

Chapter 2 Problems

1. A 1.00-L bulb containing H_2 at a pressure of 2.50 bar is connected to a 2.00-L bulb containing N_2 at a pressure of 1.50 bar, both at the same temperature. Calculate (a) the total pressure of the system, (b) the mole fraction of H_2 , and (c) the partial pressure of each gas.

Answer: (a) The easiest way to work this kind of problem is to convert to moles. For the 1.00-L bulb:

$$n_{H_2} = PV/RT = 2.50 \text{ bar } 1.00 \text{ L}/RT = 2.50 \text{ L bar}/RT$$

for the 2.00-L bulb:

$$n_{N_2} = 1.50 \text{ bar } 2.00 \text{ L}/RT = 3.00 \text{ L bar}/RT$$

the total pressure is given by the total moles, $n = n_{H_2} + n_{N_2}$ in the total volume $V = 3.00 \text{ L}$, Eq. 2.1.3°:

$$P = nRT/V = (2.50 \text{ L bar}/RT + 3.00 \text{ L bar}/RT) RT/3.00 \text{ L} = 1.833 \text{ bar}$$

(b) The mole fractions are:

$$y_{H_2} = n_{H_2}/n = \frac{2.50 \text{ L bar}/RT}{5.50 \text{ L bar}/RT} = 0.4545$$

and $y_{N_2} = n_{N_2}/n = \frac{3.00 \text{ L bar}/RT}{5.50 \text{ L bar}/RT} = 0.5455$

(c) The partial pressures are given by Eq. 2.1.10°:

$$P_{H_2} = y_{H_2} P = 0.4545 (1.833 \text{ bar}) = 0.833 \text{ bar}$$

$$P_{N_2} = y_{N_2} P = 0.5455 (1.833 \text{ bar}) = 1.000 \text{ bar}$$

2. Dry air is 20.946% by volume O_2 and 79.054% N_2 . Consider a constant pressure piston filled with dry air at 1.000 atm or 1.01325 bar pressure at 298.2 K. A small amount of water is admitted and allowed to evaporate to give the equilibrium vapor pressure of water in the piston. Calculate the partial pressure of O_2 at 298.2 K.

Answer: Think through this problem first: At constant pressure, admission of water vapor into the piston will cause an increase in the total moles of gas and a corresponding increase in volume. The moles of O_2 remain the same, but with the increase in volume, the partial pressure of O_2 will decrease. Assume the initial volume is V_0 . In dry air $P = P_{O_2} + P_{N_2}$, with $P_{O_2} = n_{O_2} RT/V_0$ and $P_{N_2} = n_{N_2} RT/V_0$ giving:

$$P = n_{O_2} RT/V_0 + n_{N_2} RT/V_0 \quad \text{or} \quad P = (n_{O_2} + n_{N_2}) RT/V_0 \quad (1)$$

Using the given mole fraction of O_2 , the partial pressure of O_2 in dry air is:

$$P_{O_2} = y_{O_2} P = 0.20946 (1.01325 \text{ bar}) = 0.2122 \text{ bar} \quad \text{or}$$

$$P_{O_2} = y_{O_2} P = 0.20946 (1.0000 \text{ atm}) = 0.2095 \text{ atm} = 159.2 \text{ torr} \quad (2)$$

After the admission of water vapor, $P = P_{O_2} + P_{N_2} + P_{H_2O}$ and the volume increases to V_1 , or:

$$P - P_{H_2O} = P_{O_2} + P_{N_2} = n_{O_2} RT/V_1 + n_{N_2} RT/V_1 = (n_{O_2} + n_{N_2}) RT/V_1 \quad (3)$$

Dividing Eq. 3 by Eq. 1 gives:

$$\frac{P - P_{\text{H}_2\text{O}}}{P} = \frac{(n_{\text{O}_2} + n_{\text{N}_2})RT/V_1}{(n_{\text{O}_2} + n_{\text{N}_2})RT/V_o} = \frac{1/V_1}{1/V_o} = \frac{V_o}{V_1} \quad (4)$$

In addition, the ratio of the wet and dry partial pressures for O_2 can be calculated from:

$$\frac{P_{\text{O}_2,1}}{P_{\text{O}_2,o}} = \frac{n_{\text{O}_2} RT/V_1}{n_{\text{O}_2} RT/V_o} = \frac{1/V_1}{1/V_o} = \frac{V_o}{V_1} \quad (5)$$

since the moles of O_2 remain constant. Combining Eq. 4 and 5 gives:

$$\frac{P_{\text{O}_2,1}}{P_{\text{O}_2,o}} = \frac{P - P_{\text{H}_2\text{O}}}{P} \quad (6)$$

Substitution of the equilibrium vapor pressure of water from Table 2.1.1 gives the ratio:

$$\frac{P_{\text{O}_2,1}}{P_{\text{O}_2,o}} = \left(\frac{101.325 \text{ kPa} - 3.168 \text{ kPa}}{101.325 \text{ kPa}} \right) = 0.9687 \quad (7)$$

Using the dry partial pressure from Eq. 1 gives the wet partial pressure:

$$P_{\text{O}_2,1} = P_{\text{O}_2,o} \left(\frac{P - P_{\text{H}_2\text{O}}}{P} \right) = 0.2122 \text{ bar} (0.9687) = 0.2056 \text{ bar}$$

or equivalently, 0.2029 atm and 154.2 torr.

3. Dry air is 20.946% by volume O_2 and 79.054% N_2 . Consider a constant volume flask filled with dry air at 1.000 atm or 1.01325 bar pressure at 298.2 K. A small amount of water is admitted and allowed to evaporate to give the equilibrium vapor pressure of water in the constant volume flask. Calculate the partial pressure of O_2 at 298.2 K.

Answer: The dry partial pressure is:

$$P_{\text{O}_2} = y_{\text{O}_2} P = 0.20946 (1.01325 \text{ bar}) = 0.2122 \text{ bar}$$

and the total pressure is given by $P_o = P_{\text{O}_2} + P_{\text{N}_2}$. The admission of water vapor to the constant volume flask will increase the total pressure to $P_1 = P_{\text{O}_2} + P_{\text{N}_2} + P_{\text{H}_2\text{O}}$. However, since the partial pressure of O_2 is the pressure the gas would exert in the flask if it were alone, the partial pressure of O_2 won't change. So the final partial pressure of O_2 is 0.2122 bar, or 0.2095 atm, or 159.2 torr.

4. An aqueous solution is prepared by adding 5.0822 g of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, to a 100-mL volumetric flask and then diluting to the mark. The final mass of the solution is 102.97 g. Calculate the molarity, molality, and the mole fraction of ammonium sulfate in this solution. Calculate the mole fraction of the solvent.

Answer: The molar mass of $(\text{NH}_4)_2\text{SO}_4$ is $132.14 \text{ g mol}^{-1}$. The number of moles of added $(\text{NH}_4)_2\text{SO}_4$ is 0.0384607 mol and the molarity is:

$$c_B = 0.0384607 \text{ mol}/0.1000 \text{ L} = 0.384605 \text{ M.}$$

The molality, using the mass of the solvent:

$$w_A = w_{\text{soln}} - w_B = 102.97 \text{ g} - 5.0822 \text{ g} = 97.888 \text{ g} = 0.097888 \text{ kg}$$

is $m_B = n_B/w_A = 0.0384607 \text{ mol}/0.097888 \text{ kg} = 0.392904 \text{ mol kg}^{-1}$

The mole fraction is given using Eq. 2.2.13:

$$x_B = \frac{m_B (1\text{kg})}{\left(\frac{1000\text{g}}{M_A}\right) + m_B (1\text{kg})} = \frac{0.392904 \text{ m (1kg)}}{\left(\frac{1000\text{g}}{18.0153 \text{ g mol}^{-1}}\right) + 0.392904 \text{ m (1kg)}}$$

$$x_B = 7.02853 \times 10^{-3}$$

Don't forget to use all constants to at least the number of significant figures justified by the problem. Then calculate the mole fraction of the solvent by difference, since $x_A + x_B = 1$:

$$x_{\text{H}_2\text{O}} = 1 - 7.02853 \times 10^{-3} = 0.992971$$

Notice that the molarity and molality differ by 2.1%.

5. An aqueous solution is prepared by adding 2.012 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to a 100-mL volumetric flask and then diluting to the mark. The final mass of the solution is 101.26 g . Calculate the molarity, molality, and the mole fraction of CaCl_2 in this solution. Calculate the mole fraction of the solvent.

Answer: We need to take into account the waters of hydration. The plan is to note that the number of moles of anhydrous CaCl_2 is equal to the moles of added $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. For the molality calculation the water of hydration is added to the mass of the solvent. The molar mass of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is $147.014 \text{ g mol}^{-1}$.

The moles of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is based on the hydrated molar mass:

$$n_B = 2.012 \text{ g}/147.014 \text{ g mol}^{-1} = 0.013686 \text{ mol}$$

and the molarity is:

$$c_B = 0.013686 \text{ mol}/0.1000 \text{ L} = 0.13686 \text{ M.}$$

The mass of the solvent includes the water of hydration, based on 0.013686 mol of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$:

$$w_A = \text{water added in making solution} + \text{water of hydration from solute}$$

$$w_A = (101.26 \text{ g} - 2.012 \text{ g}) + 2 (18.02 \text{ g mol}^{-1})(0.013686 \text{ mol})$$

$$= 99.741 \text{ g} = 0.99741 \text{ kg}$$

The molality is then:

$$m_B = n_B/w_A = 0.013686 \text{ mol}/0.99741 \text{ kg} = 0.13721 \text{ mol kg}^{-1}$$

The mole fraction is given using Eq. 2.2.13:

$$x_B = \frac{m_B (1\text{kg})}{\left(\frac{1000\text{g}}{\mathcal{M}_A}\right) + m_B (1\text{kg})} = \frac{0.13721 \text{ m (1kg)}}{\left(\frac{1000\text{g}}{18.0153 \text{ g mol}^{-1}}\right) + 0.13721 \text{ m (1kg)}}$$

$$x_B = 2.466 \times 10^{-3}$$

Don't forget to use all constants to at least the number of significant figures justified by the problem. Then calculate the mole fraction of the solvent by difference, since $x_A + x_B = 1$:

$$x_{\text{H}_2\text{O}} = 1 - 2.466 \times 10^{-3} = 0.9975$$

Notice that the molarity and molality differ only by 0.26% in this problem.

6. Calculate the molality and mole fraction of an 0.851 M aqueous NH_4Cl solution ($\mathcal{M}_B = 53.50 \text{ g mol}^{-1}$). The density of the solution is 1.0140 g mL^{-1} .

Answer: Using Eq. 2.2.7, the molality is:

$$m = \frac{c (1\text{L})}{\left(\frac{1000\text{mL } d_{\text{soln}} - c (1\text{L}) \mathcal{M}_B}{1000\text{g/kg}}\right)} = \frac{0.851 \text{ mol L}^{-1} (1\text{L})}{\frac{1000\text{mL} (1.0140 \text{ g mL}^{-1}) - 0.851 \text{ mol L}^{-1} (1\text{L}) 53.50 \text{ g mol}^{-1}}{1000\text{g/kg}}}$$

$$= 0.879 \text{ m}$$

The molality and molarity differ by 3.3%. The mole fraction is given by Eq. 2.2.14:

$$x_B = \frac{c_B (1\text{L})}{\left(\frac{1000\text{mL } d_{\text{soln}} - c_B (1\text{L}) \mathcal{M}_B}{\mathcal{M}_A}\right) + c_B (1\text{L})}$$

$$= \frac{0.851 \text{ mol L}^{-1} (1\text{L})}{\left(\frac{1000\text{mL } 1.0140 \text{ g mL}^{-1} - 0.851 \text{ mol L}^{-1} (1\text{L}) 53.50 \text{ g mol}^{-1}}{18.02 \text{ g mol}^{-1}}\right) + 0.851 \text{ mol L}^{-1} (1\text{L})}$$

$$x_B = 0.01558 = 0.0156$$

7. The intensity of a 552 nm light beam is decreased to 18.2% of its original intensity on passing through 3.00 cm of a $2.13 \times 10^{-4} \text{ M}$ solution of an absorbing solute. What is the molar absorption coefficient?

Answer: The plan is to first calculate the absorbance of the solution and then use the Beer-Lambert Law. The absorbance is given by Eq. 2.4.8:

$$A = \log \frac{I_0}{I} = \log 1/T = \log \frac{100}{\%T} = \log \frac{100}{18.2} = 0.73993$$

The uncertainty can be easily evaluated by changing the %T to 18.3 and noting the change in the absorbance: $\log(100/18.3) = 0.7375$. The result changed in the third significant figure past the decimal point. So $A = 0.7399$ or just 0.740. Alternatively, you can use significant figure rules for

$\log x$ with $x = 100/18.2 = 5.49$ for three significant figures for x . The resulting $\log x$ should also have three significant figures past the decimal point, that is in the mantissa, $A = 0.734$.

Now using the Beer-Lambert Law, $A = \epsilon \ell c$, Eq. 2.4.7:

$$\epsilon = \frac{A}{\ell c} = \frac{0.7399}{3.00 \text{ cm} (2.13 \times 10^{-4} \text{ M})} = 1157. \text{ mol}^{-1} \text{ L cm}^{-1} = 1.16 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$$

8. Explicitly do the integration of Eq. 2.4.1 to give Eq. 2.4.3.

Answer: Starting with Eq. 2.4.1

$$dJ = -\beta c J(x) dx$$

Separate the variables by dividing both sides of the equation by J :

$$\frac{dJ}{J} = -\beta c dx$$

At $x=0$ $J = J_0$, the incident intensity. Integrating x from 0 to ℓ :

$$\int_{J_0}^J \frac{dJ}{J} = - \int_0^{\ell} \beta c dx$$

The integral on the left is in the form of $\int \frac{dx}{x} = \ln x$ and the constants β and c can factor out in front of the integral on the right:

$$(\ln J) \Big|_{J_0}^J = -\beta c \int_0^{\ell} dx = -\beta c (x) \Big|_0^{\ell}$$

Evaluating at the endpoints of the integral gives:

$$\ln J - \ln J_0 = -\beta c \ell$$

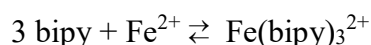
Combining the \ln terms:

$$\ln \frac{J}{J_0} = -\beta \ell c$$

and multiplying by -1 gives:

$$-\ln \frac{J}{J_0} = \ln \frac{J_0}{J} = \beta \ell c$$

9. Bipyridine forms an intense red color when mixed with aqueous solutions of Fe(II):



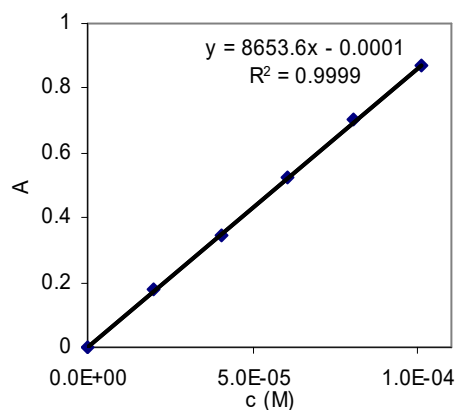
This complex is commonly used for low level spectrophotometric determinations of Fe(II) in natural waters. A standard solution of 5.04×10^{-4} M Fe(II) was added, using volumetric pipettes, to a series of 50.0-mL volumetric flasks and diluted to the mark with excess bipyridine solution according to the following table. The absorbance of the solutions was determined at the wavelength of maximum absorbance, 522 nm, using a cuvette path length of 1.00 cm. (a). What color corresponds to 522 nm? (b). Determine the molar absorption coefficient. (c). A 20.000-mL sample of water from a stream that drains a bog was treated in the same fashion producing an absorbance of 0.271. Calculate the concentration of Fe(II) in the stream.

Fe(II) added, (mL)	2.00	4.00	6.00	8.00	10.00
A	0.176	0.345	0.523	0.702	0.870

Answer: (a). The wavelength of 522 nm is in the green to blue-green region of the spectrum. The important point is the wavelength of maximum absorption is not red.

(b). According to the Beer-Lambert Law, $A = \epsilon \ell c$, Eq. 2.4.7, absorbance is a linear function with slope $\epsilon \ell$ and zero intercept when plotted as A versus c. An Excel spreadsheet was set up and `linest()` used to calculate the molar absorption coefficient from the slope of the plot. A plot of the data with the best fit line is also shown below:

V(total) =	50	mL	
[A] (stand.)=	5.04E-04	M	
V (mL)	c (M)	A	
0	0.00E+00	0	
2	2.02E-05	0.176	
4	4.03E-05	0.345	
6	6.05E-05	0.523	
8	8.06E-05	0.702	
10	1.01E-04	0.87	
slope	8653.628	-0.00014	intercept
±	37.65683	0.002298	±
r ²	0.999924	0.003176	st.dev. Y
F	52809.12	4	df
SSreg	0.532618	4.03E-05	SSresidual



It is always good idea to use the (0,0) data point, assuming the absorbance scale was calibrated properly. The molar absorption coefficient is $8654 \pm 38 \text{ M}^{-1} \text{ cm}^{-1}$. The uncertainty is 0.44%.

(c). The unknown absorbance is 0.271, which when substituted into $A = \epsilon \ell c$ gives:

$$c = 0.271/8654 \text{ M}^{-1} \text{ cm}^{-1}/1.00 \text{ cm} = 3.131 \times 10^{-5} \text{ M}$$

To find the uncertainty in the final result, note that the relative uncertainty in the unknown absorbance is $0.001/0.271 = 0.37\%$. Relative variances add on multiplication and division. Assuming that the intercept is zero with no uncertainty, the total relative uncertainty in the result is then $\sqrt{0.0044^2 + 0.0037^2} = 0.0057$ or 0.57%. The uncertainty in the result is:

$$\begin{aligned} \delta c &= (0.0057)(3.131 \times 10^{-5} \text{ M}) = 0.018 \times 10^{-5} \text{ M, giving:} \\ c &= 0.271/8654 \text{ M}^{-1} \text{ cm}^{-1}/1.00 \text{ cm} = 3.131 \times 10^{-5} \pm 0.018 \times 10^{-5} \text{ M} = 3.13 \times 10^{-5} \text{ M} \end{aligned}$$

Please consult a text on Analytical Chemistry for a more complete discussion on the propagation of errors for calibration problems, such as this. This result is the concentration in the 50-mL volumetric flask. The concentration in the original 20-mL stream sample is:
 $(50 \text{ mL}/20 \text{ mL})(3.131 \times 10^{-5} \pm 0.018 \times 10^{-5} \text{ M}) = 7.828 \times 10^{-5} \pm 0.045 \times 10^{-5} \text{ M}$.

10. What is the absorbance of the column of water that corresponds to $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the depth of the euphotic zone? What absorbance corresponds to the depth of the euphotic zone?

Answer: The euphotic zone corresponds to 99% of the incident light absorbed or a percent transmission of 1%. Using Eq. 2.4.8:

$$A = \log \frac{I_0}{I} = \log 1/T = \log \frac{100}{\%T} = \log \frac{100}{1} = 2.00$$

The other absorbances can be determined using the Beer-Lambert Law, $A = \epsilon l c$, Eq. 2.4.7, and direct proportions assuming the molar absorption coefficient and concentration of absorber are constant with depth:

$$\frac{A_2}{A_1} = \frac{\epsilon l_2 c}{\epsilon l_1 c} = \frac{l_2}{l_1}$$

So at $\frac{1}{4}$ of the depth of the euphotic zone $A = 0.5$, at $\frac{1}{2}$ of the depth of the euphotic zone $A = 1.00$, and at $\frac{3}{4}$ of the full depth $A = 1.5$. These absorbances correspond to %T of 31.6%, 10%, and 3.16%, respectively.

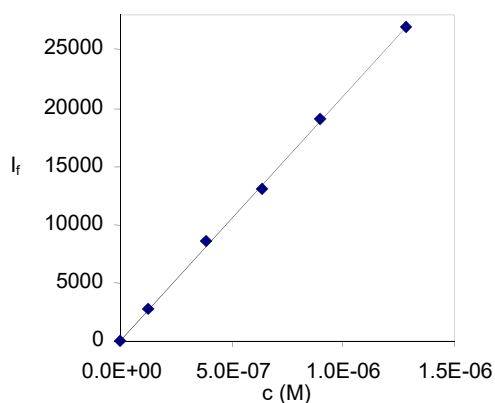
11. The concentration of quinine sulfate in tonic water can easily be determined using fluorescence emission. A series of standard solutions in 0.05 M sulfuric acid was prepared and the fluorescence emission at 470 nm was determined as shown below. The standard stock concentration was $1.00 \times 10^{-3} \text{ g L}^{-1}$ or $1.28 \times 10^{-6} \text{ M}$. The volumes of the quinine stock solution, listed below, were added to 100-mL volumetric flasks and diluted to the mark with 0.05 M sulfuric acid. Fluorescence light fluxes, or intensities, are usually measured in arbitrary units, which could be in millivolts or the unscaled computer digitized output from the detector. The units are immaterial since fluorescence must always be calibrated with standard solutions and then the fluorescence units cancel out. A commercial tonic water sample was diluted 0.5 mL to 100 mL with 0.05 M sulfuric acid and the fluorescence intensity was determined to be 22167 units. Determine the molar concentration of the quinine in the tonic water.

stock added, (mL)	10.00	30.00	50.00	70.00	100.00
fluorescence intensity	2741	8214	13586	18983	27319

Answer: The fluorescence is assumed to be directly proportional to concentration, Section 2.4, $I_f = k c$. A plot of fluorescence intensity, or flux, versus concentration should give a straight line with slope k . An Excel spreadsheet was developed and `linest()` was used to determine the slope

of the curve (essentially the same spreadsheet as for Problem 9). A plot of the data with the best fit line is also shown at right:

V(total) =	100	mL	
[A] (stand.)=	1.28E-06	M	
V (mL)	c (M)	I _f	
0	0.00E+00	0	
10	1.28E-07	2761	
30	3.84E-07	8514	
50	6.40E-07	13086	
70	8.96E-07	18983	
100	1.28E-06	27019	
slope	2.102E+10	69.83178	intercept
±	2.706E+08	191.8388	±
r ²	0.9993371	292.5832	st.dev. Y
F	6030.4259	4	df
SS _{reg}	516234315	342419.8	SS _{residual}



The calibration constant is $k = 2.102 \times 10^{10} \pm 0.027 \times 10^{10}$ M. The unknown intensity is 22167, so solving for the corresponding concentration from $I_f = k c$ gives:

$$c = I_f/k = 22167/2.102 \times 10^{10} = 1.055 \times 10^{-6} \text{ M}$$

To find the uncertainty, note that relative variances add on multiplication and division. The relative uncertainty in k is 1.3%. We can use the standard deviation of the Y values from the curve fit as a measure of the uncertainty of the fluorescence intensities, which gives a relative uncertainty of the unknown intensity as $293/22167 = 1.3\%$. The relative uncertainty in the result is then $\sqrt{0.013^2 + 0.013^2} = \sqrt{2} \cdot 0.013 = 0.018$, which gives the final result as $1.055 \times 10^{-6} \pm 0.019 \times 10^{-6}$ M.

12. Photovoltaic cells convert sunlight into electrical energy. The units often used for the electrical energy are kW hours, or kWh. Calculate the conversion factor from kWh to joules.

Answer: Given that 1 Watt = 1 J s⁻¹ then:

$$1 \text{ kWh} = 1000 \text{ J s}^{-1} (1 \text{ hr}) (3600 \text{ s/1 hr}) = 3.6 \times 10^6 \text{ J}$$

13. The peak sun solar flux that reaches a surface pointed directly at the sun is about 1000 W m^{-2} . The solar insolation is the total amount of solar energy for a given location for a specific time. The solar insolation is the average incident energy for a specific time that takes into account the tilt of the sun during the day and the effects of clouds. Calculate the factor for the conversion of the peak sun flux of 1000 W m^{-2} to the yearly average flux for Phoenix ($6.08 \text{ kWh m}^{-2} \text{ day}^{-1}$), Seattle ($3.69 \text{ kWh m}^{-2} \text{ day}^{-1}$), Boston ($4.16 \text{ kWh m}^{-2} \text{ day}^{-1}$), and Miami ($5.45 \text{ kWh m}^{-2} \text{ day}^{-1}$). (The yearly average insolation for the United States is given in color plate 1 at the end of this section, from data from the National Renewable Resource Laboratory, NREL, <http://www.nrel.gov/gis/solar.html>).

Answer: The tabulated yearly average value for Phoenix from NREL is $6.08 \text{ kWh m}^{-2} \text{ day}^{-1}$. First convert the insolation into the equivalent averaged flux.

$$J = 6.08 \text{ kWh m}^{-2} \text{ day}^{-1} (3.6 \times 10^6 \text{ J/1 kWh}) (1 \text{ day}/24 \text{ hr}) (1 \text{ hr}/3600 \text{ s}) = 253.33 \text{ J m}^{-2} \text{ s}^{-1}$$

Remember that $1 \text{ J s}^{-1} = 1 \text{ W}$ so $J = 253 \text{ W m}^{-2}$. We want to find the factor, k , for the conversion:

$$k = \text{averaged flux/peak sun flux} = 253.3 \text{ W m}^{-2}/1000 \text{ W m}^{-2} = 0.253 \text{ or } 25.3\%$$

Let's check this result. The solar insolation should be given by

$$\begin{aligned} \text{solar insolation} &= k (\text{peak sun flux}) (24 \text{ hr}/1 \text{ day}) \\ &= 0.25333 (1 \text{ kW m}^{-2}) (24 \text{ hr}/1 \text{ day}) = 6.08 \text{ kWh m}^{-2} \text{ day}^{-1} \end{aligned}$$

The values for the other cities are given in the table below:

City	flux (W m^{-2})	k	Insolation ($\text{kWh m}^{-2} \text{ day}^{-1}$)
Phoenix	253	25.3%	6.08
Miami	227	22.7%	5.45
Boston	173	17.3%	4.16
Seattle	154	15.4%	3.69

14. A photovoltaic panel can convert about 17-23% of the light flux into electrical power. The conversion of the DC power from a solar panel to AC power that can be used to power appliances or to feed into the power grid is about 77% efficient. Use the solar insolation values listed in Problem 13. (a) Calculate the AC power available per square meter per day from photovoltaic cells operating at 23% efficiency in each of the four cities listed in the previous problem. (b) A typical refrigerator requires 450 kWh hours of energy per year. Calculate the photovoltaic panel area needed to provide all the energy for this refrigerator.

Answer: The tabulated yearly average value for Phoenix from NREL is $6.08 \text{ kWh m}^{-2} \text{ day}^{-1}$. First convert the insolation into the equivalent averaged flux:

$$J = 6.08 \text{ kWh m}^{-2} \text{ day}^{-1} (3.6 \times 10^6 \text{ J/1 kWh}) (1 \text{ day}/24 \text{ hr}) (1 \text{ hr}/3600 \text{ s}) = 253.33 \text{ J m}^{-2} \text{ s}^{-1}$$

Remember that $1 \text{ J s}^{-1} = 1 \text{ W}$ so $J = 253 \text{ W m}^{-2}$. The AC power from a 23% efficient solar photovoltaic cell is:

$$\text{AC power} = (253 \text{ W m}^{-2})(0.23)(0.77) = 44.87 \text{ W m}^{-2}.$$

and in kWh per year:

$$\text{AC energy} = 44.87 \text{ W} (365 \text{ day}/1 \text{ yr})(24 \text{ hr}/1 \text{ day}) = 393 \text{ kWh m}^{-2} \text{ yr}^{-1}$$

The refrigerator requires 450 kWh yr^{-1} . The panel area necessary is:

$$\text{panel area} = (450 \text{ kWh yr}^{-1}) / 393 \text{ kWh m}^{-2} \text{ yr}^{-1} = 1.15 \text{ m}^2$$

The values for the other cities are given in the table below:

City	flux (W m ⁻²)	Insolation (kWh m ⁻² day ⁻¹)	AC power (W m ⁻²)	AC energy (kWh m ⁻² yr ⁻¹)	Collector area (m ²)
Phoenix	253	6.08	44.9	393	1.15
Miami	227	5.45	40.2	352	1.28
Boston	173	4.16	30.7	269	1.67
Seattle	154	3.69	27.2	239	1.89

This calculation is optimistic, because most current commodity photovoltaics have an efficiency closer to 19%. This calculation also doesn't have any inefficiency added for energy storage. Battery storage is 80-90% efficient. So in Boston with 19% efficiency and battery storage, the roof area to be energy neutral for a refrigerator is in the range of 2.25-2.5 m². This refrigerator power corresponds to an averaged 51 W. So the roof areas listed in the table would also be needed for roughly 15 "100 watt-equivalent" LED light bulbs (10 W), assuming they are on a third of the time.

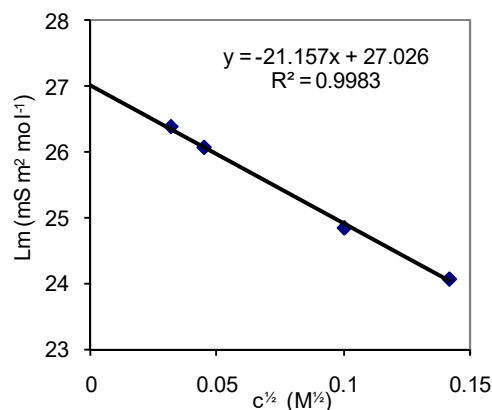
15. Calculate the value for the limiting molar conductivity, Λ_m° , for CaCl₂ from the following data, taken at 25°C.

c (M)	1.00x10 ⁻³	2.00x10 ⁻³	10.00x10 ⁻³	0.100
Λ_m (mS m ² mol ⁻¹)	26.386	26.072	24.850	24.072

Answer: From Eq. 2.4.14, $\Lambda_m = \Lambda_m^\circ - \mathcal{K}c^{1/2}$, we need to plot the molar conductivity as a function of the square root of the concentration. The y-intercept is then the value of Λ_m° . The following spreadsheet and plot were constructed and `linest()` was used to find the intercept:

c (M)	c ^{1/2} (M ^{1/2})	Λ_m (mS m ² mol ⁻¹)
1.00E-03	0.031623	26.386
2.00E-03	0.044721	26.072
1.00E-02	0.1	24.85
0.02	0.141421	24.072

slope	-21.1568	27.02572	intercept
±	0.621326	0.056435	±
r ²	0.998278	0.05472	st.dev. Y
F	1159.469	2	df
SSreg	3.471775	0.005989	SSresidual



The intercept gives $\Lambda_m^\circ(\text{CaCl}_2) = 27.02 \pm 0.06 \text{ mS m}^2 \text{ mol}^{-1}$.

16. Conductivity electrodes are calibrated using standard KCl solutions. The conductivity of 0.001000 M KCl is 0.14695 S m⁻¹. Many meters and texts list conductivities in mS m⁻¹, S cm⁻¹, mS cm⁻¹, and $\mu\text{S cm}^{-1}$. Find the conductivity of 0.001000 M KCl in these additional units.

Answer: $\kappa = 0.14695 \text{ S m}^{-1} (1000 \text{ mS/1S}) = 146.95 \text{ mS m}^{-1}$
 $\kappa = 0.14695 \text{ S m}^{-1} (1 \text{ m/100 cm}) = 0.0014695 \text{ S cm}^{-1}$
 $\kappa = 0.14695 \text{ S m}^{-1} (1 \text{ m/100 cm})(1000 \text{ mS/1S}) = 1.4695 \text{ mS cm}^{-1}$
 $\kappa = 0.14695 \text{ S m}^{-1} (1 \text{ m/100 cm})(1 \times 10^6 \text{ }\mu\text{S/1S}) = 1469.5 \text{ }\mu\text{S cm}^{-1}$

17. Conductivity electrodes are calibrated using standard KCl solutions. The conductivity of 0.01000 M KCl is 0.14127 S m⁻¹ or 1412.7 $\mu\text{S cm}^{-1}$. The resistance of a conductance cell containing 0.0100 M KCl is 552.2 ohm at 25°C. The resistance of the same cell when filled with a solution containing 2.380 g of MgCl₂ per liter is 151.0 ohm. (a). Calculate the cell constant, which is defined as (ℓ/A), where ℓ is the distance between the electrodes and A is the cross-sectional area of the electrodes. (b). Calculate the conductivity of the MgCl₂ solution. (c). Calculate the molar conductivity in mS m² mol⁻¹, S cm² mol⁻¹, and $\mu\text{S cm}^{-1} \text{ mol}^{-1}$.

Answer: (a). Using Eq. 2.4.11: $\kappa = \frac{1}{R} \left(\frac{\ell}{A} \right)$

Solving for (ℓ/A) gives:

$$= R \kappa = 552.2 \text{ ohm} (0.14127 \text{ S m}^{-1}) = 78.009 \text{ m}^{-1}$$

or $\left(\frac{\ell}{A} \right) = R \kappa = 552.2 \text{ ohm} (1412.7 \text{ }\mu\text{S cm}^{-1}) (1 \times 10^{-6} \text{ ohm}^{-1}/1 \text{ }\mu\text{S}) = 0.78009 \text{ cm}^{-1}$

(b). The conductivity of the MgCl₂ solution is:

$$\kappa = \frac{1}{R} \left(\frac{\ell}{A} \right) = \frac{1}{151.0 \text{ ohms}} 78.009 \text{ m}^{-1} = 0.5166 \text{ S m}^{-1}$$

or $\kappa = \frac{1}{R} \left(\frac{\ell}{A} \right) = \frac{1}{151.0 \text{ ohms}} 0.78009 \text{ cm}^{-1} = 5.166 \times 10^{-3} \text{ S cm}^{-1} = 5166. \text{ }\mu\text{S cm}^{-1}$

(c). The concentration of the MgCl₂ solution is:

$$\begin{aligned} c &= 2.380/95.21 \text{ g mol}^{-1}/1 \text{ L} = 0.02500 \text{ mol L}^{-1} \\ &= 2.380/95.21 \text{ g mol}^{-1}/1 \text{ L} (1000 \text{ L/1m}^3) = 25.00 \text{ mol m}^{-3} \\ &= 2.380/95.21 \text{ g mol}^{-1}/1 \text{ L} (1 \text{ L/1000 cm}^3) = 2.500 \times 10^{-5} \text{ mol cm}^{-3} \end{aligned}$$

The molar conductivity is then defined by Eq. 2.4.12

$$\Lambda_m = \frac{\kappa}{c} = \frac{0.5166 \text{ S m}^{-1}}{25.00 \text{ mol m}^{-3}} = 0.02066 \text{ S m}^2 \text{ mol}^{-1} = 20.66 \text{ mS m}^2 \text{ mol}^{-1}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{5166. \text{ }\mu\text{S cm}^{-1}}{2.500 \times 10^{-5} \text{ mol cm}^{-3}} = 2.066 \times 10^8 \text{ }\mu\text{S cm}^2 \text{ mol}^{-1}$$

Another common set of units for molar conductivity are S cm² mol⁻¹:

$$\Lambda_m = 0.02066 \text{ S m}^2 \text{ mol}^{-1} (100 \text{ cm/1m})^2 = 206.6 \text{ S cm}^2 \text{ mol}^{-1}$$

18. Ammonia is a weak electrolyte and weak base: $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. The fraction of NH₄OH is always small in aqueous solution, so the limiting molar conductivity cannot be

measured directly. However, NH_4Cl , NaCl , and NaOH are all strong electrolytes. Given $\Lambda_m^\circ(\text{NH}_4\text{Cl}) = 14.97 \text{ mS m}^2\text{mol}^{-1}$, $\Lambda_m^\circ(\text{NaCl}) = 12.64 \text{ mS m}^2\text{mol}^{-1}$, and $\Lambda_m^\circ(\text{NaOH}) = 24.80 \text{ mS m}^2\text{mol}^{-1}$, calculate the limiting molar conductivity of NH_4OH .

Answer: At infinite dilution the conductivity of ions is independent, because negligible forces act between the ions. Then $\Lambda_m^\circ(\text{NH}_4\text{OH}) = \Lambda_m^\circ(\text{NH}_4\text{Cl}) - \Lambda_m^\circ(\text{NaCl}) + \Lambda_m^\circ(\text{NaOH})$:

$$\Lambda_m^\circ(\text{NH}_4\text{OH}) = 14.97 - 12.64 + 24.80 \text{ mS m}^2\text{mol}^{-1} = 27.13 \text{ mS m}^2\text{mol}^{-1}$$

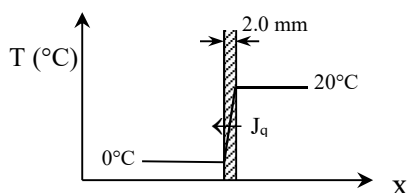
19. Thermal conductivity can be expressed as a linear flux-force relationship:

$$J_q = -\kappa \frac{dT}{dx}$$

where κ is the thermal conductivity and dT/dx is the temperature gradient. The units of the thermal flux are $\text{J m}^{-2} \text{ s}^{-1}$ giving the units of κ as $\text{J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$. Some manufactures sell thermopane windows with argon as the fill gas between the panes. Calculate the thermal flux with air and with argon as the fill gas in a thermopane window with a spacing of 2.00 mm between the panes of glass. Assume the outside air temperature is 0.0°C and the inside is 20.0°C . The thermal conductivity of air is 0.0252 and argon is $0.0233 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$ at 15°C and 1 atm. Assume a linear temperature gradient.

Answer: Note that for temperature differences, a $^\circ\text{C}$ is the same as a degree K. Analogously to Eq. 2.3.4 for a linear temperature gradient:

$$\frac{dT}{dx} = \frac{(T' - T)}{\delta}$$



For air:

$$J_q = -\kappa \frac{dT}{dx} = -0.0252 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1} (20.0 - 0.0^\circ\text{C}) / 2.00 \text{ mm} (1000 \text{ mm}/1 \text{ m})$$

$$= -252 \text{ J m}^{-2} \text{ s}^{-1} \quad \text{the flux direction is } \leftarrow \text{ (hotter to colder)}$$

For argon:

$$J_q = -\kappa \frac{dT}{dx} = -0.0233 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1} (20.0 - 0.0^\circ\text{C}) / 2.00 \text{ mm} (1000 \text{ mm}/1 \text{ m})$$

$$= -233 \text{ J m}^{-2} \text{ s}^{-1}$$

The difference is about 7.5%.

20. Thermal conductivity can be expressed as a linear flux-force relationship:

$$J_q = -\kappa \frac{dT}{dx}$$

where κ is the thermal conductivity and dT/dx is the temperature gradient. The units of the thermal flux are $\text{J m}^{-2} \text{s}^{-1}$ giving the units of κ as $\text{J m}^{-1} \text{K}^{-1} \text{s}^{-1}$. Why are stainless steel cooking pans often sold with a thin copper cladding on the bottom? The thermal conductivity of aluminum is 250, copper is 401, and stainless steel is $16 \text{ J m}^{-1} \text{K}^{-1} \text{s}^{-1}$ at 25°C .

Answer: Note that for temperature differences, a $^\circ\text{C}$ is the same as a degree K. Analogously to Eq. 2.3.4 for a linear temperature gradient:

$$\frac{dT}{dx} = \frac{(T' - T)}{\delta}$$

For the same temperature gradient, a substance with a higher thermal conductivity will conduct more energy in a given amount of time. The chemical resistance of stainless steel is much better than copper and aluminum, but the thermal conductivity is poor. The copper cladding distributes the heat more evenly from the cooking surface. Even heat distribution helps to minimize food sticking and carbonizing on the bottom of the pot. Copper is more expensive than aluminum.

21. Often in practical applications of membrane diffusion the membrane thickness is not known. When the membrane thickness is not known, the flux across the membrane from Eqs. 2.3.3 and 2.3.4 is written as:

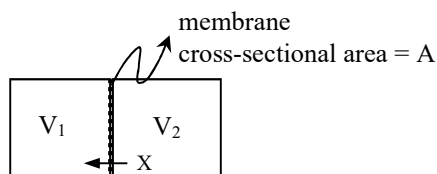
$$J_m = -D \frac{(c' - c)}{\delta} = -P (c' - c)$$

where the permeability, P , is defined as $P = D/\delta$, and δ is the thickness of the membrane. A linear concentration gradient through the membrane is assumed. The permeability of a cellulose-based dialysis membrane was found to be $6.3 \times 10^{-4} \text{ m s}^{-1}$ for KCl. Calculate the initial flux of KCl through the membrane if one side of the membrane is a well-stirred solution of 0.100 M KCl and the other side is distilled water.

Answer: Using $J_m = -P (c' - c) = -6.3 \times 10^{-4} \text{ m s}^{-1} (0 - 0.100 \text{ mol L}^{-1})(1000 \text{ L/1 m}^3)$
 $= 0.063 \text{ mol m}^{-2} \text{ s}^{-1}$

The flux will decrease as the two solutions approach the same concentration, so this value is only for short times.

22. Assume two well-mixed compartments with volumes V_1 and V_2 are separated by a membrane. Substance X diffuses through the membrane, which has cross-sectional area A :



(a). Prove for diffusion of substance X across a membrane that the rate of concentration change in compartment 1 is given by:

$$\frac{d[X]}{dt} = \frac{dc_X}{dt} = J_m (A/V_1)$$

(b). Using the data in the last problem calculate the initial rate for the concentration change for compartment 1 assuming a 3.00 cm diameter circular membrane and $V_1 = 50.0$ mL.

Answer: (a). The flux is the amount per unit time per unit area. Starting with Eq. 2.3.1:

$$\frac{dn_X}{dt} = J_m A$$

gives the change in moles of X flowing into compartment 1 per unit time. The change in concentration is then just the change in moles from the last equation divided by the volume for compartment 1:

$$\frac{d[X]}{dt} = \frac{dc_X}{dt} = \frac{1}{V_1} \frac{dn_X}{dt} = J_m \left(\frac{A}{V_1} \right)$$

(b). The cross-sectional area of the membrane is $A = \pi r^2 = 7.07 \times 10^{-4} \text{ m}^2$. The volume should be converted to liters, since we normally express rates in mol L^{-1} . From the last problem, $J_m = 0.063 \text{ mol m}^{-2} \text{ s}^{-1}$ giving the rate as:

$$\frac{d[X]}{dt} = J_m \left(\frac{A}{V_1} \right) = 0.063 \text{ mol m}^{-2} \text{ s}^{-1} \left(\frac{7.07 \times 10^{-4} \text{ m}^2}{0.050 \text{ L}} \right) = 8.91 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

The rate will decrease as the two solutions approach the same concentration, so this value is only for short times. However, to check the order of magnitude of the result to see if it is reasonable, if the flux were constant after 112 s the concentration would increase to 0.10 M.

23. A constant volume flow reactor is used to convert used vegetable oil to biodiesel fuel. The input stream contained vegetable oil, 1% KOH and 20% methanol. The yield of biodiesel for a constant flow at 50°C was 73.0% and the yield when the reactor was run at 65°C was 92.1%. Assume a constant flow. (a). Show that the ratio of the reaction yields under two different conditions is equal to the ratio of the product fluxes out of the reactor. Assume the flow cross-sectional area for the input and output are the same. (b). Show that the ratio of the reaction yields is equal to the ratio of the average chemical reaction rates under the two different conditions. [Hint: the average reaction rate for the formation of product over the time interval Δt is given by $\bar{v} = \Delta[P]/\Delta t$, where $\Delta[P]$ is the change in product concentration.]

Answer: (a). The yield for a reaction is given by:

$$y = \frac{\text{moles product}}{\text{moles reactant}} \quad 1$$

Using Eq. 2.3.2, the amount can be related to the flux into and out of the reactor. Assume the input cross-sectional area is A_{in} and for the output A_{out} . The yield for a time in the reactor of Δt is given by:

$$y = \frac{\text{moles product}}{\text{moles reactant}} = \frac{n_P}{n_R} = \frac{J_{mP} A_{out} \Delta t}{J_{mR} A_{in} \Delta t} \quad 2$$

where J_{mR} and J_{mP} are the fluxes for the reactant into the reactor and the product out of the reactor, respectively. If the cross-sectional area of the input and output to the flow reactor are equal then $y = J_{mP}/J_{mR}$ for a given experiment. For two different experiments with the same input, the ratio is given by:

$$y_1 = (J_{mP1}/J_{mR}) \quad y_2 = (J_{mP2}/J_{mR}) \quad \text{and} \quad \frac{y_2}{y_1} = \frac{J_{mP2}}{J_{mP1}} \quad 3$$

which is just the ratio of the output product fluxes.

(b). Assuming a constant average reaction rate over the time in the reactor, \bar{v} , the amount of product formed is given by:

$$\bar{v} = \frac{\Delta[P]}{\Delta t} \quad \text{or} \quad \Delta[P] = \bar{v} \Delta t \quad 4$$

Note that $n_P = \Delta[P]V$, where V is the total volume flowing through the reactor in time Δt . Substitution of this last result with Eq. 4 into Eq. 2 gives for a given experiment:

$$y = \frac{n_P}{n_R} = \frac{\bar{v} V \Delta t}{n_R} \quad 5$$

For two different experiments the ratio is given by:

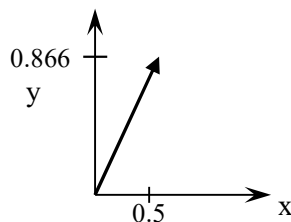
$$y_1 = \frac{\bar{v}_1 V \Delta t}{n_R} \quad y_2 = \frac{\bar{v}_2 V \Delta t}{n_R} \quad \text{and} \quad \frac{y_2}{y_1} = \frac{\bar{v}_2}{\bar{v}_1} \quad 6$$

The ratio of the average reaction rates over the fixed time interval is given by the ratio of the yields in a constant volume flow reactor.

24. By drawing vectors in an x-y coordinate plot, show that matrix multiplication: $\underline{\underline{a}} = \underline{\underline{M}} \underline{\underline{b}}$ with the matrix:

$$\underline{\underline{M}} = \begin{pmatrix} \sqrt{3}/2 & -1/2 \\ 1/2 & \sqrt{3}/2 \end{pmatrix}$$

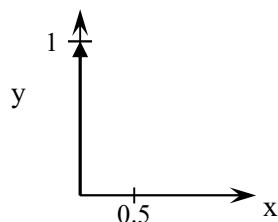
corresponds to a rotation of the vector by 30° around the z-axis. Use $\underline{\underline{b}} = \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix}$, which is diagrammed at right:



Answer:

$$\underline{\underline{a}} = \underline{\underline{M}} \underline{\underline{b}} = \begin{pmatrix} \sqrt{3}/2 & -1/2 \\ 1/2 & \sqrt{3}/2 \end{pmatrix} \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix} = \begin{pmatrix} \sqrt{3}/4 - \sqrt{3}/4 \\ 1/4 + 3/4 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

which lies along the y-axis:



To verify the angle we can remember from your General Physics course that the dot product is related to the angle between the vectors, $\underline{\underline{u}} \cdot \underline{\underline{v}} = |\underline{\underline{u}}| |\underline{\underline{v}}| \cos \theta$. Both $\underline{\underline{a}}$ and $\underline{\underline{b}}$ are unit length; that is, $|\underline{\underline{a}}| = |\underline{\underline{b}}| = 1$, giving:

$$\cos \theta = \frac{\underline{\underline{a}} \cdot \underline{\underline{b}}}{|\underline{\underline{a}}| |\underline{\underline{b}}|} = (1/2(0) + \sqrt{3}/2(1)) = \sqrt{3}/2 = 0.866 \quad \text{or} \quad \theta = 30^\circ$$

25. How are 3D computer graphics done? Many of the operations in computer games and molecular graphics correspond to rotation about the axis perpendicular to the computer screen. We showed in the last problem that matrix multiplication can generate such rotations. Show that the matrix:

$$\underline{\underline{R}}_z(\theta) = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$$

generates a rotation around the z-axis of θ degrees, by showing that $\underline{\underline{R}}_z(30^\circ)$ gives the matrix in the last problem.

$$\text{Answer: } \underline{\underline{R}}_z(30^\circ) = \begin{pmatrix} \cos 30^\circ & -\sin 30^\circ \\ \sin 30^\circ & \cos 30^\circ \end{pmatrix} = \begin{pmatrix} \sqrt{3}/2 & -1/2 \\ 1/2 & \sqrt{3}/2 \end{pmatrix}$$

26. In computer graphics, the apparent distance between the observer and the object on the screen is determined by scaling the object. Show that the diagonal matrix:

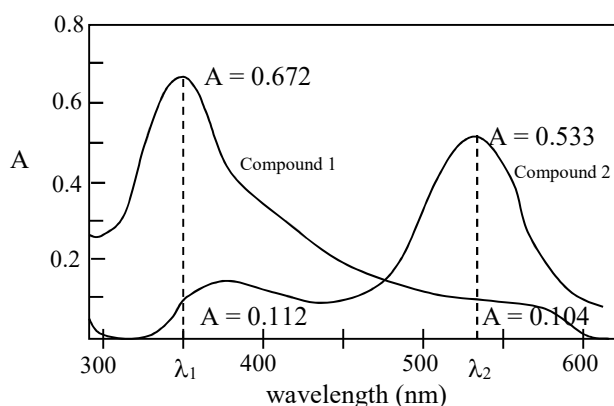
$$\underline{\underline{M}} = \begin{pmatrix} n & 0 \\ 0 & n \end{pmatrix} \quad \text{with} \quad \underline{\underline{a}} = \underline{\underline{M}} \underline{\underline{b}}$$

changes the length of the vector \underline{b} but not the direction. Use $\underline{b} = \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix}$, which is diagrammed in Problem 24.

Answer: $\underline{a} = \underline{M} \underline{b} = \begin{pmatrix} n & 0 \\ 0 & n \end{pmatrix} \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix} = \begin{pmatrix} n(1/2) \\ n(\sqrt{3}/2) \end{pmatrix}$ which is in the same direction but is longer if $n > 1$ and shorter if $n < 1$. To verify the angle we can remember from your General Physics course that $\underline{u} \cdot \underline{v} = |\underline{u}| |\underline{v}| \cos \theta$. Note that $|\underline{a}| = \sqrt{n^2(1/2)^2 + n^2(\sqrt{3}/2)^2} = n$ and \underline{b} is unit length; that is, $|\underline{b}| = 1$. The angle is given by:

$$\cos \theta = \frac{\underline{a} \cdot \underline{b}}{|\underline{a}| |\underline{b}|} = \frac{n(1/2)(1/2) + \sqrt{3}/2(n\sqrt{3}/2)}{n} = 1 \quad \text{or} \quad \theta = 0^\circ$$

27. The UV-visible absorption spectra of two compounds is shown below. The concentration of each is 5.00×10^{-5} M. The absorbances at the two chosen analytical wavelengths, λ_1 and λ_2 are listed.



The path length of the cuvette is 1.00 cm. An unknown mixture has an absorbance of 0.419 at λ_1 and an absorbance of 0.546 at λ_2 . (a). Determine, without calculations, the component with the larger concentration. (b). Calculate the concentrations of the two compounds.

Answer: (a). The absorbance at the second wavelength for the unknown is bigger than at the first. As a pure substance, compound 2 has the bigger absorbance at wavelength 2. This shows that component 2 is in higher concentration than component 1 in the unknown.

(b). The plan is to first find $\epsilon \ell$ for each compound at each wavelength. Then invert the matrix in Excel to do the matrix multiplication based on the Beer-Lambert Law, Eq. 2.6.8.

Using the Beer-Lambert Law, $A = \epsilon \ell c$, Eq. 2.4.7 gives $\epsilon \ell = A/c$:

$$\begin{array}{cc}
 \text{compound 1} & \text{compound 2} \\
 \downarrow & \downarrow \\
 (\underline{\epsilon \ell}) = \begin{pmatrix} 13440 & 2240 \\ 2080 & 10660 \end{pmatrix} & \begin{array}{l} \leftarrow \lambda_1 \\ \leftarrow \lambda_2 \end{array}
 \end{array}$$

Excel was then used to invert the matrix and do the multiplication, as in Figure 2.8.2:

		compound 1	compound 2						
	$\epsilon l =$			$(\epsilon l)^{-1}$		*	A	=	c
wavelength 1		13440	2240	7.6906E-05	-1.6160E-05		0.419		2.340E-05
wavelength 2		2080	10660	-1.5006E-05	9.6962E-05		0.546		4.665E-05

One difficulty with simultaneous concentration determinations is that the uncertainties are a bit harder to determine. Since we are using Excel, we can use the trick of changing an absorbance by ± 1 in the last significant figure and recalculating to see how the final results change. For example, changing 0.419 to 0.420 changes the results to $(2.348 \times 10^{-5}$ and $4.664 \times 10^{-5} \text{M})$. In other words the results change roughly in the third significant figure. Of course, there are uncertainties in every measurement, which compound to increase the uncertainty in the result. But at least the results are certainly not known to better than three significant figures. Changing a few values simultaneously at random will give an even better estimate of the overall uncertainty. Using three significant figures, the final results are $c_1 = 2.34 \times 10^{-5} \text{M}$ and $c_2 = 4.67 \times 10^{-5} \text{M}$.

28. Show that $\underline{\underline{A}}(\underline{\underline{B}} + \underline{\underline{C}}) = \underline{\underline{A}}\underline{\underline{B}} + \underline{\underline{A}}\underline{\underline{C}}$ explicitly using $\underline{\underline{A}} = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$, $\underline{\underline{B}} = \begin{pmatrix} e & f \\ g & h \end{pmatrix}$, and $\underline{\underline{C}} = \begin{pmatrix} i & j \\ k & l \end{pmatrix}$

Answer: The plan is to work on the left-hand side and then the right-hand side and compare to see if the results from both sides are equal. For the left-hand side:

$$\underline{\underline{A}}(\underline{\underline{B}} + \underline{\underline{C}}) = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \left[\begin{pmatrix} e & f \\ g & h \end{pmatrix} + \begin{pmatrix} i & j \\ k & l \end{pmatrix} \right] = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} e+i & f+j \\ g+k & h+l \end{pmatrix} = \begin{pmatrix} a(e+i)+b(g+k) & a(f+j)+b(h+l) \\ c(e+i)+d(g+k) & c(f+j)+d(h+l) \end{pmatrix}$$

For the right-hand side:

$$\begin{aligned} \underline{\underline{A}}\underline{\underline{B}} + \underline{\underline{A}}\underline{\underline{C}} &= \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} e & f \\ g & h \end{pmatrix} + \begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} i & j \\ k & l \end{pmatrix} = \begin{pmatrix} ae+bg & af+bh \\ ce+dg & cf+dh \end{pmatrix} + \begin{pmatrix} ai+bk & aj+bl \\ ci+dk & cj+dl \end{pmatrix} \\ &= \begin{pmatrix} ae+bg+ai+bk & af+bh+aj+bl \\ ce+dg+ci+dk & cf+dh+cj+dl \end{pmatrix} = \begin{pmatrix} a(e+i)+b(g+k) & a(f+j)+b(h+l) \\ c(e+i)+d(g+k) & c(f+j)+d(h+l) \end{pmatrix} \end{aligned}$$

The left-hand and right-hand sides agree. Matrices are distributive.

29. Find the determinant of the following matrix:

$$\underline{\underline{M}} = \begin{pmatrix} 2 & 0 & 1 \\ 3 & 5 & 0 \\ 0 & 1 & 4 \end{pmatrix}$$

Answer: We can expand across any row or down any column. Expanding down the first column, we need the first and second minors:

$$\underline{\underline{M}} = \begin{pmatrix} 2 & 0 & 1 \\ 3 & 5 & 0 \\ 0 & 1 & 4 \end{pmatrix} \quad \text{and} \quad \underline{\underline{M}} = \begin{pmatrix} 2 & 0 & 1 \\ 3 & 5 & 0 \\ 0 & 1 & 4 \end{pmatrix}$$

We need to take into account the signs of the associated minors: $\begin{pmatrix} + & - & + \\ - & + & - \\ + & - & + \end{pmatrix}$

Expanding in terms of the minors gives: $|M| = 2 \begin{vmatrix} 5 & 0 \\ 1 & 4 \end{vmatrix} - 3 \begin{vmatrix} 0 & 1 \\ 1 & 4 \end{vmatrix}$

The determinants of the 2x2 minors are:

$$\begin{vmatrix} 5 & 0 \\ 1 & 4 \end{vmatrix} = 5(4) - 1(0) = 20 \quad \text{and} \quad \begin{vmatrix} 0 & 1 \\ 1 & 4 \end{vmatrix} = 0(4) - 1(1) = -1$$

giving the final determinant: $|M| = 2(20) - 3(-1) = 43$.

30. Find the determinant of the following matrix (which we will use in Chapter 6):

$$\underline{\underline{M}} = \begin{pmatrix} -k_1 - \lambda_i & 0 & 0 \\ k_1 & -k_1' - \lambda_i & 0 \\ 0 & k_1' & -\lambda_i \end{pmatrix}$$

Answer: We can expand across any row or down any column. Expanding across the first row, we only need the first minor, since the second and third elements across the row are zero.

Striking out the first row and column:

$$\underline{\underline{M}} = \begin{pmatrix} -k_1 - \lambda_i & 0 & 0 \\ k_1 & -k_1' - \lambda_i & 0 \\ 0 & k_1' & -\lambda_i \end{pmatrix}$$

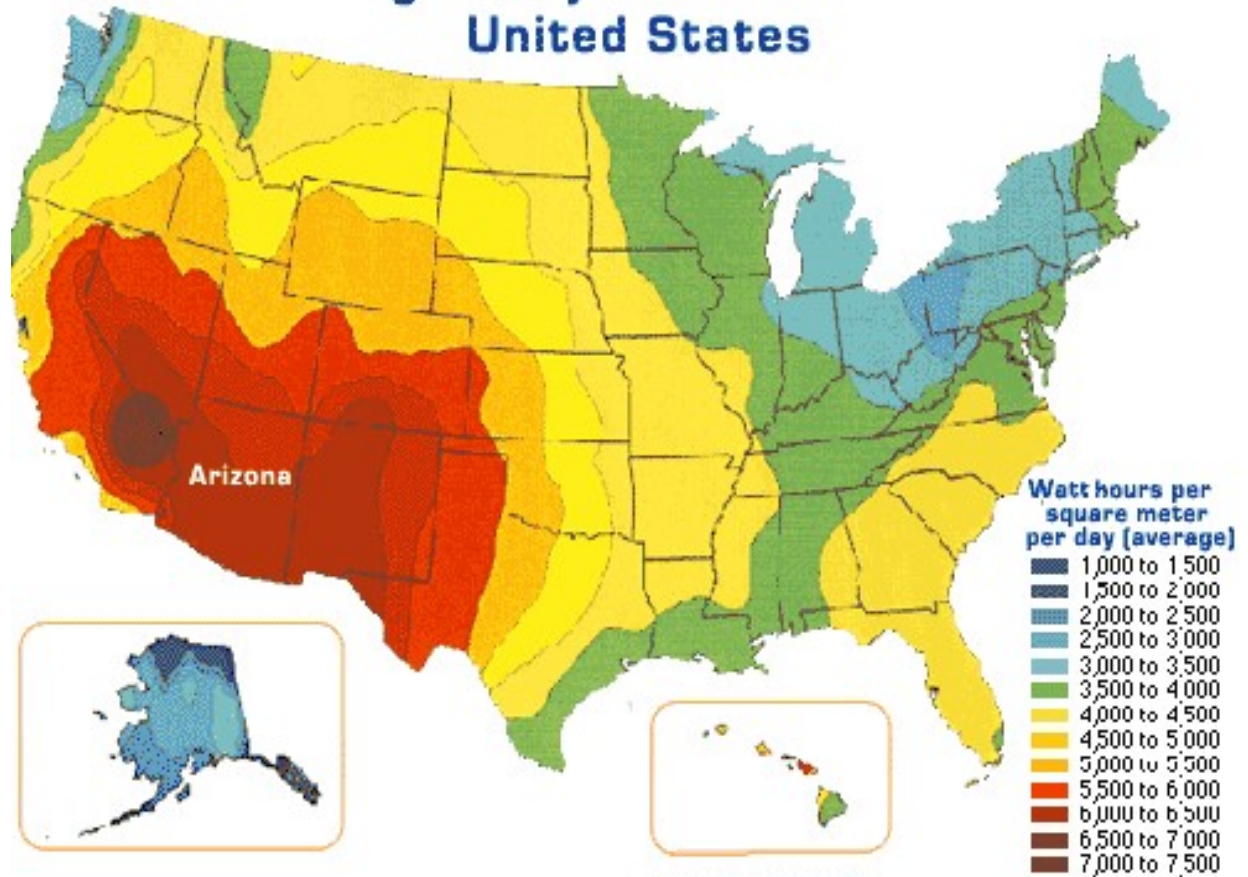
and then the first minor gives:

$$\begin{vmatrix} -k_1' - \lambda_i & 0 \\ k_1' & -\lambda_i \end{vmatrix} = (-k_1' - \lambda_i)(-\lambda_i)$$

Overall, then the determinant is:

$$|M| = (-k_1 - \lambda_i)(-k_1' - \lambda_i)(-\lambda_i)$$

Average Daily Solar Insolation: United States



Color Plate1: Average Daily Solar Insolation. The solar insolation is the average daily energy falling on a surface parallel to the ground per day averaged over the year. (Map source: http://projectsol.aps.com/solar/data_insolation.asp)(See also: <http://www.nrel.gov/gis/solar.html>)