of the bubble becomes constant when all the forces balance.

$$F_{buoy} = F_{weight} + F_{drag}$$

The buoyant force is equal to the volume of water displaced. Substituting into the force balance gives:

$$\rho_w V_{bubble} g = \rho_{bubble} V_{bubble} g + 6\pi\mu vr_o$$

Substituting for the volume of the bubble and solving for the velocity gives:

$$v = \frac{2}{9\mu} r_o^2 g (\rho_w - \rho_{bubble}) = \frac{2}{9(1)} (0.0025)^2 9.8 (1250 - 1) = 0.017 \frac{m}{s}$$

15. A 100 kg man is preparing to spend the day on a dive. If we can approximate the man as a cylinder, 2 m long and 0.2 m in radius, how much weight must he carry to insure he is neutrally buoyant?
-

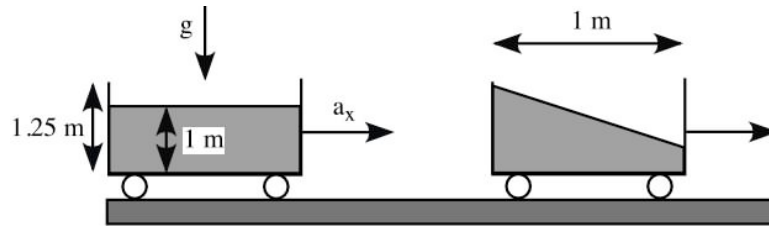
To be neutrally buoyant, the man will be totally submerged. Thus the buoyant force on him will be equal to the weight of the water displaced. This is just the volume of the man times the density of water.

$$F_{buoy} = V_{man} g \rho_{water} = \pi r_{man}^2 L g \rho_{water} = \pi (0.2m)^2 (2m) \left(9.8 \frac{m}{s^2} \right) \left(1000 \frac{kg}{m^3} \right) = 2463N$$

The force exerted by the man must be equal to the buoyant force. The force exerted by the man is 100kg = 980N. Thus the amount of mass the man must carry is:

$$mass = \frac{F_{buoy} - F_{man}}{g} = \frac{2463 - 980}{9.8} = 151.3 \text{ kg}$$

16. An open rectangular tank, 0.5 m wide and 1 m long contains water to a depth of 1 m. If the height of the tank is 1.25 m, what is the maximum horizontal acceleration (along a line parallel to the long axis of the tank) that can be sustained before the water spills.



The equation representing the pressure distribution in the liquid are:

$$-\frac{\partial P}{\partial x} + \rho g_x = \rho a_x \quad -\frac{\partial P}{\partial y} + \rho g_y = \rho a_y$$

Here $g_x = 0$, $a_y = 0$, and $g_y = g$. Thus:

$$\frac{\partial P}{\partial x} = -\rho a_x \quad \frac{\partial P}{\partial y} = \rho g$$

Dividing the equation in the x-direction by that in the y-direction yields an equation for the surface.

$$\frac{dy}{dx} = -\frac{a_x}{g} \quad y = -\left(\frac{a_x}{g}\right)x + C$$

There are two equations and two unknowns, C and a_x . We have one piece of information not used the volume of fluid. The volume of fluid in the tank is $V = (1)(1)(0.5) = 0.5 \text{ m}^3$. Integrating the above equation over x and multiplying by the tank width we find:

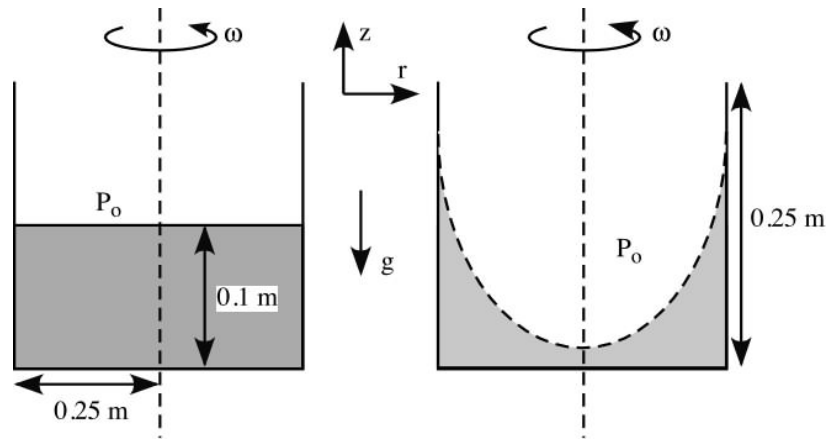
$$V = 0.5 = 0.5 \int_0^1 \left(-\frac{a_x}{g}x + C\right) dx = 0.5 \left[-\left(\frac{a_x}{2g}\right) + C\right]$$

$$C = 1 - \frac{a_x}{2g}$$

$$y = 1 - \frac{a_x}{g} \left(x - \frac{1}{2}\right)$$

Now we know that when the fluid is about to spill, at $x = 0$, $y = 1.25$. Thus $a_x = 0.5g$.

17. An open, cylindrical tank of depth 0.25 m is partially filled with water. The depth of the water is 0.1 m and the diameter of the tank is 0.5 m. If the tank is rotated about its vertical axis, what will be the shape of the surface of the liquid?



The governing equation for this problem is:

$$-\nabla P + \rho \mathbf{g} = \rho \mathbf{a}$$

This problem is two-dimensional in the r and z directions. The two components of interest are:

$$-\frac{\partial P}{\partial r} + \rho g_r = \rho a_r \quad -\frac{\partial P}{\partial z} + \rho g_z = \rho a_z$$

For this problem, where the surface shape is constant, $g_r = 0$, $a_r = 0$, and $g_z = g$. The acceleration in the radial direction is $r\omega^2$. Plugging in we have:

$$-\frac{\partial P}{\partial r} = \rho r \omega^2 \quad -\frac{\partial P}{\partial z} + \rho g = 0$$

The total pressure at any point in the fluid is given by:

$$dP = \left(\frac{\partial P}{\partial r} \right) dr + \left(\frac{\partial P}{\partial z} \right) dz$$

$$dP = -\rho r \omega^2 dr + \rho g dz$$

Integrating and using the fact that at the free surface and centerline of the cylinder we have $r = 0$, $z = z_o$ and $P = P_o$, we can integrate to give:

$$P - P_o = -\left(\frac{\rho \omega^2}{2} \right) r^2 + \rho g (z - z_o)$$

At the free surface, $P = P_o$ everywhere so the equation of the surface is a parabola:

$$z = \left(\frac{\omega^2}{2g} \right) r^2 + z_o$$

18. For the tank and water system of problem 17, how fast can we spin the tank before the bottom surface of the tank is exposed? How fast can we spin the tank before water reaches the rim?

To answer these questions we need to know the volume of water in the tank for any given surface shape.

$$V = \pi r^2 h_{\text{water}} = \frac{\pi}{160} m^3 \quad \text{before rotation}$$

$$V = \int_0^{2\pi} \int_0^r z r \, dr \, d\theta = \int_0^{2\pi} \int_0^r \left(\frac{\omega^2}{2g} r^2 + z_o \right) r \, dr \, d\theta$$

after rotation

$$= \frac{\pi \omega^2 r^4}{4g} + \pi z_o r^2$$

If $r = 0.25$ m, then if we want $z_o = 0$ and expose the tank bottom,

$$\omega = \sqrt{6.4g}.$$

If we want the fluid to reach the rim, then $z = h_{\text{tank}} = 0.25$ m at $r = r_o$. Using the equation for the surface to solve for z_o and then substituting into the volume equation lets us solve for the acceleration.

$$z_o = h_{\text{tank}} - \frac{\omega^2}{32g}$$

$$\frac{\pi \omega^2}{1024g} + \frac{\pi h_{\text{tank}}}{16} - \frac{\pi \omega^2}{512g} = \frac{\pi}{160}$$

$$\text{Solving shows } \omega = \sqrt{4.8g}$$

Chapter #2 Problems

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

$$v_r = v_o (r^2 \theta + \theta^2 z - r^2 z) \quad v_\theta = v_o (\theta^2 z - \theta^2 r + \theta^3)$$

$$v_z = v_o (zr^2 - z^2 \theta)$$

- a) What are the 9 stresses for this fluid?
 b) 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:

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

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

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

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 $\nabla \cdot \mathbf{v} = 0$. If we plug in for \mathbf{v} using Darcy's Law we have:

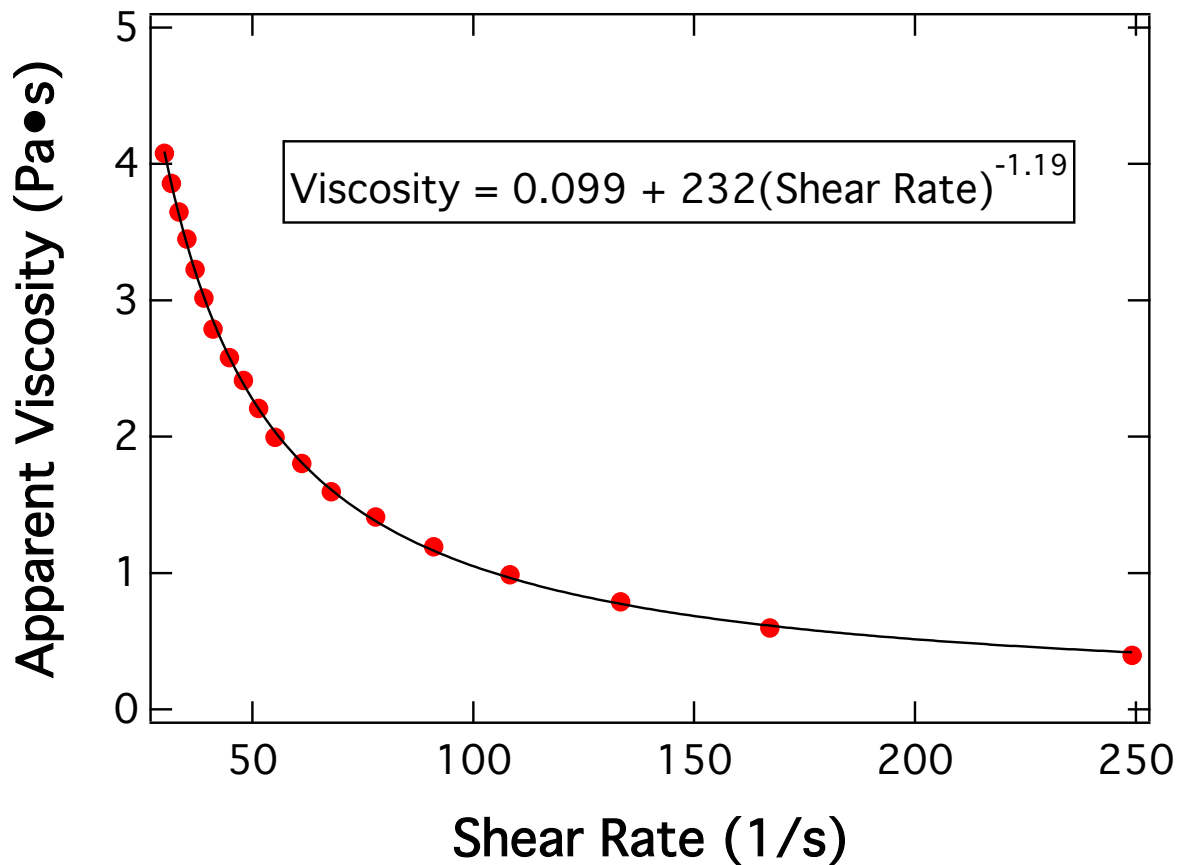
$$-\frac{k}{\mu} \vec{\nabla} \cdot \vec{\nabla} P = 0 = -\frac{k}{\mu} \nabla^2 P$$

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).

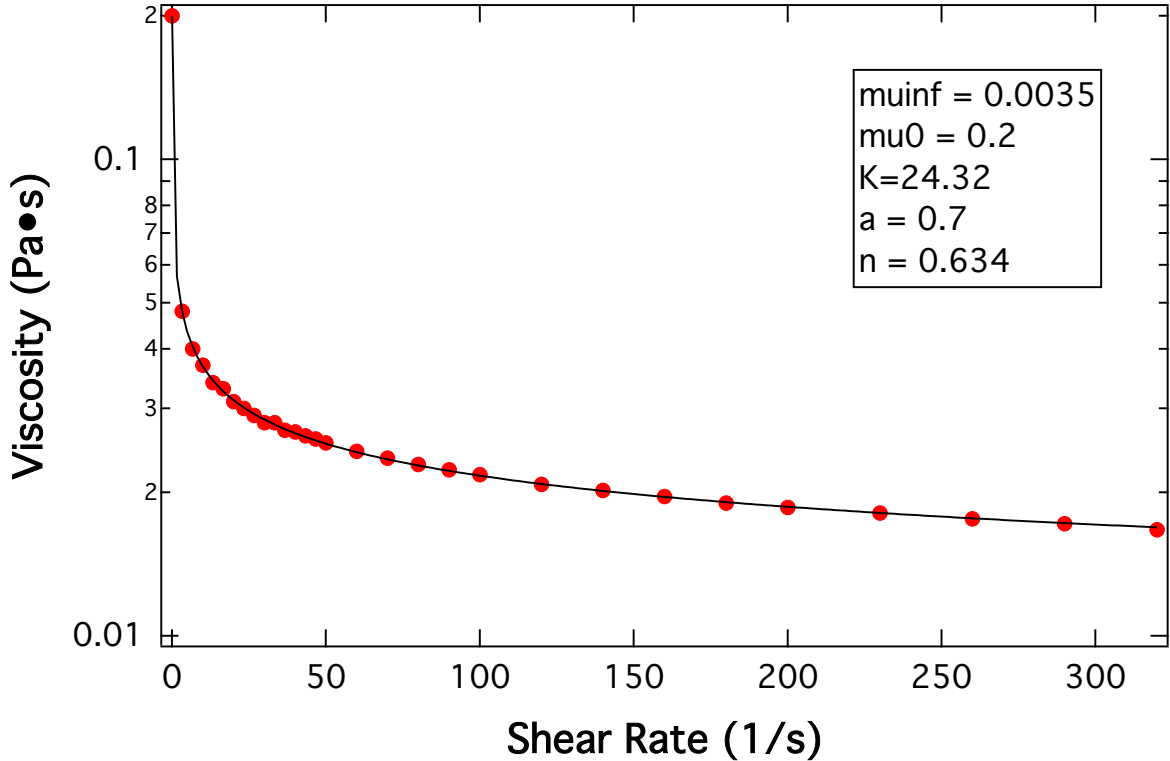


4. The Carreau-Yasuda model is a popular formulation for representing non-Newtonian fluid behavior. The model is:

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

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 (\vec{N}_{Li} , \vec{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 $\vec{N}_{\text{Li}} = -2\vec{N}_{\text{SO}_4}$:

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

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

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

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

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

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

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.

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

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

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

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

Now multiplying by V_t in the same way we have:

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

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:

$$\mu_i^c = \mu_{i0}^c + RT \ln x_i$$

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?

$$\mu_i^c = \mu_{i0}^c + RT \ln(\gamma_i x_i)$$

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:

$$\vec{\mathbf{j}}_a = D_{ab} x_a \vec{\nabla} [\mu_{a0}^c + RT \ln x_a] \qquad \vec{\mathbf{j}}_b = D_{ab} x_b \vec{\nabla} [\mu_{b0}^c + RT \ln x_b]$$

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

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:

$$\vec{\mathbf{j}}_a = D_{ab} x_a \vec{\nabla} [\mu_{a0}^c + RT \ln(\gamma_a x_a)] \qquad \vec{\mathbf{j}}_b = D_{ab} x_b \vec{\nabla} [\mu_{b0}^c + RT \ln(\gamma_b x_b)]$$

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

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

Combining all the terms we find:

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

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

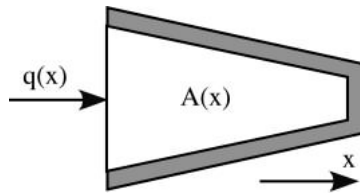
If the activity coefficients are constant the equation is automatically satisfied. If they are a function of \mathbf{x}_a , then we must satisfy the relationship above.

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.

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

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

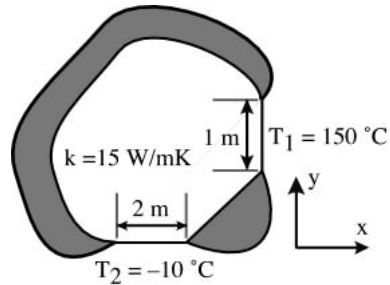
The highest heat flux is at $x = 0.2$ where the area is the smallest.

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

$$q''(0) = -59,683.5 \frac{\text{W}}{\text{m}^2} \quad q''(0.2) = -93.255.5 \frac{\text{W}}{\text{m}^2}$$

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:

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

- a) Is the heat transfer at steady-state, i.e. is the rate constant?
b) 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.

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

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

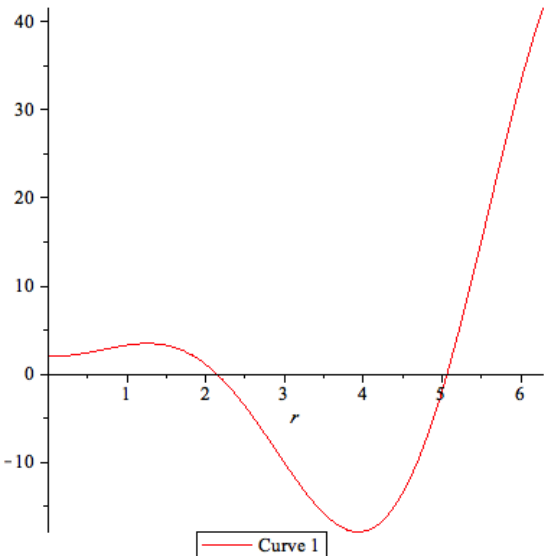
We integrate to get the temperature profile.

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

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

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

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.

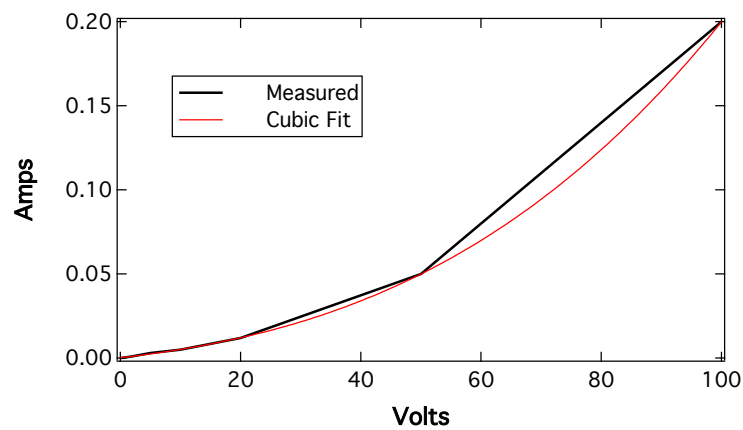


15. The voltage(V) – current(I) behavior for a new material was measured and found to be:

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 $T = 298\text{K}$?
- 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:

$$\vec{J}_i = -\underbrace{D_{ij0}}_{D_{ij}} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln x_i} \right) \vec{\nabla} c_i = c_i (\vec{v}_i - \vec{v}^c)$$

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

$$\vec{\nabla} \mu_i = \frac{RTx_j}{D_{ij0}} (\vec{v}_j - \vec{v}_i)$$

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.

$$\vec{\nabla} \mu_i = RT \vec{\nabla} \ln x_1 + RT \vec{\nabla} \ln \gamma_1 = \frac{RTx_2}{D_{120}} (\vec{v}_2 - \vec{v}_1)$$

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.

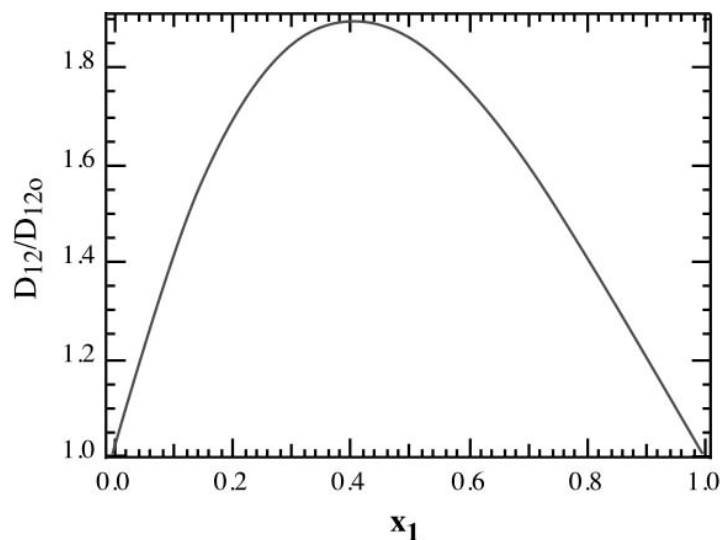
For the binary system, $D_{12} = D_{21}$ so we only need consider one of the terms. Thus:

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

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. $c_i = 63055 \text{ mol/m}^3$; $D_{ab} = 1.0 \times 10^{-9} \text{ m}^2/\text{s}$; $L = 5 \text{ cm}$. 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:

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

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

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.

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

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

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

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

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

$$= \exp(0.03z)$$

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:

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

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

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:

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

$$x_m = 0.34$$

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

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:

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

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. D_{im} is the pseudo-binary diffusion coefficient.

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

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

c) Use your result to calculate the pseudo-binary diffusion coefficient for each species in the system H₂O, He, N₂:

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

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 H₂O (1), He(2), and N₂(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.