Chapter 2: Concentrations and Partial Pressures

> The euphotic zone is the layer in a natural body of water that can support photosynthesis. The euphotic zone extends to the depth that corresponds to 1% of the light flux incident on the surface. Colored dissolved organic matter, CDOM, is one component in the water column that limits the penetration of light in lakes and rivers. A typical component of CDOM has a molar absorption coefficient of 1.8×10^7 M^{-1} cm^{-1} and a concentration of 2.7×10^{-10} M. Calculate the depth of the euphotic zone for this concentration.

Before we begin our study of kinetics and chemical equilibrium, we need to discuss how concentrations and partial pressures are measured. In the last chapter we learned that the state of a system is defined by V, P, T, S, and the amounts of each substance. The amounts of substances can alternatively be specified using moles, concentrations, or partial pressures. The measurement of concentration is central to all aspects of chemistry. To study chemical reactivity we need to monitor changes in concentration during an experiment. Concentrations can be expressed in different ways. We start with gases and then discuss solutions. Hopefully, you are already quite familiar with most of this material on concentration measures from your General Chemistry course, and only a quick review is necessary.

   We also consider systems with non-uniform concentrations, where molecular diffusion transports molecules from regions of high concentration to regions of low concentration. Molecular diffusion is an example of a generalized flux-force relationship.

2.1 Gas Phase Concentrations and Partial Pressures

Dalton's Law of Partial Pressures states that the partial pressure of a gas, P_i, is the pressure the gas would exert if it were alone in the flask:

$$P_i V = n_i RT \qquad \text{(ideal gas)} \qquad 2.1.1°$$

The total pressure is the sum of the partial pressures, assuming an ideal mixture:

$$P = \sum_{i=1}^{n_s} P_i \qquad \text{(ideal mixture)} \qquad 2.1.2°$$

for n_s constituents. Since from Eq. 2.1.1°, $P_i = n_i RT/V$, the total pressure is related to the total volume and temperature through Eq. 2.1.2°:

$$P = \sum_{i=1}^{n_s} P_i = \sum_{i=1}^{n_s} n_i RT/V = \frac{RT}{V} \sum_{i=1}^{n_s} n_i = \frac{n RT}{V} \qquad \text{(ideal mixture of ideal gases) } 2.1.3°$$

given that the total number of moles of gas is:

$$n = \sum_{i=1}^{n_s} n_i \qquad 2.1.4$$

In other words, PV = nRT for the mixture of gases. The ideal gas law assumes that the gas molecules have no volume and no forces between the molecules. An ideal mixture assumes that the forces between the different molecular species are equal to the forces between molecules of the same species. The ideal mixture approximation is better, in general, than the ideal gas law.

The concentration of a species, c_i, is given as n_i/V in moles per m^3 or moles per liter:

$$c_i = \frac{n_i}{V} = \frac{P_i}{RT}$$
(ideal gas)   2.1.5°

The mole fraction of a species i, y_i, is defined as:

$$y_i = \frac{n_i}{\sum\limits_{j=1}^{n_s} n_j} = \frac{n_i}{n}$$
2.1.6

For example, for a two-component mixture $y_1 = n_1/(n_1 + n_2)$. We use y_i for gas phase mole fractions and x_i for solution phase mole fractions to avoid confusion when we discuss volatile liquid solutions. Mole fraction based concentrations are very useful because the fractions for all constituents add to one:

$$\sum\limits_{i=1}^{n_s} y_i = 1$$
2.1.7

We can relate the partial pressures to the total pressure by dividing Eq. 2.1.1° by $PV = n\,RT$ for the total mixture:

$$\frac{P_i V}{PV} = \frac{n_i\,RT}{nRT}$$
(ideal mixture of ideal gas)   2.1.8°

Cancelling terms gives:

$$\frac{P_i}{P} = \frac{n_i}{n} = y_i$$
(ideal mixture of ideal gases) 2.1.9°

Solving for the partial pressure gives:

$$P_i = y_i\,P$$
(ideal mixture of ideal gases) 2.1.10°

where P is the total pressure of the mixture. Eqs. 2.1.1° and 2.1.10° are both expressions of Dalton's Law of Partial Pressures. The concentrations, c_i or y_i, and the partial pressures, P_i, can all be used to study the concentration dependence of reaction rates and chemical equilibrium.

We often like to work with gases in equilibrium with aqueous solutions in the environment, for example gas exchange with the surface of lakes, streams, or the ocean. For these problems we need to take into account water vapor as one of the components of the gas phase. The vapor pressure of water, P^*_{H2O}, is given in Table 2.1.1. We will use the symbol θ for temperature in degrees Centigrade; T is always in kelvins.

Table 2.1.1: Vapor Pressure of Water[1]. Values in kPa and torr.

θ (°C)	P^*_{H2O} (kPa)	P^*_{H2O} (torr)	θ (°C)	P^*_{H2O} (kPa)	P^*_{H2O} (torr)	θ (°C)	P^*_{H2O} (kPa)	P^*_{H2O} (torr)
0.0	0.611	4.579	20.0	2.339	17.535	50.0	12.344	92.51
10.0	1.228	9.209	25.0	3.168	23.756	75.0	38.556	289.10
15.0	1.705	12.788	36.6	6.140	46.050	90.0	70.117	525.76

The relative humidity of air is defined as the percentage ratio of the ambient vapor pressure of water to the equilibrium vapor pressure at the current temperature:

$$RH = \frac{P_{H2O}}{P^*_{H2O}} \ (100\%) \hspace{6cm} 2.1.11$$

Example 2.1.1: *Volume Fractions and Mole Fractions*
Dry air is 20.946% by volume O_2 and 79.054% N_2. For many partial pressure problems we need to know the mole fractions. Show that volume fractions are equivalent to mole fractions.

Answer: Assuming the system is at constant total pressure, P, the corresponding volume of O_2 is given by:

$$PV_{O2} = n_{O2} \ RT$$

where V_{O2} is the volume that the O_2 would occupy if it were alone in the container. Using Dalton's Law of Partial Pressures, the total pressure is given by Eq. 2.1.3°:

$$PV = (n_{O2} + n_{N2}) \ RT$$

Where V is the total volume, $V = V_{O2} + V_{N2}$. Dividing these two equations gives:

$$\frac{PV_{O2}}{PV} = \frac{n_{O2} \ RT}{(n_{O2} + n_{N2}) \ RT}$$

Canceling common factors gives the mole fraction from the volume fraction:

$$\frac{V_{O2}}{V} = \frac{n_{O2}}{(n_{O2} + n_{N2})} = y_{O2}$$

proving that volume fractions and mole fractions are identical.

Example 2.1.2: *Partial Pressures and Relative Humidity*
Dry air is 20.946% by volume O_2 and 79.054% N_2. (a) Calculate the number of moles of O_2 in 1.00 m^3 of dry air at 1.00 bar pressure at 298.15K. (b) Calculate the number of moles of O_2 in 1.00 m^3 of air at a relative humidity of 60.0% for the same conditions as part (a).

Answer: (a.) In dry air $P = P_{O2} + P_{N2}$, with $P_{O2} = n_{O2} \ RT/V$ and $P_{N2} = n_{N2} \ RT/V$ giving:

$$P = n_{O2} \ RT/V + n_{N2} \ RT/V \hspace{1cm} \text{or} \hspace{1cm} (n_{O2} + n_{N2}) = PV/RT$$

Noting that 1 bar = 1×10^5 Pa and using V in m^3 and R in J mol^{-1} K^{-1} gives the total moles of gas:

$$(n_{O2} + n_{N2}) = PV/RT = \frac{1.000 \times 10^5 \ \text{Pa} \ (1.000 \ \text{m}^3)}{8.3145 \ \text{J mol}^{-1} \ \text{K}^{-1}(298.15 \ \text{K})} = 40.34 \ \text{mol}$$

Using the given mole fraction of O_2 gives $n_{O2} = y_{O2} \ (n_{O2} + n_{N2}) = 0.20946 \ (40.34 \ \text{mol}) = 8.450 \ \text{mol}$.

(b). In humid air $P = P_{O2} + P_{N2} + P_{H2O}$. All we need to do is subtract the partial pressure of the water from both sides of the equation and then proceed as before:

$$P - P_{H2O} = P_{O2} + P_{N2} = n_{O2}\ RT/V + n_{N2}\ RT/V = (n_{O2} + n_{N2})RT/V$$

Solving for the moles of O_2 and N_2 gives:

$$(n_{O2} + n_{N2}) = (P - P_{H2O})V/_{RT}$$

At 298.15 K the equilibrium vapor pressure of water from Table 2.1.1 is 3.168 kPa. At 60.0% relative humidity the vapor pressure of water is $P_{H2O} = 0.600\ (3.168\ \text{kPa}) = 1.900\ \text{kPa} = 1.900 \times 10^3\ \text{Pa} = 0.01900 \times 10^5\ \text{Pa}$. The moles of O_2 and N_2 are then:

$$(n_{O2} + n_{N2}) = \frac{(P - P_{H2O})V}{RT} = \frac{(1.000 \times 10^5 - 0.01900 \times 10^5\ \text{Pa})\ 1.000\ \text{m}^3}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}\ (298.15\ \text{K})} = 39.57\ \text{mol}$$

The relative fractions of O_2 and N_2 are the same as for dry air. To see this, consider admitting a known number of moles of O_2 and N_2 into a constant pressure container. Now admit enough water vapor to reach the desired partial pressure of water; the number of moles of O_2 and N_2 haven't changed so that the relative ratio of O_2 to N_2 is constant, even though water vapor is present. Using the dry mole fraction to find the relative amounts of O_2 and N_2 gives $n_{O2} = 0.20946\ (39.58\ \text{mol}) = 8.289\ \text{mol}$. The net result is that there is about 2% less O_2 available on the humid day. Air is actually a mixture of O_2, N_2, CO_2, and Ar. No changes are needed for our calculation for O_2 if we use P_{N2} to represent the combined partial pressure of N_2, CO_2, and Ar.

2.2 Concentrations of Solutions

The mole fraction of a component i in solution, x_i, is the most fundamental expression of concentration:

$$x_i = \frac{n_i}{\sum_{j=1}^{n_s} n_j} = \frac{n_i}{n} \qquad\qquad 2.2.1$$

for n_s constituents in solution. Just as for gases, the sum of all mole fractions is one:

$$\sum_{i=1}^{n_s} x_i = 1 \qquad\qquad 2.2.2$$

The concentration of the solvent in solution is almost always given in terms of mole fraction. The concentration of solutes can also be expressed in **molar** units, which is defined as the number of moles per liter of solution:

$$c_i = n_i/_V \qquad\qquad 2.2.3$$

The units are designated as "M." The problem with molar concentration units is that they are temperature dependent. The temperature dependence results from the fact that the density and, therefore, the volume of a solution depends on temperature. To avoid the temperature dependence, a more useful measure of concentration, called the **molality**, is expressed as the number of moles of solute divided by the mass of the solvent in kg, $w_{solvent}$:

$$m_i = \frac{n_i}{w_{solvent}} \qquad\qquad 2.2.4$$

The units for molality are "m." Thermodynamic reference tables are often given assuming molal concentrations. In equilibrium expressions, the symbol [A] is often used for concentration, which can be expressed either in molar or molal units. Use the listed units in data tables to determine the concentration measure. Note that mole fraction is unitless, which is another good reason for using mole fractions. It is often necessary to convert among the concentration measures.

  To convert from <u>molarity to molality</u>, assume an amount of a c molar solution of 1L total volume. The moles of solute is $n_i = c$ (1 L) and the mass of the solution is $w_{soln} =$ (volume)(density of solution):

$$w_{soln} = 1000mL\ d_{soln} \qquad\qquad 2.2.5$$

where d_{soln} is the density of the solution in g mL^{-1}. The mass of the solvent is calculated by difference:

$$w_{solvent} = \text{mass of solution} - \text{mass of solute} = \frac{1000mL\ d_{soln} - c\ (1L)\ \mathfrak{M}_B}{1000g/kg} \qquad 2.2.6$$

where $\mathfrak{M}_B$ is the molar mass of the solute, B, in g mol^{-1}. The molality is then just the moles of solute divided by the mass of the solvent in kg, Eq. 2.2.4:

$$m = \frac{c\ (1L)}{\dfrac{1000mL\ d_{soln} - c\ (1L)\ \mathfrak{M}_B}{1000g/kg}} \qquad\qquad 2.2.7$$

For dilute solutions, the mass of the solute is negligible compared to the mass of the solvent and Eq. 2.2.7 reduces to:

$$m \cong \frac{c}{d_{soln}}\left(\frac{1L}{1000\ mL}\right)\left(\frac{1000\ g}{1\ kg}\right) \qquad\qquad \text{(very dilute)} \qquad 2.2.8$$

For very dilute solutions the density of the solution is very close to the density of water, Table 2.2.1. For very dilute solutions at 25°C, the density of water is 0.99705 g mL^{-1} so that molarity and molality differ by 0.3%.

Table 2.2.1. Density of Water[2]

Temperature (°C)	d (g mL^{-1})	Temperature (°C)	d (g mL^{-1})
0.0	0.9998425	30.0	0.9956502
4.0	0.9999750	36.6	0.9934748
10.0	0.9997026	50.0	0.9880393
20.0	0.9982071	75.0	0.9748519
25.0	0.9970479	100.0	0.9583665

$d = a_o + a_1\theta + a_2\theta^2 + a_3\,\theta^3$, with $a_o = 0.9998425$, $a_1 = 5.3322 \times 10^{-5}$, $a_2 = -7.5899 \times 10^{-6}$, $a_3 = 3.6719 \times 10^{-8}$ g mL^{-1}.

To convert <u>molality to molarity,</u> assume an amount of an m molal solution that contains 1 kg of solvent. The moles of solute is $n_i = m$ (1 kg) and the mass of the solution:

$$w_{soln} = 1000g + m\ (1kg)\ \mathfrak{M}_B \qquad\qquad 2.2.9$$

$$\text{volume of solution} = \text{mass/density} = \frac{1000g + m\ (1kg)\ \mathfrak{M}_B}{d_{soln}\ 1000\ mL/L} \qquad 2.2.10$$

giving the molarity as:

$$c = \frac{m\ (1kg)}{\dfrac{1000g + m\ (1kg)\ \mathfrak{M}_B}{d_{soln}\ 1000mL/L}} \qquad\qquad 2.2.11$$

and in very dilute solution, neglecting the mass of the solute compared to the solvent, Eq. 2.2.11 reduces to:

$$c \cong m\ d_{soln}\left(\frac{1000\ mL}{1L}\right)\left(\frac{1\ kg}{1000\ g}\right) \qquad\qquad \text{(very dilute)} \quad 2.2.12$$

Similarly, to convert from <u>molality or molarity to mole fraction</u>:

$$x_B = \frac{m_B\ (1kg)}{\left(\dfrac{1000g}{\mathfrak{M}_A}\right) + m_B\ (1kg)} \qquad\qquad 2.2.13$$

$$x_B = \frac{c_B\ (1L)}{\left(\dfrac{1000mL\ d_{soln} - c_B\ (1L)\ \mathfrak{M}_B}{\mathfrak{M}_A}\right) + c_B\ (1L)} \qquad\qquad 2.2.14$$

where $\mathfrak{M}_A$ is the molar mass of the solvent, A. The solvent is often water. In very dilute solution the amount of solute is negligible compared to the amount of solvent in the denominator and:

$$x_B \cong \frac{m_B\ (1kg)}{\left(\dfrac{1000g}{\mathfrak{M}_A}\right)} \qquad \text{aqueous solutions: } x_B \cong \frac{m_B\ (1kg)}{55.51\ mol} \qquad \text{(very dilute)} \quad 2.2.15$$

$$x_B \cong \frac{c_B\ (1L)}{\left(\dfrac{1000mL\ d_{soln}}{\mathfrak{M}_A}\right)} \qquad\qquad \text{(very dilute)} \qquad 2.2.16$$

and for water as the solvent at 25°C, 1L of water corresponds to 55.33 moles and then:

$$x_B \cong \frac{c_B\ (1L)}{55.33\ mol} \qquad\qquad \text{(very dilute)} \qquad 2.2.17$$

We will use these equations often in the chapters on solutions and equilibria.

Example 2.2.1: *Molarity, Molality, and Mole Fraction*
A sodium chloride solution is prepared by adding 3.752 g of sodium chloride to a 100-mL volumetric flask and then diluting to the mark. The molar mass is 58.442 g mol⁻¹. The final mass of the solution is 102.4 g. Calculate the molarity, molality, and the mole fraction of sodium chloride in this solution. Calculate the mole fraction of the solvent.

Answer: The number of moles of added NaCl is 0.06420 moles and the molarity is:

$$c_B = 0.06420 \text{ mol}/0.1000 \text{ L} = 0.6420 \text{ M}.$$

The molality is based on the mass of the solvent, which is $w_A = 102.4 \text{ g} - 3.752 \text{ g} = 98.65 \text{ g}$. The molality is then $m = 0.06420 \text{ mol}/0.09865 \text{ kg} = 0.6508 \text{ m}$.

   In many problems, the density is given instead of the final total weight of the solution. Eq. 2.2.7 must then be used to calculate the molality. Let's do the problem using the density to gain some more experience with concentration conversions. The density of the solution is the final mass divided by the volume, $d = 102.4 \text{ g}/100.0 \text{ mL} = 1.024 \text{ g mL}^{-1}$. It is wise to write an Excel spreadsheet to do concentration conversions. You can use this example to test your spreadsheet. You will be doing these calculations often. Using Eq. 2.2.7, the molality is:

$$m_B = \frac{c \, (1L)}{\dfrac{1000 \text{mL } d_{soln} - c \, (1L) \, \mathfrak{M}_B}{1000 \text{g/kg}}} = \frac{0.6420 \text{ M } (1L)}{\dfrac{1000 \text{mL } 1.024 \text{ g mL}^{-1} - 0.6420 \text{ M } (1L) \, 58.442 \text{ g mol}^{-1}}{1000 \text{g/kg}}}$$

$$m_B = 0.6508 \text{ m}$$

The mole fraction is given using Eq. 2.2.13:

$$x_B = \frac{m_B \, (1\text{kg})}{\left(\dfrac{1000\text{g}}{\mathfrak{M}_A}\right) + m_B \, (1\text{kg})} = \frac{0.6508 \text{ m } (1\text{kg})}{\left(\dfrac{1000\text{g}}{18.02 \text{ g mol}^{-1}}\right) + 0.6508 \text{ m } (1\text{kg})}$$

$$x_B = x_{NaCl} = 0.01159$$

We then calculate the mole fraction of the solvent by difference, since $x_A + x_B = 1$:

$$x_{H2O} = 1 - 0.01159 = 0.9884$$

Notice that the molarity and molality differ by 1.4%. This solution is within the salinity range of normal sea water. This solution is 3.66% NaCl by mass or 36.6 ‰ (‰ indicates parts per thousand by mass, which is the concentration measure used by oceanographers for salinity).

Example 2.2.2: *Solution Preparation by Mass*
Making up solutions by mass avoids the need for using volumetric glassware, and is usually more accurate. You can work with volumes smaller than your available volumetric glassware. A mass of 0.00987 g of levulose, molar mass 180.16 g mol^{-1}, and 1.006 g of water were added to a small tube. Calculate the molality and molarity, if the density of the solution is 1.0039 g mL^{-1}.

Answer: Remember that spreadsheet idea? A spreadsheet sure would make this calculation easier. Here are the results. The molality and molarity are:

$$m = \frac{\text{moles solute}}{\text{mass solvent}} = \frac{0.00987 \text{ g}/180.16 \text{ g mol}^{-1}}{1.006 \times 10^{-3} \text{ kg}} = 0.05446 \text{ m}$$

$$c = \frac{m \, (1\text{kg})}{\dfrac{1000\text{g} + m \, (1\text{kg}) \, \mathfrak{M}_B}{d_{soln} \, 1000 \text{mL/L}}} = \frac{0.0545 \text{ m } (1\text{kg})}{\dfrac{1000\text{g} + 0.0545 \text{ m } (1\text{kg}) \, 180.16 \text{ g mol}^{-1}}{1.0039 \text{ g mL}^{-1} \, 1000 \text{mL/L}}} = 0.05414 \text{ M}$$

The results are almost good to four significant figures, since the mass of levulose was almost 0.01000 g, which would have had four significant figures. When the last digit isn't significant, the digit is shown in a smaller font, or underlined, 0.05414 M. Always carry more significant figures than you are allowed through intermediate calculations to avoid round-off error.

2.3 Molecules in Motion—Mass Transport

Chemical systems are often dynamic. In other words, the concentrations of chemical species change as a function of time. Concentrations can change because of flow processes and chemical reactions. In flow processes, molecules move from place to place. In this section we consider the effect of flow processes. In the next chapter we will discuss the time dependence of chemical reactions. The flow of molecules is often called mass transport. Mass transport processes include bulk flow, convection, and diffusion. An example of bulk flow includes flow in pipes and tubing. An example of convection is the flow in stirred solutions. This type of flow is called streaming flow. In stationary, non-stirred solutions molecules move only by a random process called diffusion. Examples of systems where flow processes are important include membrane systems, flow reactors, electrochemistry, and chromatography. Most biological processes involve flow in some way or another, and many of the problems in energy applications involve overcoming flow restrictions. The change in the amount of a substance caused by a flow process is characterized as a flux. The concept of a flux is quite general and useful. Fluxes are used to characterize the flow of chemical species, charge, and energy.

Fluxes measure flow: The flux is the flow of something per unit time per unit area. We normalize to unit area because we often don't care how large the system is; we want an intrinsic measure of the transport properties of the system for any size. The flows of matter, charge, or energy per unit area are all fluxes, Figure 2.3.1. Chemical fluxes involve the flow of chemical species. A flux of charge results if the chemical species are ions. Charge fluxes also occur from electron flow in a conductor. Light is one example of an energy flux. Energy transfer in the form of heat can also be treated as a flux.

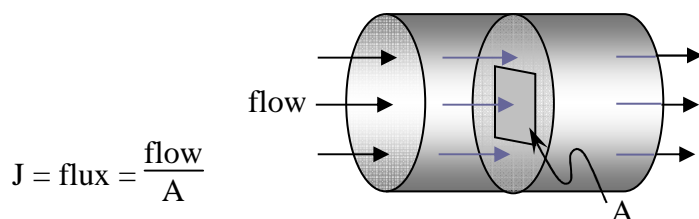$$J = \text{flux} = \frac{\text{flow}}{A}$$

Figure 2.3.1: The flux is the flow of matter, charge, or energy through a surface of unit area per unit time. For uniform flow, the flux is independent of the size of the surface chosen, because the flux is normalized to unit area. For non-uniform flow, the flux is the average over the chosen surface.

The chemical flux, J_m, is given as the number of moles of a given species passing through a surface per unit area per unit time. Bulk flow is the simplest case. For a solution of concentration c flowing through a tube at velocity υ the flux is just $J_m = c\upsilon$. If the solution velocity is not uniform, then the velocity is the local velocity at the point of interest. (Note that for pump-driven

flow through a tube that the solution close to the wall of the tube travels slower than the bulk of the solution.) Convection is quite analogous. The velocity is the local velocity of the stirred solution, and $J_m = c\upsilon$ applies as before. If the solute concentration is not uniform, then the concentration is the local concentration at the point of interest.

We can also relate the flux to the volumetric flow rate. If the **volumetric flow rate**, F, is given in L s^{-1} and the concentration of the solution, c, is given in mol L^{-1} then the flux is also $J_m = Fc/A$, where the cross-sectional area is usually given in m^2. The flux calculated in this way is the average over the total flow area.

Once the flux is known, the change in moles of a given species, n, can be calculated. For a portion of the sample with cross sectional area A:

$$\frac{dn}{dt} = J_m A \qquad\qquad\qquad 2.3.1$$

If the flux is constant, the number of moles of a species transported across this area in a time Δt is given as:

$$n = J_m \, A \, \Delta t \qquad\qquad (\text{cst. } J_m) \qquad 2.3.2$$

Example 2.3.1: *Flux and Moles*
Consider a large reservoir filled with 0.1 M sucrose that is emptied by a small tube with an internal diameter of 5.00 mm. Assume the reservoir empties at a rate of 1.00 mL s^{-1}. (a) Calculate the average sucrose molar flux in mol m^{-2} s^{-1} across the tube. (b) From the flux, calculate the number of moles of sucrose delivered in 1.00 minute.

Answer: (a) The cross sectional area of the tube is A = πr^2 = 3.1416 (5.00x10^{-3} m/2)^2 = 1.96x10^{-5} m^2. The velocity of the solution through the tube is the volumetric flow rate, F, divided by the cross sectional area:

   υ = F/A = 1.00 mL s^{-1} (1 m^3/1x10^{6}mL)/1.96x10^{-5} m^2 = 0.0510 m s^{-1}

The molar flux is then:

   J_m = cυ = 0.1 mol L^{-1} (1000 L/1m^3) 0.0510 m s^{-1} = 5.10 mol m^{-2} s^{-1}.

(b) The amount of sucrose delivered in 1.00 minute using this flux and Eq. 2.3.2 is:

   n = J_m A Δt = 5.10 mol m^{-2} s^{-1} (1.96x10^{-5} m^2)(60 s) = 6.00x10^{-3} mol

As a check on our calculations, we can alternatively use the volumetric flow rate and concentration directly: n = FcΔt = 1.00 mL s^{-1}(0.1 mol L^{-1})(1 L/1000 mL)(60 s) = 6.00x10^{-3} mol.

Concentration Gradients Are Reduced by Diffusion: For a system at equilibrium, the concentrations of all species are uniform in each phase. For non-equilibrium systems, the concentrations can vary from place to place. The difference in concentration with position produces a concentration gradient. Without the input of energy or matter, concentration gradients disappear through diffusion, and the concentrations become uniform at equilibrium. A solution with a linear concentration gradient is diagrammed in Figure 2.3.2. To calculate the local concentration, the total volume is divided into small intervals, as indicated by the light gray lines. These light gray lines are not physical barriers, but are used only to delineate small equal increments. The concentration gradient is defined as the derivative of the concentration with

respect to distance, dc/dx. The gradient in Figure 2.3.2 is given in terms of the number of molecules in the volume increment, V_{inc}. The number of molecules is converted to molar units by division by the increment volume and Avogadro's number, N_A:

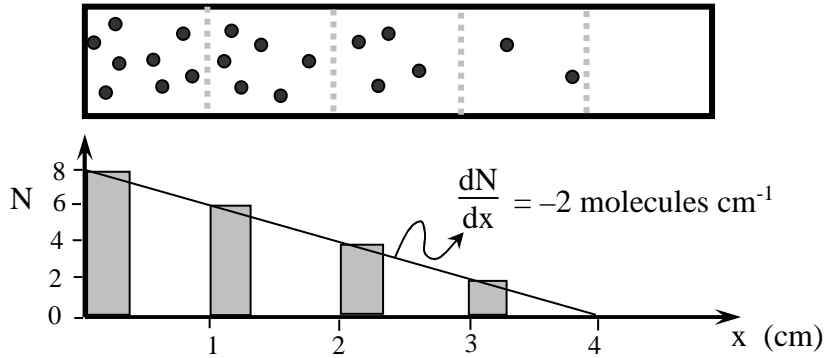$$\frac{dc}{dx} = \frac{1}{V_{inc} N_A} \frac{dN}{dx} \qquad\qquad 2.3.3$$

Figure 2.3.2: A solution with a linear concentration gradient. The local concentration is calculated by dividing the total volume into small increments. The number of molecules in each volume increment is plotted as a histogram, with the horizontal axis indicating the position of the volume increment along the x axis. The concentration gradient is the derivative of the curve for the number of molecules per unit volume as a function of distance.

More generally, if the concentration in a solution varies linearly between c and c' over a distance δ, then the gradient is:

$$\frac{dc}{dx} = \frac{(c' - c)}{\delta} \qquad\qquad \text{(linear gradient)} \qquad 2.3.4$$

Molecules move through a solution by diffusion, which is characterized by a diffusion coefficient, D. The diffusion coefficient is dependent on the particular solute species and solvent. The larger the diffusion coefficient, the higher the intrinsic mobility of the species. The molar flux of a species through the solution is directly proportional to its concentration gradient:

$$J_m = -D \frac{dc}{dx} \qquad\qquad 2.3.5$$

where J_m is the molar flux. In short, concentration gradients drive mass transfer from regions of high concentration to regions of low concentration. Eq. 2.3.5 is called **Fick's First Law**. For a linear gradient, substituting Eq. 2.3.4 into Eq. 2.3.5, gives Fick's First Law as:

$$J_m = -\frac{D}{\delta}(c' - c) \qquad\qquad \text{(linear gradient)} \qquad 2.3.6$$

The units of the flux are mol m^{-2} s^{-1}. The units of the diffusion coefficient are m^2 s^{-1}, giving the corresponding units for the concentration gradient as mol m^{-4}. Typical values for the diffusion coefficient are given in Table 2.3.1.

Table 2.3.1. Diffusion Coefficients in water at 293 K.[3]

Species	Molar Mass (g mol^{-1})	D (m^2 s^{-1})
CH_3OH	32	13.7×10^{-10}
urea, H_2NCONH_2	60	11.8×10^{-10}
sucrose	342	5.7×10^{-10}
insulin	41,000	8.2×10^{-11}
horse hemoglobin	68,000	6.3×10^{-11}

The data in Table 2.3.1 show an inverse relationship of molecular size with the diffusion coefficient. Large molecules move slowly. Diffusion coefficients also decrease as the viscosity of the solvent increases.

Example 2.3.2: *Diffusion Across a Membrane*
A membrane is placed between two stirred solutions. The solution on the left of the membrane contains 0.010 M sucrose and on the right is pure water. The membrane is 0.100 mm thick and has an area of 5.00 cm^2. Assume the diffusion coefficient of sucrose in the membrane is the same as in pure water, 5.7×10^{-10} m^2 s^{-1}. Calculate the number of moles of sucrose that diffuse across the membrane in one hour.

Answer: Assuming a linear change in concentration across the membrane, the concentration gradient using Eq. 2.3.4 is:

$$\frac{dc}{dx} = \frac{(c' - c)}{\delta} = \frac{0 - 0.01 \text{ mol L}^{-1}(1000\text{L}/1\text{m}^3)}{0.100 \text{ mm } (1 \text{ m}/1000 \text{ mm})} = \frac{-10. \text{ mol m}^{-3}}{1.00 \times 10^{-4}\text{m}} = -1.00 \times 10^5 \text{ mol m}^{-4}$$

Using Fick's First Law, Eq. 2.3.5, the flux is given by:

$$J_m = -D\frac{dc}{dx} = -(5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1})(-1.00 \times 10^5 \text{ mol m}^{-4}) = 5.7 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$$

The cross sectional area of the membrane is A = 5.00 cm^2 (1 m/100 cm)^2 = 5.00×10^{-4} m^2
The total amount of sucrose passing through the membrane in one hour is then:

$$n = J_m \, A \, \Delta t = 5.7 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \, (5.00 \times 10^{-4} \text{ m}^2)(1 \text{ hr})(3600 \text{ s}/1\text{hr}) = 1.03 \times 10^{-4} \text{ mol}$$

This membrane is quite thin and the gradient is quite large. Even so, the amount of sucrose that is transported across the membrane is quite small.
   Since we approximated the diffusion coefficient through the membrane as the diffusion coefficient in bulk water, this problem gives the same numerical result as diffusion through an equivalent slice of a bulk solution with a comparable gradient. In either the membrane or bulk solution case, we note that the diffusion of molecules is quite slow. That slow mobility is why vigorous stirring is necessary when making up solutions. Diffusion alone is insufficient; convection is also required for rapid mixing.

2.4 Experimental Determination of Concentration: Some Tools of the Trade

There are a vast variety of methods for determining concentrations in the gas phase and in solution. We will encounter many such methods throughout this text. As a prelude to kinetics and equilibrium studies, however, we will discuss just three representative techniques: UV-visible absorption spectroscopy, emission spectroscopy, and conductivity. Within wide concentration ranges, these techniques show a linear or near-linear response with concentration. In general, most techniques for measuring concentration can be put into a linear form. These three methods will help you get a quick start on your experimental work. We discuss the theoretical background for these techniques later in the text.

Absorption Spectroscopy: The diagram of a simple absorbance spectrophotometer is shown in Figure 2.4.1. Light from a source is focused on a diffraction grating. The dispersed light from the grating passes through a slit selecting a narrow range of wavelengths. This arrangement of a grating with slits for selection of a small range of wavelengths is called a **monochromator**. The incident light flux on the sample is J_o. This flux is the energy per unit time per unit area. As with all fluxes, we normalize to unit area because we don't care how large the incident light beam is; we want an intrinsic measure of the ability of the sample to absorb light for any size sample and incident beam area. How do we relate the light flux to the concentration of the sample?
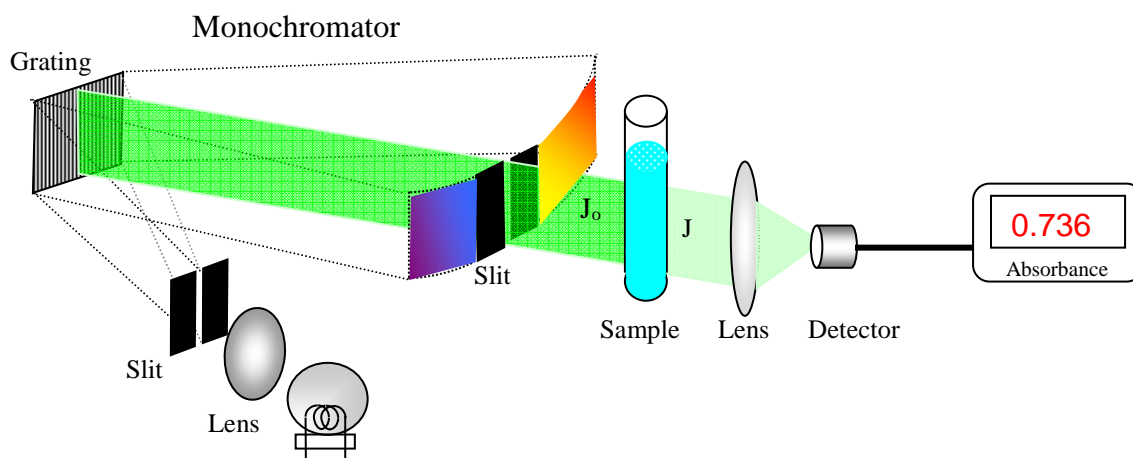

Figure 2.4.1: A simple absorbance spectrophotometer. A narrow band of excitation wavelengths is produced by a monochromator.

Let c be the concentration of the sample, ℓ the path length of the cuvette, and β the intrinsic ability of the molecules in the sample to absorb light at the given wavelength. β is the fraction of the light flux absorbed by the molecules, which is the probability of absorbing photons. The units of the concentration are usually molar units, mol L^{-1}, but molal units, mol kg^{-1}, can also be used. The path length is usually measured in cm. The distance that the light has traveled through the sample is x. The light flux, $J(x)$, decreases as it passes through the sample because of absorption by the molecules. Consider a thin slice of solution of thickness dx, Figure 2.4.2.

The change in flux over the distance dx is proportional to the intrinsic ability of the molecules to absorb light, the concentration of the sample, the light flux at distance x incident on the slice, and the thickness of the slice:

$$dJ = - \beta \, c \, J(x) \, dx \qquad\qquad 2.4.1$$

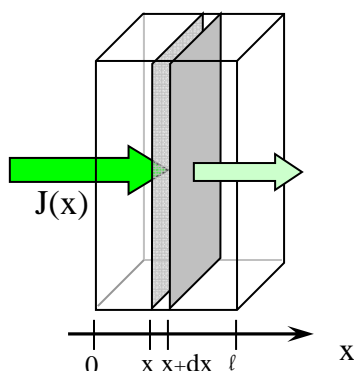The negative sign is necessary because the flux decreases with distance.

Figure 2.4.2: Absorption of light by a thin slice of solution of thickness dx.

Eq. 2.4.1 can easily be integrated, because it is in the general form of $df = -a \, f \, dx$ given in general pattern ℘1 in Section 1.3. After separation of variables and setting the flux to J_o at $x = 0$ and J at $x = \ell$:

$$\int_{J_o}^{J} \frac{dJ}{J} = - \int_0^\ell \beta \, c \, dx \qquad\qquad 2.4.2$$

$$\ln \frac{J}{J_o} = - \beta \, \ell \, c \qquad\qquad 2.4.3$$

$$J = J_o \, e^{-\beta \ell c} \qquad\qquad 2.4.4$$

The flux is an exponentially decreasing function of distance through the sample. Multiplying Eq. 2.4.3 by –1 gives the **Beer-Lambert Law**:

$$\ln(J_o/J) = \beta \, \ell \, c \qquad\qquad 2.4.5$$

The absorbance of the solution is defined as:

$$A \equiv \log(J_o/J) \qquad\qquad 2.4.6$$

using base 10 logarithms. To convert Eq. 2.4.5 from base-e logarithms to base-10, remember that $\ln x = 2.303 \log x$:

$$A = \log \frac{J_o}{J} = \frac{\beta}{2.303} \, \ell \, c \qquad\qquad 2.4.7$$

Defining the **molar absorption coefficient** as $\varepsilon \equiv \beta/2.303$ gives the final linear result:

$$A = \varepsilon \, \ell \, c \qquad\qquad 2.4.8$$

The importance of this equation is that the concentration of a solution can be easily obtained from the absorbance, if the molar absorption coefficient and path length of the cuvette are

known. The value of ε is wavelength dependent, and is determined by calibration with solutions of known concentration at a fixed wavelength, Figure 2.4.3. Molecular spectra typically consist of more than one transition, each transition resulting from a different excited state of the molecule. The wavelength of maximum absorption for a band is usually used for determinations. The value of ε is typically in the range of zero to 10^5 M^{-1} cm^{-1}.

The molar absorption coefficient is also alternatively called the extinction coefficient or the molar absorptivity. The units are L mol^{-1} cm^{-1}, or M^{-1} cm^{-1}. The light flux, J, is equivalent to the power per unit area, P, and also the intensity, I. The absorbance can be expressed using any of these equivalent measures of light intensity. The transmittance, T, is defined as the fraction of the light that is transmitted through the sample, $T = I/I_o$, and the percent transmittance is just the transmittance on a percentage basis, $\%T = (I/I_o)\,100\%$:

$$A = \log \frac{J_o}{J} = \log \frac{P_o}{P} = \log \frac{I_o}{I} = \log 1/T = \log \frac{100}{\%T} \qquad 2.4.9$$

Spectrophotometers may use any of these measures of light absorption.

Absorption spectroscopy isn't always linear with concentration. Non-linearity results from equilibria that change the speciation of the substance that is being determined. For example, many dyes dimerize in solution, $A + A \rightleftarrows A_2$. Changes in pH or ionic strength can also cause non-linearity. Highly absorptive solutions also show non-linearity caused by stray light in the monochromator.
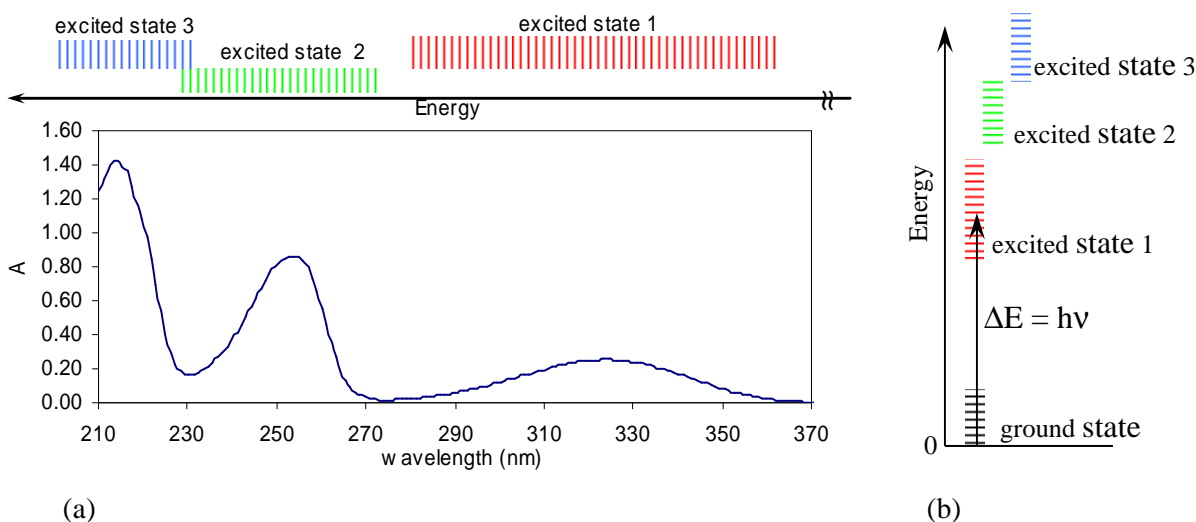

Figure 2.4.3: (a) Absorption spectrum of 8.00×10^{-5} M salicylaldehyde, for a 1 cm path length. The absorbance at 255 nm is 0.848 giving $\varepsilon = A/(\ell c) = 10{,}600$ M^{-1} cm^{-1} at 255 nm. The absorbance spectrum shows three absorption bands corresponding to three molecular electronic excited states. (b) The three excited states are shown in the corresponding energy level diagram. (There is no horizontal axis for an energy level diagram.)

Example 2.4.1: *Beer-Lambert Law and the Euphotic Zone*
The euphotic zone is the layer in a natural body of water that can support photosynthesis. The euphotic zone extends to the depth that corresponds to 1% of the light flux incident on the

surface. Colored dissolved organic matter, CDOM, is one component in the water column that limits the penetration of light in lakes and rivers. CDOM includes polyphenolic compounds that are secondary metabolites in plants. Anthocyanins are one class of polyphenolics that are responsible for the coloration of many fruits, berries, and some leaves. A typical anthocyanin, cyanidin 3-O-glucoside chloride, has a molar absorption coefficient at 525 nm of 1.8×10^7 M^{-1} cm^{-1}.[4] Photosynthetically active light, or PAR, is in the 380-710 nm range.
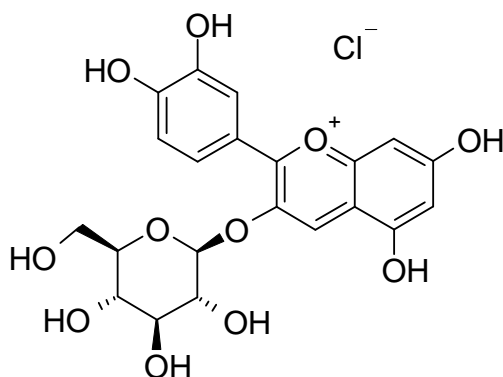

Figure 2.4.4: Cyanidin 3-O-glucoside chloride.

The molar mass is 484.84 g mol^{-1}. (a) What is the %T and absorbance from the surface to the bottom of the euphotic zone? (b) Calculate the absorbance at 525 nm of a 2.7×10^{-10} M solution of cyanidin 3-O-glucoside chloride for a 1.00 cm path length cuvette. (c) Calculate the depth of the euphotic zone for this concentration.

Answer: (a) 1% of the light flux incident on the surface corresponds to 1 %T and the absorbance is $A = \log(J_o/J) = \log(1/0.01) = 2$
(b) The absorbance is given by the Beer-Lambert Law:

$$A = \varepsilon \ell c = 1.8 \times 10^7 \text{ M}^{-1} \text{ cm}^{-1} (1.00 \text{ cm})(2.7 \times 10^{-10} \text{ M}) = 4.9 \times 10^{-3} \approx 0.005$$

For a 1 cm path length the absorbance is quite small.
(c) To find the euphotic zone depth, we set $A = 2$ and solve for the corresponding path length:

$$A = 2 = \varepsilon \ell c = 1.8 \times 10^7 \text{ M}^{-1} \text{ cm}^{-1} \ell (2.7 \times 10^{-10} \text{ M}) \qquad \text{or} \qquad \ell = 410 \text{ cm} = 4.1 \text{ m}$$

The depth of the euphotic zone in a lake is usually measured using a Secchi disk, a disk with white and black areas that is lowered into the lake until the disk is no longer visible. A lake with a Secchi depth of 4 m looks clean. Such a lake would be classified as mesotrophic. Eutrophic lakes have Secchi depths in the 1-3 m range. Algae can be the major contributor to the light attenuation, which is in addition to CDOM.

Example 2.4.2: *Concentration Determination Using Light Absorption*
The following solutions were prepared and the absorbance measured at 535 nm using a 1.00 cm path length. An unknown was determined to have an absorbance of 0.632 at 535 nm. Calculate the concentration of the unknown.

concentration (M)	1.23×10^{-6}	2.34×10^{-5}	3.52×10^{-5}	4.46×10^{-5}	5.45×10^{-5}
absorbance	0.018	0.339	0.496	0.647	0.781

Answer: Eq. 2.4.7, $A = \varepsilon \ell c$, is a linear function with zero intercept, that is $y = mx + b$ with $b=0$ and the slope $m = \varepsilon \ell$. The best way to do this problem is to use least squares curve fitting in Excel or using a calculator. An Excel spreadsheet is shown below with the curve fit data, using the linest() function. The function output is a 5x2 array, and the values are labeled. The "ss" acronym stands for "sum of squares." The best "goodness of fit" criteria are the uncertainties of the slope and the intercept, which are labeled with a "±". The data point (0,0) should always be included for absorbance experiments, unless you have an experimental value for the absorbance at zero concentration that is different from zero. The resulting slope gives the molar absorption coefficient, which is $14349. \pm 119.$ M^{-1} cm^{-1}. The molar absorption coefficient is best reported as 1.43×10^4 M^{-1} cm^{-1} if you are using significant figure rules to show the precision. The fit intercept is zero to within experimental uncertainty. The "fit absorbance" column is calculated using:

$$\hat{A} = 14349.33\ c + 7.69E\text{-}05, \qquad \text{that is, just } y = mx + b.$$

concentration (M)	absorbance	fit absorbance			slope	intercept	
0	0	0.000					
1.23E-06	0.018	0.018	m		14349.33	7.69E-05	b
2.34E-05	0.339	0.336	±		118.9366	0.003989	±
3.52E-05	0.496	0.505	r^2		0.999725	0.005992	st. dev. y
4.46E-05	0.647	0.640	F		14555.66	4	df
5.45E-05	0.781	0.782	SSregression		0.522527	0.000144	SSresidual

The unknown absorbance is 0.632. Working backwards using $A = \varepsilon \ell c$:

$$0.632 = (14350. \pm 120.\ M^{-1}\ cm^{-1})(1.00\ cm)\ c$$

giving $c = 4.40 \times 10^{-5} \pm 0.04 \times 10^{-5}$ M.

Emission Spectroscopy: Fluorescence and NMR are examples of emission spectroscopy. In **fluorescence** spectroscopy a sample is excited by a beam of light. The molecules in the sample absorb the input light and reemit light a short time later. The average time between the absorption and emission is called the fluorescence lifetime, which is typically in the ~5 ns to 10 µs range. Fluorescence is relatively rare but is a very sensitive technique for determining concentration. The spectrum of the fluorescence emission of a compound is determined using a spectrofluorimeter, Figure 2.4.5. The excitation wavelength is set to maximize the fluorescence intensity of the dye. The emission monochromator is then scanned to determine the fluorescence spectrum. Even though the fluorescence emission is isotropic, that is in all directions, the fluorescence is sampled at a 90° angle to the excitation light beam to minimize the amount of excitation light that reaches the emission monochromator.

Fluorescence, at low concentrations, and NMR are inherently linear. The signal intensity is directly proportional to concentration, $I_f = k\ c$, where k is a calibration constant. The calibration constant is determined from known solutions by linear curve fitting, similar to Example 2.4.2.

Fluorescence spectroscopy is complementary to absorption spectroscopy. When a molecule absorbs light, it is left in an excited state. Most often, the excited state loses the excess energy through collisions with the solvent and returns to the ground state with the production of heat. This process is called a **non-radiative** process. However, some molecules release their excess energy by emitting light. The emitted light is called fluorescence if the excited state lifetime is

~5 ns to 10 µs. The emitted light is called **phosphorescence** for longer lifetimes. We will discuss fluorescence and phosphorescence in greater detail in the spectroscopy portion of this text.

Excitation monochromator

Emission monochromator

Grating

Grating
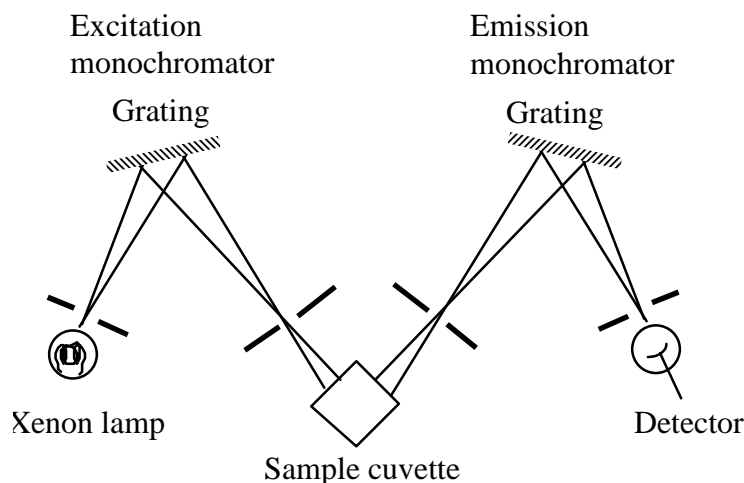
Xenon lamp

Detector

Sample cuvette

Figure 2.4.5. Fluorescence Spectrophotometers use two monochromators (or filters), one for selection of the excitation wavelength and one for selection of the emission wavelength.

The relationship of absorption spectroscopy to emission spectroscopy is shown by the **Jablonski diagram** in Figure 2.4.6. The energy difference for the transition, ΔE, is proportional to the frequency of the light; $\Delta E = h\nu$. Fluorescence emission is redder, that is at longer wavelength, than the absorption. Remember from your General Physics and Chemistry courses that $\nu\lambda = c$, where ν is the frequency of the light, λ is the wavelength, and c is the speed of light. Redder light has a lower frequency and since $\lambda = c/\nu$, redder corresponds to a longer wavelength.

E 1st excited state

vibrational relaxation

excitation
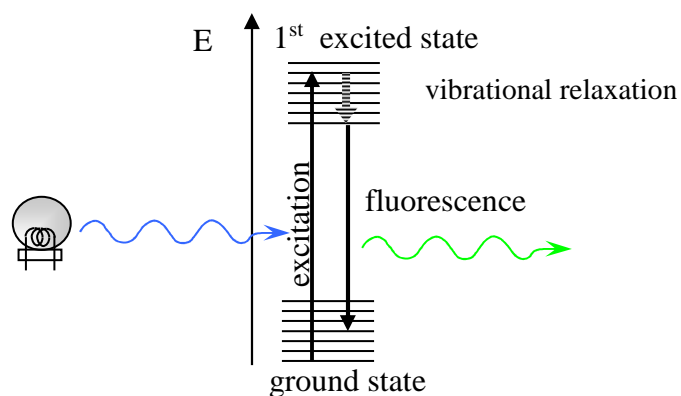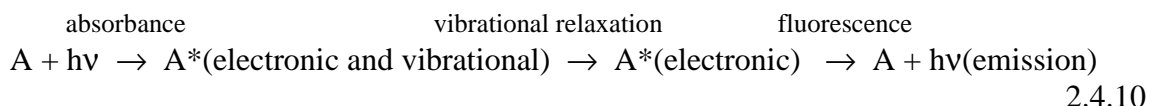
fluorescence

ground state

Figure 2.4.6: The relationship between absorption and fluorescence. The molecule is excited into an excited state by the absorption of light. Fluorescence results in the emission of light as the molecule returns to its ground state. This figure is called a Jablonski diagram.

When molecules absorb visible or ultraviolet light, the molecule is excited into a higher energy molecular excited state and vibrational state. The range of excited vibrational states makes the

absorption bands broad, as we see in Figure 2.4.3. Without vibrational excitation, the absorption band for each excited state would be quite narrow. The range of vibrational excited states is indicated schematically by the closely spaced horizontal lines in Figures 2.4.3b and 2.4.6. After excitation, the molecule rapidly drops to the first excited state and loses excess vibrational energy through collisions with the solvent and the corresponding creation of heat. This rapid loss of vibrational energy is called vibrational relaxation. The molecule then fluoresces from the lowest energy vibrational state of the first excited state back down to the ground state. The reason that the fluorescence is redder than the absorption is explained by the transition arrows in Figure 2.4.6. A shorter arrow corresponds to a smaller change in energy, which corresponds to a longer, redder wavelength. Fluorescence is, therefore, a three step process:

$$\underset{\text{absorbance}}{} \quad \underset{\text{vibrational relaxation}}{} \quad \underset{\text{fluorescence}}{}$$
$$A + h\nu \ \rightarrow \ A^*(\text{electronic and vibrational}) \ \rightarrow \ A^*(\text{electronic}) \ \rightarrow \ A + h\nu(\text{emission})$$
$$2.4.10$$

The "*" is often used to symbolize a molecule in an excited state. The shift to longer wavelength makes it easy to discriminate between the excitation light and the fluorescence. Fluorescence is an absolute intensity measurement rather than a difference in intensity as is absorbance, which makes fluorescence more sensitive than absorbance spectroscopy.

Fluorescence isn't always linear with concentration. For concentrated solutions, the fluorescence intensity becomes non-linear as the fluorescing molecules interact with each other and share excitation energy through **molecular energy transfer**. Fluorescence also can be susceptible to interferences through energy sharing with other solutes. Such concentration dependent transfer usually causes a decrease in the fluorescence, which is called **quenching**.

The distinction between fluorescence and phosphorescence can be illustrated using the electron configurations for the diatomic molecule Cl_2, Figure 2.4.7. (Please review the section on molecular orbital theory from your General Chemistry text.) The ground state of iodine has all spin-paired electrons, which results in a **singlet** state. If one of the outer electrons is excited, the resulting state can still have all paired electrons, half-up and half-down, which results in an excited singlet state. The excited electron can also undergo a spin flip to yield two electrons with parallel spins. Two electrons with parallel spins results in a **triplet** state.
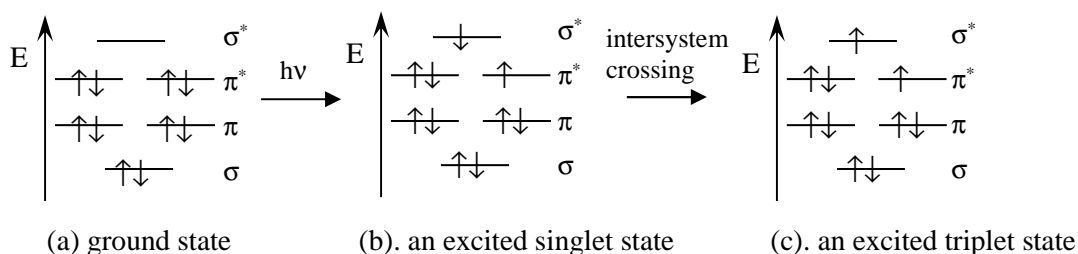

(a) ground state   (b). an excited singlet state   (c). an excited triplet state

Figure 2.4.7: Ground and excited states for Cl_2.

Most molecules have singlet ground states. The absorption of light cannot flip the spin of the electron. Therefore, if the molecule has a ground singlet state, the excited state produced from the absorption of light will also be a singlet state. Emission of light from the excited singlet state back to the ground singlet state is called fluorescence. On the other hand, collisions of the molecule can result in a spin flip from the excited singlet state to produce an excited triplet state. This process is called **intersystem crossing**. Emission from the excited triplet state back to the

ground singlet state requires a change in energy and a spin flip, which requires a longer time than a fluorescent transition. The emission from the excited triplet state to the ground singlet state is called phosphorescence. Iodine can be detected with high sensitivity using laser induced phosphorescence. Glow-in-the-dark watch dials and plastic stick-on stars are examples of phosphorescent materials. Fluorescent light bulbs are actually based on phosphorescence.

Conductivity: Conductivity is a widely used technique for determining concentration. Many pH meters can be equipped with a conductivity probe, and dedicated meters are also common. Conductivity is widely used in water quality determinations for lakes and rivers and in oceanography for salinity determinations. Gas phase conductivity is used in fire alarms. Electron capture and photoionization detectors for gas chromatography are also based on conductivity. The theory of conductivity is central for separations techniques such as gel and capillary electrophoresis and electrodialysis. More importantly, however, conductivity is a general property of solids and solutions. The general theory of conductivity is particularly important for understanding membrane systems. Conductivity is an example of a generalized flux-force relationship. Understanding conductivity will be a good introduction to fluxes.

  Ions conduct electric current through solutions. Solutions of ionic substances, like NaCl, are called electrolyte solutions. You are familiar with Ohm's Law for metallic conductors, $\Delta\phi = IR$, and Ohm's Law also holds for electrolyte solutions. Consider a solution with two electrodes of cross sectional area A, Figure 2.4.8. A small potential difference is placed across the two electrodes, $\Delta\phi = \phi_R - \phi_L$. Cations migrate to the cathode and anions will migrate to the anode. The measured current is given by $\Delta\phi = IR$, with R the resistance of the solution.
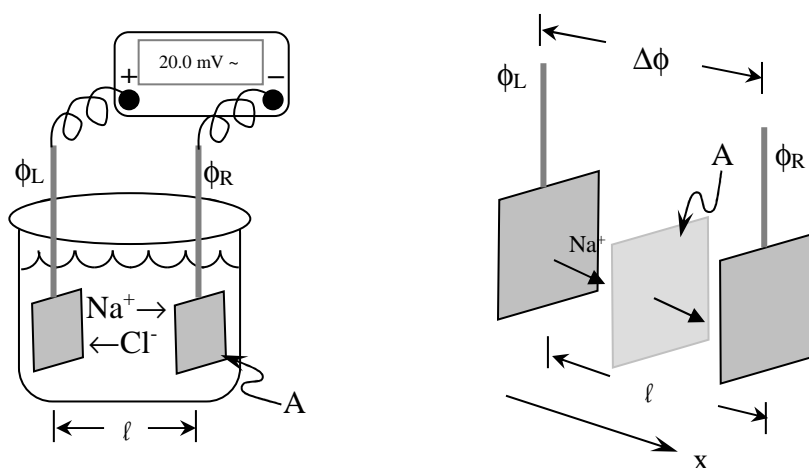

Figure 2.4.8: Electrical conductivity is determined by placing a potential difference between two electrodes, $\Delta\phi$, and measuring the current, I.

  The resistance is inversely proportional to the concentration of the solution for a strong electrolyte. As the solute concentration increases the resistance decreases. A direct proportionality is more convenient than an inverse relationship. The solution is more directly characterized by the **conductance**, G, which is defined as the inverse of the resistance:

$$G \equiv 1/R \qquad\qquad 2.4.11$$

The units are ohms^{-1}; the SI units are called siemens, $1\ S = 1\ ohm^{-1}$.

The conductance of the solution is directly proportional to the cross sectional area of the electrodes, A, and inversely proportional to the distance between the electrodes, ℓ. Normalizing the conductance to these geometric variables provides an intrinsic measure of the solution to conduct current. The **conductivity** is defined as:

$$\kappa \equiv \frac{1}{R}\left(\frac{\ell}{A}\right) = \frac{G\,\ell}{A} \qquad\qquad 2.4.12$$

Conductivity meters give the conductivity directly. The units are S m^{-1} or S cm^{-1}. For example, the recommended conductivity for a goldfish aquarium is 40 mS m^{-1}, or equivalently, 400 μS cm^{-1}. The units are related by 1 mS m^{-1} = 1x10^{-3} S m^{-1} and 1 μS cm^{-1} = 1x10^{-6} S cm^{-1}. Drinking water is usually below 150 μS cm^{-1}. The conductivity depends on the solute concentration; the higher the concentration the higher the conductivity. The higher the conductivity the better the solution conducts electricity. The molar conductivity is defined as:

$$\Lambda_m = \kappa/c \qquad\qquad 2.4.13$$

where c is the molar concentration. Extensive tables are available of molar conductivities. The use of conductivity for concentration determinations is based on Eq. 2.4.13; solving for the conductivity gives:

$$\kappa = \Lambda_m\, c \qquad\qquad 2.4.14$$

The molar conductivity is just the proportionality constant for the linear dependence of conductivity on concentration. Conductivity can then be used to monitor the course of chemical reactions just like absorbance, fluorescence, and NMR measurements, as long as the reaction has a change in the conductivity.

Unfortunately, the molar conductivity is concentration dependent. For strong electrolytes, experimental data shows that the molar conductivity over a large concentration range is given by:

$$\Lambda_m = \Lambda_m^\circ - \mathcal{K}\, c^{1/2} \qquad\qquad \text{(strong electrolytes)} \quad 2.4.15$$

where Λ_m° is the limiting molar conductivity and $\mathcal{K}$ is a constant that is dependent on the electrolyte. The limiting molar conductivity, Λ_m°, is the molar conductivity extrapolated to zero concentration, where the ions are infinitely far apart giving no forces between ions. The concentration dependence comes from the interactions among the ions; the attractions between cations and anions act as a drag that slows the ion movements. For example, the molar conductivity of 1 M HCl is about 25% less than the limiting molar conductivity. However, if the range of concentrations is kept small enough, linear behavior is observed and conductivity is an easy and general measurement of concentration for ionic substances. For strong electrolytes over larger concentration ranges or for more accurate concentration determinations, Eq. 2.4.15 can be substituted into Eq. 2.4.14 to give a non-linear calibration equation:

$$\kappa = (\Lambda_m^\circ - \mathcal{K}\, c^{1/2})\, c = \Lambda_m^\circ\, c - \mathcal{K}\, c^{3/2} \qquad\qquad \text{(strong electrolytes)} \quad 2.4.16$$

where Λ_m° and $\mathcal{K}$ are available in reference tables or they can also be determined by calibration using known standard solutions. The conductivity of <u>weak</u> electrolytes is a strong function of concentration; we will consider the conductivity of weak electrolytes in the chapter on chemical equilibrium.

Example 2.4.3: *Limiting Molar Conductivity*

The limiting molar conductivity can be calculated from contributions of individual ionic species using $\Lambda_m^\circ = \nu_+\lambda_+ + \nu_-\lambda_-$ where ν_+ and ν_- are the number of ions in the formula, $M_{\nu+}X_{\nu-}$, while λ_+ and λ_- are limiting ionic conductivities. For example, $CaCl_2$ corresponds to $\nu_+ = 1$ and $\nu_- = 2$. There are extensive compilations of limiting ionic conductivities in standard references.[1] The limiting ionic conductivities of the Na^+ and Cl^- ions are 5.01 and 7.63 mS m^2 mol^{-1}, respectively. Calculate the NaCl concentration that corresponds to the recommended conductivity for a goldfish aquarium of 40 mS m^{-1}, or equivalently, 400 µS cm^{-1}.

Answer: For NaCl, $\nu_+ = 1$ and $\nu_- = 1$, giving the limiting molar conductivity for NaCl as:
$$\Lambda_m^\circ = \nu_+\lambda_+ + \nu_-\lambda_- = 5.01 + 7.63 \text{ mS m}^2 \text{ mol}^{-1} = 12.64 \text{ mS m}^2 \text{ mol}^{-1}$$

Approximating the molar conductivity of the solution as the limiting value, $\Lambda_m \approx \Lambda_m^\circ$ and using Eq. 2.4.13 with the target conductivity gives:
$$c = \frac{\kappa}{\Lambda_m} = \frac{40 \text{ mS m}^{-1}}{12.64 \text{ mS m}^2 \text{ mol}^{-1}} \ (1 \text{ m}^3/1000 \text{ L}) = 3.16\text{x}10^{-3} \text{ mol L}^{-1}$$

How accurate is our approximation that $\Lambda_m \approx \Lambda_m^\circ$? From standard reference tables, the molar conductivity of a 0.005 M solution of NaCl is 12.059 mS m^2 mol^{-1}, which is close enough to our concentration.[1] So the error in using the limiting, zero concentration value of 12.64 compared to 12.059 mS m^2 mol^{-1} is 5%, which is good enough for many purposes.

2.5 Generalized Flux-Force Relationships

Electrical conductivity involves the movement of ions through the solution as they are "pulled" by the applied electric potential. This motion of ions is a flux, and the flux is controlled by the applied potential. Electrophoresis uses this flux as a separations tool, and electro-blotting and related techniques use these fluxes to transfer ions from place to place. We now consider the electric potential dependence of the ion flux. Consider a surface, of area A, placed between the two electrodes, each of area A, in Figure 2.4.8. The electrical flux, J_{el}, is the flow of charge through this surface per unit time per unit area. The current through the cell is proportional to the flux and the surface area, $I = -J_{el} A$. The negative sign is necessary because, when the current in the external circuit flows from right to left, the corresponding current of cations in the solution is from left to right. The units of current are amps, or equivalently coulombs per second, 1 amp = 1 C s^{-1}. The units of the electric flux are amps per m^2, or equivalently C m^{-2} s^{-1}. Ohm's Law can be rearranged to give the current,

$$I = \frac{1}{R} \Delta\phi \qquad\qquad 2.5.1$$

Solving Eq. 2.4.12 for 1/R in terms of the conductivity and substituting into Eq. 2.5.1 gives:

$$I = \left(\frac{\kappa A}{\ell}\right) \Delta\phi \qquad\qquad 2.5.2$$

Given that $I = -J_{el} A$, dividing both sides of Eq. 2.5.2 by the surface area, A, gives:

$$J_{el} = -\kappa \left(\frac{\Delta\phi}{\ell} \right)$$ 2.5.3

This equation for the electric flux can be generalized by noting that the $\Delta\phi/\ell$ term is the electric field between two parallel plates. In other words, the electric flux, which is the flow of charge, is proportional to the electric field that the ions experience. The greater the electric field the greater the "pull" on the ions. The electric field, $\mathscr{E}_x$, is the negative of the gradient of the electric potential, which in turn is $-\Delta\phi/\ell$ for two parallel plates, Figure 2.5.1:

$$\mathscr{E}_x = -\frac{d\phi}{dx} = -\left(\frac{(\phi_R - \phi_L)}{\ell} \right) = -\left(\frac{\Delta\phi}{\ell} \right)$$ 2.5.4
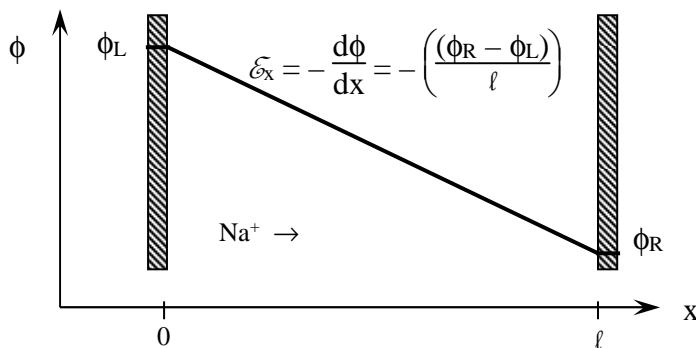

Figure 2.5.1: The electric potential decreases linearly between two parallel plates. The electric field is the negative of the gradient of the electric potential.

Note the similarity of Eqs. 2.5.4 and 2.3.4. The magnitude of the electric field increases as the electrodes get closer together, for a fixed potential difference. For different geometries other than parallel plates, it is best to write Eq. 2.5.3 in terms of the electric field or the potential gradient. Substituting $d\phi/dx$ for $\Delta\phi/\ell$ in Eq. 2.5.3, gives the electric flux in terms of the negative gradient of the electric potential:

$$J_{el} = -\kappa \frac{d\phi}{dx}$$ 2.5.5

Cations flow from regions of high electric potential to regions of low electric potential.

§2

General Pattern 2: Generalized Flux-Force relationships: Fick's First Law for diffusion, Eq. 2.3.5, and electrical conductivity, Eqs. 2.5.3 and 2.5.5, are examples of generalized flux-force relationships. This form is quite general and we will encounter similar linear flux relationships when we consider conductive heat transfer and chemical reactions close to equilibrium. The general form is often written as:

$$J_i = L_i X_i$$ 2.5.6

where J_i is the flux, which is the flow per unit time per unit area

X_i is the generalized force for transfer, which is a gradient with units per unit distance

and L_i is a linear coefficient

The generalized force is the gradient of an intensive parameter. For electrical conductivity, the force is the gradient of the electric potential and the linear coefficient is the conductivity, κ. The linear relationships make these flow processes easy to model. We will use the interactions of diffusion, conductive heat transfer, and chemical reactions when we consider non-equilibrium steady states. These ideas are central for understanding membrane potentials and membrane-based energy transduction during metabolism and photosynthesis. One way to help understand these relationships is to compare generalized flux relationships with Ohm's Law:

$$J_i = L_i X_i \qquad \longleftrightarrow \qquad I = \frac{1}{R} \Delta\phi$$

The flux is analogous to a current. The linear coefficient is a conductance, which increases with increasing ability of the system to conduct matter, charge, or energy. The force is the potential gradient. A potential gradient is a difference in potential divided by the distance. The gradient of the potential drives the flow. The difference between the flux equation and Ohm's Law is that the flux is per unit area.

Fick's First Law, Eq. 2.3.5, is also a linear flux-force relationship. The "generalized force" for concentration change is the concentration gradient. For diffusion, the concentration gradient is not an actual force, but rather an expression of the statistical probability for molecules to spread out over time. However, associating the concentration gradient with other generalized forces is a useful way of understanding molecular diffusion. Concentration gradients drive mass transfer.

Not all flux relationships are linear. For example, heat flux can be nonlinear for large temperature gradients. Flux-force relationships based on chemical reactions are often nonlinear.

For a system at equilibrium, all fluxes are equal to zero, averaged over time. A system in a steady state has at least one non-zero constant flux, since the steady state must be maintained away from equilibrium by the constant input of matter or energy. In the next chapter on kinetics, we consider fluxes that are caused by chemical reactions.

℘2

2.6 Absorbance of Mixtures

UV-visible absorbance is particularly useful for measuring concentrations because the spectrum of a solution can be used to determine the concentration of more than one component. If the absorbance spectra of two constituents in solution have negligible overlap at the wavelengths of maximum absorption for the two components, then Eq. 2.4.6 can be solved separately for the two components. However, the absorption spectra for substances often show considerable overlap, Figure 2.6.1. The absorbance of a mixture is just the sum of the absorbances of the constituents, assuming that there are no interactions between the constituents. Consider a two-component mixture. Let constituent 1 have a molar absorbance coefficient at wavelength λ of $\varepsilon_{\lambda 1}$ and constituent 2 have a molar absorbance coefficient at the same wavelength of $\varepsilon_{\lambda 2}$. The absorbance of the solution is:

$$A_\lambda = \varepsilon_{\lambda 1} \, \ell \, c_1 + \varepsilon_{\lambda 2} \, \ell \, c_2 \qquad\qquad 2.6.1$$

where the concentration of components 1 and 2 are c_1 and c_2, respectively. The molar absorption coefficients are determined by calibration on solutions with just constituent 1 or 2 alone. In the analysis of an unknown, Eq. 2.6.1 alone is not sufficient to determine the concentrations. A measurement at a second wavelength is necessary. Call the two wavelengths λ_1 and λ_2. The two measurements then provide two simultaneous equations with two unknowns:

$$A_1 = \varepsilon_{11}\, \ell\, c_1 + \varepsilon_{12}\, \ell\, c_2 \qquad \leftarrow \text{ for } \lambda 1$$
$$A_2 = \varepsilon_{21}\, \ell\, c_1 + \varepsilon_{22}\, \ell\, c_2 \qquad \leftarrow \text{ for } \lambda 2 \qquad\qquad 2.6.2$$

The molar absorbance coefficients are illustrated in Figure 2.6.1. For an unknown solution, the absorbances at the two wavelengths, A_1 and A_2, are determined and then Eqs. 2.6.2 are solved for the concentrations of the unknowns, c_1 and c_2.
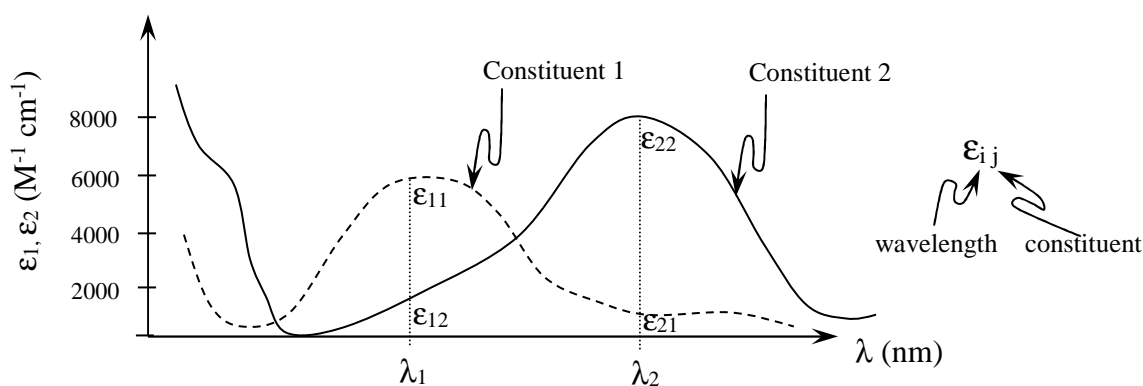

Figure 2.6.1: Absorbance of a solution is the sum of the absorbances of the constituents. Measurements at two wavelengths are necessary to determine the composition of a two-constituent solution if the absorbance bands overlap. The first subscript indexes the constituent and the second subscript indexes the wavelength.

We have an ulterior motive in dealing with absorbance of mixtures. We want to introduce you to a little matrix algebra. Matrix algebra is a general purpose tool for solving simultaneous equations, among many uses. Matrix algebra is also a handy way to simplify the way equations are written that helps us focus on the underlying issues. Matrix techniques will be central in several upcoming sections. This application to the solution of simultaneous equations will be a good way to help you get used to powerful matrix techniques.

Eqs. 2.6.2 are straightforward enough. However, it is often convenient to write simultaneous equations in matrix form. Assuming the path length, ℓ, is 1 cm for convenience:

$$\overset{\text{constituent 1 \quad constituent 2}}{\underset{\downarrow \qquad\qquad \downarrow}{}}$$

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad \begin{matrix} \leftarrow \lambda_1 \\ \leftarrow \lambda_2 \end{matrix} \qquad\qquad (\ell = 1 \text{ cm}) \qquad 2.6.3$$

Eq. 2.6.3 and Eqs. 2.6.2 are completely equivalent. The absorbance vector and the concentrations vector are given symbols with one underscore "~":

$$\underset{\sim}{A} = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} \quad \text{and} \quad \underset{\sim}{c} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad \text{2.6.4}$$

You are familiar with vectors from General Physics; however, the vectors in General Physics had three components, one each for the x, y, and z directions. Vectors in general can have any number of components. In mechanics, you probably used a symbol like $\vec{v}$ to indicate a vector. Both types of notation are used interchangeably. The matrix of coefficients for the simultaneous set of equations is given a symbol with an underscore "$\approx$" to indicate it is a matrix:

$$\underset{\approx}{\varepsilon} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix} \qquad \text{2.6.5}$$

Using this notation, Eq. 2.6.3 becomes:

$$\underset{\sim}{A} = \underset{\approx}{\varepsilon} \, \underset{\sim}{c} \qquad (\ell = 1 \text{ cm}) \qquad \text{2.6.6}$$

Matrices in general have rows and columns:

$$\begin{array}{cc} \text{column 1} & \text{column 2} \\ \downarrow & \downarrow \end{array}$$

$$\begin{array}{c} \text{row 1} \rightarrow \\ \text{row2} \rightarrow \end{array} \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix}$$

For each element in the matrix, ε_{ij}, the first index is for the row number and the second index is for the column number. Eq. 2.6.5 is a square matrix with 2 rows and 2 columns, that is, it is a 2x2 matrix. For more information on matrix algebra, please consult the Addendum, Section 2.8.

Example 2.6.1: *Matrices and the Absorbance of Mixtures*
Use Figure 2.6.1 to estimate the coefficient matrix for the corresponding set of linear simultaneous equations.

Answer: Following the dotted curve for constituent 1, the molar absorption coefficient at wavelength one is $\varepsilon_{11} = 6000$ M^{-1} cm^{-1}, but the molar adsorption coefficent at wavelength 2 is much smaller, $\varepsilon_{21} = 1000$ M^{-1} cm^{-1}. Following the solid curve for component 2, at wavelength 1 the value is small, $\varepsilon_{12} = 1800$ M^{-1} cm^{-1}, but much larger at wavelength 2, $\varepsilon_{22} = 8000$ M^{-1} cm^{-1}. Building the matrix gives:

$$\underset{\approx}{\varepsilon} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix} = \begin{pmatrix} 6000 & 1800 \\ 1000 & 8000 \end{pmatrix} \qquad \text{2.6.7}$$

Example 2.6.2: *Absorbance of a Mixture*
Using the molar absorption coefficients from Eq. 2.6.7, assume that the concentration of constituent 1 is 2.54×10^{-5} M and constituent 2 is 0.86×10^{-5} M, and a cuvette pathlength of 1 cm. Calculate the absorbance of the solution at the two wavelengths. Assume the molar absorption coefficients are known to three significant figures.

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Answer: From Eq. 2.6.3:

$$A = \underset{\approx}{\varepsilon} \, \underset{\sim}{c} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 6000 & 1800 \\ 1000 & 8000 \end{pmatrix} \begin{pmatrix} 2.54 \times 10^{-5} \text{ M} \\ 0.86 \times 10^{-5} \text{ M} \end{pmatrix} =$$

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} 6000(2.54 \times 10^{-5}) + 1800(0.86 \times 10^{-5}) \\ 1000(2.54 \times 10^{-5}) + 8000(0.86 \times 10^{-5}) \end{pmatrix} = \begin{pmatrix} 0.168 \\ 0.094 \end{pmatrix}$$

The pattern for the multiplication can be seen from comparison of Eq. 2.6.2 and 2.6.3. The general case is discussed in the Addendum on matrix algebra, Section 2.8. The absorbance at the first wavelength is 0.168 and at the second is 0.094.

The form of the matrix in Eq. 2.6.7 is particularly useful. The elements ε_{11} and ε_{22} are called the diagonal elements; they lie along the main diagonal of the matrix. These coefficients show the major absorptions. The elements ε_{12} and ε_{21} are called off-diagonal elements. These off-diagonal elements would be zero if the absorption bands of the two constituents showed no overlap. The non-zero values in our example show that the two components cause an interaction between the absorbances of the two constituents. In this case, there is no chemical interaction; the interaction is just that both components absorb at both wavelengths. In cases that we will see in later chapters, the off-diagonal elements indicate a chemical interaction or a coupling of processes. Putting the equations in matrix form helps to make these interactions easier to see— it's a "can't see the forest for the trees" thing.

The big advantage of using matrix notation for simultaneous equations is that these equations have general solutions. In other words, the algebra is pretty much automatic, saving you a lot of work. The formal solution to Eq. 2.6.3 is calculated using the inverse of the matrix:

$$\underset{\approx}{\varepsilon}^{-1} \, \underset{\sim}{A} = \underset{\sim}{c} \qquad\qquad (\ell = 1 \text{ cm}) \qquad 2.6.8$$

If the path length is not 1 cm then including the path length gives $(\underset{\approx}{\varepsilon}\ell)^{-1} \, \underset{\sim}{A} = \underset{\sim}{c}$. Eq. 2.6.8 looks a little abstruse, but it is really quite simple to implement, especially using Excel, a handheld calculator, or a mathematical analysis package like *Mathematica*, *Maple*, or *MatLab*. Let's switch into general notation for a moment to highlight the general pattern in Eqs. 2.6.3 and 2.6.8.

℘3

General Pattern 3: The Matrix Solution of Simultaneous Linear Equations:

Consider the set of simultaneous linear equations:

$$a_1 = M_{11} b_1 + M_{12} b_2$$
$$a_2 = M_{21} b_1 + M_{22} b_2 \qquad\qquad 2.6.9$$

The corresponding general matrix equation for the simultaneous linear equations is:

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \qquad\qquad 2.6.10$$

which is equivalent to:

$$\underset{\sim}{a} = \underset{\approx}{M} \, \underset{\sim}{b} \qquad\qquad 2.6.11$$

where $\underset{\approx}{M}$ is the matrix of coefficients for the simultaneous set of equations. Assume the matrix $\underset{\approx}{M}$ and the vector $\underset{\sim}{a}$ are known. We solve for the vector $\underset{\sim}{b}$ by multiplying from the left by $\underset{\approx}{M}^{-1}$:

$$\underset{\approx}{M}^{-1} \underset{\sim}{a} = \underset{\sim}{b} \tag{2.6.12}$$

where $\underset{\approx}{M}^{-1}$ is the matrix inverse of $\underset{\approx}{M}$:

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}^{-1} = \frac{1}{|M|}\begin{pmatrix} M_{22} & -M_{12} \\ -M_{21} & M_{11} \end{pmatrix} \tag{2.6.13}$$

and |M| is the determinant of the matrix:

$$|M| = M_{11} M_{22} - M_{12} M_{21} \tag{2.6.14}$$

The Addendum, Section 2.8, gives the instructions for calculating inverses for larger matrices and for using Excel to calculate Eq. 2.6.12.

℘3

Example 2.6.3: *Concentration Determination of Mixtures Using Light Absorption*
Using the molar absorption coefficients from Eq. 2.6.7, calculate the concentrations of constituents 1 and 2 given that the absorbance of an unknown at wavelength 1 is 0.168 and at wavelength 2 is 0.094. The cuvette path length is 1 cm. Assume the molar absorption coefficients are known to three significant figures.

Answer: We need to solve the equation Eq. 2.6.3, $\underset{\sim}{A} = \underset{\approx}{\varepsilon}\,\underset{\sim}{c}$, for the concentration vector $\underset{\sim}{c}$.

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \qquad \text{or explicitly} \qquad \begin{pmatrix} 0.168 \\ 0.094 \end{pmatrix} = \begin{pmatrix} 6000 & 1800 \\ 1000 & 8000 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

The determinant of the matrix is $|\varepsilon| = 6000(8000)-1000(1800) = 4.62 \times 10^7$. The inverse, using Eq. 2.6.13 is:

$$\underset{\approx}{\varepsilon}^{-1} = \frac{1}{4.62 \times 10^7}\begin{pmatrix} 8000 & -1800 \\ -1000 & 6000 \end{pmatrix} = \begin{pmatrix} 1.732 \times 10^{-4} & -3.896 \times 10^{-5} \\ -2.164 \times 10^{-5} & 1.299 \times 10^{-4} \end{pmatrix}$$

Substitution into Eq. 2.6.8 gives:

$$\underset{\sim}{c} = \underset{\approx}{\varepsilon}^{-1}\underset{\sim}{A} = \begin{pmatrix} 1.732 \times 10^{-4} & -3.896 \times 10^{-5} \\ -2.164 \times 10^{-5} & 1.299 \times 10^{-4} \end{pmatrix}\begin{pmatrix} 0.168 \\ 0.094 \end{pmatrix} = \begin{pmatrix} 2.54 \times 10^{-5}\,M \\ 0.86 \times 10^{-5}\,M \end{pmatrix}$$

The concentration of constituent 1 is 2.54×10^{-5} M and constituent 2 is 0.86×10^{-5} M. Of course normally, we would just use Excel, but doing the problem by hand should help you feel more confident. This example is the reverse of Example 2.6.2, so we can compare to check that we got the correct answer and to look for self-consistency. See Problem 27 for suggestions on error analysis.

2.7 Summary—The Goal of Physical Chemistry

Chemical systems can be at equilibrium with uniform concentrations in each phase. Chemical systems can also be quite dynamic, with chemical reactions and fluxes of chemical species, charge, and energy. Our goal now is to understand as completely as possible the response of chemical systems to changes in conditions and the approach to equilibrium.

   Looking at the progression of this text, we first discuss the kinetics of chemical reactions. The remainder of Part 1 is devoted to equilibrium thermodynamics and linear non-equilibrium thermodynamics. Part 2 moves into the microscopic world to discuss the nature of the chemical bond and other quantum chemical concepts. Part 3 is devoted to statistical mechanics. Statistical mechanics is the bridge that joins the microscopic and macroscopic world. The goal of statistical mechanics is to derive the values of the equilibrium constants and rate constants for any chemical process from quantum chemical calculations or spectroscopic information.

   The goal of physical chemistry is to be able to sit at our desk and make accurate quantitative predictions of the equilibrium constants and rate constants for any given chemical process. We then want to use that information to design solutions for life's pressing needs.

2.8 Addendum: A Brief Introduction to Matrix Algebra

General Properties of Matrices: Matrices are characterized by the number of rows and columns:

$$\text{A 2x4 matrix:} \begin{pmatrix} 2 & 3 & 1 & 5 \\ 3 & 7 & 1 & 0 \end{pmatrix} \qquad \text{A 3x3 square matrix:} \begin{pmatrix} 2 & 5 & 0 \\ 3 & 5 & 1 \\ 4 & 5 & 1 \end{pmatrix}$$

A column vector is an nx1 matrix, which is a matrix with a single column. A row vector is a 1xn matrix, which is a matrix with a single row:

$$\text{A 4x1 column vector:} \begin{pmatrix} 2 \\ 4 \\ 3 \\ 5 \end{pmatrix} \qquad \text{A 1x4 row vector:} \begin{pmatrix} 2 & 5 & 3 & 5 \end{pmatrix}$$

Vectors follow the same algebra rules as matrices. Matrices add element by element for the matching row and column:

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} + \begin{pmatrix} N_{11} & N_{12} \\ N_{21} & N_{22} \end{pmatrix} = \begin{pmatrix} M_{11}+N_{11} & M_{12}+N_{12} \\ M_{21}+N_{21} & M_{22}+N_{22} \end{pmatrix} \qquad 2.8.1$$

Multiplication of each element of a matrix by a number is called **scalar multiplication**:

$$c \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \\ M_{31} & M_{32} \end{pmatrix} = \begin{pmatrix} c\,M_{11} & c\,M_{12} \\ c\,M_{21} & c\,M_{22} \\ c\,M_{31} & c\,M_{32} \end{pmatrix} \qquad 2.8.2$$

The number, c, is called a scalar. To multiply a vector by a matrix, $\underset{\approx}{M}\ \underset{\sim}{a}$, the row elements of the matrix are multiplied by the column elements of the vector. The first element in the result is:

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} M_{11}\,a_1 + M_{12}\,a_2 \\ \text{---} \end{pmatrix} \qquad 2.8.3$$

For the second element in the result:

$$\left(\begin{array}{cc} M_{11} & M_{12} \\ \hline M_{21} & M_{22} \end{array}\right) \left(\begin{array}{c} a_1 \\ a_2 \end{array}\right) = \left(\begin{array}{c} M_{11}\, a_1 + M_{12}\, a_2 \\ M_{21}\, a_1 + M_{22}\, a_2 \end{array}\right)$$

2.8.4

Take a moment and verify the relationship between Eqs. 2.6.3, 2.8.3, and 2.8.4. A matrix multiplied by a matrix follows the same pattern, for each column of the product matrix:

$$\left(\begin{array}{cc} M_{11} & M_{12} \\ M_{21} & M_{22} \end{array}\right) \left(\begin{array}{cc} N_{11} & N_{12} \\ N_{21} & N_{22} \end{array}\right) = \left(\begin{array}{cc} M_{11}\,N_{11} + M_{12}\,N_{21} & M_{11}\,N_{12} + M_{12}\,N_{22} \\ M_{21}\,N_{11} + M_{22}\,N_{21} & M_{21}\,N_{12} + M_{22}\,N_{22} \end{array}\right)$$

2.8.5

For matrix multiplication to work, the left matrix must have the same number of columns as the right matrix has rows. Note that the order of multiplication is important. Matrices are not commutative, that is $\underset{\approx}{M}\,\underset{\approx}{N} \neq \underset{\approx}{N}\,\underset{\approx}{M}$, except for unusual circumstances. For example, notice that Eqs. 2.8.3 and 2.8.4 rearranged as $\underset{\sim}{a}\,\underset{\approx}{M}$ does not work following the rules of matrix multiplication.

The unit matrix has 1's on the diagonal and 0's for the off-diagonal elements:

$$\underset{\approx}{I} = \left(\begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}\right)$$

2.8.6

The unit matrix is the identity element for matrix operations. The unit matrix acts just like the number 1 in multiplication:

$$\underset{\approx}{M}\,\underset{\approx}{I} = \underset{\approx}{M}$$

2.8.7

The zero matrix has elements that are all zero:

$$\underset{\approx}{0} = \left(\begin{array}{cc} 0 & 0 \\ 0 & 0 \end{array}\right)$$

2.8.8

The zero matrix acts just like the number zero:

$$\underset{\approx}{M} + \underset{\approx}{0} = \underset{\approx}{M}$$

2.8.9

The transpose of a matrix exchanges all the rows for columns. The transpose of matrix M is indicated by $\underset{\approx}{M}^{\mathrm{T}}$:

$$\text{given}\quad \underset{\approx}{M} = \left(\begin{array}{cccc} 2 & 3 & 1 & 5 \\ 4 & 7 & 6 & 0 \end{array}\right)\qquad \underset{\approx}{M}^{\mathrm{T}} = \left(\begin{array}{cc} 2 & 4 \\ 3 & 7 \\ 1 & 6 \\ 5 & 0 \end{array}\right)$$

2.8.10

In other words, you just switch the subscripts: given matrix $\underset{\approx}{M}$ with elements M_{ij} the transpose has elements M_{ji}. The transpose of a column vector is a row vector. Notice that, because of the rules of matrix multiplication you can't multiply a column vector by a column vector. However, you can multiply the transpose of a column vector by a column vector as long as both vectors have the same dimension:

$$\underset{\sim}{A}^{\mathrm{T}}\,\underset{\sim}{B} = \left(\begin{array}{c} A_1 \\ A_2 \end{array}\right)^{\mathrm{T}} \left(\begin{array}{c} B_1 \\ B_2 \end{array}\right) = (A_1\, A_2) \left(\begin{array}{c} B_1 \\ B_2 \end{array}\right) = A_1\,B_1 + A_2\,B_2$$

2.8.11

Notice that this result is the dot product of the two vectors, which you used many times in physics; $\underset{\sim}{A}^T \underset{\sim}{B} = \vec{A} \cdot \vec{B}$.

The properties of matrices are almost the same as for scalar numbers, except the lack of matrix commutivity for multiplication. Given matrices $\underset{\sim}{A}$, $\underset{\sim}{B}$, and $\underset{\sim}{C}$ and scalar numbers c and d, the general properties are given in Table 2.8.1. Note that a vector $\underset{\sim}{A}$ is just an nx1 or 1xn matrix, so row or column vectors can be substituted for any of the matrices, assuming the dimensions match the required values for the operation.

Table 2.8.1: Properties of Matrices. For addition, matrices must have the same dimensions. For multiplication, the dimensions must match pxq with qxr.

$\underset{\sim}{A}+(\underset{\sim}{B}+\underset{\sim}{C}) = (\underset{\sim}{A}+\underset{\sim}{B})+\underset{\sim}{C}$	Additive associative law
$\underset{\sim}{A}+\underset{\sim}{B} = \underset{\sim}{B}+\underset{\sim}{A}$	Additive commutative law
$c(\underset{\sim}{A}+\underset{\sim}{B}) = c\underset{\sim}{A}+c\underset{\sim}{B}$	Scalar distributive law
$(c+d)\underset{\sim}{A} = c\underset{\sim}{A}+d\underset{\sim}{A}$	Scalar distributive law
$\underset{\sim}{A}(\underset{\sim}{B}\underset{\sim}{C}) = (\underset{\sim}{A}\underset{\sim}{B})\underset{\sim}{C}$	Multiplicative associative law
$\underset{\sim}{A}(\underset{\sim}{B}+\underset{\sim}{C}) = \underset{\sim}{A}\underset{\sim}{B} + \underset{\sim}{A}\underset{\sim}{C}$	Distributive law
$(\underset{\sim}{A}+\underset{\sim}{B})\underset{\sim}{C} = \underset{\sim}{A}\underset{\sim}{C} + \underset{\sim}{B}\underset{\sim}{C}$	Distributive law
$(\underset{\sim}{A}+\underset{\sim}{B})^T = \underset{\sim}{A}^T + \underset{\sim}{B}^T$	Transpose of a sum
$(c\underset{\sim}{A})^T = c(\underset{\sim}{A}^T)$	Transpose of a scalar multiple
$(\underset{\sim}{A}\underset{\sim}{B})^T = \underset{\sim}{B}^T\underset{\sim}{A}^T$	Transpose of a matrix product

Example 2.8.1:

Do the matrix multiplication: $\begin{pmatrix} 2 & 5 & 2 \\ 3 & 6 & 1 \end{pmatrix}\begin{pmatrix} 4 \\ 5 \\ 1 \end{pmatrix}$

Answer: For the first element in the result:

$$\begin{pmatrix} 2 & 5 & 2 \\ 3 & 6 & 1 \end{pmatrix} \begin{pmatrix} 4 \\ 5 \\ 1 \end{pmatrix} = \begin{pmatrix} 2(4) + 5(5) + 2(1) \\ \text{---} \end{pmatrix}$$

For the second element:

$$\begin{pmatrix} 2 & 5 & 2 \\ 3 & 6 & 1 \end{pmatrix} \begin{pmatrix} 4 \\ 5 \\ 1 \end{pmatrix} = \begin{pmatrix} 2(4) + 5(5) + 2(1) \\ 3(4) + 6(5) + 1(1) \end{pmatrix}$$

Giving the final result:

$$\begin{pmatrix} 2 & 5 & 2 \\ 3 & 6 & 1 \end{pmatrix}\begin{pmatrix} 4 \\ 5 \\ 1 \end{pmatrix} = \begin{pmatrix} 35 \\ 43 \end{pmatrix}$$

Example 2.8.2:

The length of a vector can be calculated by $|\underline{B}| = \sqrt{\underline{B}^T\underline{B}}$. Find the length of the vector $\begin{pmatrix} 4 \\ 5 \\ 1 \end{pmatrix}$.

Answer: $\underline{B}^T\underline{B} = (4 \ 5 \ 1)\begin{pmatrix} 4 \\ 5 \\ 1 \end{pmatrix} = 4(4) + 5(5) + 1(1) = 42$. The length is then $\sqrt{42} = 6.48$

Example 2.8.3:

Calculate $\begin{pmatrix} 1 & 3 \\ 2 & 4 \end{pmatrix}\begin{pmatrix} 5 & 1 \\ 3 & 6 \end{pmatrix}$

Answer: $\begin{pmatrix} 1 & 3 \\ 2 & 4 \end{pmatrix}\begin{pmatrix} 5 & 1 \\ 3 & 6 \end{pmatrix} = \begin{pmatrix} 1(5)+3(3) & 1(1)+3(6) \\ 2(5)+4(3) & 2(1)+4(6) \end{pmatrix} = \begin{pmatrix} 14 & 19 \\ 22 & 26 \end{pmatrix}$

Matrix Inverses: When we want to solve a normal algebraic equation we use the inverse:

$$x \ y = z \qquad \text{solving for y} \qquad y = \left(\frac{1}{x}\right) z = x^{-1} z \qquad\qquad 2.8.12$$

where $1/x$ is the inverse of x; $x^{-1} = 1/x$. We do a similar trick with matrices. The inverse of $\underline{\underline{M}}$ is defined so that:

$$\underline{\underline{M}}^{-1} \underline{\underline{M}} = \underline{\underline{I}} \qquad\qquad 2.8.13$$

just like $(1/x)(x) = 1$. For the matrix equation:

$$\underline{a} = \underline{\underline{M}} \ \underline{b} \qquad\qquad 2.8.14$$

we can solve for $\underline{b}$ by multiplying both sides of Eq. 2.8.14 from the left by $\underline{\underline{M}}^{-1}$:

$$\underline{\underline{M}}^{-1} \ \underline{a} = \underline{\underline{M}}^{-1} \underline{\underline{M}} \ \underline{b} \qquad\qquad 2.8.15$$

The right-hand side simplifies, using Eq. 2.8.13, to:

$$\underline{\underline{M}}^{-1} \ \underline{a} = \underline{b} \qquad\qquad 2.8.16$$

All we need now is the inverse of our original matrix. The inverse of a 2x2 matrix is:

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}^{-1} = \frac{1}{|M|}\begin{pmatrix} M_{22} & -M_{12} \\ -M_{21} & M_{11} \end{pmatrix} \qquad\qquad 2.8.17$$

where $|M|$ is the determinant of the matrix:

$$|M| = M_{11} M_{22} - M_{12} M_{21} \qquad\qquad 2.8.18$$

You can visualize the determinant by following the multiplications:

$$\begin{pmatrix} M_{11} & M_{12} \\ & \\ M_{21} & M_{22} \end{pmatrix}$$

However, note the change in sign for the product of the off-diagonal elements.

The inverse of a 3x3 matrix is more complicated. We list the result to show you how it can be calculated. However, it will be much easier to use Excel, *Mathematica*, *Maple*, or a programmable calculator for normal use. The inverse of a 3x3 matrix is:

$$\begin{pmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{pmatrix}^{-1} = \frac{1}{|M|} \begin{pmatrix} M_{33}M_{22}-M_{32}M_{23} & -(M_{33}M_{12}-M_{32}M_{13}) & M_{23}M_{12}-M_{22}M_{13} \\ -(M_{33}M_{21}-M_{31}M_{23}) & M_{33}M_{11}-M_{31}M_{13} & -(M_{23}M_{11}-M_{21}M_{13}) \\ M_{32}M_{21}-M_{31}M_{22} & -(M_{32}M_{11}-M_{31}M_{12}) & M_{22}M_{11}-M_{21}M_{12} \end{pmatrix}$$

with $|M| = M_{11}(M_{33}M_{22}-M_{32}M_{23})-M_{21}(M_{33}M_{12}-M_{32}M_{13})-M_{31}(M_{23}M_{12}-M_{22}M_{13})$ \qquad 2.8.19

We will discuss a general algorithm for calculating determinants below. A matrix must be a square matrix to have an inverse. However, not all square matrices can be inverted; the determinant must be non-zero.

The MINVERSE() function in Excel is particularly handy for finding inverses. Here is an example solving a 3x3 matrix. We will solve the following equation for x, y, and, z:

$$\begin{pmatrix} 2 \\ 3 \\ 2 \end{pmatrix} = \begin{pmatrix} 2 & 3 & 2 \\ 3 & 0 & 4 \\ 1 & 2 & 3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad\qquad 2.8.20$$

First input the matrix of coefficients, this example uses cells C6:E8, Figure 2.8.1. To calculate the inverse, you highlight the 3x3 range of cells in the spreadsheet where you want to place the inverse, and then input the array formula by pressing the fx button and setting up MINVERSE as =MINVERSE(C6:E8).
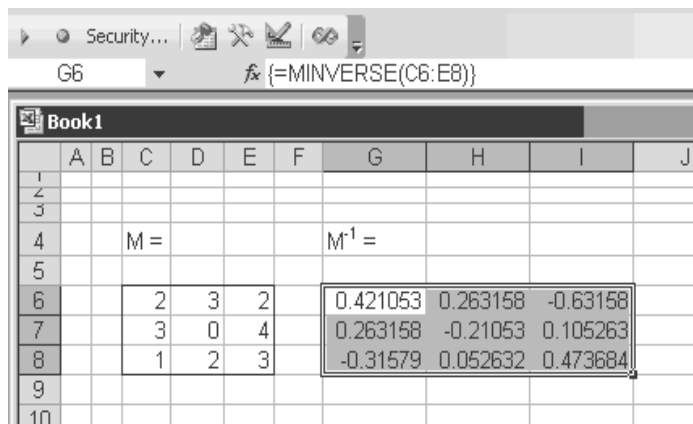

Figure 2.8.1: Calculating the inverse of a matrix in Excel. To specify an array formula, after entering the formula, highlight the entire formula in the formula bar, press and hold "Ctrl" and "Shift", and then press "Enter". Excel enters the "{" and "}" for you.

The inverse matrix is an array, so you need to specify the formula as an array formula. An array is another name for a matrix. To do this, highlight the entire formula in the formula bar including the equals sign, and press and hold "Ctrl" and "Shift" and then press "Enter". (For a Macintosh, the keys are the "Apple" key and "Return.") Excel places braces, "{ }", around the formula and converts the currently highlighted range of cells in the spreadsheet to the corresponding array: {=MINVERSE(C6:E8)}. To do the matrix multiplication in Eq. 2.7.20, you use the =MMULT() function in a similar fashion. Highlight the column cells where you want to place the result, M6:M8 in our example, and then input the array formula by pressing the *fx* button and setting up MMULT. MMULT() is also an array formula so you need to do the same trick with "Ctrl" and "Shift", and "Enter" to input the formula: {=MMULT(G6:I8,K6:K8)}. The completed spreadsheet is given in Figure 2.8.2:

A2	B	C	D	E	F	G	H	I	J	K	L	M
3												
4		M =				M⁻¹ =				a=		b=
5												
6		2	3	2		0.4211	0.2632	-0.6316		2		0.3684
7		3	0	4		0.2632	-0.2105	0.1053		3	=	0.1053
8		1	2	3		-0.3158	0.0526	0.4737		2		0.4737

Figure 2.8.2: Calculating the solution for three equations in three unknowns in Excel.

The final answer is then x = 0.3684, y = 0.1053, and z = 0.4737.

Calculating determinants: The determinant of a 2x2 matrix is given by Eq. 2.8.18. How do you calculate determinants for larger matrices? Take the case of a 3x3 matrix:

$$|M| = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} \qquad \text{2.8.21}$$

The determinant of a large matrix can be written in terms of smaller matrices called minors. The minor of a given element is the matrix obtained by striking out the row and column of the chosen element. For example, the minor for element a is given by:

$$\begin{vmatrix} \cancel{a} & \cancel{b} & \cancel{c} \\ \cancel{d} & e & f \\ \cancel{g} & h & i \end{vmatrix} = \begin{vmatrix} e & f \\ h & i \end{vmatrix} \qquad \text{2.8.22}$$

Minors have an associated sign, alternating through the matrix:

$$\begin{vmatrix} + & - & + & - \\ - & + & - & + \\ + & - & + & - \\ - & + & - & + \end{vmatrix} \qquad \text{2.8.23}$$

For example the minor for element a is positive and the minor for element d is negative. We can expand the determinant in terms of the minors of any row or column. For example, choosing the first column:

$$|M| = a \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} - d \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} + g \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} \qquad \text{2.8.24}$$

The resulting 2x2 determinants can be evaluated using Eq. 2.8.18:

$$|M| = a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - d \begin{vmatrix} b & c \\ h & i \end{vmatrix} + g \begin{vmatrix} b & c \\ e & f \end{vmatrix} \qquad \text{2.8.25}$$

The second term in this last equation is negative because the minor associated with element d has a negative sign, using Eq. 2.8.23.

We could also have expanded in terms of a row. For example, choosing the second row:

$$|M| = - d \begin{vmatrix} b & c \\ h & i \end{vmatrix} + e \begin{vmatrix} a & c \\ g & i \end{vmatrix} - f \begin{vmatrix} a & b \\ g & h \end{vmatrix} \qquad \text{2.8.26}$$

In general we pick the row or column with the most zeros for the expansion.

For larger matrices, the expansion is done in steps. For example, a 4x4 is expanded in terms of 3x3 minors and then the 3x3 determinants are expanded in terms of 2x2 minors.

Example 2.8.4:

Find the determinant of the matrix: $\quad \underset{\approx}{M} = \begin{pmatrix} 3 & 2 & 0 \\ 1 & 0 & 5 \\ 0 & 4 & 2 \end{pmatrix}$

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

$$\begin{pmatrix} 3 & 2 & 0 \\ 1 & 0 & 5 \\ 0 & 4 & 2 \end{pmatrix} \qquad \text{and} \qquad \begin{pmatrix} 3 & 2 & 0 \\ 1 & 0 & 5 \\ 0 & 4 & 2 \end{pmatrix}$$

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

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

The determinants of the 2x2 minors are:

$$\begin{vmatrix} 0 & 5 \\ 4 & 2 \end{vmatrix} = 0(2) - 4(5) = \text{-20} \quad \text{and} \quad \begin{vmatrix} 1 & 5 \\ 0 & 2 \end{vmatrix} = 1(2) - 0(5) = 2$$

giving the final determinant: $|M| = 3(\text{-20}) - 2(2) = \text{-64}$.

Excel can be used to easily calculate determinants using the "=MDETERM()" function:

A1	B	C	D	E	F	G	H
2							
3		M=				|M|=	-64
4		3	2	0			
5		1	0	5			
6		0	4	2			

The formula in H3 is "=MDETERM(C4:E6)".

Matrix algebra is widely used in statistics, economics, population biology, engineering, computer graphics, and in ranking sports teams. Knowing some matrix tricks will come in handy.

Chapter Summary

1. Dalton's Law of Partial Pressures states that the partial pressure of a gas, P_i, is the pressure the gas would exert if it were alone in the flask: $P_i V = n_i RT$ and $P_i = y_i P$ with $Y_i = n_i/n$.

2. $PV = n RT$ for the mixture of gases with $n = \sum_{i=1}^{n_s} n_i$.

3. Gas phase concentrations are defined as $c_i = {}^{n_i}/_V = {}^{P_i}/_{RT}$.

4. Mole fractions sum to one for a phase: $\sum_{i=1}^{n_s} y_i = 1$ for the gas phase, $\sum_{i=1}^{n_s} x_i = 1$ for solutions.

5. Molarity is $c_i = n_i/V$, with V in liters. Molality is $m_i = n_i/w_{solvent}$, with $w_{solvent}$ in kg.

6. Mole fractions and molality are independent of temperature. Molarity depends on temperature.

7. A flux is a flow per unit area per unit time for matter, charge, or energy.

8. The molar flux for bulk flow or convection is $J_m = c\upsilon$.

9. Fick's First Law shows that concentration gradients drive mass transfer through diffusion:

$$J_m = - D\frac{dc}{dx} .$$

10. Light flux is the power per unit area or equivalently the intensity.

11. Absorbance is defined as $A = \log(J_o/J)$.

12. The Beer Lambert Law for absorption is $A = \varepsilon \ell c$. By using absorbance, instead of the flux or intensity directly, the relationship to concentration is linear.

13. Emission intensity is also linear, or nearly-linear, with concentration, $I_f = k c$.

14. Absorption and emission bands are broad because the molecules are changing molecular electronic states and vibrational states at the same time. The width of an absorption band or an emission band in solution is given by the range of vibrational excitations.

15. Molecules have more than one excited state, and therefore often have more than one absorption band in the UV-visible range of the spectrum.

16. Fluorescence is redder than the corresponding absorption. Fluorescence always occurs from the lowest vibrational energy state of the first molecular excited state.

17. The loss of vibrational energy within a molecular excited state in absorption or the molecular ground state in emission is called vibrational relaxation.

18. Conductance is defined as $G = 1/R$. Conductivity is normalized for the geometry of the conductance cell electrodes, $\kappa = 1/R (\ell/A)$.

19. Molar conductivity is defined as $\Lambda_m = \kappa/c$.

20. For strong electrolytes, conductivity is approximately linear with concentration, $\kappa = \Lambda_m c$. However, see the following.

21. For strong electrolytes over wide concentration ranges, $\Lambda_m = \Lambda_m^o - \mathcal{K}c^{\frac{1}{2}}$. Λ_m^o is the limiting molar conductivity, which is the molar conductivity that is extrapolated to zero concentration so that the inter-ionic forces are negligible.

22. Diffusion and electrical conductivity are examples of linear flux-force relationships.

23. The absorbance of a mixture is the sum of the absorbances of the constituents.

24. The simultaneous linear equations for the absorbance of mixtures can be expressed in matrix form, $\underset{\sim}{A} = \underset{\approx}{\varepsilon\ell}\ \underset{\sim}{c}$, The matrix formulation allows the concentrations of an unknown to be calculated easily, $\underset{\approx}{\varepsilon\ell}^{-1}\ \underset{\sim}{A} = \underset{\sim}{c}$. or more simply $\underset{\approx}{\varepsilon}^{-1}\ \underset{\sim}{A} = \underset{\sim}{c}$. assuming $\ell = 1$ cm.

℘2 Generalized flux-force relationships have the form $J_i = L_i X_i$, with L_i a linear coefficient and X_i the generalized force for the transfer. The generalized force is the gradient of a potential.

℘3 The set of simultaneous linear equations:

$a_1 = M_{11}\ b_1 + M_{12}\ b_2$
$a_2 = M_{21}\ b_1 + M_{22}\ b_2$

can be written in matrix form:

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} M_{11}\ M_{12} \\ M_{21}\ M_{22} \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} \qquad \text{or equivalently}\quad \underset{\sim}{a} = \underset{\approx}{M}\ \underset{\sim}{b}$$

The solution to this equation for $\underset{\sim}{b}$ is: $\underset{\approx}{M}^{-1}\ \underset{\sim}{a} = \underset{\sim}{b}$

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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.

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.

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.

4. An aqueous solution is prepared by adding 5.0822 g of ammonium sulfate, $(NH_4)_2SO_4$, 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.

5. An aqueous solution is prepared by adding 2.012 g of $CaCl_2 \cdot 2H_2O$ 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.

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

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 2.13×10^{-4} M solution of an absorbing solute. What is the molar absorption coefficient?

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

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

$$3 \text{ bipy} + Fe^{2+} \rightleftarrows Fe(bipy)_3^{2+}$$
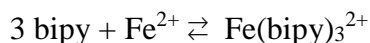
This complex is commonly used for low level spectrophotometric determinations of Fe(II) in natural waters. A standard solution of 5.04×10^{-4} M Fe(II) was added, using volumetric pipettes, to a series of 50.0-mL volumetric flasks and diluted to the mark with excess bipyridine solution according to the 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

10. What is the absorbance of the column of water that corresponds to ¼, ½, and ¾ of the depth of the euphotic zone? What absorbance corresponds to the depth of the euphotic zone?

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 1.00×10^{-3} g L^{-1} or 1.28×10^{-6} 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

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.

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. The yearly average insolation for the United States is given below from data from the National Renewable Resource Laboratory, NREL, (http://www.nrel.gov/gis/solar.html). 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 kWh m^{-2} day^{-1}), Seattle (3.69 kWh m^{-2} day^{-1}), Boston (4.16 kWh m^{-2} day^{-1}), and Miami (5.45 kWh m^{-2} day^{-1}).
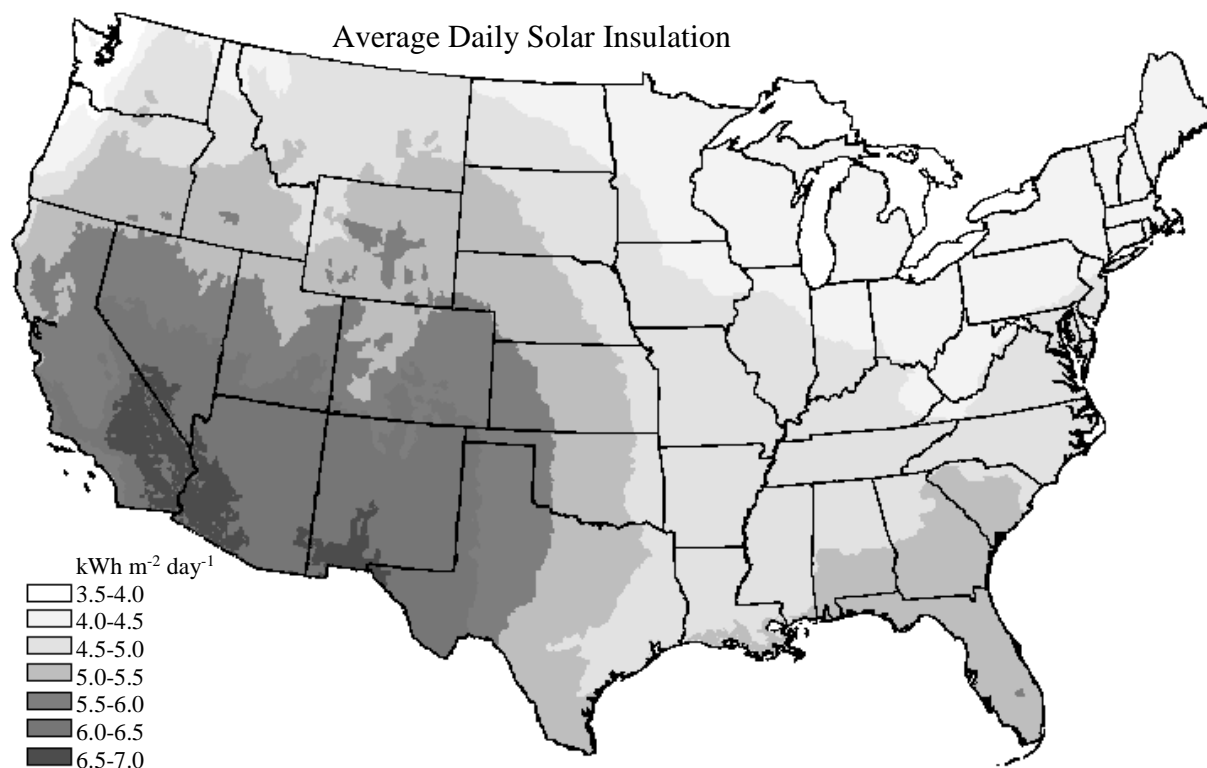

Figure P2.1: Average Daily Solar Insolation. The solar insolation is the average daily energy falling on a surface parallel to the ground per day averaged over the year. (Map source: http://www.nrel.gov/gis/images/map_pv_us_annual10km_dec2008.jpg)

14. A photovoltaic panel can convert about 6-12% 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 12% efficiency in each of the four cities. (b) A typical refrigerator requires 450 kW hours of energy per year. Calculate the photovoltaic panel area needed to provide all the energy for this refrigerator.

15. Calculate the value for the limiting molar conductivity, Λ_m°, for $CaCl_2$ from the following data, taken at 25°C.

c (M)	1.00×10^{-3}	2.00×10^{-3}	10.00×10^{-3}	0.100
Λ_m (mS m^2 mol^{-1})	26.386	26.072	24.850	24.072

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 µS cm^{-1}. Find the conductivity of 0.001000 M KCl in these additional units.

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 µS 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 $MgCl_2$ 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 $MgCl_2$ solution. (c). Calculate the molar conductivity in mS m^2 mol^{-1}, S cm^2 mol^{-1}, and µS cm^{-1} mol^{-1}.

18. Ammonia is a weak electrolyte and weak base: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$. The fraction of NH_4OH 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 $\Lambda_m^\circ(NH_4Cl) = 14.97$ mS m^{2}mol^{-1}, $\Lambda_m^\circ(NaCl) = 12.64$ mS m^{2}mol^{-1}, and $\Lambda_m^\circ(NaOH) = 24.80$ mS m^{2}mol^{-1}, calculate the limiting molar conductivity of NH_4OH.

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 J m^{-2} s^{-1} giving the units of κ as J m^{-1} K^{-1} 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 J m^{-1} K^{-1} s^{-1} at 15°C and 1 atm. Assume a linear temperature gradient.

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 J m^{-2} s^{-1} giving the units of κ as J m^{-1} K^{-1} 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 J m^{-1} K^{-1} s^{-1} at 25°C.

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 6.3×10^{-4} 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.

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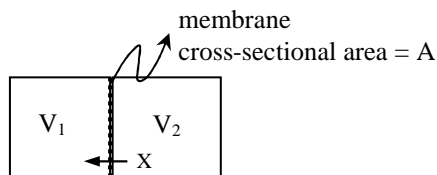
 (a). Prove for diffusion of substance X across a membrane that the rate of concentration change in compartment 1 is given by:

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

(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.

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 $\bar{\upsilon} = \Delta[P]/\Delta t$, where $\Delta[P]$ is the change in product concentration.]

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

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

corresponds to a rotation of the vector by 30° around the z-axis. Use $\underset{\sim}{b} = \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix}$, which is diagrammed at right:
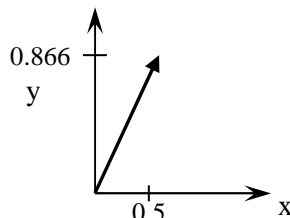
25. How are 3D computer graphics done? Many of the operations in computer games and molecular graphics correspond to rotation about the axis perpendicular to the computer screen. We showed in the last problem that matrix multiplication can generate such rotations. Show that the matrix,

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

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

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:

$$\underset{\approx}{M} = \begin{pmatrix} n & 0 \\ 0 & n \end{pmatrix} \qquad \text{with} \quad \underset{\sim}{a} = \underset{\approx}{M} \underset{\sim}{b}$$

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

27. The UV-visible absorption spectra of two compounds is shown below. The concentration of each is 5.00×10^{-5} M. The absorbencies at the two analytical wavelengths, λ_1 and λ_2 are listed in the figure.
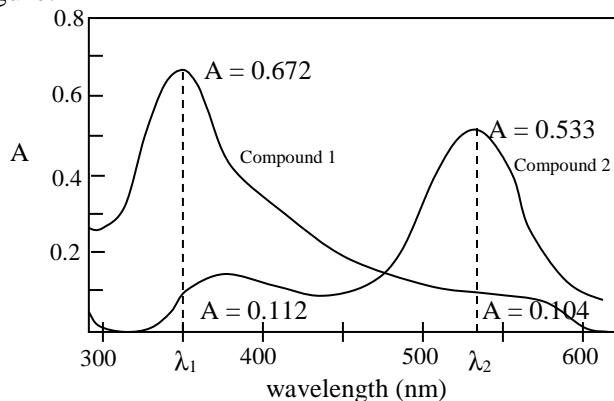
The path length of the cuvette is 1.00 cm. An unknown mixture has an absorbance of 0.419 at λ_1 and an absorbance of 0.546 at λ_2. (a). Determine, without calculations, the component with the larger concentration. (b). Calculate the concentrations of the two compounds.

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

29. Find the determinant of the following matrix:

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

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

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