Physical Chemistry:
Answers to Problems

(To accompany the text in Physical Chemistry)

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Chapter

Chapter 1 Problems: Chemical Reactivity

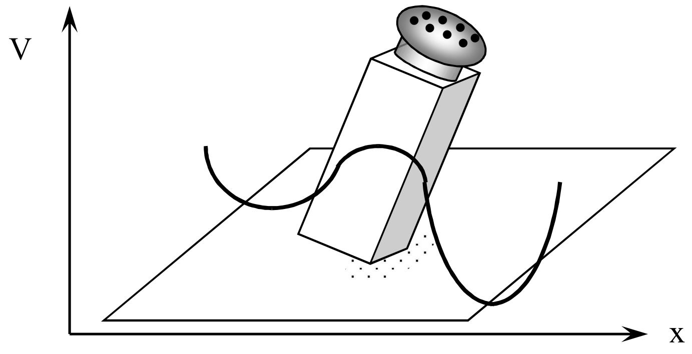
1. Consider a bowl of sugar. Sugars are our primary source of energy, so the oxidation of sucrose in our body must be thermodynamically favorable. How can a bowl of sugar exist in the open atmosphere for very long times?

Answer: A bowl of sugar is an example of meta-stable system. The oxidation of sucrose at room temperature is kinetically hindered. The addition of a catalyst or an ignition spark greatly accelerates this process. The oxidation of sucrose is thermodynamically favorable but kinetically unfavorable.

2. Consider a salt shaker balanced on one edge, Figure P.1. This state is often possible if a few salt grains are sprinkled on the table. Characterize the state of the system with respect to change in position. If the system is not at equilibrium, state the equilibrium position. Describe any spontaneous processes that might occur if the salt grains were gently blown away.

Answer: This system is meta-stable. With a small perturbation, in other words a small push, the shaker would flop over. The normal vertical position of the shaker is also meta-stable; the vertical position is a local minimum. The overall global equilibrium is with the salt shaker on its side, flat against the table. After the salt grains are gently blown away, the system is unstable and falls to equilibrium.

A plot of the potential energy of the system as a function of the x position of the center of mass is shown below.



3. Our bodies, at rest, can be considered as being in a steady state. Describe the incoming flows that keep us away from equilibrium. What are the outgoing flows? What is the equilibrium state for our bodies?

Answer: Living systems in general need an energy source, a source of electrons, and a source of carbon. The electrons are available from redox reactions involving good reducing agents, which as you might remember from your Organic course include compounds rich in hydrogen. In other words, we need food as a source of carbon and electrons, and O_2 in combination with food as a source of energy. Of course, humans also need sources of N, P, S, Na^+, K^+, Ca^{2+}, Fe^{3+}, and other trace elements, which we obtain from food. The outgoing flows are heat, water vapor from perspiration, water loss through breathing, CO_2, feces, and urine as waste products.

4. Are spontaneous processes always irreversible? Explain.

Answer: Yes: Returning a spontaneous process to its initial state requires energy input from the surroundings in the form of heat and work that is different from the heat and work for the forward process. The reverse of a spontaneous process is not the exact reverse of the change for the original forward process. The forward spontaneous process is irreversible. Equilibrium processes are reversible (always). The only way for a process to be reversible is for the system to be at equilibrium.

5. (a). In what way is a steady state and an equilibrium system similar? (b). In what ways are a steady state and an equilibrium system different?

Answer: (a). Steady state and equilibrium systems are time invariant. In other words, the concentrations of the various chemical species are constant. (b). They are different in that a steady state process requires the continual input of energy or matter to remain at steady state. For a system at equilibrium, all heat and work transfers are zero. For steady state systems, heat and work transfers per unit time are constant and may be non-zero. Heat is evolved at a constant rate for a steady-state process. For a steady state system, the forward processes are not the exact reverse of all the reverse processes. For an equilibrium system, the forward rates are equal and opposite to all the reverse rates.

6. Determine if the following processes are spontaneous, non-spontaneous, or reversible.

(a). 1 J of heat is transferred from a hot cup of coffee to the table top.
(b). Sugar is added to a cup of coffee and the sugar dissolves.
(c). Water decomposes into $H_2$and O_2 from a cup of coffee.
(d). A small amount of ice melts in a cup of iced coffee at 0°C.
(e). A small amount of ice melts in a cup of coffee at 5°C.
(f). A small amount of water freezes in a cup of iced coffee at 0°C
(g). A small amount of water freezes in a cup of coffee that is placed outdoors at -10°C.
(h). Too much sugar is added to a cup of coffee producing a super-saturated solution. After bumping the cup on the table, some of the sugar crystallizes out of solution.

Answers: (a). 1 J of heat is transferred from a hot cup of coffee to the table top: spontaneous.
(b). Sugar is added to a cup of coffee and the sugar dissolves: spontaneous.
(c). Water decomposes into H_2 and O_2 from a cup of coffee: non-spontaneous.
Rather, $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ (l) is the spontaneous direction; the reverse of a spontaneous process is non-spontaneous.
(d). A small amount of ice melts in a cup of iced coffee at 0°C: reversible.
Any amount of ice and water can coexist, without any further changes at 0°C. Starting with an initial amount of ice at 0°C, the system begins at equilibrium. Then, if a small amount of ice melts, the final system is also at equilibrium. A reversible process occurs through a sequence of equilibrium states.
(e). A small amount of ice melts in a cup of coffee at 5°C: spontaneous.
The melting of ice is reversible only at 0°C, the normal melting point.
(f). A small amount of water freezes in a cup of iced coffee at 0°C: reversible.
As in part (d), any amount of ice and water can coexist at the normal melting point, so the system remains at equilibrium and can reversed by melting a small amount of ice, without any change in the surroundings for the overall forward and reverse process.
(g). A small amount of water freezes in a cup of coffee that is placed outdoors at -10°C: spontaneous.
This process is spontaneous in the same way as making ice in a freezer is spontaneous (otherwise ice would not exist; the formation of ice must be spontaneous under some circumstances).
(h). Too much sugar is added to a cup of coffee producing a super-saturated solution. After bumping the cup on the table, some of the sugar crystallizes out of solution: spontaneous.
A super-saturated solution is a meta-stable system with a kinetic bottleneck. Bumping provides a bubble or a fresh surface that acts as a nucleation center for sugar crystal formation. The sugar concentration in a super-saturated solution exceeds the amount the solution can hold at equilibrium, at the given temperature.

7. Prove that if the reverse of a spontaneous process is also spontaneous, it is possible to construct a perpetual motion machine.[1,2]

Answer: A cyclic process is a process that begins and ends at the same state of the system. Consider a cyclic process that is made from the combined forward process and the reverse process, so that the system remains unchanged. Since the forward process is spontaneous and the reverse process is spontaneous, the cyclic process is overall spontaneous. The system is unchanged by the cyclic process, which can then reoccur, again spontaneously. The net result is that the cyclic process can reoccur an infinite number of times, which is an example of perpetual motion. Perpetual motion has never been observed, and because of our experience, we never expect perpetual motion to occur.

In proving a statement we often assume the converse and work through the ramifications until we come to an impossibility. Having reached an impossible condition we must conclude the original assumption was wrong. In this problem we show that the forward and reverse processes cannot both be spontaneous. We therefore conclude: the reverse of a spontaneous process is non-spontaneous.

8. Calculate the molar density, in mol m^{-3}, and the mass density, in kg m^{-3} and g L^{-1}, for an ideal gas at standard pressure, P° = 1.00 bar, and 298.15 K. Assume the gas is air with an effective molar mass given by Eq. 1.3.17.

Answer: P° = 1.00 bar = $1.00 \text{x} 10^5$ Pa. The molar density is:

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.000\text{x}10^5 \text{ Pa}}{8.314 \text{ J K}^{-1} \text{mol}^{-1}(298.15 \text{ K})} = 40.3 \text{ mol m}^{-3}$$

and in mol L^{-1}

$$\frac{n}{V} = 40.3 \text{ mol m}^{-3} \text{ (1 m}^3\text{/1000 L)} = 0.0403 \text{ mol L}^{-1}$$

The mass density can be calculated from the molar density by

$$d = \frac{\mathcal{M} n}{V} = \frac{\mathcal{M} P}{RT} = 28.8\text{x}10^{-3} \text{ kg mol}^{-1} \text{ (40.3 mol m}^{-3}) = 1.16 \text{ kg m}^{-3}$$

or $\quad d = 28.8 \text{ g mol}^{-1} \text{ (0.0403 mol L}^{-1}) = 1.16 \text{ g L}^{-1}$

Alternatively, directly using R = 0.082058 L atm K^{-1} mol^{-1} and 1 bar = 0.9869 atm:

$$d = \frac{\mathcal{M} n}{V} = \frac{\mathcal{M} P}{RT} = \frac{28.8\text{x}10\text{g mol}^{-1}(0.9869 \text{ atm})}{0.082058 \text{ L atm K}^{-1} \text{mol}^{-1}(298.15 \text{ K})} = 1.16 \text{ g L}^{-1}$$

9. Calculate the number of moles of an ideal gas in a volume of 1.000 L for a pressure of 1.000 bar and a temperature of 298.15 K. Do this problem using three different sets of units and the corresponding value for R: (a) using L atm, (b) using Pa m^3, and (c) using L bar.

Answer: Note that 1 bar = 0.9869 atm , 1 bar = $1.00\text{x}10^5$ Pa , 1 m^3 = 1000 L.

(a) using L atm,

$$n = \frac{PV}{RT} = \frac{0.9869 \text{ atm (1.000 L)}}{0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})} = 0.04034 \text{ mol}$$

(b) using Pa m^3:

$$n = \frac{PV}{RT} = \frac{1.000\text{x}10^5 \text{ Pa } (1.000\text{x}10^{-3} \text{ m}^3)}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})} = 0.04034 \text{ mol}$$

(c) using L bar:

$$n = \frac{PV}{RT} = \frac{1.000 \text{ bar (1.000 L)}}{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})} = 0.04034 \text{ mol}$$

10. The density of a mixture of H_2 and O_2 is 0.982 g L^{-1} at 298.2 K and 1.00 bar pressure. Calculate the mole fraction of H_2 in the mixture.

Answer: The plan is to calculate the effective molar mass of the sample, using Eq. 1.3.9°, and then use the weighted average to calculate the original composition, as was done in Eq. 1.3.17.

Convenient units for this problem are L and bar, with R = 0.083145 L bar K^{-1} mol^{-1}. The effective molar mass is given from the mass density as:

$$d = \frac{\mathcal{M}\,P}{RT}$$

$$0.982 \text{ g L}^{-1} = \frac{\mathcal{M}\,(1.00 \text{ bar})}{0.083145 \text{ L bar K}^{-1}\text{ mol}^{-1}(298.15 \text{ K})} \quad \text{or} \quad \mathcal{M} = 24.3_4 \text{ g mol}^{-1}$$

The effective molar mass is the weighted average of the pure molar masses, as in Eq. 1.3.17:

$$\mathcal{M} = x\,(2.02 \text{ g mol}^{-1}) + (1 - x)\, 32.00 \text{ g mol}^{-1} = 24.3_4 \text{ g mol}^{-1}$$

Solving for x gives x = 0.2555 or 25.5%. We will show in the next chapter that volume and mole fractions are equivalent.

11. Two containers, which are separated by a stopcock, are held in a constant temperature bath at 298.2 K, Figure P10.1. The first container has a volume of 24.80 L and the second 12.39 L. The two containers are filled with 2.00 mol and 1.00 mol of ideal gas, respectively. Calculate the intial pressures. After the stopcock is opened, calculate the final volume and pressure. Of P, V, and n, in this experiment, which are intensive and which are extensive?

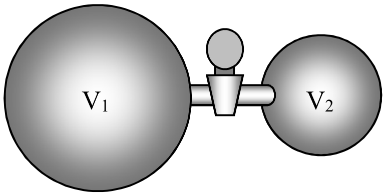


Figure P10.1: Two closed containers are opened to form a combined system.

Answer: The initial pressures are calculated using the ideal gas law in each separate volume:

$$P_1 = n_1RT/V_1 = 2.00 \text{ mol}(0.083145 \text{ bar L K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})/24.80 \text{ L} = 2.00 \text{ bar}$$
$$P_2 = n_2RT/V_2 = 1.00 \text{ mol}(0.083145 \text{ bar L K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})/12.39 \text{ L} = 2.00 \text{ bar}$$

After the stopcock is opened, the total volume is $V_{tot} = V_1 + V_2 = 37.19$ L and total moles of gas is $n_{tot} = n_1 + n_2 = 3.00$ mol. The final pressure is:

$$P_{tot} = n_{tot}\, RT/V_{tot} = 3.00 \text{ mol}(0.083145 \text{ bar L K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})/37.19 \text{ L} = 2.00 \text{ bar}$$

The mole amount and volume add, so they are extensive. The pressure remains the same and is intensive. Repeating a similar problem with constant pressures shows that the temperature is the same before and after, so the temperature is also intensive.

12. Classify the following variables as intensive or extensive:

(a). molar concentration of a solution.
(b). molar density.
(c). density (mass density).
(d). surface area of an interface between two dissimilar phases. The air-water, olive oil-water, and olive oil-glass interfaces are three examples. The interface can be the planar interface between two bulk samples or the surface of a spherical droplet.

(e). surface tension, which is defined as the change in surface energy of an interface divided by the change in surface area: $\gamma = dU/d\sigma$.

(f). temperature.

(g). coefficient of thermal expansion at constant pressure, which is defined as:

$$\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

where $(\partial V/\partial T)_P$ is the rate of change of the volume of a sample with temperature, while holding the pressure constant.

Answers: The ratio of any two extensive properties of a system is intensive.

(a). molar concentration = n/V, which is the ratio of two extensive quantities: intensive. The concentration of a drop or a bucket full of solution is the same.

(b). molar density = n/V, which is the ratio of two extensive quantities of the system: intensive

(c). density = d = w/V, where w is the mass of the system. The density is the ratio of two extensive quantities of the system: intensive

(d). surface area depends on the size of an interface or a droplet: extensive

(e). surface tension = $\gamma = dU/d\sigma$, where dU is the change in surface energy and $d\sigma$ is the change in surface area. Surface tension is the ratio of two extensive quantities: intensive

(f). temperature is independent of the size of the system: intensive. Combining 50 mL of water at 25°C with another 50 mL of water at 25°C gives 100 mL of water at 25°C

(g) coefficient of thermal expansion, $\alpha = (1/V)(\partial V/\partial T)_P$. $(\partial V/\partial T)_P$ is the ratio of the change in volume, which is extensive, to the change in temperature which is intensive, giving the derivative as extensive. The coefficient of thermal expansion is the ratio of $(\partial V/\partial T)_P$, which is extensive, to the total volume, which is also extensive, giving an overall intensive property. The coefficient of thermal expansion is a primary property of a substance. The coefficient of thermal expansion for a drop and a gallon of water is the same.

13. Calculate the pressure inside your mouth that would be necessary to drink a soft drink through a straw of length 20.0 cm. Assume the drink has the density of water at 20.0°C, 0.9982 g mL^{-1} and the atmospheric pressure is 1.000 bar.

Answer: This problem is just like a closed end manometer, with your mouth acting as the volume in the closed end. Then $P_{ext} = P_{in} + P_{liq}$ and $P_{liq} = dgh$. The density of water at 20.0°C is needed in kg m^{-3} to match the units of g:

$d = 0.9982 \text{ g mL}^{-1} (1 \text{ kg}/1000 \text{ g})(1\times10^3 \text{ mL}/1 \text{ L})(1000 \text{ L}/1 \text{ m}^3) = 998.2 \text{ kg m}^{-3}$

Then $P_{liq} = dgh = 998.2 \text{ kg m}^{-3} (9.807 \text{ m s}^{-2})(0.200 \text{ m}) = 1958 \text{ Pa}$

Solving $P_{ext} = P_{in} + P_{liq}$ for P_{in} gives:

$P_{in} = P_{ext} - P_{liq} = 1.00\times10^5 \text{ Pa} - 1958 \text{ Pa} = 98042 \text{ Pa} = 0.980 \text{ bar}$

If you would like to see the pressure in torr:

$P_{in} = 0.980 \text{ bar } (1 \text{ atm}/1.01325 \text{ bar})(760 \text{ torr}/1 \text{ atm}) = 735. \text{ torr}$

So, by decreasing the pressure in your mouth, the atmosphere pushes the water up the straw.

<u>14</u>. Calculate the height of a column of water at 20.0°C in a closed end manometer for an atmospheric pressure of 1.000 bar. Assume the liquid has a constant density. The density of water at 20°C is 0.9982 g mL^{-1}. The vapor pressure of water at 20.0°C is 2.338 kPa.

Answer: For a closed end manometer, $P_{ext} = P_{in} + P_{liq}$ with P_{liq} = dgh and P_{in} given by the vapor pressure of the liquid in the manometer, 2.338 kPa. Solving for P_{liq}:

$$P_{liq} = P_{ext} - P_{in} = 1.000\text{x}10^5 \text{ Pa} - 2338 \text{ Pa} = 97662 \text{ Pa}$$

The density of water at 20.0°C is needed in kg m^{-3} to match the units of g:

$$d = 0.9982 \text{ g mL}^{-1} (1 \text{ kg}/1000 \text{ g})(1\text{x}10^3 \text{ mL}/1 \text{ L})(1000 \text{ L}/1 \text{ m}^3) = 998.2 \text{ kg m}^{-3}$$

Then $P_{liq} = 97662 \text{ Pa} = dgh = 998.2 \text{ kg m}^{-3} (9.807 \text{ m s}^{-2})\, h$

Solving for h = 9.976 m

In English units for comparison:

$$h = 9.976 \text{ m } (100 \text{ cm}/1 \text{ m})(1 \text{ in}/2.540 \text{ cm})(1 \text{ ft}/12 \text{ in}) = 32.7 \text{ ft}$$

<u>15.</u> Long's Peak in the Colorado Rocky Mountains is 3962. m high. What is the predicted pressure on the top of Long's Peak? Assume a constant temperature of 20.0°C. Compare the molar density on top of Long's Peak with the molar density of air at sea level.

Answer: Assuming the atmospheric pressure at sea level is 1 atm and the mole fraction averaged molar mass of air is 28.8 g mol^{-1} gives the barometric formula as:

$$\left(\frac{-\mathfrak{M}_{gas}\, g\, h}{RT}\right) = \frac{-28.8\text{x}10^{-3} \text{ kg}(9.807 \text{ m s}^{-2})(3962. \text{ m})}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}(293.15 \text{ K})} = -0.4591$$

$$P = P_o\, e^{\left(\frac{-\mathfrak{M}_{gas}\, g\, h}{RT}\right)} = 1.00 \text{ atm } e^{-0.4591} = 0.632 \text{ atm}$$

The molar density at sea level assuming 1 atm = 1.01325x10^5 Pa and at 293.15 K, is:

$$\frac{n}{V} = \frac{P}{RT} = \frac{1.01325\text{x}10^5 \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}(293.15 \text{ K})} = 41.6 \text{ mol m}^{-3}$$

The molar density at the top of the mountain is based on P = 0.632 atm(1.01325x10^5 Pa/1 atm) = 6.404x10^4 Pa:

$$\frac{n}{V} = \frac{P}{RT} = \frac{6.404\text{x}10^4 \text{ Pa}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}(293.15 \text{ K})} = 26.3 \text{ mol m}^{-3}$$

which is why hiking at high altitude is so difficult.

<u>16</u>. Calculate the altitude in the atmosphere that corresponds to a pressure of 0.500 bar if the surface pressure is 1.000 bar. Assume the temperature is constant at 18°C.

Answer: Use Eq. 1.3.15°:

$$\ln \frac{P}{P_o} = -\frac{\mathfrak{M}_{gas}\, g\, h}{RT}$$

$$\ln(0.500/1.00) = -\frac{28.8\text{x}10^{-3}\ \text{kg}\ (9.807\ \text{m s}^{-2})\ h}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\ (291.2\ \text{K})} = -1.1667\text{x}10^{-4}\ h$$

$h = -0.6931/-1.1667\text{x}10^{-4} = 5941\ \text{m} = 5.94\text{x}10^3\ \text{m}$

17. For liquids with moderate changes in pressure, the density is given by:

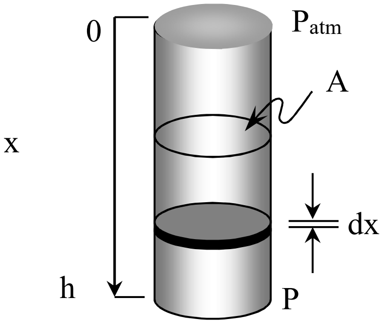
$$d = d_o\,[1 + \kappa_T\,(P - P_o)]$$

where κ_T is the isothermal compressibility, d_o is the density of the liquid at the surface pressure P_o and d is the density at final pressure P. (a). Show that the formula for the pressure as a function of depth is given by:

$$\frac{1}{\kappa}\ln(1 + \kappa_T\,(P - P_o)) = d_o\,g\,h$$

(b). Calculate the pressure in the Mariana Trench at a depth of 10911 m (35798 ft) given $\kappa_T = 4.587\text{x}10^{-10}\ \text{Pa}^{-1}$ at 20°C. Use the density of pure water, 0.9982 g mL^{-1} at 1 bar, for this problem, instead of the density of sea water. Assume the surface pressure is 1.000 bar.

Answer: The depth below the surface is x. The surface corresponds to the depth x = 0. The change in pressure for a thin disk of water is given by dP = df/A = d g dx. The differential has a positive sign since as x increases the column of water above your head increases and the pressure increases.



Substituting the density as a function of pressure gives:

$$dP = [1 + \kappa_T\,(P - P_o)]\,d_o\,g\,dx$$

Separating variables gives:

$$\frac{dP}{[1 + \kappa_T\,(P - P_o)]} = d_o\,g\,dx$$

Integrating gives:

$$\int_{P_o}^{P} \frac{dP}{[1 + \kappa_T\,(P - P_o)]} = \int_0^h d_o\,g\,dx$$

The general form of the left-hand integral is $\int \frac{1}{1 + ax}\, dx \;=\; \frac{1}{a} \ln(1 + ax)$. Which gives:

$$\int_{P_o}^{P} \frac{dP}{[1 + \kappa_T (P - P_o)]} \;=\; \frac{1}{\kappa} \left(\ln(1 + \kappa_T (P - P_o))\right|_{P_o}^{P} \;=\; \frac{1}{\kappa_T} \ln(1 + \kappa_T (P - P_o))$$

The final result is then:

$$\frac{1}{\kappa_T} \ln(1 + \kappa_T (P - P_o)) = d_o\, g\, h$$

We can solve for P by rearranging in the following steps:

$$\ln(1 + \kappa_T (P - P_o)) = \kappa_T\, d_o\, g\, h$$

$$1 + \kappa_T (P - P_o) = e^{\kappa_T\, d_o g h}$$

$$(P - P_o) = \frac{1}{\kappa} \left(e^{\kappa_T\, d_o g h} - 1 \right)$$

With $h = 10911.$ m, $d_o = 998.2\ \text{kg m}^{-3}$, and $\kappa_T = 4.587\text{x}10^{-10}\ \text{Pa}^{-1}$:

$$\kappa_T\, d_o g h = (4.587\text{x}10^{-10}\ \text{Pa}^{-1})(998.2\ \text{kg m}^{-3})(9.8067\ \text{m s}^{-2})(10911.\ \text{m}) = 4.8993\text{x}10^{-2}$$

Notice that the units are $1\ \text{Pa} = 1\ \text{N m}^{-2} = 1\ \text{kg m}^{-1}\ \text{s}^{-2}$

and then $\left(e^{\kappa_T\, d_o g h} - 1 \right) = 5.0213\text{x}10^{-2}$ giving:

$$(P - P_o) = \frac{1}{\kappa} \left(e^{\kappa_T\, d_o g h} - 1 \right) = \frac{5.0213\text{x}10^{-2}}{4.587\text{x}10^{-10}\ \text{Pa}^{-1}} = 1094.7\text{x}10^{5}\ \text{Pa}$$

and the total pressure at depth is $1095.7\text{x}10^{5}$ Pa or $1.096\text{x}10^{3}$ bar.
What would we have gotten if we had assumed an incompressible fluid with $P_{liq} = dgh$:

$P_{liq} = 1068.1\ \text{x}10^{5}$ or a total pressure of $1069.1\text{x}10^{5}$ Pa

or 2.4% less. So the density of water can be considered as a constant for all but extreme conditions.

<u>18</u>. (a). Find the derivative of the atmospheric pressure with respect to altitude from the barometric formula, Eq. 1.3.16°. (b). Show that this derivative satisfies the original differential equation, Eq. 1.3.10°.

Answer: (a). The barometric formula at height x is: $P = P_o\, e^{\left(\frac{-\mathcal{M}_{gas}\, g\, x}{RT}\right)}$

The general form of the derivative using the chain rule is: $\frac{de^{-cx}}{dx} = (-c)\, e^{-cx}$

The derivative is: $\frac{dP}{dx} = \left(\frac{-\mathfrak{M}_{gas}\, g}{RT}\right) P_o\, e^{\left(\frac{-\mathfrak{M}_{gas}\, g\, x}{RT}\right)} = \left(\frac{-\mathfrak{M}_{gas}\, g}{RT}\right) P$

(b). The original differential equation, Eq. Eq. 1.3.10°, rearranges to give: $\frac{dP}{dx} = \left(\frac{-\mathfrak{M}_{gas}\, g}{RT}\right) P$ which shows that the barometric formula is the proper solution to the differential equation.

19. Chemical kinetic equations are good examples of first-order homogeneous differential equations with a constant coefficient. The rate of change of the concentration of a substance A with time in a first-order chemical reaction is given as:

$$\frac{d[A]}{dt} = -k\,[A]$$

where k is the rate constant. (a). Show that this expression is a first-order homogeneous differential equation with a constant coefficient. (b). Integrate the equation from an initial concentration of $[A]_o$ at time t = 0 to a final concentration of [A] at time t.

Answer: (a). Multiplying both sides of the rate expression by dt gives:

$$d[A] = -k\,[A]\,dt$$

Comparison with Eq. 1.3.18 shows that this expression is a first-order homogeneous differential equation with a constant coefficient, where f is replaced by [A] and the constant coefficient is the rate constant, k.
(b). Dividing both sides of the equation by [A] to separate the variables gives:

$$\frac{d[A]}{[A]} = -k\,dt$$

Now the terms involving the concentration are on the left of the equal sign, and the terms involving time are on the right. The limits for the integration are at t = 0 the initial concentration of A is $[A]_o$ and at time t the concentration of A is given as [A]:

$$\int_{[A]o}^{[A]} \frac{d[A]}{[A]} = -\int_0^t k\,dt$$

$$\ln\,[A]\,\Big|_{[A]_o}^{[A]} = -k\,t\Big|_0^t$$

$$\ln\,[A] - \ln\,[A]_o = -k\,t$$

The difference in the logs is the log of the ratio, ln x – ln y = ln(x/y):

$$\ln\left(\frac{[A]}{[A]_o}\right) = -k\,t$$

Solving for [A]:

$$[A] = [A]_o\, e^{-kt}$$

20. Do the Taylor expansion for $\sqrt{1\text{-}x}$ for $x \approx 0$, keeping terms up to x^2.

Answer: We need the first and second derivatives:

$$\frac{d\,(1\text{-}x)^{1/2}}{dx} = \frac{-(1-x)^{-1/2}}{2} = \frac{-1}{2(1\text{-}x)^{1/2}} = \frac{-1}{2(1\text{-}x)^{1/2}}$$

$$\frac{d^2\,(1\text{-}x)^{1/2}}{dx^2} = \frac{d\left(\frac{-1}{2(1\text{-}x)^{1/2}}\right)}{dx} = \frac{-1}{4(1\text{-}x)^{3/2}}$$

Evaluating at $x = x_o = 0$

$$(\,(1\text{-}x)^{1/2})_{x=0} = 1$$

$$\left(\frac{d\,(1\text{-}x)^{1/2}}{dx}\right)_{x=0} = \frac{-1}{2(1\text{-}0)^{1/2}} = \frac{-1}{2}$$

$$\left(\frac{d^2\,(1\text{-}x)^{1/2}}{dx^2}\right)_{x=0} = \frac{-1}{4(1\text{-}0)^{3/2}} = \frac{-1}{4}$$

Substituting into the Taylor series gives:

$$f \approx f(x_o) + \left(\frac{df}{dx}\right)_{x=x_o}(x - x_o) + \left(\frac{d^2f}{dx^2}\right)_{x=x_o}\frac{(x - x_o)^2}{2} = 1 - \frac{1}{2}(x) - \frac{1}{4}\left(\frac{x^2}{2}\right)$$

Giving the same result as Table 1.4.2:

$$\sqrt{1\text{-}x} \approx 1 - \frac{x}{2} - \frac{x^2}{8}$$

21. Using a Taylor series expansion, what is the linear approximation for $\ln(f_2/f_1)$ for $f_2 \approx f_1$.

Answer: From Table 1.4.2: $\ln x \approx (x - 1)$ for $x \approx 1$

Substitute $x = f_2/f_1$ giving:

$$\ln\frac{f_2}{f_1} \approx \left(\frac{f_2}{f_1} - 1\right)$$

Now we should derive $\ln x \approx (x - 1)$. The function at $x = x_o = 1$ is:

$$(\ln x)_{x=1} = 0$$

The derivative evaluated at $x = x_o = 1$:

$$\left(\frac{d\ln x}{dx}\right)_{x=1} = \left(\frac{1}{x}\right)_{x=1} = 1$$

Substituting into the Taylor series:

$$f \approx f(x_o) + \left(\frac{df}{dx}\right)_{x=x_o}(x - x_o) = 0 + (1)\,(x - 1) = (x - 1)$$

<u>22</u>. Determine the number of terms in the Taylor series expansion of ln(1 – x) that are necessary for 1% and 0.1% accuracy, if x = 0.100.

Answer: First, note that the exact value is ln(1 – 0.100) = -0.10536. Using Example 1.5.6, keeping the first two terms gives a 5% error. We need to generate the next few terms in the Taylor expansion. From Example 1.5.6:

$$\ln(1-x)\big|_{x=0} = 0$$

$$\frac{d\ln(1-x)}{dx} = -\left.\frac{1}{(1-x)}\right|_{x=0} = -1$$

$$\frac{d^2\ln(1-x)}{dx^2} = \frac{d\dfrac{-1}{(1-x)}}{dx} = -\left.\frac{1}{(1-x)^2}\right|_{x=0} = -1$$

$$\frac{d^3\ln(1-x)}{dx^3} = \frac{d\dfrac{-1}{(1-x)^2}}{dx} = -\left.\frac{2}{(1-x)^3}\right|_{x=0} = -2$$

$$f \cong f(x_o) + \left(\frac{df}{dx}\right)_{x=x_o}(x-x_o) + \left(\frac{d^2f}{dx^2}\right)_{x=x_o}\frac{(x-x_o)^2}{2} + \left(\frac{d^3f}{dx^3}\right)_{x=x_o}\frac{(x-x_o)^3}{3!}$$

$$\ln(1-x) \cong (0) - 1\,x - \frac{x^2}{2!} - \frac{2\,x^3}{3!} - \frac{3\,x^4}{4!} = -x - \frac{x^2}{2} - \frac{2\,x^3}{6} - \frac{3\,x^4}{24} = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{8}$$

$\ln(1-0.1) \cong -0.1$	with 5 % error for two terms
$\cong -0.1 - 0.05 = -0.105$	with 0.34 % error for three terms
$\cong -0.1 - 0.05 - 0.0033 = -0.10533$	with 0.03 % error for four terms

Three terms, including the first zero term, are sufficient for 1% accuracy. Four terms are needed for 0.1 % accuracy. The approximation ln(1 – x) ≅ – x is appropriate only for x < 0.022, for 1% error.

<u>23</u>. Calculate the derivative of $h(x) = e^{-cx}/(1-e^{-cx})$, with respect to x for c equal to a constant.

Answer: Using the product rule with $f = e^{-cx}$ and $g = 1/(1-e^{-cx})$:

$$\frac{d\,(f\,g)}{dx} = f\frac{dg}{dx} + g\frac{df}{dx} = e^{-cx}\frac{d\,(1/(1-e^{-cx}))}{dx} + \frac{1}{(1-e^{-cx})}\frac{d\,e^{-cx}}{dx}$$

Using the chain rule:

$$\frac{d\,e^{-cx}}{dx} = -c\,e^{-cx}$$

and (see Eq. 1.4.7-9):

$$\frac{d\,(1/(1-e^{-cx}))}{dx} = \frac{-1}{(1-e^{-cx})^2}\,(-(-c)\,e^{-cx}) = \frac{-c\,e^{-cx}}{(1-e^{-cx})^2}$$

Substituting back into the product rule result:

$$\frac{dh}{dx} = e^{-cx}\left(\frac{-c\,e^{-cx}}{(1-e^{-cx})^2}\right) + \frac{1}{(1-e^{-cx})}\,(-\,c\,e^{-cx})$$

$$\frac{dh}{dx} = \left(\frac{-c\,e^{-2cx}}{(1-e^{-cx})^2}\right) - \frac{c\,e^{-cx}}{(1-e^{-cx})}$$

This derivative is actually useful; it is related to the heat capacity of a normal mode of vibration.

<u>24</u>. Find the derivative of $P = \frac{nRT}{(V-nb)} - a\,\frac{n^2}{V^2}$, with respect to V. Assume that n, R, T, a, and b are all equal to a constant.

Answer: We hold n, R, T, a, and b constant and take the derivative of the two terms:

$$\frac{dP}{dV} = nRT\,\frac{d\left(\frac{1}{(V-nb)}\right)}{dV} - a\,n^2\,\frac{d\left(\frac{1}{V^2}\right)}{dV} \qquad \text{(cst. n, R, T, a, \& b)}$$

Consulting Table 1.5.1, we find:

$$\frac{d(1/x^n)}{dx} = \frac{-\,n}{x^{n+1}}$$

For the first derivative, we can use the substitution z = (V – nb). The first derivative, using the chain rule, is:

$$\frac{d\left(\frac{1}{(V-nb)}\right)}{dV} = \frac{d\left(\frac{1}{z}\right)}{dz}\,\frac{dz}{dV} = \frac{-\,1}{z^2}\left(\frac{dz}{dV}\right) = \frac{-\,1}{(V-nb)^2}\left(\frac{d(V-n\,b)}{dV}\right) = \frac{-\,1}{(V-nb)^2} \qquad (1)$$

The next derivative is then:

$$\frac{d\left(\frac{1}{V^2}\right)}{dV} = \frac{-\,2}{V^3}$$

Then the partial derivative is given by:

$$\frac{dP}{dV} = -\,\frac{nRT}{(V-nb)^2} + \frac{2an^2}{V^3} \qquad \text{(cst. n, R, T, a, \& b)}$$

This derivative is actually useful; it is related to the compressibility of a real (Van der Waals) gas. In Ch. 7 we will note that this derivative is better written as $(\partial P/\partial V)_T$.

25. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true. If the statement is true, but too restrictive, give the more general statement.

(a). For a spontaneous process, no work can be done by the surroundings on the system.

(b). Fast processes are spontaneous.

(c). On an average day at sea level, supporting a column of mercury in a closed tube higher than 760 mm requires more force per unit area than the atmosphere can provide.

(d). Your mouth provides a partial vacuum that pulls a soft drink into your mouth through a straw.

(e). The derivative of the potential energy with respect to a displacement in a system is zero for a system at equilibrium.

Answers: (a). False: Spontaneous processes can have heat and work transfers with the surroundings in both directions. The heat and work necessary to return the system to the initial state are different than the heat and work for the forward process. The overall result of the forward process and then returning the system back to the initial state requires a net transfer of energy from the surroundings into the system. In other words, there is a net change in the surroundings for the cyclic overall process. A true statement is "The work done in a spontaneous process is not equal to the work required to return the system to the initial state."

(b). False: Don't confuse kinetic and equilibrium considerations. Spontaneous processes can be fast or slow. Spontaneous processes have equilibrium constants greater than one. The equilibrium constant is the ratio of the forward and reverse overall reaction rates, $K_p = k_f/k_r$. If the forward rate constant is large, the reverse rate can be even larger, which would make the equilibrium constant small. A true statement is "spontaneous processes may be fast or slow."

(c). True.

(d). False: A vacuum provides no force. Rather, "a partial vacuum in your mouth decreases the downward pressure on the liquid, so that the pressure of the atmosphere can provide sufficient force to raise the liquid higher in the straw."

(e). True but too restrictive: The complete statement is "the derivative of the potential energy with respect to a displacement in the system is zero for metastable and equilibrium systems."

26. (*Challenge Problem*) Three definitions of a reversible process are:

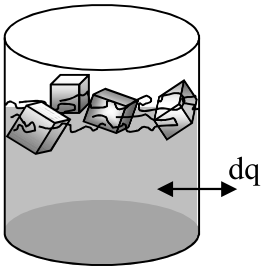
(a). A reversible process is one in which the system never deviates from equilibrium by more than an infinitesimal amount.

(b). A reversible process is not a real process, but a hypothetical succession of equilibrium states.

(c). A reversible process is one for which the system can be returned to its initial state with no net change in the surroundings.

Consider the melting of 1 mole of ice at 0°C as an example. Show how each of the three definitions is equivalent.

Answer: Consider a glass of iced tea in a refrigerator at 0°C, illustrated below, and the melting of one mole of water: $H_2O\ (s) \rightleftarrows H_2O\ (l)$. Small amounts of energy can be withdrawn or added to the glass of iced tea through heat transfers from the system, dq, to the refrigerator. To transfer heat from the system, the temperature of the refrigerator is decreased by an infinitesimal amount, until an infinitesimal amount of heat is transferred. To transfer heat to the system, the temperature of the refrigerator is increased an infinitesimal amount, until an infinitesimal amount of heat is transferred. Any amount of ice and water are in equilibrium at the normal melting point, as long as both phases are present. If the temperature of the refrigerator and the iced tea are exactly the same, no heat is transferred and the net amount of ice and liquid remain constant.



(a). An infinitesimal change in temperature gives rise to either melting or fusion, but the system remains at equilibrium as long as the temperature is returned to 0°C, after the heat transfer. One mole of ice may be melted or one mole of liquid may be frozen by a series of heat transfers using infinitesimal changes in the temperature of the refrigerator. The system remains at equilibrium during the process, or infinitesimally close to equilibrium during the heat transfers.

(b). An infinitesimal is the limit of a small change. Let the temperature of the refrigerator be $T + \delta T$. The infinitesimal change dT is the limit $\delta T \rightarrow 0$. So even though infinitesimal changes are hypothetical, such processes are realized through extrapolation of practical processes at $\delta T \rightarrow 0$. Any amount of ice and water are in equilibrium at the normal melting point, as long as both phases are present. So the process occurs through a succession of equilibrium states as one mole of ice melts or one mole of liquid freezes.

(c). If we freeze a small amount of ice by infinitesimally lowering the temperature of the refrigerator, the energy flows into the refrigerator. Because the process is an infinitesimal process, the freezing can be reversed by the transfer of exactly the same amount of heat back into the glass of iced tea: $dq_{melt} = -\, dq_{fuse}$. The net result is no change for the refrigerator, which acts as the surroundings in this example. Because the melting of one mole of ice or the freezing of one mole of liquid can be accomplished through a sequence of such transfers, the net change in the refrigerator (surroundings) is always zero for the overall combined forward and reverse process, no matter how big the overall transfer.

Literature Cited:

1. A. M. Lesk, *Introduction to Physical Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1982, Ch. 5.
2. P. T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations*, Wiley-Interscience, New York, NY, 1961, p. 95.

Chapter 2 Problems: Concentrations and Partial Pressures

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

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

$$n_{H2} = PV/RT = 2.50 \text{ bar } 1.00 \text{ L}/RT = 2.50 \text{ L bar}/RT$$

for the 2.00-L bulb:

$$n_{N2} = 1.50 \text{ bar } 2.00 \text{ L}/RT = 3.00 \text{ L bar}/RT$$

the total pressure is given by the total moles, $n = n_{H2} + n_{N2}$ in the total volume V= 3.00 L, Eq. 2.1.3°:

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

(b) The mole fractions are:

$$y_{H2} = n_{H2}/n = \frac{2.50 \text{ L bar}/RT}{5.50 \text{ L bar}/RT} = 0.4545$$

and $$y_{N2} = n_{N2}/n = \frac{3.00 \text{ L bar}/RT}{5.50 \text{ L bar}/RT} = 0.5455$$

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

$$P_{H2} = y_{H2}\,P = 0.4545\ (1.833 \text{ bar}) = 0.833 \text{ bar}$$
$$P_{N2} = y_{N2}\,P = 0.5455\ (1.833 \text{ bar}) = 1.000 \text{ bar}$$

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

Answer: Think through this problem first: At constant pressure, admission of water vapor into the piston will cause an increase in the total moles of gas and a corresponding increase in volume. The moles of O_2 remain the same, but with the increase in volume, the partial pressure of O_2 will decrease. Assume the initial volume is V_o. In dry air $P = P_{O2} + P_{N2}$, with $P_{O2} = n_{O2}\,RT/V_o$ and $P_{N2} = n_{N2}\,RT/V_o$ giving:

$$P = n_{O2}\,RT/V_o + n_{N2}\,RT/V_o \quad \text{or} \quad P = (n_{O2} + n_{N2})\,RT/V_o \tag{1}$$

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

$$P_{O2} = y_{O2}\,P = 0.20946\ (1.01325 \text{ bar}) = 0.2122 \text{ bar or}$$
$$P_{O2} = y_{O2}\,P = 0.20946\ (1.0000 \text{ atm}) = 0.2095 \text{ atm} = 159.2 \text{ torr} \tag{2}$$

After the admission of water vapor, $P = P_{O2} + P_{N2} + P_{H2O}$ and the volume increases to V_1, or:

$$P - P_{H2O} = P_{O2} + P_{N2} = n_{O2}\,RT/V_1 + n_{N2}\,RT/V_1 = (n_{O2} + n_{N2})RT/V_1 \tag{3}$$

Dividing Eq. 3 by Eq. 1 gives:

$$\frac{P - P_{H2O}}{P} = \frac{(n_{O2} + n_{N2})RT/V_1}{(n_{O2} + n_{N2})RT/V_o} = \frac{1/V_1}{1/V_o} = \frac{V_o}{V_1} \tag{4}$$

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

$$\frac{P_{O2,1}}{P_{O2,o}} = \frac{n_{O2}\,RT/V_1}{n_{O2}\,RT/V_o} = \frac{1/V_1}{1/V_o} = \frac{V_o}{V_1} \tag{5}$$

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

$$\frac{P_{O2,1}}{P_{O2,o}} = \frac{P - P_{H2O}}{P} \tag{6}$$

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

$$\frac{P_{O2,1}}{P_{O2,o}} = \left(\frac{101.325\text{ kPa} - 3.168\text{ kPa}}{101.325\text{ kPa}}\right) = 0.9687 \tag{7}$$

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

$$P_{O2,1} = P_{O2,o}\left(\frac{P - P_{H2O}}{P}\right) = 0.2122\text{ bar }(0.9687) = 0.2056\text{ bar}$$

or equivalently, 0.2029 atm and 154.2 torr.

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

Answer: The dry partial pressure is:

$$P_{O2} = y_{O2}\,P = 0.20946\ (1.01325\text{ bar}) = 0.2122\text{ bar}$$

and the total pressure is given by $P_o = P_{O2} + P_{N2}$. The admission of water vapor to the constant volume flask will increase the total pressure to $P_1 = P_{O2} + P_{N2} + P_{H2O}$. However, since the partial pressure of O_2 is the pressure the gas would exert in the flask if it were alone, the partial pressure of O_2 won't change. So the final partial pressure of O_2 is 0.2122 bar, or 0.2095 atm, or 159.2 torr.

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

Answer: The molar mass of $(NH_4)_2SO_4$ is 132.14 g mol^{-1}. The number of moles of added $(NH_4)_2SO_4$ is 0.0384607 mol and the molarity is:

c_B = 0.0384607 mol/0.1000 L = 0.384605 M.

The molality, using the mass of the solvent:

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

is $m_B = n_B/w_A$ = 0. 0.0384607 mol/0.097888 kg = 0.392904 mol kg^{-1}

The mole fraction is given using Eq. 2.2.13:

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

$$x_B = 7.02853\text{x}10^{-3}$$

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

$x_{H2O} = 1 - 7.02853\text{x}10^{-3} = 0.992971$

Notice that the molarity and molality differ by 2.1%.

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

Answer: We need to take into account the waters of hydration. The plan is to note that the number of moles of anhydrous $CaCl_2$ is equal to the moles of added $CaCl_2{\cdot}2H_2O$. For the molality calculation the water of hydration is added to the mass of the solvent. The molar mass of $CaCl_2{\cdot}2H_2O$ is 147.014 g mol^{-1}.

The moles of $CaCl_2{\cdot}2H_2O$ is based on the hydrated molar mass:

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

and the molarity is:

c_B = 0.013686 mol/0.1000 L = 0.13686 M.

The mass of the solvent includes the water of hydration, based on 0.013686 mol of $CaCl_2{\cdot}2H_2O$:

w_A = water added in making solution + water of hydration from solute
w_A = (101.26 g – 2.012 g) + 2 (18.02 g mol^{-1})(0.013686 mol)
= 99.741 g = 0.99741 kg

The molality is then:

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

The mole fraction is given using Eq. 2.2.13:

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

$$x_B = 2.466\text{x}10^{-3}$$

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

$$x_{H2O} = 1 - 2.466\text{x}10^{-3} = 0.9975$$

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

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

Answer: Using Eq. 2.2.7, the molality is:

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

$$= 0.879\text{ m}$$

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

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

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

$$x_B = 0.01558 = 0.0156$$

7. The intensity of a 552 nm light beam is decreased to 18.2% of its original intensity on passing through 3.00 cm of a 2.13x10^{-4} M solution of an absorbing solute. What is the molar absorption coefficient?

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

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

The uncertainty can be easily evaluated by changing the %T to 18.**3** and noting the change in the absorbance: log(100/18.**3**) = 0.73**7**5. The result changed in the third significant figure past the decimal point. So A = 0.7399 or just 0.740. Alternatively, you can use significant figure rules for log x with x = 100/18.2 = 5.49 for three significant figures for x. The resulting log x should also have three significant figures past the decimal point, that is in the mantissa, A = 0.734.

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

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

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

Answer: Starting with Eq. 2.4.1

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

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

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

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

$$\int_{J_o}^{J} \frac{dJ}{J} = -\int_{0}^{\ell} \beta\, c\, dx$$

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

$$\left(\ln J \right|_{J_o}^{J} = -\beta\, c \int_{0}^{\ell} dx = -\beta\, c \left(x \right|_{0}^{\ell}$$

Evaluating at the endpoints of the integral gives:

$$\ln J - \ln J_o = -\beta\, c\, \ell$$

Combining the ln terms:

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

and multiplying by -1 gives:

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

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

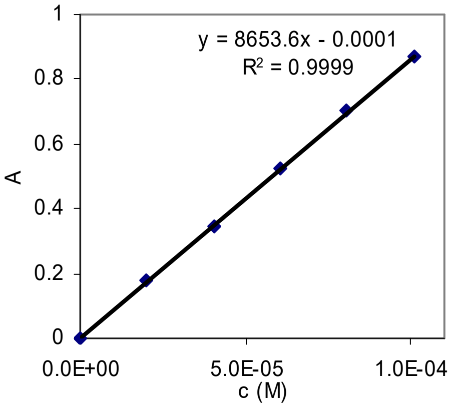
$$3\ \text{bipy} + \text{Fe}^{2+} \rightleftarrows \ \text{Fe(bipy)}_3{}^{2+}$$

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

Answer: (a). The wavelength of 522 nm is in the green to blue-green region of the spectrum. The important point is the wavelength of maximum absorption is not red.
(b). According to the Beer-Lambert Law, $A = \varepsilon \ell c$, Eq. 2.4.7, absorbance is a linear function with slope $\varepsilon\ell$ and zero intercept when plotted as A versus c. An Excel spreadsheet was set up and linest() used to calculate the molar absorption coefficient from the slope of the plot. A plot of the data with the best fit line is also shown below:

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



It is always good idea to use the (0,0) data point, assuming the absorbance scale was calibrated properly. The molar absorption coefficient is 8654. ± 38 M^{-1} cm^{-1}. The uncertainty is 0.44%.
(c). The unknown absorbance is 0.271, which when substituted into $A = \varepsilon \ell c$ gives:

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

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

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

Please consult a text on Analytical Chemistry for a more complete discussion on the propagation of errors for calibration problems, such as this. This result is the concentration in the 50-mL volumetric flask. The concentration in the original 20-mL stream sample is:
(50 mL/20 mL)($3.131\times10^{-5} \pm 0.018\times10^{-5}$ M) = $7.828\times10^{-5} \pm 0.045\times10^{-5}$ M.

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?

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

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

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

$$\frac{A_2}{A_1} = \frac{\varepsilon \ell_2 c}{\varepsilon \ell_1 c} = \frac{\ell_2}{\ell_1}$$

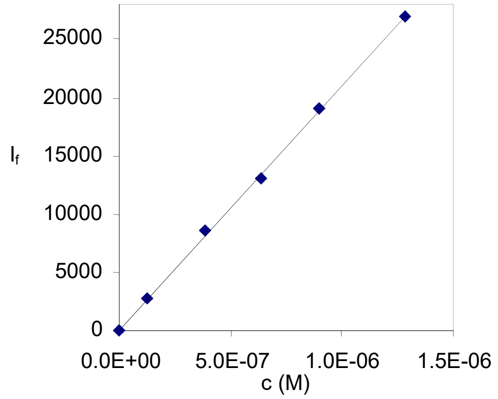
So at ¼ of the depth of the euphotic zone A = 0.5, at ½ of the depth of the euphotic zone A= 1.00, and at ¾ of the full depth A = 1.5. These absorbances correspond to %T of 31.6%, 10%, and 3.16%, respectively.

11. The concentration of quinine sulfate in tonic water can easily be determined using fluorescence emission. A series of standard solutions in 0.05 M sulfuric acid was prepared and the fluorescence emission at 470 nm was determined as shown below. The standard stock concentration was 1.00×10^{-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

Answer: The fluorescence is assumed to be directly proportional to concentration, Section 2.4, $I_f = k\,c$. A plot of fluorescence intensity, or flux, versus concentration should give a straight line with slope k. An Excel spreadsheet was developed and linest() was used to determine the slope of the curve (essentially the same spreadsheet as for Problem 9). A plot of the data with the best fit line is also shown at right:

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



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

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

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

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

Answer: Given that 1 Watt = 1 J s^{-1} then:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

and in kWh per year:

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

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

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

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

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

This calculation is optimistic, because most current commodity photovoltaics have an efficiency closer to 19%. This calculation also doesn't have any inefficiency added for energy storage. Battery storage is 80-90% efficient. So in Boston with 19% efficiency and battery storage, the roof area to be energy neutral for a refrigerator is in the range of 2.25-2.5 m^2. This refrigerator power corresponds to an averaged 51 W. So the roof areas listed in the table would also be needed for roughly 15 "100 watt-equivalent" LED light bulbs (10 W), assuming they are on a third of the time.

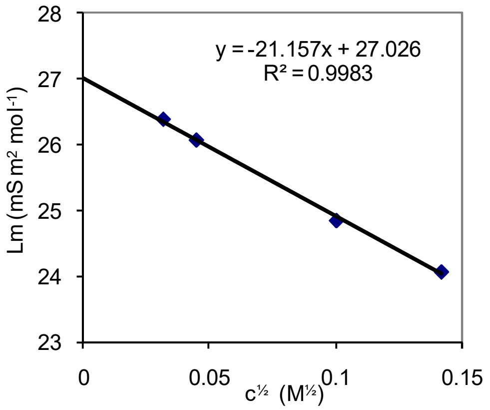
15. Calculate the value for the limiting molar conductivity, Λ^{o}_{m}, for $CaCl_2$ from the following data, taken at 25°C.

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

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

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

slope	-21.1568	27.02572	intercept
±	0.621326	0.056435	±
r^2	0.998278	0.05472	st.dev. Y
F	1159.469	2	df
ss_{reg}	3.471775	0.005989	$ss_{residual}$



The intercept gives $\Lambda^{o}_{m}(CaCl_2) = 27.02 \pm 0.06\ mS\ m^2\ mol^{-1}$.

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

Answer: $\kappa = 0.14695 \text{ S m}^{-1} \text{ (1000 mS/1S)} = 146.95 \text{ mS m}^{-1}$

$\kappa = 0.14695 \text{ S m}^{-1} \text{ (1 m/100 cm)} = 0.0014695 \text{ S cm}^{-1}$

$\kappa = 0.14695 \text{ S m}^{-1} \text{ (1 m/100 cm)(1000 mS/1S)} = 1.4695 \text{ mS cm}^{-1}$

$\kappa = 0.14695 \text{ S m}^{-1} \text{ (1 m/100 cm)(1x}10^{6} \ \mu\text{S/1S)} = 1469.5 \ \mu\text{S cm}^{-1}$

17. Conductivity electrodes are calibrated using standard KCl solutions. The conductivity of 0.01000 M KCl is 0.14127 S m^{-1} or 1412.7 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}.

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

Solving for (ℓ/A) gives:

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

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

(b). The conductivity of the $MgCl_2$ solution is:

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

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

(c). The concentration of the $MgCl_2$ solution is:

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

The molar conductivity is then defined by Eq. 2.4.12

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

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

Another common set of units for molar conductivity are S cm^2 mol^{-1}:

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

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 $\Lambda^o_m(NH_4Cl) = 14.97$ mS m^{2}mol^{-1}, $\Lambda^o_m(NaCl) = 12.64$ mS m^{2}mol^{-1}, and $\Lambda^o_m(NaOH) =$ 24.80 mS m^{2}mol^{-1}, calculate the limiting molar conductivity of NH_4OH.

Answer: At infinite dilution the conductivity of ions is independent, because negligible forces act between the ions. Then $\Lambda^o_m(NH_4OH) = \Lambda^o_m(NH_4Cl) - \Lambda^o_m(NaCl) + \Lambda^o_m(NaOH)$:

$$\Lambda^o_m(NH_4OH) = 14.97 - 12.64 + 24.80 \text{ mS m}^2\text{mol}^{-1} = 27.13 \text{ mS m}^2\text{mol}^{-1}$$

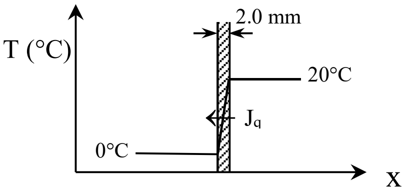
19. Thermal conductivity can be expressed as a linear flux-force relationship:

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

where κ is the thermal conductivity and dT/dx is the temperature gradient. The units of the thermal flux are 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.

Answer: Note that for temperature differences, a °C is the same as a degree K. Analogously to Eq. 2.3.4 for a linear temperature gradient:

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



For air:

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

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

For argon:

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

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

The difference is about 7.5%.

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

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

where κ is the thermal conductivity and dT/dx is the temperature gradient. The units of the thermal flux are 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.

Answer: Note that for temperature differences, a °C is the same as a degree K. Analogously to Eq. 2.3.4 for a linear temperature gradient:

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

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

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

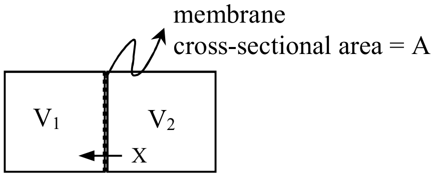
$$J_m = -D\frac{(c' - c)}{\delta} = -P\,(c' - c)$$

where the permeability, P, is defined as P = D/δ, 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 $6.3\text{x}10^{-4}$ 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.

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

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

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



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

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

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

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

$$\frac{dn_x}{dt} = J_m\,A$$

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

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

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

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

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

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

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

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

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

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

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

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

which is just the ratio of the output product fluxes.
(b). Assuming a constant average reaction rate over the time in the reactor, $\bar{\upsilon}$, the amount of product formed is given by:

$$\bar{\upsilon} = \frac{\Delta[P]}{\Delta t} \qquad \text{or} \quad \Delta[P] = \bar{\upsilon}\, \Delta t \tag{4}$$

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

$$y = \frac{n_P}{n_R} = \frac{\bar{\upsilon}\, V\, \Delta t}{n_R} \tag{5}$$

For two different experiments the ratio is given by:

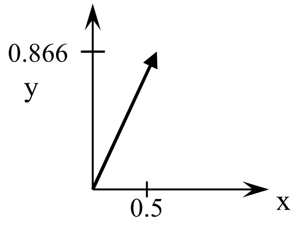
$$y_1 = \frac{\bar{\upsilon}_1\, V\, \Delta t}{n_R} \qquad y_2 = \frac{\bar{\upsilon}_2\, V\, \Delta t}{n_R} \qquad \text{and} \quad \frac{y_2}{y_1} = \frac{\bar{\upsilon}_2}{\bar{\upsilon}_1} \tag{6}$$

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

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

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

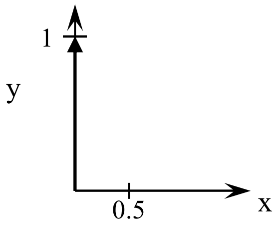
corresponds to a rotation of the vector by 30° around the z-axis. Use $\underset{\sim}{b} = \begin{pmatrix} 1/2 \\ \sqrt{3}/2 \end{pmatrix}$, which is diagrammed at right:



Answer:

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

which lies along the y-axis:



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

$$\cos\theta = \frac{\underset{\sim}{a}\cdot\underset{\sim}{b}}{|a|\,|b|} = \left(1/2(0) + \sqrt{3}/2(1)\right) = \sqrt{3}/2 = 0.866 \qquad \text{or} \quad \theta = 30°$$

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.

Answer: $\underset{\approx}{R}_z(30°) = \begin{pmatrix} \cos 30° & -\sin 30° \\ \sin 30° & \cos 30° \end{pmatrix} = \begin{pmatrix} \sqrt{3}/2 & -1/2 \\ 1/2 & \sqrt{3}/2 \end{pmatrix}$

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

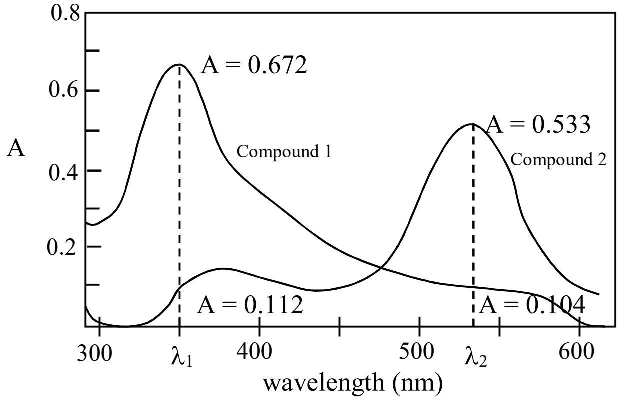
$$\underset{\approx}{M} = \begin{pmatrix} n & 0 \\ 0 & n \end{pmatrix} \qquad \text{with} \quad \underset{\sim}{a} = \underset{\approx}{M}\,\underset{\sim}{b}$$

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.

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

$$\cos\theta = \frac{\underset{\sim}{a} \cdot \underset{\sim}{b}}{|a|\,|b|} = \frac{n(1/2(1/2) + \sqrt{3}/2(\sqrt{3}/2))}{n} = 1 \qquad \text{or} \quad \theta = 0°$$

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



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

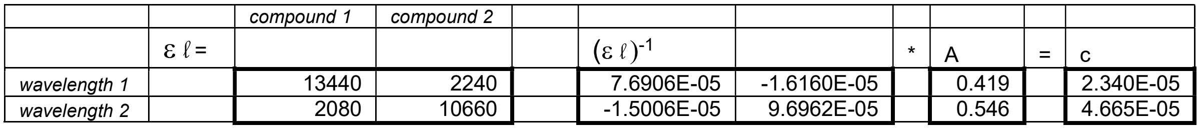
Answer: (a). The absorbance at the second wavelength for the unknown is bigger than at the first. As a pure substance, compound 2 has the bigger absorbance at wavelength 2. This shows that component 2 is in higher concentration than component 1 in the unknown.

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

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

$$\begin{array}{cccc} & \overset{\textit{compound 1}}{\downarrow} & \overset{\textit{compound 2}}{\downarrow} & \\ (\underset{\approx}{\varepsilon\ell}) = & \left(\begin{matrix} 13440 \\ 2080 \end{matrix}\right. & \left.\begin{matrix} 2240 \\ 10660 \end{matrix}\right) & \begin{matrix} \leftarrow \lambda_1 \\ \leftarrow \lambda_2 \end{matrix} \end{array}$$

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



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

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

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 $\underset{\approx}{C} = \begin{pmatrix} i & j \\ k & l \end{pmatrix}$

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

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

For the right-hand side:

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

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

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

29. Find the determinant of the following matrix:

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

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

$$\underset{\approx}{M} = \begin{pmatrix} \cancel{2} & \cancel{0} & \cancel{1} \\ \cancel{3} & 5 & 0 \\ \cancel{0} & 1 & 4 \end{pmatrix} \qquad \text{and} \quad \underset{\approx}{M} = \begin{pmatrix} \cancel{2} & 0 & 1 \\ \cancel{3} & \cancel{5} & \cancel{0} \\ \cancel{0} & 1 & 4 \end{pmatrix}$$

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

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

The determinants of the 2x2 minors are:

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

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

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

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

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

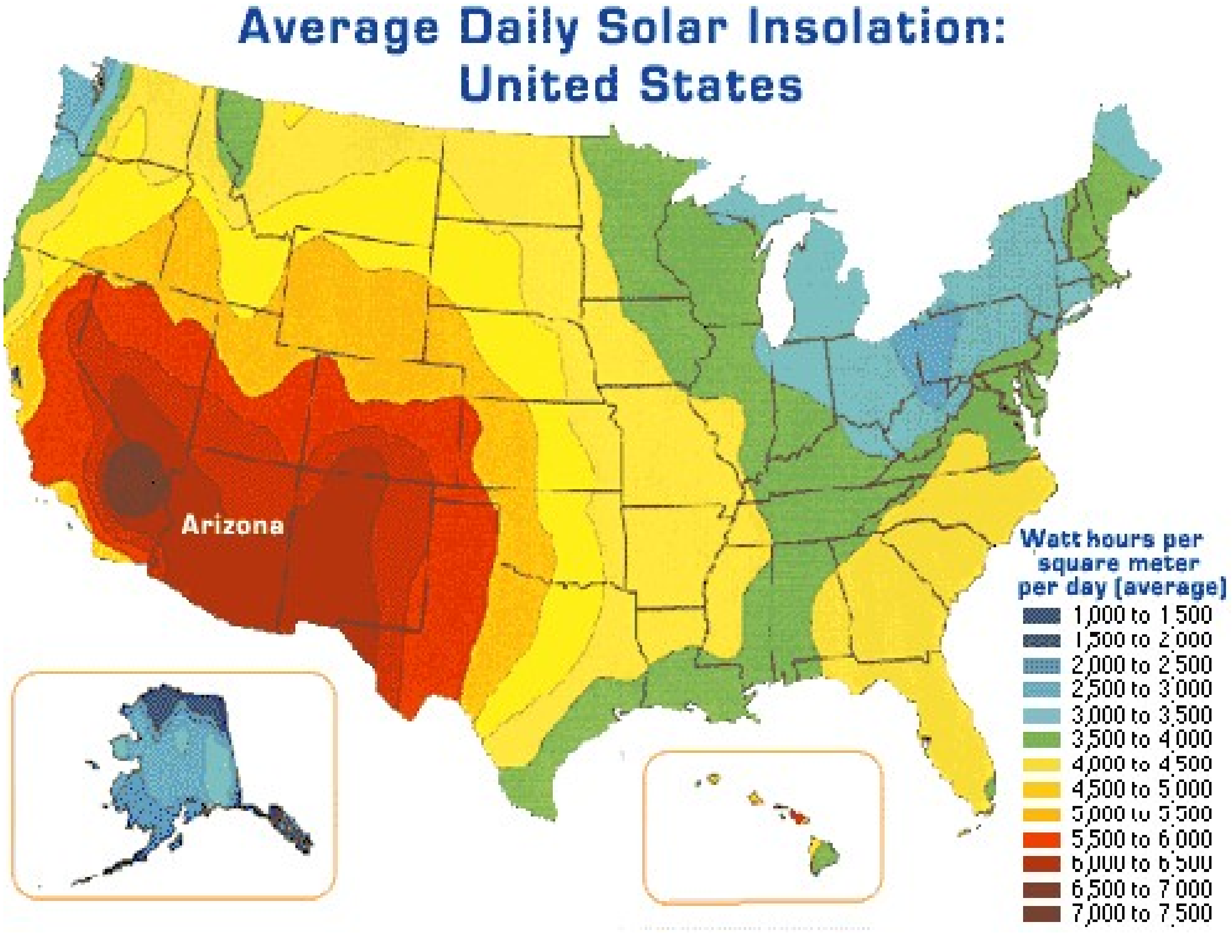
$$\underset{\approx}{M} = \begin{pmatrix} \cancel{-k_1-\lambda_i} & \cancel{0} & \cancel{0} \\ \cancel{k_1} & -k_1'-\lambda_i & 0 \\ \cancel{0} & k_1' & -\lambda_i \end{pmatrix}$$

and then the first minor gives:

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

Overall, then the determinant is:

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



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

Chapter 3 Problems: Kinetics

1. In Example 3.3.1 we discussed denitrification of contaminated ground water. The literature assumes a half-order reaction with respect to NO_3^-, but the differential method for the particular data set gives ¾ order. The best fit values for the corresponding rate constants are $k_{\frac{1}{2}} = 26.71$ and $k_{\frac{3}{4}} = 7.12$. Give the units for the rate constants with the concentration expressed in mg L^{-1}.

Answer: For a half-order reaction the rate law is in the form: $-\frac{d[A]}{dt} = k_{\frac{1}{2}} [A]^{\frac{1}{2}}$

The units of the rate, based on the data, are mg L^{-1} hr^{-1}. The units of $[A]^{\frac{1}{2}}$ are $mg^{\frac{1}{2}}$ $L^{-\frac{1}{2}}$, giving the rate constant as: $k_{\frac{1}{2}} = 26.71$ $mg^{\frac{1}{2}}$ $L^{-\frac{1}{2}}$ hr^{-1}

For a ¾-order reaction the rate law is in the form: $-\frac{d[A]}{dt} = k_{\frac{3}{4}} [A]^{\frac{3}{4}}$

The units of the rate are mg L^{-1} hr^{-1} and $k_{\frac{3}{4}} = 7.12$ $mg^{\frac{1}{4}}$ $L^{-\frac{1}{4}}$ hr^{-1}.

2. The half-life of the pesticide aldicarb (trade name Temik) is 30.0 days. The decomposition of aldicarb is first-order. Calculate the time necessary for the amount of adicarb in a soil sample to drop to 10.0% of its initial value.

Answer: First we calculate the rate constant and from the integrated rate law, Eq. 3.2.5, solve for the time to achieve $[A] = 0.100\ [A]_o$. Solving, Eq. 3.2.11:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k_1} = \frac{0.6931}{k_1} \qquad \text{rearranges to} \qquad k_1 = \frac{0.6931}{30.0\text{ days}} = 0.0231\text{ days}^{-1}$$

Then from Eq. 3.2.5, when $[A] = 0.100\ [A]_o$:

$$\ln\left(\frac{0.100\ [A]_o}{[A]_o}\right) = -\ 0.0231\text{ days}^{-1}\ t$$

$t = 99.7$ days.

3. Organisms require iron for survival. Reduced iron in the form of Fe^{2+} is readily available for acquisition by living systems. However, Fe^{2+} is oxidized by O_2 from the air to produce Fe^{3+}, which precipitates from solution as mixed hydrated oxides and hydroxides. Iron(II) stability is strongly pH dependent. The oxidation of Fe^{2+} in aqueous 0.5 M $HClO_4$ solution at 35°C follows the rate law:

$$-\frac{d[Fe^{2+}]}{dt} = k\ [Fe^{2+}]^2\ P_{O2}$$

where P_{O2} is the partial pressure of O_2 above the solution and $k = 3.65x10^{-3}$ mol^{-1} L atm^{-1} hr^{-1}. Assume that the air above the solution is at constant $P_{O2} = 0.200$ atm. (a) Calculate the half-time of the reaction in days for an initial concentration of 0.100 M Fe^{2+}. (b)How long would it take for the concentration of Fe^{2+} to drop to 0.0100 M?

Answer: For a constant P_{O2} the reaction is pseudo-second order with effective rate constant, $k_{eff} = k\,P_{O2} = 7.30\text{x}10^{-4}\ \text{mol}^{-1}\ \text{L hr}^{-1}$.

(a) The half-time is given by Eq. 3.2.30:

$$t_{½} = \frac{1}{[A]_o k_{eff}} = \frac{1}{0.100\ \text{M}(7.30\text{x}10^{-4}\ \text{mol}^{-1}\ \text{L hr}^{-1})} = 1.370\text{x}10^{4}\ \text{hr} = 571\ \text{days}$$

(b) The integrated rate law is given by Eq. 3.2.27 with [A] = 0.0100 M:

$$\frac{1}{[A]} - \frac{1}{[A]_o} = k_{eff}\,t$$

or

$$\frac{1}{0.0100\ \text{M}} - \frac{1}{0.100\ \text{M}} = (7.30\text{x}10^{-4}\ \text{mol}^{-1}\ \text{L hr}^{-1})\ t$$

Solving for t: $t = 1.233\text{x}10^{5}$ hr = $5.14\text{x}10^{3}$ days. Unfortunately for living organisms, the half-life of Fe^{2+} at neutral pH is many orders of magnitude shorter.

4. The concentration of ozone, O_3, in the stratosphere is dependent on interactions with the odd electron reactive nitrogen species, NO. The concentration of NO in the atmosphere is determined in part by the rate of oxidation by O_2:

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2$$

An initial rate study at 25°C was completed with the following results. Determine the rate law and the rate constant. The initial rate is the slope of the time course for very short times, $t \approx 0$:

$$\text{initial rate} = \upsilon_o = -\left(\frac{d[O_2]}{dt}\right)_o$$

Exp	$[O_2]_o$ (mol L^{-1})	$[NO]_o$ (mol L^{-1})	υ_o (mol L^{-1} s^{-1})
1	$1.44\text{x}10^{-3}$	$0.28\ \text{x}10^{-3}$	$6.90\text{x}10^{-7}$
2	$1.44\ \text{x}10^{-3}$	$0.93\ \text{x}10^{-3}$	$7.50\ \text{x}10^{-6}$
3	$1.44\ \text{x}10^{-3}$	$2.69\ \text{x}10^{-3}$	$6.00\ \text{x}10^{-5}$
4	$6.60\ \text{x}10^{-5}$	$2.69\ \text{x}10^{-3}$	$3.00\ \text{x}10^{-6}$

Answer: The order with respect to O_2 can be calculated from experiments 3 and 4. Just looking at the ratios, since they are about equal, first-order behavior is indicated. To be more precise, using Eq. 3.3.4 gives:

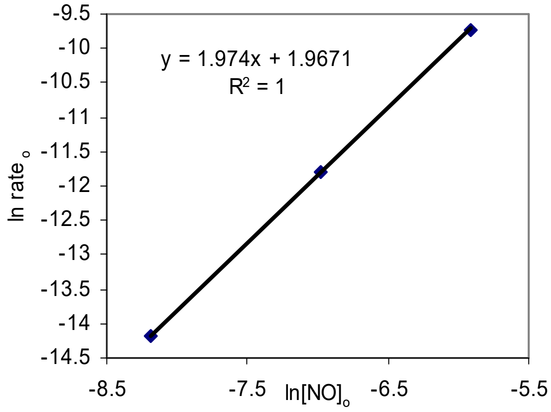
$$\ln\left(\frac{\upsilon_{o2}}{\upsilon_{o1}}\right) = n \ln\left(\frac{[A]_{o2}}{[A]_{o1}}\right)$$

$$\ln\left(\frac{3.00\ \text{x}10^{-6}}{6.00\ \text{x}10^{-5}}\right) = n \ln\left(\frac{6.60\ \text{x}10^{-5}}{1.44\ \text{x}10^{-3}}\right)$$

$$-2.996 = n\,(-3.083) \qquad \text{or} \quad n = 0.972$$

To determine the order with respect to NO we could just do the same. In fact with just three data points, using Eq. 3.3.4 is the best approach. But, if we did have more data points a curve fitting approach would make better use of the experimental uncertainties. So as an example, a spreadsheet was constructed based on the left and right-hand sides of Eq. 3.3.4:

$[NO]_o$	$rate_o$	$\ln[NO]_o$	$\ln rate_o$
2.80E-04	6.90E-07	-8.1807	-14.187
9.30E-04	7.50E-06	-6.9803	-11.801
2.69E-03	6.00E-05	-5.9182	-9.7212



The order with respect to NO is then 1.97, which rounds to 2. It would be silly to do any serious error analysis using linest() with only three data points. So we won't bother, other than using significant figure rules. The ln values are good to 2-3 significant figures, so the final order is good to about 2-3 significant figures. The rate law is then: $\upsilon = k_3 [O_2][NO]^2$. The rate constant can be calculated from each run and then the averaged result can be calculated. Using run 1:

$$\upsilon = k_3 [O_2][NO]^2$$

gives $6.90\text{x}10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k_3 (1.44\text{x}10^{-3} \text{ mol L}^{-1})(0.28 \text{ x}10^{-3} \text{ mol L}^{-1})^2$

solving for k_3: $k_3 = 6.11\text{x}10^3 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$

5. The decomposition of acetaldehyde:

$$CH_3CH{=}O \rightarrow CH_4 + C{\equiv}O$$

at 518°C and at an initial pressure of 363 mm Hg can be monitored by measuring the total pressure of the reaction at constant volume.[1] What is the order of the reaction and the rate constant? Use non-linear curve fitting. [Hint: you need to solve for the partial pressure of acetaldehyde from the total pressure.]

t (s)	42	73	105	190	242	310
P (mm Hg)	397	417	437	477	497	517
t (s)	384	480	665	840	1070	1440
P (mm Hg)	537	557	587	607	627	647

Answer: The total pressure during the reaction is the sum for the reactants and products:

$$P = P_{CH_3CHO} + P_{CH_4} + P_{CO} \qquad 1$$

The stoichiometric relationships for the initial pressure, P_o, give:

$$CH_3CH{=}O \rightarrow CH_4 + C{\equiv}O$$

P_i : $P_o - \xi$ $\quad \xi \quad \xi$ 2

Substituting these values into the total pressure gives:

$$P = P_o - \xi + \xi + \xi = P_o + \xi \qquad 3$$

solving for ξ gives:

$$\xi = P - P_o \text{ and then } P_{CH_3CHO} = P_o - \xi = 2P_o - P \qquad 4$$

The transformation from Eq. 4 was used in an Excel spreadsheet to calculate the acetaldehyde partial pressures:

t (s)	P (mm Hg)	$2P_o$-P (mm Hg)
0	363	363
42	397	329
73	417	309
105	437	289
190	477	249
242	497	229
310	517	209
384	537	189
480	557	169
665	587	139
840	607	119
1070	627	99
1440	647	79

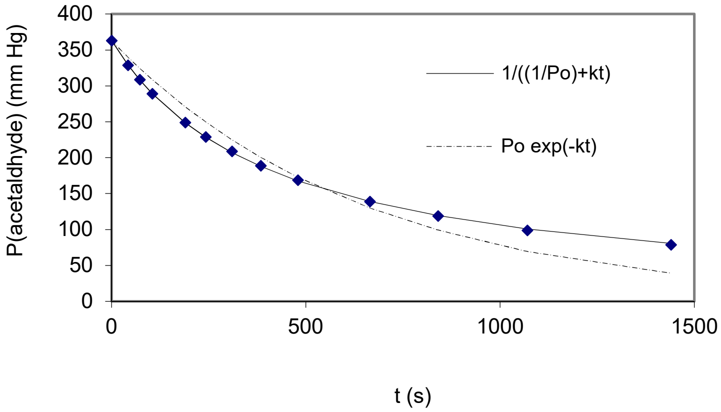
Using the "Nonlinear Least Squares Curve Fit" applet on the text book Web site and on the companion CD with the "a exp(–bx)" fitting function for a first-order fit gives:

```
===============   Results   =============
 a= 337.6 +- 8.8
 b= 0.00133 +- 0.000091
-----------------------------------------
 sum of squared residuals= 2912
 stand. dev. y values= 16.27
 correlation between a & b= 0.6541
```

Using the "1/((1/a)+bx)" fitting function for a second-order fit gives:

```
===============   Results   =============
 a= 363.24 +- 0.76
 b= 0.000006674 +- 3.5e-8
-----------------------------------------
 sum of squared residuals= 13.9
 stand. dev. y values= 1.124
 correlation between a & b= 0.5758
```

The corresponding plots are:



The second-order fit is much better, giving the rate constant as:

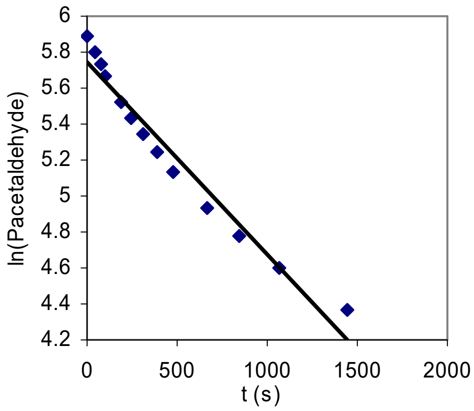
$k = 6.674\text{x}10^{-6} \pm 0.035\text{x}10^{-6}$ mm Hg^{-1} s^{-1}.

6. Redo the kinetic analysis for the data from Problem 5 using the linearized forms of the integrated rate laws.

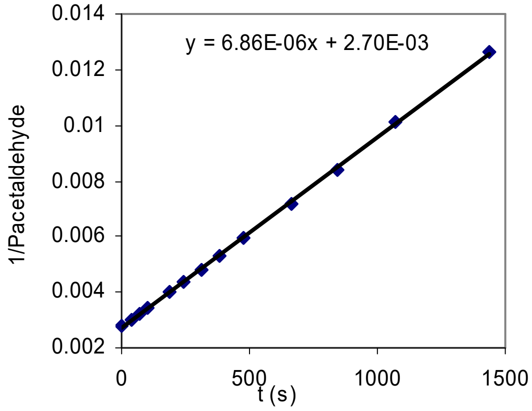
Answer: The data transformations using Eqs. 3.2.18 and 3.2.25 are given below as an Excel spreadsheet:

t (s)	P (mm Hg)	$2P_o$-P (mm Hg)	ln(P_{CH_3CHO})	1/P_{CH_3CHO}
0	363	363	5.894	0.0027548
42	397	329	5.796	0.0030395
73	417	309	5.733	0.0032362
105	437	289	5.666	0.0034602
190	477	249	5.517	0.0040161
242	497	229	5.434	0.0043668
310	517	209	5.342	0.0047847
384	537	189	5.242	0.005291
480	557	169	5.13	0.0059172
665	587	139	4.934	0.0071942
840	607	119	4.779	0.0084034
1070	627	99	4.595	0.010101
1440	647	79	4.369	0.0126582

The corresponding plots are:



(a) First-order plot



(b) Second-order plot

The output from the linest() spreadsheet linear fit for the second-order plot is:

slope	6.864E-06	2.703E-03	intercept
±	3.745E-08	2.312E-05	±
r2	0.99967	5.715E-05	st.dev. y
F	33585.36	11	df
ss_{reg}	1.097E-04	3.593E-08	ss_{resid}

The reaction is second order with a rate constant of $6.864 \times 10^{-6} \pm 0.037 \times 10^{-6}$ mm Hg^{-1} s^{-1}. Notice that the difference between the non-linear fit rate constant and this current value is greater than the estimated uncertainty. This underestimate of the uncertainty from the linearized forms is another reason to rely on non-linear curve fitting, which has a firmer statistical basis. The reson for the better statistical treatment is that the random errors are evaluated directly and not in the transformed 1/P form.

7. Use the differential method during the time course for the data in Problem 5.

Answer: First note that $\upsilon = -\,dP_{CH3CHO}/dt$. We next need to calculate the average rate for each time interval. For example, for the first interval:

$$\bar{\upsilon} = -\frac{P_i(t_2) - P_i(t_1)}{t_2 - t_1} = -\frac{329 - 363}{42 - 0} = 0.8095 \text{ mm Hg s}^{-1}$$

and the partial pressure in the middle of this first time interval is:

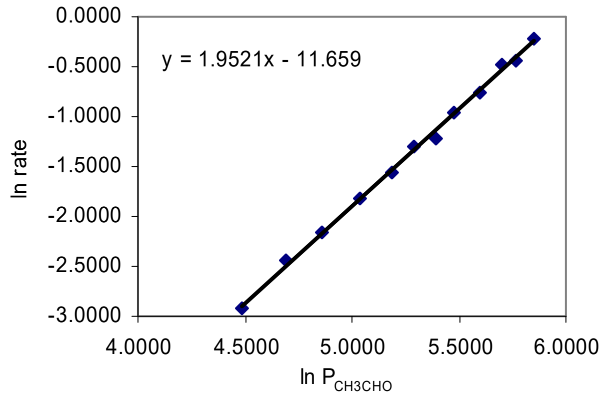
$$\bar{P}_{CH3CHO} = \frac{P_i(t_1) + P_i(t_2)}{2} = \frac{329 + 363}{2} = 346 \text{ mm Hg}$$

A spreadsheet was constructed with rates and average acetaldehyde partial pressures, as shown below. The ln of the average partial pressure and the ln of the rate are also included.

t (s)	$2P_o$-P (mm Hg)	average rate	average P_{CH3CHO}	ln P_{CH3CHO}	ln rate
0	363				
42	329	0.8095	346	5.8464	-0.2113
73	309	0.6452	319	5.7652	-0.4383

105	289	0.6250	299	5.7004	-0.4700
190	249	0.4706	269	5.5947	-0.7538
242	229	0.3846	239	5.4765	-0.9555
310	209	0.2941	219	5.3891	-1.2238
384	189	0.2703	199	5.2933	-1.3083
480	169	0.2083	179	5.1874	-1.5686
665	139	0.1622	154	5.0370	-1.8192
840	119	0.1143	129	4.8598	-2.1691
1070	99	0.0870	109	4.6913	-2.4423
1440	79	0.0541	89	4.4886	-2.9178

The plot of ln(rate) versus ln P is given below:



The output from the linest() spreadsheet linear fit is:

slope	1.9521	-11.659	intercept
±	0.0303	0.1603	±
r^2	0.9976	0.0439	st.dev. y
F	4159	10	df
ss_{reg}	8.0012	0.0192	ss_{resid}

The reaction order is 1.95±0.03, which is close enough to the integer 2.

You'll probably agree that the non-linear curve fitting method is easiest, flowed by the linearized equation fitting. However, the differential method is somewhat less susceptible to problems arising from offsets than the linearized methods.

8. Pharmacokinetics is the study of the absorption, disposition, metabolism, and excretion (ADME) of drugs in living organisms. Pharmacokinetics uses chemical kinetics as a tool to predict drug levels in the body and anticipate drug distribution problems that might arise. Your study of chemical kinetics puts you in a good position to understand ADME properties of drug substances. In the terminology of pharmacology, a bolus dose is a drug given in a short period of time, for example by intravenous injection or oral tablet administration. The table, below, gives the plasma concentration as a function of time for the administration of a 184-mg bolus dose of ceftriaxone to a newborn infant.[2,3] Ceftriaxone is an antibiotic. Find the effective kinetic order for the time course of the drug concentration, the rate constant, and half-life of the drug in the body.

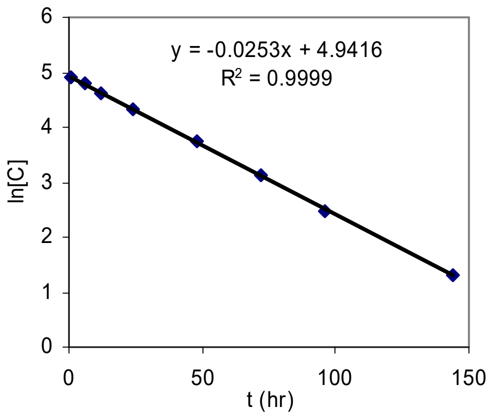
t (hr)	1.0	6.0	12.	24.	48.	72.	96.	144.

Concentration (mg L^{-1})	137.	120.	103.	76.	42.	23.	12.	3.7

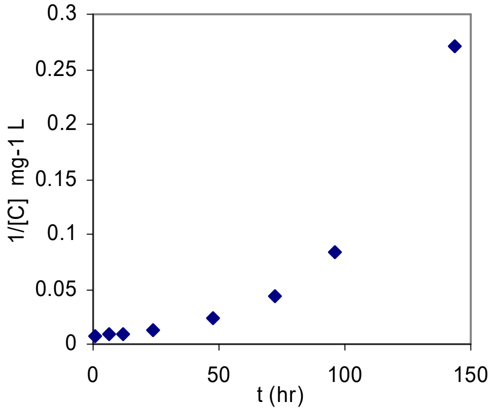
Answer: To construct kinetic plots based on the linear forms of the integrated rate laws, Eq. 3.2.18 for first-order and Eq. 3.2.27 for second-order, the following spreadsheet was constructed:

t (hr)	[C] (mg L^{-1})	ln [C]	1/[C]
1	137	4.919981	0.007299
6	120	4.787492	0.008333
12	103	4.634729	0.009709
24	76	4.330733	0.013158
48	42	3.73767	0.02381
72	23	3.135494	0.043478
96	12	2.484907	0.083333
144	3.7	1.308333	0.27027

The corresponding plots are given below:



(a) first-order plot



(b) second-order plot

The output from the linest() linear least squares curve fitting function in Excel for the first-order plot is:

slope	-0.02529	4.941594	intercept
±	0.000109	0.007509	±
r^2	0.999889	0.014537	st. dev. Y
F	54177.75	6	df
ss_{reg}	11.44938	0.001268	$ss_{residuals}$

The plasma concentrations clearly decrease by first-order kinetics. The slope of the ln[C] versus t curve gives the rate constant: slope = $-k_1$. The half-time for a first-order reaction is given by $t_{½} = \ln(2)/k_1$. The final results are then:

$$k_1 = 0.02529 \pm 0.00011 \text{ hr}^{-1} \quad \text{and} \quad t_{½} = \ln(2)/k_1 = 0.6931/0.02529 = 27.4 \pm 0.1 \text{ hr}$$

The uncertainty in the half-time was calculated from the relative standard deviation in the slope, which is 0.43 %. In other words the relative uncertainty in 1/x is the relative uncertainty in x, since multiplication and division are involved.

9. The absorption of UV light by benzophenone creates a long-lived excited state. When isopropanol-water mixtures are used as the solvent, the excited state of benzophenone rapidly reacts with isopropanol to produce protonated benzophenone ketyl $(C_6H_5)_2CO^{\bullet}H$, which is a free radical:

$$(C_6H_5)_2CO^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2CO^{\bullet}H + (CH_3)_2C^{\bullet}OH$$

The "*" indicates an electronic excited state. In basic solution protonated benzophenone ketyl rapidly looses a proton to produce the benzophenone ketyl radical anion:

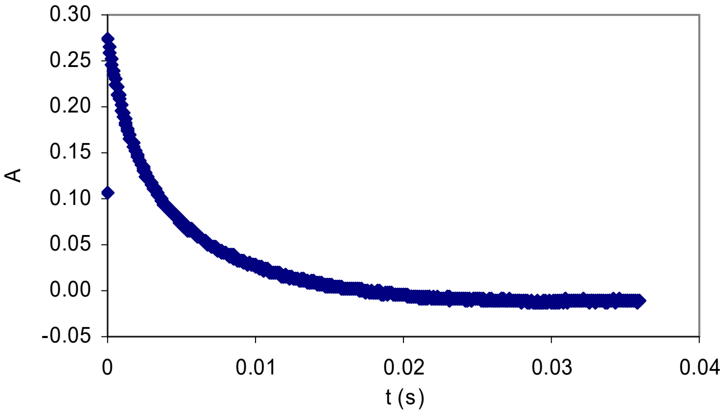
$$(C_6H_5)_2CO^{\bullet}H \rightleftarrows (C_6H_5)_2CO^{\bullet-} + H^+$$

The benzophenone ketyl radical anion then reacts with the protonated form to produce benzpinacol:

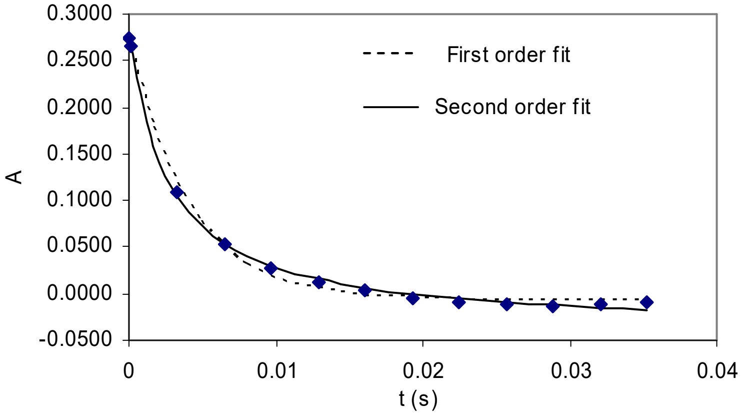
$$(C_6H_5)_2CO^{\bullet}H + (C_6H_5)_2CO^{\bullet-} \xrightarrow{k_2} (C_6H_5)_2C(OH)\text{-}C(OH)(C_6H_5)_2$$

The benzophenone ketyl radical anion has an absorption maximum at 630 nm, which allows the disappearance of the radical anion to be followed as a function of time in a laser flash photolysis instrument. The absorbance time course for the reaction is given below. The data table is extracted from the much larger data file from the instrument, which is plotted at right. Find the order of the reaction and the rate constant with respect to benzophenone ketyl radical anion using non-linear least squares curve fitting.

t (ms)	A
0.064	0.2736
0.128	0.2660
3.264	0.1080
6.464	0.0540
9.664	0.0282
12.864	0.0129
16.064	0.0029
19.264	-0.0039
22.464	-0.0084
25.664	-0.0109
28.864	-0.0125
32.064	-0.0111
35.264	-0.0102



Answer: The long-time portion of the absorbance time course is negative, which shows that the data has a constant offset. That is, A_∞ in Eq. 3.2.38 is negative. The long-time behavior of the time course has some low frequency noise, such that the time course has a minimum before the end of the time course. This level of noise is common for real world kinetics runs. The noise makes the determination of A_∞ in Eq. 3.2.38 very difficult. Therefore, the curve fit equations chosen included a constant offset as a fit parameter. The data table was pasted into the "Nonlinear Least Squares Curve Fitting" applet, which is available on the textbook companion Web site and the and on the companion CD. For first-order fitting, Eq. 3.2.6 with a constant offset, is the "a exp(-bx) + c" option. For second-order curve fitting, Eq. 3.2.26 with a constant offset, is the "1/((1/a)+bx) + c" option. The results are plotted below.



The first-order fit results are:

```
===================   Results   =====================
 a= 0.2821 +- 0.0051
 b= 242 +- 12
 c= -0.0076 +- 0.0025
-----------------------------------------------------
 sum of squared residuals= 0.0003994
 stand. dev. y values= 0.00632
 correlation between a & b= 0.05997
 correlation between b & c= 0.5454
 correlation between a & c= -0.4078
```

The second-order fit results are:

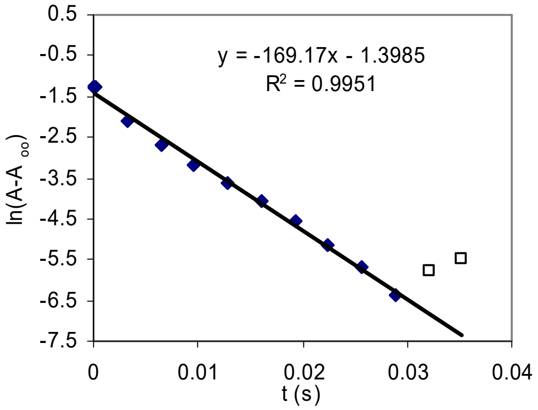
```
===================   Results   =====================
 a= 0.3208 +- 0.0031
 b= 1180 +- 6.3
 c= -0.0395 +- 0.0023
----------------------------------------------------
 sum of squared residuals= 0.0001139
 stand. dev. y values= 0.003375
 correlation between a & b= -0.4096
 correlation between b & c= 0.8893
 correlation between a & c= -0.5629
```

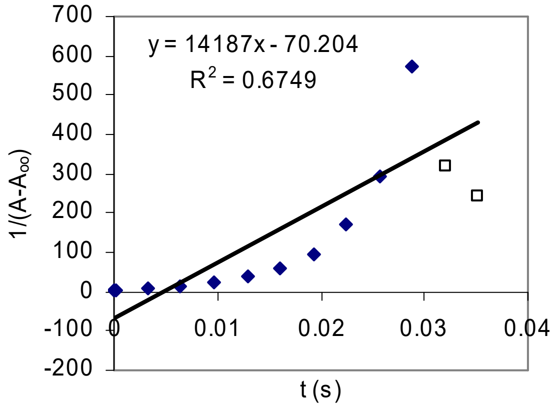
The second-order fit appears to reproduce the time-course better. In addition, in agreement with our visual inspection, the standard deviation of the y values for the second-order plot, 0.003375, is about half that for the first-order plot. The effective second-order rate constant is 1180 ± 6 s^{-1}. Note that a second-order rate constant should have units M^{-1} s^{-1}. Because the absorbance is plotted instead of the actual concentration, an effective rate constant using Eq. 3.2.37 is the result, $k_{eff} = k_2/\varepsilon b$, which has units of s^{-1}. Absorbance is unitless. To distinguish this result from a first-order rate constant you might give the result as 1180 ± 6 au^{-1} s^{-1}, where "au" stands for absorbance units (which are officially unitless). The fit parameter correlation coefficients are acceptable. However, notice that the "correlation between b & c= 0.8893" value shows that final rate constant is very dependent on the choice of the offset constant, A_∞.

10. Use the data in the last problem with linear curve fitting to determine the order of the reaction and the rate constant.

Answer: In the last problem, the long-time portion of the absorbance time course is negative, which shows that the data has a constant offset. The difficulty in using the linear integrated rate law forms, Eq. 3.2.18 for first-order and Eq. 3.2.27 for second-order, is that the constant offset must be handled explicitly. As a first approach, choose the minimum value for the offset, $A_\infty = -0.0125$. Then the corresponding data point can't be used in the fit, since ln 0 is undefined. A spreadsheet that is set up to do the transformations is given below with the resulting curve fits:

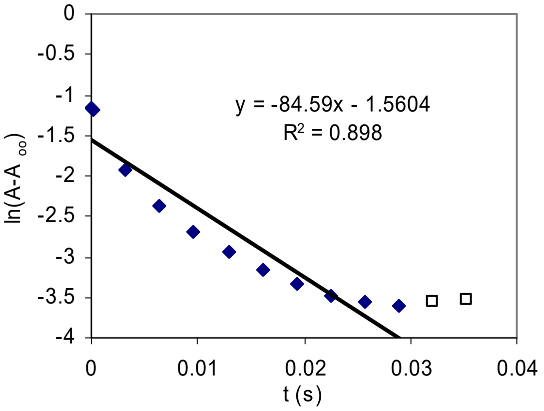
t (s)	A	A - A∞	ln[A]	1/[A]
0.000064	0.2736	0.2861	-1.251	3.4956
0.000128	0.2660	0.2785	-1.278	3.5910
0.003264	0.1080	0.1205	-2.116	8.3002
0.006464	0.0540	0.0665	-2.710	15.031
0.009664	0.0282	0.0407	-3.202	24.600
0.012864	0.0129	0.0254	-3.672	39.337
0.016064	0.0029	0.0154	-4.173	64.968
0.019264	-0.0039	0.0086	-4.761	116.897
0.022464	-0.0084	0.0041	-5.508	246.592
0.025664	-0.0109	0.0016	-6.445	629.445

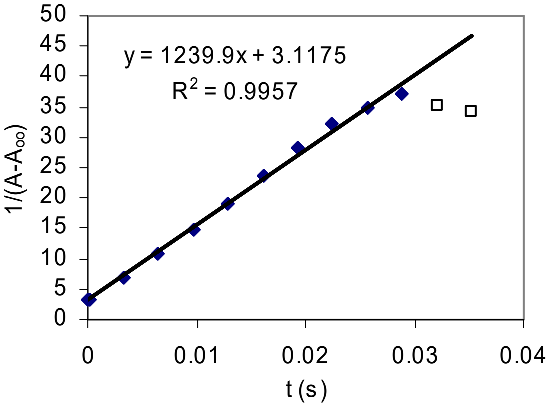




The last two data points are included in the plot to show the effect of noise, but they weren't used in the curve fitting. Notice that these plots predict a first-order reaction in contradiction to Problem 5. If instead of the minimum value from the time course, the A_∞ value from the non-linear curve fits is used, $A_\infty = -0.0395$, then the following plots are obtained:

t (s)	A	A - A∞	ln[A]	1/[A]
0.000064	0.2736	0.3131	-1.161	3.1941
0.000128	0.2660	0.3055	-1.185	3.2736
0.003264	0.1080	0.1475	-1.914	6.7806
0.006464	0.0540	0.0935	-2.369	10.691
0.009664	0.0282	0.0677	-2.693	14.780
0.012864	0.0129	0.0524	-2.948	19.076
0.016064	0.0029	0.0424	-3.160	23.589
0.019264	-0.0039	0.0356	-3.336	28.125
0.022464	-0.0084	0.0311	-3.471	32.200





In which case the reaction appears to be second-order with a rate constant of 1240 s^{-1} (please see the answer to the last problem concerning units). This problem shows that non-linear curve fitting is often the best method. If you choose an incorrect value for the long time value, the resulting kinetic plots can be so distorted that you determine the incorrect order. Non-linear curve fitting provides a non-biased method to determine the long time value because A_∞ can be treated as an adjustable parameter.

11. Determine the fluorescence lifetime for anthracene using the following fluorescence intensity measurements.

t (ns)	0	2	4	6	8	10
Intensity	62620	41250	27218	17708	11352	7560

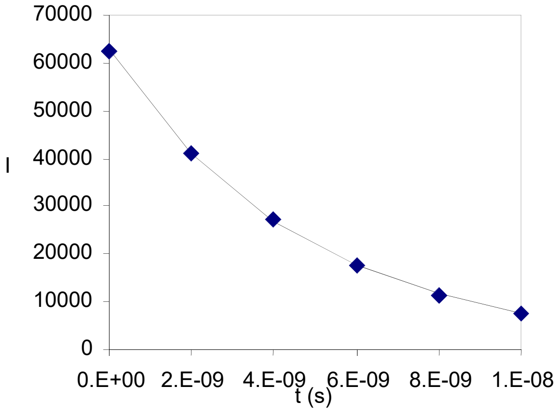
Answer: First convert the times from nano-seconds to seconds. Using the “Nonlinear Least Squares Curve Fit” applet on the text book Web site and on the companion CD with the “a exp(–bx)” fitting function for a first-order fit gives:

```
============   Results   ===============
 a= 62720 +- 170
 b= 210700000.0 +- 1100000
----------------------------------------
 sum of squared residuals= 145100
 stand. dev. y values= 190.5
 correlation between a & b= 0.5655
```

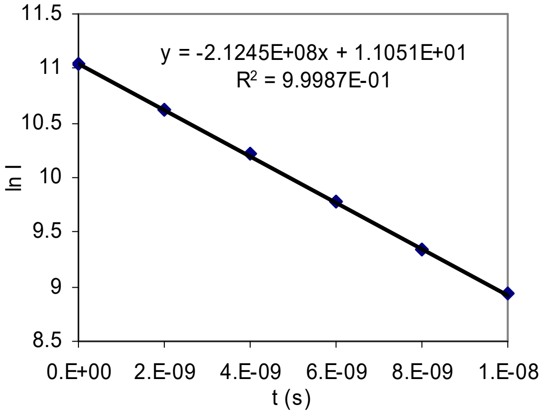
with the fluorescence lifetime τ from the slope: $\tau = 2.11\text{x}10^8 \pm 0.011\text{x}10^8$ s^{-1}. You could also do the linear fit as ln I versus t using the following spreadsheet.

t (s)	Intensity	ln I
0.00E+00	62620	11.04483999
2.00E-09	41250	10.62740639
4.00E-09	27218	10.2116338
6.00E-09	17708	9.781771794
8.00E-09	11352	9.337149219
1.00E-08	7560	8.930626469

The plot from the non-linear fit and the linear version are shown below:



(a) Non-linear fit



(b) First-order plot

<u>12</u>. Determine the integrated rate law for a zeroth-order reaction with stoichiometry 2 A → P. Use definite integrals. Zeroth-order reactions are common with reactions involving surfaces. Find the half-time for a zeroth-order reaction with this stocihiometry.

Answer: The rate law is $-\frac{1}{2}\frac{d[A]}{dt} = k_o$.

The rate of the reaction is independent of the amount of reactant. Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$d[A] = -2k_o\, dt$$

The integral limits are at t = 0, [A] = [A]ₒ, and at time t the concentration is [A]. The definite integrals are:

$$\int_{[A]_o}^{[A]} d[A] = -\int_0^t 2k_o\, dt$$

The integrals are:

$$[A]\Big|_{[A]_o}^{[A]} = -2k_o\, t\Big|_0^t$$

Evaluating the integrals at the limits gives:

$$[A] - [A]_o = -2k_o\, t$$

This equation can be rearranged into the linear form by adding $[A]_o$ to both sides:

$$[A] = [A]_o - 2k_o\, t$$

which has slope = $-2k_o$ and intercept $[A]_o$. The half-time is when $[A] = [A]_o/2$:

$$[A]_o/2 - [A]_o = -2k_o t_{½}$$

Solving for the half-time:

$$t_{½} = \frac{[A]_o}{4k_o} \qquad \text{(for } 2\text{ A} \rightarrow \text{P)}$$

The half-time is greater when you start with more material, since the rate of the reaction is independent of the starting amount.

13. The half-time for a chemical reaction is the time when ½ the original amount of reactant remains. However, the choice of the half-time point as a measure of the reaction rate is not unique. We can also determine the time when ¼ of the original amount remains, or when 1/p of the original amount remains. Find the formula that relates the time to reach the 1/p point to the rate constant, for a first-order and a second-order reaction.

Answer: For a first order reaction, starting with the integrated rate law in the form, Eq. 3.2.5:

$$\ln\left(\frac{[A]}{[A]_o}\right) = -k_1 t$$

The 1/p time corresponds to the concentration of a dropping to $[A] = [A]_o/p$. Substituting into the integrated rate law gives:

$$\ln\left(\frac{[A]_o/p}{[A]_o}\right) = -k_1 t_{1/p}$$

Simplifying the ln term:

$$\ln\left(\frac{[A]_o/p}{[A]_o}\right) = \ln(1/p) = -\ln p$$

Then solving for $t_{1/p}$ gives:

$$t_{1/p} = \frac{\ln p}{k_1}$$

which for p = 2 reduces to Eq. 3.2.11. As an example, assume that the half-time for a first order reaction is $t_{½} = 10$ s, or $k_1 = 0.0693\ \text{s}^{-1}$. The ¼ time would occur at 20 s, which is 2 $t_{½}$, and the $^{1}/_{8}$ time at 30 s, which is 3 $t_{½}$.

For a second-order reaction, from Eq. 3.2.27:

$$\frac{1}{[A]_o/p} - \frac{1}{[A]_o} = k_2\, t_{1/p}$$

Simplifying the left-hand side gives:

$$\frac{1}{[A]_o/p} - \frac{1}{[A]_o} = \frac{p}{[A]_o} - \frac{1}{[A]_o} = \frac{p-1}{[A]_o} = k_2\, t_{1/p}$$

Solving for the 1/p time gives:

$$t_{1/p} = \frac{p-1}{[A]_o\, k_2}$$

which reduces to Eq. 3.2.30 when p = 2. As an example, assume that the half-time for a second order reaction is $t_{½} = 10$ s. The ¼ time would occur at 30 s and the $^1/_8$ time at 70 s.

14. Determine the integrated rate law and the half-time for a third-order reaction with the stoichiometry A → P.

Answer: The rate law is:

$$-\frac{d[A]}{dt} = k_3\,[A]^3$$

Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$-\frac{d[A]}{[A]^3} = k_3\,dt$$

The indefinite integrals are:

$$-\int \frac{1}{[A]^3}\,d[A] = \int k_3\,dt$$

Note that $-\int \frac{1}{x^3}\,dx = \frac{1}{2x^2}$

Combining the integration constants:

$$\frac{1}{2[A]^2} = k_3t + c$$

The boundary condition is at t = 0, [A] = $[A]_o$, the initial concentration:

$$c = \frac{1}{2[A]_o^2}$$

Substituting the integration constant back in to the integrated rate law gives the linear form:

$$\frac{1}{2[A]^2} = k_3t + \frac{1}{2[A]_o^2}$$

Rearranging gives the standard form often seen in texts:

$$\frac{1}{2[A]^2} - \frac{1}{2[A]_o^2} = k_3t$$

Or solving for the time course gives:

$$[A] = \frac{1}{\left(\frac{1}{[A]_o^2} + 2k_3t\right)^{½}}$$

For the half-time:

$$\frac{1}{2([A]_o/2)^2} - \frac{1}{2[A]_o^2} = \frac{2}{[A]_o^2} - \frac{1}{2[A]_o^2} = \frac{3}{2[A]_o^2} = k_3\, t_{½}$$

Solving for the half-time gives:

$$t_{½} = \frac{3}{2[A]_o^2\, k_3}$$

15. Determine the integrated rate law for a half-order reaction with the stoichiometry A → P.

Answer: The rate law is:

$$-\frac{d[A]}{dt} = k_{½}\, [A]^{½}$$

Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$-\frac{d[A]}{[A]^{½}} = k_{½}\, dt$$

The indefinite integrals are:

$$\int \frac{1}{[A]^{½}}\, d[A] = -\int k_{½}\, dt$$

Note that $\int \frac{1}{x^{½}}\, dx = 2\, x^{½}$ or conversely in proof: $\frac{d(2\, x^{½})}{dx} = x^{-½}$

Combining the integration constants:

$$2\, [A]^{½} = -\, k_{½}t + c$$

The boundary condition is at t = 0, [A] = [A]ₒ, the initial concentration:

$$c = 2\, [A]_o^{½}$$

Substituting the integration constant back in to the integrated rate law gives the linear form:

$$2\, [A]^{½} = -\, k_{½}t + 2\, [A]_o^{½} \qquad \text{and} \quad [A]^{½} = -\frac{k_{½}}{2}\, t + [A]_o^{½}$$

Solving for the time course gives:

$$[A] = \left([A]_o^{½} - \frac{k_{½}}{2}\, t\right)^2$$

16. In biology, exponential population growth arises from the rate law:

$$\frac{d[P]}{dt} = k\,[P]$$

where [P] is the population of a given organism and d[P]/dt is the birth rate. In short, the greater the number of individuals the greater the birth rate. Find the integrated rate law for the population.

Answer: Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$\frac{1}{[P]}\,d[P] = k\,dt$$

The indefinite integrals are:

$$\int \frac{1}{[P]}\,d[P] = \int k\,dt$$

Integrating and combining the integration constants gives:

$$\ln [P] = kt + c$$

The boundary condition is at t = 0, $[P] = [P]_o$; if you don't start with at least a few individuals, there can be no population growth. Evaluating the integration constant:

$$c = \ln [P]_o$$

Substituting the integration constant back into the integrated rate law gives:

$$\ln [P] = kt + \ln [P]_o$$

Combining the ln terms gives:

$$\ln [P] - \ln [P]_o = kt \qquad \text{or} \quad \ln\frac{[P]}{[P]_o} = kt$$

Solving for the population gives:

$$[P] = [P]_o\, e^{kt}$$

which is Malthusian exponential population growth.

17. Determine the integrated rate law for a ¾-order reaction with the stoichiometry A → P.

Answer: The rate law is:

$$-\frac{d[A]}{dt} = k_{3/4}\,[A]^{3/4}$$

Separation of variables to isolate all concentration dependent terms on the left side of the equality and all the time dependent terms on the right side gives:

$$-\frac{d[A]}{[A]^{3/4}} = k_{3/4}\, dt$$

The indefinite integrals are:

$$\int \frac{1}{[A]^{3/4}}\, d[A] = -\int k_{3/4}\, dt$$

Note that $\int \frac{1}{x^{3/4}}\, dx = 4\, x^{1/4}$ or conversely in proof: $\frac{d(4\, x^{1/4})}{dx} = x^{-3/4}$

Combining the integration constants:

$$4\, [A]^{1/4} = -\, k_{3/4}t + c$$

The boundary condition is at t = 0, [A] = $[A]_o$, the initial concentration:

$$c = 4\, [A]_o^{1/4}$$

Substituting the integration constant back in to the integrated rate law gives the linear form:

$$4\, [A]^{1/4} = -\, k_{3/4}t + 4\, [A]_o^{1/4} \qquad \text{and} \quad [A]^{1/4} = -\frac{k_{3/4}}{4}\, t + [A]_o^{1/4}$$

Solving for the time course gives:

$$[A] = \left([A]_o^{1/4} - \frac{k_{3/4}}{4}\, t \right)^4$$

<u>18</u>. In Example 3.3.1 we discussed denitrification of contaminated ground water. The literature assumes a half-order reaction with respect to NO_3^-, but the differential method for the data set gives ¾ order. Plot the time course for a ½-order and a ¾-order reaction using $[NO_3^-]_o$ = 409 mg L^{-1} for 0 hr to 1.7 hr. Include the data points from Example 3.3.1. The best fit values for the rate constants are $k_{1/2}$ = 26.71 $mg^{-1/2}\, L^{1/2}\, hr^{-1}$ and $k_{3/4}$ = 7.12 $mg^{-3/4}\, L^{3/4}\, hr^{-1}$. [Hint: restrict the time interval for the half-order plot so that $([A]_o^{1/2} - k_{1/2}\, t/2) \geq 0$ or for the ¾-order plot, $([A]_o^{1/4} - k_{3/4}\, t/4) \geq 0$]

Answer: The following spreadsheet was set up using the equations from Problems 15 and 17, or alternatively from the Chapter Summary Table:

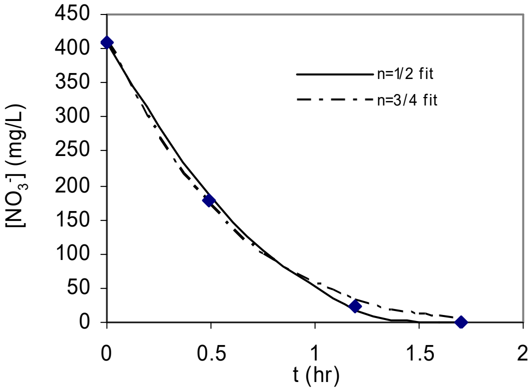
$$\text{For ½-order: } [A] = \left([A]_o^{1/2} - \frac{k_{1/2}}{2}\, t \right)^2$$

$$\text{For ¾-order: } [A] = \left([A]_o^{1/4} - \frac{k_{3/4}}{4}\, t \right)^4$$

A spreadsheet based on these equations and the corresponding plot is:

t (hr)	$[NO_3^-]$	n=1/2 fit	n=3/4 fit
0	409	409	409
0.25		285.11	269.53
0.49	178.2	187.14	172.56

0.75		104.20	99.88
1.19	23.8	18.76	31.96
1.5		0.04	11.11
1.6		0	7.37
1.7	0	0	4.66



The values for the half–order fit for 1.6 and 1.7 hr were just manually set to zero since $([A]_o^{1/2} - k_{1/2}\, t/2)$ was negative for these times. The plots show that both orders fit fairly well. The key time range for determining the correct order is the long-time region where the concentrations get close to zero. More data points in the 1.25-1.5 hr range would be helpful.

19. Find the integrated rate law for a third-order reaction that is second-order in A and first-order in B for the stoichiometry: 2 A + B → products. In actual examples, B is often called a "third body" and is often an inert gas, an N_2 molecule from the air, a particle, or the walls of the container. If the third body were not present, the collision of two A molecules would not be stable and would dissociate back to form two A molecules. The third body is necessary to carry away the excess energy of the collision.

Answer: The rate law would be given as:

$$\upsilon = -\frac{1}{2}\frac{d[A]}{dt} = k_3\,[A]^2[B]$$

Given the stoichiometric relationships, $[A] = ([A]_o - 2\xi)$ and $[B] = ([B]_o - \xi)$:

$$\frac{d\xi}{dt} = k_3\,([A]_o - 2\xi)^2\,([B]_o - \xi)$$

Separating variables: $\dfrac{d\xi}{([A]_o - 2\xi)^2\,([B]_o - \xi)} = k_3\,dt$

The indefinite integrals are: $\displaystyle\int \frac{d\xi}{([A]_o - 2\xi)^2\,([B]_o - \xi)} = \int k_3\,dt$

Integral tables give:

$$\int \frac{dx}{(a + bx)^2\,(a' + b'x)} = \frac{1}{ab' - a'b}\left(\frac{1}{a + bx} + \frac{b'}{ab' - a'b}\ln\frac{(a' + b'x)}{(a + bx)}\right)$$

With b = -2 and b' = -1:

$$\int \frac{d\xi}{([A]_o - 2\xi)^2\,([B]_o - \xi)} = \frac{1}{2\,[B]_o - [A]_o}\left(\frac{1}{[A]_o - 2\xi} - \frac{1}{2[B]_o - [A]_o}\ln\left(\frac{[B]_o - \xi}{[A]_o - 2\xi}\right)\right)$$

The integrated rate law is:

$$\frac{1}{2\,[B]_o - [A]_o}\left(\frac{1}{[A]_o - 2\xi} - \frac{1}{2[B]_o - [A]_o}\ln\left(\frac{[B]_o - \xi}{[A]_o - 2\xi}\right)\right) = k_3\,t + c$$

The boundary condition is at $t = 0$, $\xi = 0$, and the integration constant is:

$$c = \frac{1}{2\,[B]_o - [A]_o}\left(\frac{1}{[A]_o} - \frac{1}{2[B]_o - [A]_o}\ln\left(\frac{[B]_o}{[A]_o}\right)\right)$$

Substituting the integration constant back into the integrated rate law and collecting common terms gives:

$$\frac{1}{2\,[B]_o - [A]_o}\left(\frac{1}{[A]_o - 2\xi} - \frac{1}{[A]_o} - \frac{1}{2[B]_o - [A]_o}\ln\left(\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - 2\xi)}\right)\right) = k_3\,t$$

This equation is often rearranged by taking a common denominator for the terms:

$$\frac{1}{[A]_o - 2\xi} - \frac{1}{[A]_o} = \frac{2\xi}{[A]_o([A]_o - 2\xi)}$$

Substitution back into the integrated rate law gives:

$$\frac{1}{2\,[B]_o - [A]_o}\left[\frac{2\xi}{[A]_o([A]_o - 2\xi)} - \frac{1}{2[B]_o - [A]_o}\ln\left(\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - 2\xi)}\right)\right] = k_3\,t$$

In the next chapter we will discuss a method of calculating numerical approximations to rate laws that avoids having to do complicated integrals. However, this rate law arises often enough that it is handy to have a closed-form solution.

20. The *cis-trans* isomeration of 1-ethyl-2-methylcyclopropane is first order in the forward and reverse directions:[4,5]

$$cis \;\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}\; trans$$

The reaction, starting with only *cis* isomer has the following time course. The long-time value for the *cis*-isomer concentration is 0.00443 M. Determine k_1 and k_{-1}.

t (s)	0	400	1000	1600	2100
[*cis*] (M)	0.01679	0.01406	0.01102	0.00892	0.00775

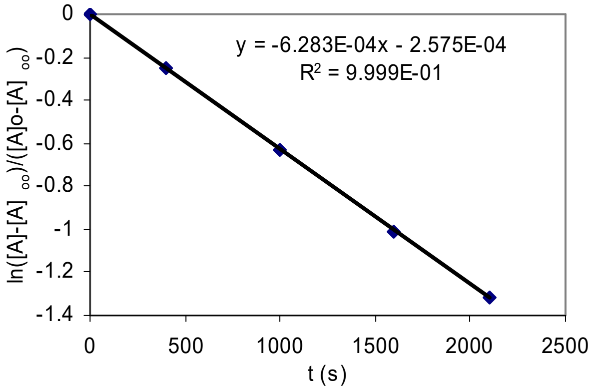
Answer: Using Eq. 3.4.23 with $A_o = 0.01679$ M and $A_\infty = 0.00443$ M, the follow spreadsheet was constructed:

t (s)	[*cis*] (M)	$\frac{([A]-[A]_\infty)}{([A]_o-[A]_\infty)}$	$\ln\frac{([A]-[A]_\infty)}{([A]_o-[A]_\infty)}$
0	0.01679	1	0

400	0.01406	0.7791	-0.2496
1000	0.01102	0.5332	-0.6289
1600	0.00892	0.3633	-1.0126
2100	0.00775	0.2686	-1.3145

The corresponding plot and linest() output is:

slope	-0.0006283	-0.000258	intercept
±	3.039E-06	0.003875	±
r^2	0.999929	0.00520	st. dev. y
F	42737.8	3	df
ss_{reg}	1.15585	8.114E-05	ss_{res}



The slope gives the sum of the rate constants: slope = $-(k_1 + k_{-1}) = -0.0006283$, or:

$$(k_1 + k_{-1}) = 0.0006283 \qquad 1$$

To calculate the rate constants separately, we can use the equilibrium constant. The long-time, equilibrium concentration of the *cis* isomer is $[cis]_\infty = 0.00443$ M, and from the 1:1 stoichiometry:

$$[\text{trans}]_\infty = [\text{cis}]_o - [\text{cis}]_\infty = 0.01679 - 0.00443 \text{ M} = 0.01236 \qquad 2$$

The ratio gives the equilibrium constant:

$$K_c = \frac{k_1}{k_{-1}} = \frac{0.01236}{0.00443} = 2.79 \qquad 3$$

We now have two equations in two unknowns, Eq. 1 and 3. Solving Eq. 3 for k_{-1} gives $k_{-1} = k_1/K_c$ and substitution into Eq . 1 gives:

$$(k_1 + k_1/K_c) = 6.283\text{x}10^{-4} \text{ s}^{-1} \qquad 4$$

Solving for k_1:

$$k_1 = \frac{6.283\text{x}10^{-4}}{1 + 1/K_c} = \frac{6.283\text{x}10^{-4}}{1 + 1/2.79} = 4.625\text{x}10^{-4} \text{ s}^{-1}$$

and then $k_{-1} = k_1/K_c = 4.625\text{x}10^{-4} \text{ s}^{-1}/2.79 = 1.658 \text{ x}10^{-4} \text{ s}^{-1}$

21. The rate of decomposition of acetaldehyde has been studied as a function of temperature. The table below gives the rate constant for the reaction as a function of temperature. Determine the activation energy and the pre-exponential factor.

T (K)	703	733	759	791	811	836
k_2 (M^{-1} s^{-1})	0.011	0.035	0.105	0.343	0.79	2.14

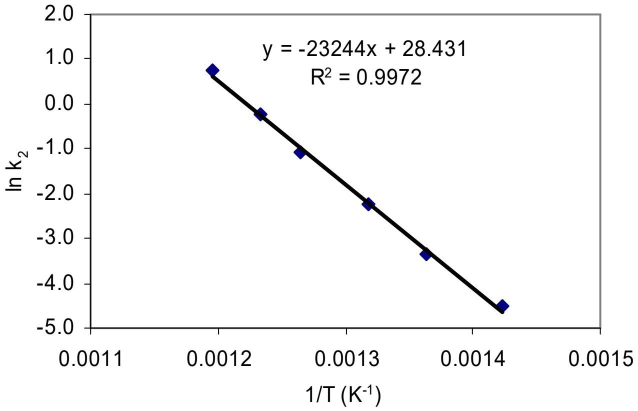
Answer: We will first do the common Arrhenius plot and then compare the results with a non-linear curve fit in the next problem. The non-linear fit gives a more realistic view of the experimental errors.

The following spreadsheet was developed to fit the linear form of the Arrhenius equation, Eq. 3.5.3.

T (K)	k_2 (M^{-1} s^{-1})	1/T (K^{-1})	ln k_2
703	0.011	0.001422	-4.5099
733	0.035	0.001364	-3.3524
759	0.105	0.001318	-2.2538
791	0.343	0.001264	-1.0700
811	0.79	0.001233	-0.2357
836	2.14	0.001196	0.7608

The linest() output and plot are:

slope	-23243.86	28.4312	intercept
±	619.84	0.8069	±
r2	0.9972	0.1176	st.dev.y
F	1406.2193	4.0000	df
ss_{reg}	19.4383	0.0553	ss_{resid}



The activation energy is given by: slope = – E_a/R or E_a = – slope(R) = 193.2 ± 5.1 kJ mol^{-1}. The pre-exponential factor is given by intercept = ln A or:

$$A = e^{28.43} = 2.2\text{x}10^{12}\ M^{-1}\ s^{-1}.$$

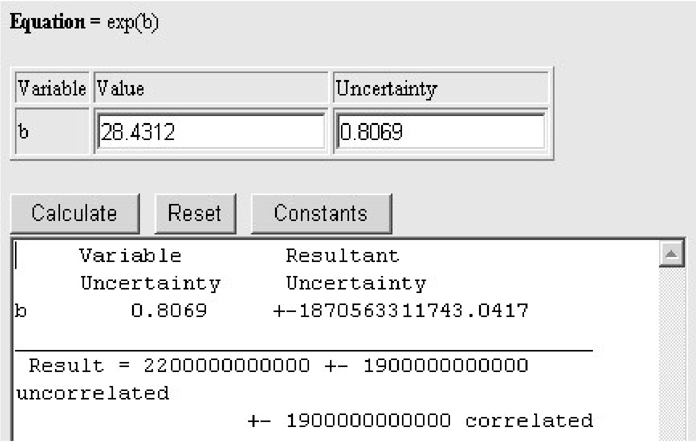
See the next problem for more on error analysis.

22. This problem concerns the error analysis of the results from the last problem. (a) Using the results from the last problem, determine the error in the activation energy and the pre-exponential factor. (b) Often a better approach is to use a non-linear fit. Do a non-linear fit to the original data in the last problem and compare the fit values and the uncertainties with the linearized fit.

Answer: From the last problem, the relative uncertainty in the slope is 2.7% giving the activation energy as uncertain to 2.7% or 193.2 ± 5.1 kJ mol^{-1}. The error for the pre-exponential factor is a bit harder. The intercept is quite uncertain: 28.43 ± 0.81. The significant figure rule is Significant Figure Rule 4 from Appendix 1:

"The number of significant figures in 10^x is the number of significant figures in the mantissa of x. Use the same rule for e^x."

Using significant figure rules, the uncertainty is in the order of magnitude; there are no significant figures in the mantissa. Using the "Uncertainty Calculator" applet on the textbook Web site and on the text companion CD:



Equation = exp(b)

Variable	Value	Uncertainty
b	28.4312	0.8069

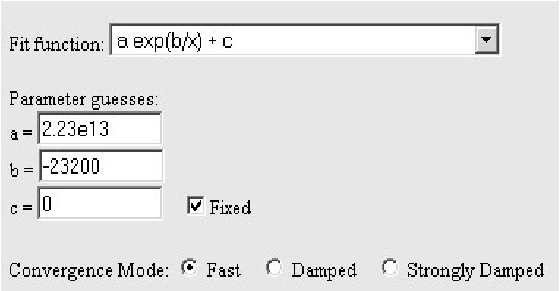
```
     Variable        Resultant
     Uncertainty     Uncertainty
b        0.8069     +-1870563311743.0417

 Result = 2200000000000 +- 1900000000000
uncorrelated
                   +- 1900000000000 correlated
```

The pre-exponential factor and uncertainty are $2.2 \times 10^{12} \pm 1.9 \times 10^{12}\ M^{-1}\ s^{-1}$, which is a bit smaller than expected by the significant figure rules.

The full propagation of errors rule is: the relative variance in e^x is equal to the variance in x (Rule 4, Appendix 1). In this case there is only one error term so we can work with standard deviations directly (Rule 5, Appendix 1). The standard deviation in x is 0.8069 so the relative standard deviation in $e^{28.43}$ is 0.8069, or in other words 81%. The final result is the same as given by the "Uncertainty Calculator."

A better approach is to do non-linear curve fitting, which is also quicker and easier. However, for non-linear curve fitting you need to specify initial guesses for the fit parameters. Sometimes these guesses can be far from the final value. For this particular function the guesses need to be pretty close to the final results. To get guesses for the fit parameters, we can use the results from the linear fit that we obtained in the last problem. The fit function is set up as:



Fit function: a exp(b/x) + c

Parameter guesses:
a = 2.23e13
b = -23200
c = 0 ☑ Fixed

Convergence Mode: ● Fast ○ Damped ○ Strongly Damped

The results of the non-linear fit are significantly different from the linear form for the pre-exponential factor:

```
============   Results   ===============
 a= 171000000000000 +- 75000000000000
 b= -26760 +- 360
```

```
-------------------------------------
 sum of squared residuals= 0.0007028
 stand. dev. y values= 0.01326
 correlation between a & b= -0.9999
```

This fit gives $E_a = 222.5 \pm 3.0$ kJ mol^{-1} and $A = 1.71\text{x}10^{14} \pm 0.75\text{x}10^{14}$ M^{-1} s^{-1}. The correlation between the fit values shows why the uncertainties are so large. This very large correlation between the fit values suggests that the value would be best reported as $\log A \approx 14$ to avoid over-representing the precision.

A Note on Convergence: If you start with a guess that results in the error message “Not Converged,” try clicking on one of the damping options. Choosing “Damped” or “Strongly Damped” allows a much larger range of input guesses to converge on the final result for this particular function. Unfortunately, damping is not always helpful for other fitting functions.

23. Calculate the activation energy and pre-exponential factor for the decomposition of N_2O_5 from the following temperature dependence.[6]

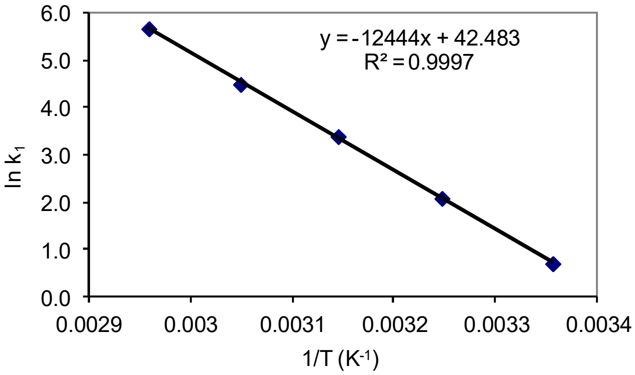
T (K)	298.0	308.0	318.0	328.0	338.0
k_1 (min^{-1})	2.03	8.09	29.9	90.1	291.5

Answer: The plan is to use the linearized form of the Arrhenius temperature dependence, Eq. 3.5.8, and linear least squares curve fitting.

The linearized form of the Arrhenius equation is $\ln k = -E_a/R + \ln A$. A fit of the $\ln k_1$ versus 1/T is done using linest() in the following spreadsheet and plot.

T (K)	k_1 (min^{-1})	1/T (K^{-1})	ln k_1
298.0	2.03	0.003356	0.7080
308.0	8.09	0.003247	2.0906
318.0	29.9	0.003145	3.3979
328.0	90.1	0.003049	4.5009
338.0	291.5	0.002959	5.6750

slope	-12443.7	42.483	intercept
±	123.38	0.389	±
r^2	0.9997	0.0387	st.dev.y
F	10171.6	3.00	df
ssreg	15.2657	0.0045	ssresid



The straight-line behavior verifies Arrhenius temperature dependence. The slope is $-E_a/R$, giving: $E_a = -(-12443.7)8.3145$ J K^{-1} mol^{-1} (1 kJ/1000 J) = 103.46 kJ mol^{-1}

Relative errors propagate upon multiplication and division, giving the uncertainty of 1.0% or $E_a = 103.5 \pm 1.0$ kJ mol^{-1}.

The pre-exponential factor is determined from the intercept, $\ln A = 42.48 \pm 0.39$, giving:

$$A = e^{42.48} = 2.81\text{x}10^{18} \text{ min}^{-1}$$

The relative uncertainty of e^x is the absolute uncertainty in x. The absolute uncertainty in the pre-exponential factor is ±0.39 or equivalently 39% of the final result:

$$A = 2.8\text{x}10^{18} \pm 1.1\text{x}10^{18} \text{ min}^{-1}$$

The pre-exponential factor always has the same units as the rate constant.

<u>24</u>. The rate constant for the disappearance of chlorine in the reaction of NO with Cl_2 to form NOCl is 4.52 $M^{-2}\ s^{-1}$ at 0.0°C and 8.03 $M^{-2}\ s^{-1}$ at 22.0°C. What are the activation energy and pre-exponential factor for this reaction?

Answer: The plan is to follow Example 3.5.1. The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln {}^{k_{T2}}/_{k_{T1}} = -\,{}^{E_a}/R\ ({}^{1}/_{T_2} - {}^{1}/_{T_1}) \qquad (3.5.7)$$

$$\ln ({}^{8.03}/_{4.52}) = -\frac{E_a}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\ ({}^{1}/_{295.15\ \text{K}} - {}^{1}/_{273.15\ \text{K}})$$

$$0.5747 = -\frac{E_a}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\ (-2.7288\text{x}10^{-4}\ \text{K}^{-1})$$

$$E_a = 17.51\ \text{kJ mol}^{-1}$$

Then $k = A\ e^{-E_a/RT}$ using the lower temperature data point:

$$4.52\ M^{-2}\ s^{-1} = A\ e^{(-17.51\text{x}10^3\ \text{J mol}^{-1}/8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}/273.15\ \text{K})} = A\ e^{-7.710} = A\ (4.484\text{x}10^{-4})$$

$$A = 1.01\text{x}10^4\ M^{-2}\ s^{-1}$$

The number of significant figures in e^x is the number of significant figures in the mantissa of x. The mantissa of the argument of the exponential is the ".710" part, or two significant figures. Either original data point gives the same pre-exponential factor. The units of the pre-exponential factor are always the same as the rate constant.

<u>25</u>. The decomposition of urea is $NH_2CONH_2 + 2\ H_2O \rightarrow 2\ NH_4^+ + CO_3^-$. The activation energy for the reaction is 128.0 kJ mol^{-1}. The rate constant 71.2°C is $2.77\text{x}10^{-5}\ min^{-1}$. Calculate the rate constants at 40.0°C.

Answer: The plan is to use the linearized form of the Arrhenius temperature dependence, Eq. 3.5.7. The temperatures must be converted to absolute temperatures.

At 71.2°C the absolute temperature is 344.4 K. The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln {}^{k_{T2}}/_{k_{T1}} = -\,{}^{E_a}/R\ ({}^{1}/_{T_2} - {}^{1}/_{T_1}) \qquad (3.5.7)$$

$$\ln ({}^{k_{T2}}/_{2.77\text{x}10^{-5}\ \text{min}^{-1}}) = -\frac{128.\ \text{x}10^3\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\ ({}^{1}/_{313.2\ \text{K}} - {}^{1}/_{344.4\ \text{K}})$$

$$\ln ({}^{k_{T2}}/_{2.77\text{x}10^{-5}\ \text{min}^{-1}}) = -\ 1.5394\text{x}10^4\ (2.892\text{x}10^{-4}\ \text{K}^{-1}) = 4.452$$

$$k_{T2} = 2.77\text{x}10^{-5}\ \text{min}^{-1}\ e^{-4.452} = 3.228\text{x}10^{-7}\ \text{min}^{-1} = 3.2\text{x}10^{-7}\ \text{min}^{-1}$$

There are only three significant figures in the inverse temperature difference:

$$(1/313.2\ \text{K} - 1/344.4\ \text{K}) = 3.\underbrace{192}_{3\ \text{SFpdpt}}85\text{x}10^{-3} - 2.\underbrace{903}_{3\ \text{SFpdpt}}60\text{x}10^{-3} \rightarrow 0.\underbrace{289}_{3\ \text{SFpdpt}}2\text{x}10^{-3}\ \text{K}$$

where "3 SF dpdt" is short for three significant figures past the decimal point. The number of significant figures in e^x is the number of significant figures in the mantissa of x. The mantissa of the argument of the exponential is the ".45₂" part, or two significant figures.

26. The rate constant for the decomposition of N_2O_5 is 8.09 min^{-1} at 308.0 K and 90.1 min^{-1} at 328.0 K.[6] Calculate the rate constant at 298.2 K.

Answer: The plan is to calculate the activation energy using Arrhenius temperature dependence and then use the same equation and one of the data points to calculate the new rate constant.

The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln {}^{k_{T2}}/_{k_{T1}} = -\,{}^{E_a}/R\ ({}^1/_{T_2} - {}^1/_{T_1}) \qquad (3.5.7)$$

$$\ln ({}^{90.1}/_{8.09}) = -\frac{E_a}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\ ({}^1/_{328.0\ \text{K}} - {}^1/_{308.0\ \text{K}})$$

$$2.410_3 \quad = -\frac{E_a}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\ (-1.97_{97}\text{x}10^{-4}\ \text{K}^{-1})$$

$$E_a = 101.{}_{23}\ \text{kJ mol}^{-1}$$

There are four significant figures in the ln because the number of significant figures in the mantissa of ln x is the number of significant figures in x; the mantissa is the ".410₃" portion. There are only three significant figures in the inverse temperature difference:

$$(1/328.0\ \text{K} - 1/308.0\ \text{K}) = 3\underbrace{.048}_{\text{3 SFpdpt}}{}_{78}\text{x}10^{-3} - 3\underbrace{.246}_{\text{3 SFpdpt}}{}_{75}\text{x}10^{-3} \rightarrow = 0\underbrace{.197}_{\text{3 SFpdpt}}{}_{97}\text{x}10^{-3}\ \text{K}$$

where "3 SFdpdt" is short for three significant figures past the decimal point.

Then using the lower temperature data point and Eq. 3.5.7 gives the rate constant at 298.2 K:

$$\ln {}^{k_{T2}}/_{k_{T1}} = -\,{}^{E_a}/R\ ({}^1/_{T_2} - {}^1/_{T_1}) \qquad (3.5.7)$$

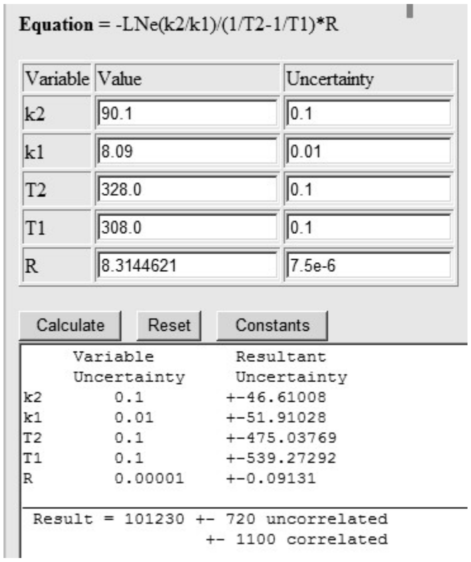
$$\ln ({}^{k_{T2}}/_{8.09\ \text{min}^{-1}}) = -\frac{101.{}_{23}\text{x}10^3\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\ ({}^1/_{298.2\ \text{K}} - {}^1/_{308.0\ \text{K}})$$

$$\ln ({}^{k_{T2}}/_{8.09\ \text{min}^{-1}}) = -\,1.21_{75}\text{x}10^4\ (-1.06_{70}\text{x}10^{-4}\ \text{K}^{-1}) = 1.29_{91}$$

$$k_{T2} = 8.09\ \text{min}^{-1}\ e^{-1.2991} = 2.2_{07}\ \text{min}^{-1} = 2.2\ \text{min}^{-1}$$

www We can verify the significant figure propagation using the "Uncertainty Calculator," from the text Web site. The activation energy calculation propagation is given by the following input.


Equation: -LNe(k2/k1)/(1/T2-1/T1)*R


Equation = -LNe(k2/k1)/(1/T2-1/T1)*R

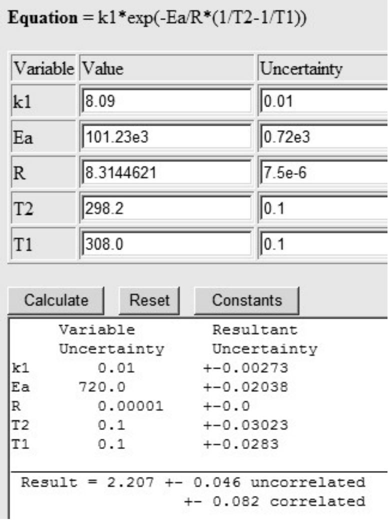
Variable	Value	Uncertainty
k2	90.1	0.1
k1	8.09	0.01
T2	328.0	0.1
T1	308.0	0.1
R	8.3144621	7.5e-6

```
     Variable        Resultant
     Uncertainty     Uncertainty
k2       0.1        +-46.61008
k1       0.01       +-51.91028
T2       0.1        +-475.03769
T1       0.1        +-539.27292
R        0.00001    +-0.09131

 Result = 101230 +- 720 uncorrelated
                 +- 1100 correlated
```

The propagation for the Arrhenius temperature dependence of the rate constant gives:


Equation: k1*exp(-Ea/R*(1/T2-1/T1))


Equation = k1*exp(-Ea/R*(1/T2-1/T1))

Variable	Value	Uncertainty
k1	8.09	0.01
Ea	101.23e3	0.72e3
R	8.3144621	7.5e-6
T2	298.2	0.1
T1	308.0	0.1

```
     Variable        Resultant
     Uncertainty     Uncertainty
k1       0.01       +-0.00273
Ea     720.0        +-0.02038
R        0.00001    +-0.0
T2       0.1        +-0.03023
T1       0.1        +-0.0283

 Result = 2.207 +- 0.046 uncorrelated
                +- 0.082 correlated
```

Significant figure rules and careful error propagation both give two significant figures in the final result: 2.207±0.046 min^{-1} = 2.2 min^{-1}. For publication, the result is best expressed as 2.207±0.046 min^{-1}. Significant figure rules are a poor substitute for careful error analysis, used only as a time saving convenience.

[Alternately, the pre-exponential factor can be determined by solving for A from $k_2 = A\,e^{-E_a/RT}$, and then the rate constant at the new temperature is determined using A and E_a. However, this approach is much more difficult to determine the proper number of significant figures in the final result. While algebraically equivalent, using Eq. 3.5.7 is the preferable approach.]

27. The half-time for the first-order denaturation of yeast invertase at 55.0°C and pH 3 is 26.7 min. The activation energy is 308. kJ mol^{-1}.[7] Calculate the time for the denaturation of the protein to be 75% complete at 60.0°C.

Answer: The plan is to calculate the rate constant at 55°C from the half-time and use the linearized form of the Arrhenius temperature dependence, Eq. 3.5.7, to calculate the rate constant at 60°C. Next the time for 75% completion is calculated using $[A]/[A]_o = 0.75$. The temperatures must be converted to absolute temperatures.

At 55.0°C the absolute temperature is 328.2 K and at 60.0 C the temperature is 333.15 K. The rate constant at 55°C is calculated from the half-time using Eq. 3.2.11, $t_{½} = \ln 2/k_2$:

$$k_{2,328K} = 0.6932/26.7 \text{ min} = 0.02596 \text{ min}^{-1}$$

The linearized form of the Arrhenius relationship for two data points is Eq. 3.5.7:

$$\ln {}^{k_{T2}}/_{k_{T1}} = -\,{}^{E_a}/R\,({}^{1}/_{T_2} - {}^{1}/_{T_1}) \qquad (3.5.7)$$

$$\ln ({}^{k_{T2}}/0.02596 \text{ min}^{-1}) = -\frac{308.\ \text{x}10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{ mol}^{-1}}\,({}^{1}/333.2 \text{ K} - {}^{1}/328.2 \text{ K})$$

$$\ln ({}^{k_{T2}}/0.02596 \text{ min}^{-1}) = -\,3.704\text{x}10^4\ (-4.5722\text{x}10^{-5} \text{ K}^{-1}) = 1.6937$$

$$k_{T2} = 0.02596 \text{ min}^{-1}\ e^{1.6937} = 1.412\text{x}10^{-7} \text{ min}^{-1} = 0.1412 \text{ min}^{-1}$$

There are only two significant figures in the inverse temperature difference:

$$(1/333.2 \text{ K} - 1/328.2 \text{ K}) = \underbrace{3.001}_{\text{3 SFpdpt}}20\text{x}10^{-3} - \underbrace{3.046}_{\text{3 SFpdpt}}92\text{x}10^{-3} = \underbrace{0.045}_{\rightarrow\ \text{2 SF}}72\text{x}10^{-3} \text{ K}$$

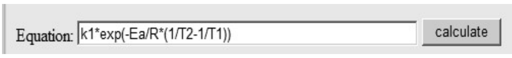
where "3 SFdpdt" is short for three significant figures past the decimal point. The number of significant figures in e^x is the number of significant figures in the mantissa of x. The mantissa of the argument of the exponential is the ".6937" part, or one significant figure.

The time for 75% completion is determined from the integrated first-order rate law:

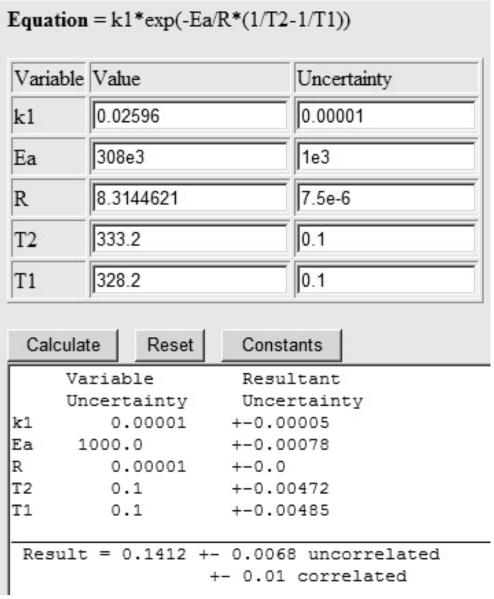
$$\ln\left(\frac{[A]}{[A]_o}\right) = -k_1t \qquad \text{giving} \quad \ln(0.75) = -(0.1412 \text{ min}^{-1})t \qquad \text{with} \qquad t = 2.0 \text{ min}$$

The reaction is greatly accelerated by the temperature increase of only 5°C because the activation energy is so large.

$\boxed{www}$ We can improve upon the significant figure propagation using the "Uncertainty Calculator," from the text Web site. The Arrhenius equation propagation is given by the following input.



Equation: k1*exp(-Ea/R*(1/T2-1/T1))



Equation = k1*exp(-Ea/R*(1/T2-1/T1))

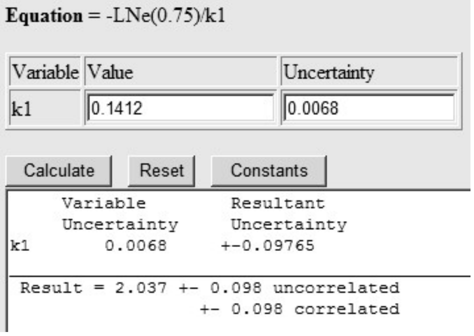
Variable	Value	Uncertainty
k1	0.02596	0.00001
Ea	308e3	1e3
R	8.3144621	7.5e-6
T2	333.2	0.1
T1	328.2	0.1

```
     Variable        Resultant
     Uncertainty     Uncertainty
k1       0.00001    +-0.00005
Ea    1000.0        +-0.00078
R        0.00001    +-0.0
T2       0.1        +-0.00472
T1       0.1        +-0.00485

 Result = 0.1412 +- 0.0068 uncorrelated
                 +- 0.01 correlated
```

The result has two significant figures, 0.14. The error in the final result is given by:

Equation: -LNe(0.75)/k1



Equation = -LNe(0.75)/k1

Variable	Value	Uncertainty
k1	0.1412	0.0068

```
     Variable        Resultant
     Uncertainty     Uncertainty
k1       0.0068     +-0.09765

 Result = 2.037 +- 0.098 uncorrelated
                +- 0.098 correlated
```

The final result is 2.037±0.098 min^{-1}, which is significantly more precise than the uncertainty based on significant figure rules, namely 2. min^{-1}. For publication, the result is best expressed as 2.037±0.098 min^{-1}. Significant figure rules are a poor substitute for careful error analysis, used only as a time saving convenience.

28. The development of biological complexity and the emergence of life have important time constraints. These time constraints in turn give a corresponding range of reaction rate constants for the production of the building blocks of life. All reactions are reversible, and the ratio of the forward and reverse rate constants is given by the equilibrium constant, $K_{eq} = k_f/k_r$. Favorable equilibrium is required to allow the significant build-up of products. A careful balancing of rate and equilibrium constants is necessary for the persistence necessary to build molecular and organizational complexity. If reactions are two fast, complexity can't be established because the lifetimes of the molecules are too short. If reactions are too slow, interdependent sets of complex reaction sequences can't develop. The range of reaction half-times that are amenable for the building of complexity is estimated to be in the 1 s to 100 yr range, which still spans more than 9 orders of magnitude.[8] Assume a range of pseudo-first order half-times of 1 s to 100 yr to

calculate the range of amenable activation energies for reactions that build complexity at 298 K. Typical pre-exponential factors are in the range of $1.0\text{x}10^{10}\ \text{s}^{-1}$ to $1.0\text{x}10^{11}\ \text{s}^{-1}$.

Answer: The plan is to use $k = A\ e^{-E_a/RT}$ to calculate a range of corresponding activation energies, where the range of rate constants is determined from the half-times, $t_{½} = \ln(2)/k_1$.

The range of half-times, 1 s to 100 years, corresponds to a range of pseudo-first order rate constants from $0.693\ \text{s}^{-1}$ to $2.20\text{x}10^{-10}\ \text{s}^{-1}$, respectively. The following table then gives the values of the activation energies, depending on the chosen value of the pre-exponential factor and half-time, using $E_a = -RT \ln(k/A)$:

Table: Activation Energies for Specific Pre-exponential Factors and Rate Constants

A	$k = 0.693\ \text{s}^{-1}$	$k = 2.20\text{x}10^{-10}\ \text{s}^{-1}$
$1.0\text{x}10^{10}\ \text{s}^{-1}$	58 kJ mol^{-1}	112 kJ mol^{-1}
$1.0\text{x}10^{11}\ \text{s}^{-1}$	64 kJ mol^{-1}	118 kJ mol^{-1}

Notice that significant activation energies are required. The activation energies are sizable fractions of typical covalent bond energies. The conclusion is that the development of complexity must be mediated through covalent bonding.[8] Non-covalent interactions, such as hydrogen bonding and π-π interactions, are insufficient to provide the persistence necessary for building complexity. However, after significant complexity is established, networks of cooperative non-covalent interactions are sufficient. For example, protein denaturation typically has high activation energies (see the previous problem). Even though the range of half-times covers nine-orders of magnitude, the corresponding activation energies vary only by a factor of two. Molecules involved in cell signaling, such as NO and acetylcholine, typically have short half-times. Structural scaffold polymers, such as cellulose and collagen, have long half-times. Both extremes are necessary to maintain complex systems.

29. In this problem we compare the integrated rate law for A + B → P with A → P for a simple first-order and second-order reaction. (a) For a second-order reaction that is first order in A and first order in B, solve Eq. 3.2.52 for ξ. Then plot $[A] = [A]_o - \xi$ using the initial conditions $[A]_o = 0.5$ M, $[B]_o = 1.0$ M and $k_2 = 0.1\ \text{M}^{-1}\ \text{s}^{-1}$. Let t range from 0 to 20 s. (b) On the same axis, plot the corresponding time course for a first-order reaction, A→P, with $[A]_o = 0.5$ M and $k_1 = 0.1\ \text{s}^{-1}$. (c) On the same axis, plot the corresponding time course for a simple second-order reaction of the form and stoichiometry A → P. For this last plot, use a rate constant of $k_2 = 0.2\ \text{M}^{-1}\ \text{s}^{-1}$ so that the initial rates for all three types of reactions are equal, to make a fair comparison. (d) Rationalize the differences in the plots.

Answer: The integrated rate law for A + B → P that is first-order in both reactants is given in Eq. 3.2.52:

$$\frac{1}{([B]_o-[A]_o)} \ln\left(\frac{[B]_o-\xi}{[A]_o-\xi}\right) = k_2 t + \frac{1}{([B]_o-[A]_o)} \ln\left(\frac{[B]_o}{[A]_o}\right)$$

Multiplying both sides of the equation by $[B]_o-[A]_o$ and exponentiating gives:

$$\left(\frac{[B]_o - \xi}{[A]_o - \xi}\right) = e^{([B]_o - [A]_o)\,k_2 t + \ln([B]_o/[A]_o)} = \frac{[B]_o}{[A]_o}\, e^{([B]_o - [A]_o)\,k_2 t}$$

Cross multiplying and multiplying out terms:

$$[B]_o - \xi \;=\; [B]_o\, e^{([B]_o - [A]_o)\,k_2 t} - \frac{[B]_o}{[A]_o}\,\xi\, e^{([B]_o - [A]_o)\,k_2 t}$$

Collecting terms in ξ:

$$\xi - \frac{[B]_o}{[A]_o}\,\xi\, e^{([B]_o - [A]_o)\,k_2 t} = [B]_o - \;[B]_o\, e^{([B]_o - [A]_o)\,k_2 t}$$

Solving for ξ:

$$\xi = [B]_o\, \frac{\left(1 - e^{([B]_o - [A]_o)\,k_2 t}\right)}{\left(1 - \dfrac{[B]_o}{[A]_o} e^{([B]_o - [A]_o)\,k_2 t}\right)}$$

Alternatively, multiplying numerator and denominator by $[A]_o/[B]_o$ gives:

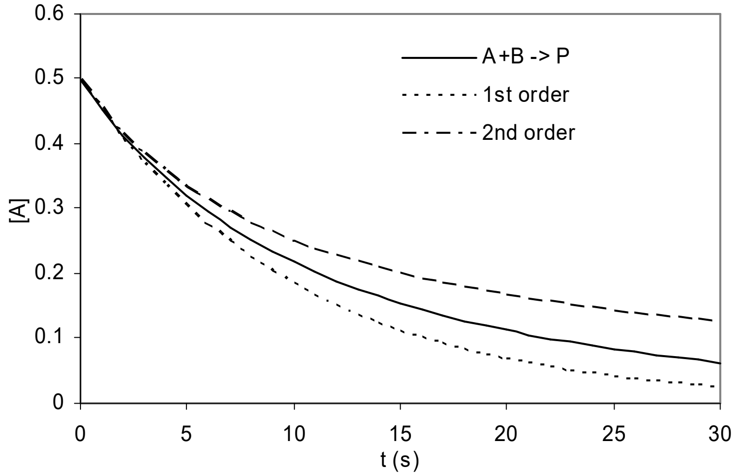
$$\xi = [A]_o\, \frac{\left(1 - e^{([B]_o - [A]_o)\,k_2 t}\right)}{\left(\dfrac{[A]_o}{[B]_o} - e^{([B]_o - [A]_o)\,k_2 t}\right)}$$

A spreadsheet was set up to calculate $e^{([B]_o - [A]_o)\,k_2 t}$, ξ, and $[A]_o - \xi$. Additional columns were added for the first-order function, $[A] = [A]_o\, e^{-k_1 t}$, and the simple second-order function:

$$[A] = \frac{1}{\left(\dfrac{1}{[A]_o} + k_2 t\right)}$$

			[A]o-ξ	[A]	[A]
t (s)	exp((b-a)kt)	ξ	A+B -> P	1st order	2nd order
0	1	0	0.5	0.5	0.5
2	1.105	0.087	0.413	0.409	0.417
4	1.221	0.153	0.347	0.335	0.357
6	1.350	0.206	0.294	0.274	0.313
8	1.492	0.248	0.252	0.225	0.278
10	1.649	0.282	0.218	0.184	0.250
12	1.822	0.311	0.189	0.151	0.227
14	2.014	0.335	0.165	0.123	0.208
16	2.226	0.355	0.145	0.101	0.192
18	2.460	0.372	0.128	0.083	0.179
20	2.718	0.387	0.113	0.068	0.167

The corresponding plot is:



(d) To rationalize the differences, we write the rate laws at 10 s as an example. At 10 s, from the table, for the A + B→ P case, [A] = 0.218 M and [B] = $[B]_o - \xi$ = 0.718 M. Substituting the actual concentrations:

2nd order overall A + B → P $-\frac{d[A]}{dt} = k_2\,[A]\,[B] = k_2\,[A]\,(0.718)$ 1

For the first-order rate law:

1st order A → P $-\frac{d[A]}{dt} = k_1\,[A]$ 2

and for the simple second-order rate law, [A] = 0.250 at t = 10 s giving:

2nd order A → P $-\frac{d[A]}{dt} = k_2\,[A]\,[A] = k_2\,[A]\,(0.250)$ 3

In Eq. 1, [A] is multiplied by (0.718) thus decreasing the rate of disappearance. In Eq. 2, [A] stands alone, so the rate of disappearance of [A] is faster than Eq. 1. In Eq. 3, $[A]^2$ is effectively [A] (0.250) which is the smallest product of all three and therefore the slowest.

30. Show that Eq. 3.4.22 reduces to simple first-order behavior, with a rate constant of just k_1, for a reaction that runs to completion.

Answer: Eq. 3.4.22 involves the sum of the rate constants:

$$\frac{d([A]-[A]_{eq})}{dt} = -\,(k_1 + k_{-1})([A]-[A]_{eq})$$

which doesn't look like it will reduce to a form that only depends on k_1. However, note that from the equilibrium constant:

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}}$$

or solving for k_{-1} gives:

$$k_{-1} = k_1/K_{eq}$$

giving:

$$\frac{d([A]-[A]_{eq})}{dt} = -k_1(1 + 1/K_{eq})([A]-[A]_{eq})$$

In addition, $[A]_{eq} = [B]_{eq}/K_{eq}$. For a reaction that runs to completion, $K_{eq} \rightarrow \infty$, $k_{-1} \rightarrow 0$, and $[A]_{eq} \rightarrow 0$, which gives Eq. 3.2.2.

31. Find the lifetime and half-time for a reversible first-order/first-order reaction from Eq. 3.4.23:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

Answer: The lifetime, τ, is the 1/e time for the course of the reaction. Since the reaction doesn't run to completion, the 1/e point is when the displacement is 1/e of the way to equilibrium:

$$\left(\frac{[A]-[A]_{eq}}{[A]_o-[A]_{eq}}\right) = 1/e$$

Then Eq. 3.4.23 reduces to:

$$\ln\left(\frac{[A]-[A]_{eq}}{[A]_o-[A]_{eq}}\right) = \ln(1/e) = -\ln e = -1 = -(k_1 + k_{-1})\,\tau$$

Solving for the lifetime gives:

$$\tau = \frac{1}{(k_1 + k_{-1})}$$

This equation should be compared to the temperature-jump relaxation time for the same reaction order and stoichiometry, Eq. 3.6.14. These two equations are the same.

Now for the half-time:

$$\left(\frac{[A]-[A]_{eq}}{[A]_o-[A]_{eq}}\right) = ½$$

Then Eq. 3.4.23 reduces to:

$$\ln\left(\frac{[A]-[A]_{eq}}{[A]_o-[A]_{eq}}\right) = \ln(1/2) = -\ln 2 = -0.6931 = -(k_1 + k_{-1})\,\tau$$

and the half-time is $t_{½} = \dfrac{\ln 2}{(k_1 + k_{-1})} = \dfrac{0.6931}{(k_1 + k_{-1})}$

32. For a reversible first-order/first-order reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

(a) Show that the displacement for A after n half-times is given by:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{2}\right)^n$$

(b)What percentage of the initial displacement for A remains after five half-times?

Answer: The half-time for a reversible first-order/first-order reaction with 1:1 stoichiometry is the time when:

$$\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}}\right) = 1/2 \quad \text{or} \quad t_{½} = \frac{\ln 2}{(k_1 + k_{-1})}$$

For n half-times, substituting $t = n\, t_{½}$ into Eq. 3.4.24 gives:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq})\, e^{-(k_1+k_{-1})n\, t½} = ([A]_o - [A]_{eq})\, e^{-n \ln 2} = ([A]_o - [A]_{eq})\, e^{\ln 2^{-n}}$$

$$= ([A]_o - [A]_{eq})\, 2^{-n} = ([A]_o - [A]_{eq}) \left(\frac{1}{2}\right)^n$$

(b) After five half-times the displacement is $[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{2}\right)^5$

and $\left(\frac{1}{2}\right)^5 = 0.0312$ or 3.1% remains compared to its equilibrium value.

33. For a reversible first-order/first-order reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

(a) Show that the displacement for A after n lifetimes is given by:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{e}\right)^n$$

A commonly quoted rule is that a reaction or process has essentially returned to equilibrium after five lifetimes. (b)What percentage of the initial displacement for A remains after five lifetimes?

Answer: The lifetime for a reversible first-order/first-order reaction with 1:1 stoichiometry is the time when:

$$\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}}\right) = 1/e \quad \text{or} \quad \tau = \frac{1}{(k_1 + k_{-1})}$$

For n lifetimes, substituting $t = n\, \tau$ into Eq. 3.4.24 gives:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq})\, e^{-(k_1+k_{-1})n\, \tau} = ([A]_o - [A]_{eq})\, e^{-n}$$

$$= ([A]_o - [A]_{eq}) \left(\frac{1}{e}\right)^n$$

(b) After five lifetimes the displacement is $[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{e}\right)^5$

and $(1/e)^5 = 6.74\text{x}10^{-3}$ or 0.67% remains compared to its equilibrium value.

34. Show that the relaxation time for a dimerization:

$$2\,A \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} A_2$$

is $\tau = \dfrac{1}{(4k_2[A]_{eq} + k_{-1})}$

Assume that the reaction is second order in the forward direction and first order in the reverse direction.

Answer: The rate law is given by:

$$\upsilon = \frac{d[A_2]}{dt} = k_2\,[A]^2 - k_{-1}[A_2] \tag{1}$$

Equilibrium is established when the forward and reverse rates are equal:

$$K_{eq} = \frac{k_2}{k_{-1}} = \frac{[A_2]_{eq}}{[A]^2_{eq}} \qquad \text{or} \quad k_2[A]^2_{eq} - k_{-1}\,[A_2]_{eq} = 0 \tag{2}$$

Subtracting Eq. 2 from Eq. 1 references the concentrations to the equilibrium values:

$$\frac{d[A_2]}{dt} = k_2\,[A]^2 - k_2[A]^2_{eq} - k_{-1}[A_2] + k_{-1}\,[A_2]_{eq} \tag{3}$$

Factoring out the rate constants gives:

$$\frac{d[A_2]}{dt} = k_2([A]^2 - [A]^2_{eq}) - k_{-1}([A_2] - [A_2]_{eq}) \tag{4}$$

Eq. 3.1.2 gives the relationship of the concentration changes, $d[A] = -2\,d[A_2]$.The displacement in the product concentration is $x = [A_2] - [A_2]_{eq}$ and then for the reactant $[A] - [A]_{eq} = -2x$ or solving for [A]:

$$[A] = [A]_{eq} - 2x \tag{5}$$

The $[A]^2$ in terms of the displacement is the square of eq. 5:

$$[A]^2 = [A]^2_{eq} - 4[A]_{eq}\,x + 4\,x^2 \approx [A]^2_{eq} - 4[A]_{eq}\,x \tag{6}$$

However for the last inequality, we assume the displacement is small so that the $4x^2$ is negligible (as we assumed for Eq. 3.6.7). Substituting Eq. 6 into Eq. 4 and using $x = [A_2] - [A_2]_{eq}$, the rate law in terms of the displacements is:

$$\frac{dx}{dt} = -\,4k_2[A]_{eq}\,x - k_{-1}\,x \tag{7}$$

Distributing out the factor of x gives:

$$\frac{dx}{dt} = -\,(4k_2[A]_{eq} + k_{-1})\,x \qquad 8$$

Setting the relaxation time to:

$$\tau = \frac{1}{(4k_2[A]_{eq} + k_{-1})} \qquad 9$$

Substituting this definition for the relaxation time gives: $\frac{dx}{dt} = -\frac{x}{\tau}$ which integrates to:

$$x = x_o\, e^{-t/\tau} \qquad 10$$

as in Eq. 3.6.13. Once again, neglecting the term in x^2 in Eq. 6 guarantees the relaxation is simple-exponential.

35. Consider the reaction: $A + B \rightleftarrows C + D$
Show that the displacement for each product is x and for each reactant is – x, independent of the initial concentrations used to prepare the reaction mixture.

Answer: Set up the following reaction table to show the stoichiometric relationships based on the extent of the reaction:

	A +	B ⇄	C +	D
Initial	$[A]_o$	$[B]_o$	$[C]_o$	$[D]_o$
During	$[A] = [A]_o - \xi$	$[B] = [B]_o - \xi$	$[C] = [C]_o + \xi$	$[D] = [D]_o + \xi$
Equilibrium	$[A]_{eq} = [A]_o - \xi_{eq}$	$[B]_{eq} = [B]_o - \xi_{eq}$	$[C]_{eq} = [C]_o + \xi_{eq}$	$[D]_{eq} = [D]_o + \xi_{eq}$
Displacement	$[A] - [A]_{eq} =$ $([A]_o\text{-}\xi)\text{-}([A]_o\text{-}\xi_{eq})$ $= \xi_{eq} - \xi = -\,x$	$[B] - [B]_{eq} =$ $([B]_o\text{-}\xi)\text{-}([B]_o\text{-}\xi_{eq})$ $= \xi_{eq} - \xi = -\,x$	$[C] - [C]_{eq} =$ $([C]_o+\xi)\text{-}([C]_o+\xi_{eq})$ $= \xi - \xi_{eq} = x$	$[D] - [D]_{eq} =$ $([D]_o\text{-}\xi)\text{-}([D]_o\text{-}\xi_{eq})$ $= \xi - \xi_{eq} = x$

36. Consider a temperature jump perturbation for a reaction that is second order in the forwards and second order in the reverse direction:

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C + D$$

Show the relaxation time is: $\tau \equiv \frac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})}$

Answer: For the displacement away from equilibrium $x \equiv [C] - [C]_{eq} = [D] - [D]_{eq}$.
Since the stoichiometry is 1:1 the displacement in A is $[A] - [A]_{eq} = [B] - [B]_{eq} = -x$. The stoichiometric relationships are summarized in Table P30.1.

Table P30.1: Concentrations for an opposed second-order/second-order reaction.

Progress	[A]	[B]	[C]	[D]
initial, new T	$[A]_o$	$[B]_o$	$[C]_o$	$[D]_o$
middle	$[A]_{eq} - x$	$[B]_{eq} - x$	$[C]_{eq} + x$	$[D]_{eq} + x$
equilibrium	$[A]_{eq}$	$[B]_{eq}$	$[C]_{eq}$	$[D]_{eq}$
displacement	$[A] - [A]_{eq} = -x$	$[B] - [B]_{eq} = -x$	$x \equiv [C] - [C]_{eq}$	$x = [D] - [D]_{eq}$

The rate law is:

$$\frac{d[C]}{dt} = k_2[A][B] - k_{-2}[C][D] \qquad 1$$

At equilibrium, the forward rate is equal to the reverse rate, $k_2[A]_{eq}[B]_{eq} = k_{-2}[C]_{eq}[D]_{eq}$, since at equilibrium the time derivative is zero:

$$k_2[A]_{eq}[B]_{eq} - k_{-2}[C]_{eq}[D]_{eq} = 0 \qquad 2$$

Using Eq. 3.6.5

$$\frac{d[C]}{dt} = \frac{d([C]_{eq}+x)}{dt} = \frac{dx}{dt} \qquad 3$$

Substituting the values from Table P30.1 and Eq. 3 into Eq. 1 gives:

$$\frac{dx}{dt} = k_2([A]_{eq} - x)([B]_{eq} - x) - k_{-2}([C]_{eq}+x)([D]_{eq}+x) \qquad 4$$

Multiplying out each term gives:

$$\frac{dx}{dt} = k_2[A]_{eq}[B]_{eq} - k_2[A]_{eq}\,x - k_2[B]_{eq}\,x + k_2x^2 - k_{-2}[C]_{eq}[D]_{eq} - k_{-2}[C]_{eq}\,x - k_{-2}[D]_{eq}\,x - k_{-2}x^2 \qquad 5$$

Since the perturbation is small, the displacement away from equilibrium, x, must be small. The term in x^2 is then negligible. Neglecting the terms in x^2 and subtracting Eq. 2 from Eq. 5 gives:

$$\frac{dx}{dt} = -k_2[A]_{eq}\,x - k_2[B]_{eq}\,x - k_{-2}[C]_{eq}\,x - k_{-2}[D]_{eq}\,x \qquad 6$$

Distributing out the common factor of –x gives:

$$\frac{dx}{dt} = -\{k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})\}\,x \qquad 7$$

All the terms in the braces are constants. We define the relaxation time:

$$\tau \equiv \frac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})} \qquad 8$$

The rate law in terms of the displacement again reduces to

$$\frac{dx}{dt} = -\frac{x}{\tau} \qquad 9$$

37. Consider a temperature jump perturbation for a reaction that is second order in the forwards and second order in the reverse direction and catalyzed by C:[9]

$$A + C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} B + C$$

Given the catalyst concentration is $[C]_o$, show that the relaxation time is: $\tau = \dfrac{1}{(k_2 + k_{-2})[C]_o}$

Answer: Assuming that the reaction as written is complete and no other mechanistic steps are involved, the concentration of the catalyst is constant. The rate law is:

$$\frac{d[B]}{dt} = k_2[A][C]_o - k_{-2}[B][C]_o$$

This reaction is pseudo-first order in both directions with effective rate constants that combine the original rate constants with the catalyst concentration:

$$\frac{d[B]}{dt} = (k_2[C]_o)\,[A] - (k_{-2}[C]_o)\,[B]$$

The reaction is then pseudo-first order in both directions, with relaxation time given by Eq. 3.6.14:

$$\tau = \frac{1}{(k_2[C]_o) + (k_{-2}[C]_o)}$$

which simplifies to: $\tau = \dfrac{1}{(k_2 + k_{-2})[C]_o}$

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Chapter 4 Problems: Kinetic Mechanisms

1. Consider the gas phase oxidation of HBr: $4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$. The following mechanism has been proposed:

$$\begin{array}{rcl} HBr + O_2 & \xrightarrow{k_1} & HOOBr \\ HOOBr + HBr & \xrightarrow{k_2} & 2\ HOBr \\ HOBr + HBr & \xrightarrow{k_3} & H_2O + Br_2 \end{array}$$

Assume all unidirectional steps. Comment on the validity of this mechanism.

Answer: The forward steps in a mechanism must add to give the overall stoichiometry of the reaction. To give the proper overall stoichiometry, the last step must be doubled.

$$\begin{array}{rcl} HBr + O_2 & \rightarrow & HOOBr \\ HOOBr + HBr & \rightarrow & 2\ HOBr \\ \underline{2x\ (\ HOBr + HBr} & \underline{\rightarrow} & \underline{H_2O + Br_2\ )} \\ 4\ HBr + O_2 & \rightarrow & 2\ H_2O + 2\ Br_2 \end{array}$$

The multiplier for a step in a mechanism is called the stoichiometric number. The stoichiometric number for Step 3 is 2. The next issue is that this mechanism can only hold far from equilibrium. Close to equilibrium a complete mechanism must include each step and its exact reverse.

2. For the $H_2 + I_2$ reaction, $H_2 + I_2 \rightarrow 2\ HI$, the empirical rate law is

$$\upsilon = \frac{d[HI]}{dt} = k\ [H_2][I_2]$$

The empirical rate law matches the stoichiometry of the reaction. Why can't you conclude that the mechanism is a simple single-step mechanism?

Answer: The reaction may occur by direct collisions of H_2 and I_2 molecules, but other mechanisms that have lower overall activation energies or larger pre-exponential factors may also be possible. The introductions to Chapters 3 and 4 discuss two alternate proposals. The direct molecular and rapid pre-equilibrium proposals are kinetically equivalent and therefore indistinguishable without additional experimental time course data for the concentrations of any and all reactive intermediates.

3. The gas phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:

(1) $CH_3COOH \rightarrow CH_4 + CO_2$ $\qquad k_1 = 3.74\ s^{-1}$

(2) $CH_3COOH \rightarrow H_2C{=}C{=}O$ $\qquad k_2 = 4.65\ s^{-1}$

What is the maximum ratio of $H_2C{=}C{=}O$ to CH_4 obtainable at this temperature?

Answer: The ratio of products during a parallel mechanism is always the same, Eq. 4.1.13:

$$\frac{[CH_4]}{[H_2C{=}C{=}O]} = \frac{k_1}{k_2} = \frac{3.74\ s^{-1}}{4.65\ s^{-1}}$$

4. The gas phase reaction, $2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$, is known to have the rate law:

$$\upsilon = k\,[NO]^2[H_2]$$

Can this mechanism be a one-step mechanism? If not, suggest a possible two-step mechanism and suggest the rate determining step. You can use unidirectional elementary steps.

Answer: The reaction cannot have a simple one-step mechanism because the empirical rate law does not agree with the stoichiometry for the reaction. The rate law suggests (but does not require) that the rate determining step may be termolecular:

$$2\ NO + H_2 \rightarrow N_2 + H_2O_2 \qquad 1$$

The product H_2O_2 is suggested by the difference: $2\ NO + H_2 - N_2 = H_2O_2$. This reaction produces stable products, which helps to justify the proposition. The hydrogen peroxide produced must be an intermediate since it does not appear in the overall reaction. To suggest the second step, we can "subtract" this first elementary step, Eq. 1, from the overall reaction, since sum of the mechanistic steps should give the overall stoichiometry:

$$\begin{array}{ll} \text{overall:} & 2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O \\ \text{first step:} & -\ (2\ NO + \ \ H_2 \rightarrow N_2 + H_2O_2) \\ \hline \text{remaining:} & H_2 + H_2O_2 \rightarrow 2\ H_2O \end{array}$$

This last step as an elementary process is a reasonable proposition for the second elementary step. For this mechanism to agree with the given empirical rate law, the first step must be the intrinsically slow step:

$$2\ NO + H_2 \rightarrow N_2 + H_2O_2 \qquad \text{(slow)}$$
$$H_2 + H_2O_2 \rightarrow 2\ H_2O \qquad \text{(fast)}$$

5. Use the finite difference approximation to integrate the rate law for a second order reaction, $A + B \rightarrow P$ with a rate constant of $0.05\ M^{-1}\ s^{-1}$. Choose the initial concentrations $[A]_o = 1.00$ M and $[B]_o = 0.50$ M. Integrate to at least 100 s. Use Excel for the integration. Compare to the exact expression and the results from the Web based "Kinetics Mechanism Simulation" applet or *MathCad* or *MatLab*.

Answer: Starting with the second-order rate law:

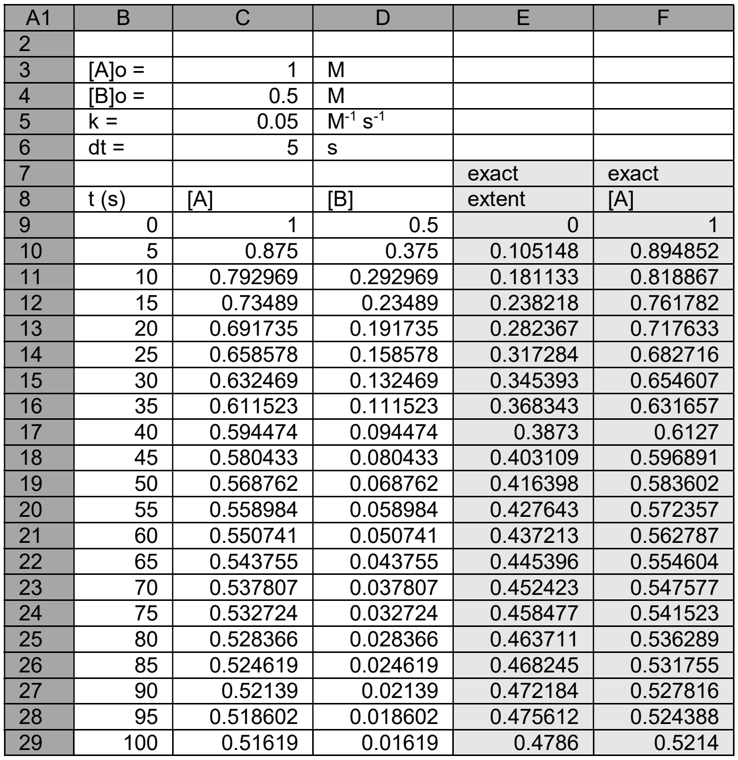
$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k\,[A][B]$$

The finite-difference iteration formulas are:

$$[A](t + \Delta t) = [A](t) - k\,[A](t)[B](t)\,\Delta t$$

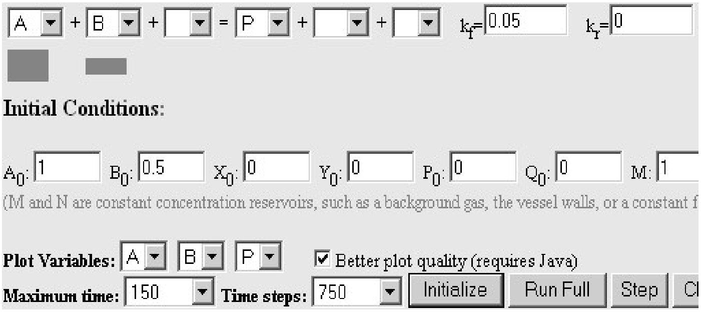
and $$[B](t + \Delta t) = [B](t) - k\,[A](t)[B](t)\,\Delta t$$

The spreadsheet for $\Delta t = 5$ s is:



A1	B	C	D	E	F
2					
3	[A]o =	1	M		
4	[B]o =	0.5	M		
5	k =	0.05	$M^{-1}\ s^{-1}$		
6	dt =	5	s		
7				exact	exact
8	t (s)	[A]	[B]	extent	[A]
9	0	1	0.5	0	1
10	5	0.875	0.375	0.105148	0.894852
11	10	0.792969	0.292969	0.181133	0.818867
12	15	0.73489	0.23489	0.238218	0.761782
13	20	0.691735	0.191735	0.282367	0.717633
14	25	0.658578	0.158578	0.317284	0.682716
15	30	0.632469	0.132469	0.345393	0.654607
16	35	0.611523	0.111523	0.368343	0.631657
17	40	0.594474	0.094474	0.3873	0.6127
18	45	0.580433	0.080433	0.403109	0.596891
19	50	0.568762	0.068762	0.416398	0.583602
20	55	0.558984	0.058984	0.427643	0.572357
21	60	0.550741	0.050741	0.437213	0.562787
22	65	0.543755	0.043755	0.445396	0.554604
23	70	0.537807	0.037807	0.452423	0.547577
24	75	0.532724	0.032724	0.458477	0.541523
25	80	0.528366	0.028366	0.463711	0.536289
26	85	0.524619	0.024619	0.468245	0.531755
27	90	0.52139	0.02139	0.472184	0.527816
28	95	0.518602	0.018602	0.475612	0.524388
29	100	0.51619	0.01619	0.4786	0.5214

The formula for C10 is: “=C9-\$C\$5*C9*D9*\$C\$6”
and for D10 is “=D9-\$C\$5*C9*D9*\$C\$6”.
The exact formula for the extent of the reaction is taken from the Chapter 3 Summary Table. The “Kinetics Mechanism Simulation” applet setup is:



A + B + = P + + k_f=0.05 k_r=0

Initial Conditions:

A_0: 1 B_0: 0.5 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1

(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant f

Plot Variables: A B P ☑ Better plot quality (requires Java)

Maximum time: 150 Time steps: 750

and the applet result at 100 s is [A] = 0.5213 M and [B] = 0.02134 M. The error for the simple Excel version at 100 s is 2% and the error for the “Kinetics Mechanism Simulation” applet compared to the exact analytical integral is 0.02%. The error for the very simple Excel version is actually quite small given the simplicity of the approach. The error could be greatly decreased by choosing a smaller Δt. The Δt for the Web applet version is Δt = max time/750 = 0.20 s, so it is not surprising that the Web applet does better than the Excel version. However, the Web applet also uses a better approximation technique, which is the "4th order Runge–Kutta" algorithm, to further decrease errors. "Numerical Analysis" courses in Mathematics cover advanced methods for integrating differential equations.

6. Use the finite difference approximation to integrate the rate law for the two step mechanism:

$$A + B \xrightarrow{k_1} X \qquad\qquad X \xrightarrow{k_2} P$$

with rate constants $k_1 = 0.05\ M^{-1}\ s^{-1}$ and $k_2 = 0.2\ s^{-1}$. Choose the initial concentrations $[A]_o = 1.00$ and $[B]_o = 0.50$ M. Use Δt = 1 s for a maximum time of at least 50 s. Use Excel and compare to the results from the Web based "Kinetics Mechanism Simulation" applet or *MathCad* or *MatLab*. A useful comparison is to find the maximum concentration of the reactive intermediate.

Answer: We can extend the spreadsheet from Problem 5. The additional rate laws are:

$$\frac{d[X]}{dt} = k_1 [A][B] - k_2[X] \qquad\qquad \frac{d[P]}{dt} = k_2 [X]$$

The corresponding iteration formulas are:

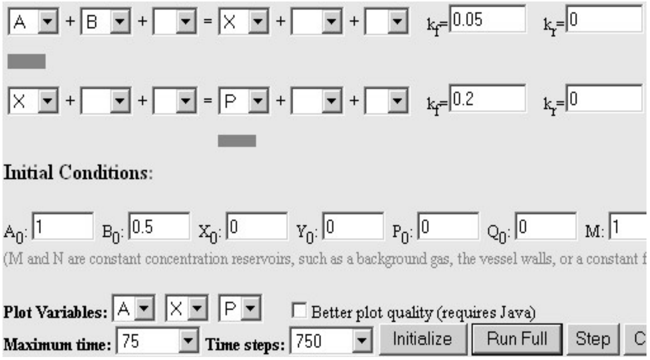
$$[A](t + \Delta t) = [A](t) - k_1 [A](t)[B](t) \Delta t$$
$$[B](t + \Delta t) = [B](t) - k_1 [A](t)[B](t) \Delta t$$
$$[X](t + \Delta t) = [X](t) + k_1 [A](t)[B](t) \Delta t - k_2 [X](t) \Delta t$$
$$[P](t + \Delta t) = [P](t) + k_2 [X](t) \Delta t$$

The first part of the spreadsheet for Δt = 1 s is:

A1	B	C	D	E	F	G
2						
3	[A]o =	1	M			
4	[B]o =	0.5	M			
5	k1 =	0.05	M^{-1} s^{-1}			
6	k2=	0.2	s^{-1}			
7	dt =	1	s			
8						check
9	t (s)	[A]	[B]	[X]	[P]	[A]+[X]+[P]
10	0	1	0.5	0	0	1
11	1	0.975	0.475	0.025	0	1
12	2	0.951844	0.451844	0.043156	0.005	1
13	3	0.93034	0.43034	0.056029	0.013631	1
14	4	0.910321	0.410321	0.064841	0.024837	1
15	5	0.891645	0.391645	0.070549	0.037805	1
16	6	0.874185	0.374185	0.0739	0.051915	1
17	7	0.857829	0.357829	0.075475	0.066695	1
18	8	0.842482	0.342482	0.075728	0.08179	1
19	9	0.828055	0.328055	0.075009	0.096936	1
20	10	0.814473	0.314473	0.07359	0.111938	1
21	11	0.801666	0.301666	0.071678	0.126656	1
22	12	0.789574	0.289574	0.069434	0.140991	1
23	13	0.778142	0.278142	0.06698	0.154878	1
24	14	0.767321	0.267321	0.064405	0.168274	1
25	15	0.757065	0.257065	0.06178	0.181155	1
26	16	0.747334	0.247334	0.059155	0.193511	1
27	17	0.738092	0.238092	0.056566	0.205342	1

The formula for [A] in C11 is: "=C10-$C$5*C10*D10*$C$7"
for [B] in D11 is "=D10-$C$5*C10*D10*$C$7"
for [X] in E11 is "=E10+$C$5*C10*D10*$C$7-$C$6*E10*$C$7"
and [P] in F11 is "=F10+$C$6*E10*$C$7".

We also added a column to act as an error check, [A]+[X]+[P], from the mass balance during the reaction. This column should always give $[A]_o$. The "Kinetics Mechanism Simulation" applet setup is:



A + B + = X + + k_f= 0.05 k_r= 0

X + + = P + + k_f= 0.2 k_r= 0

Initial Conditions:

A_0: 1 B_0: 0.5 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1

(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant f

Plot Variables: A X P ☐ Better plot quality (requires Java)

Maximum time: 75 **Time steps:** 750

The initial part of the applet output is:

time	A	B	X	P
0	1	0.5	0	0
2.5	0.9428	0.4428	0.04416	0.01302
5	0.8948	0.3948	0.06388	0.04135
7.5	0.8539	0.3539	0.07029	0.07582
10	0.8187	0.3187	0.06975	0.1115
12.5	0.7883	0.2883	0.06582	0.1459
15	0.7617	0.2617	0.06047	0.1779
17.5	0.7382	0.2382	0.05476	0.207
20	0.7175	0.2175	0.04921	0.2333
22.5	0.6991	0.1991	0.04408	0.2568
25	0.6826	0.1826	0.03946	0.2779

The maximum concentration for the reactive intermediate from the simple Excel version is 0.0757 M at 8.0 s, while the more accurate applet version gives 0.0703 M at about the same time. At 10 s, where we have data for both approaches, the error is 6%. So the $\Delta t = 1$ s is too long and the Excel simulation should be repeated with much shorter Δt. The Web applet used $\Delta t = 75$ s/750 = 0.10 s, so the result of the Web applet should be much more accurate.

7. The purpose of this exercise is to understand the statement: "the intrinsically slow step is the rate determining step." (a) Plot the integrated time course for the first-order mechanism:

$$A \xrightarrow{k_a} P$$

using $k_a = 0.05\ s^{-1}$ and $0.20\ s^{-1}$. Plot both [A] and [P] for each case. Use an initial concentration of $[A]_o = 1$. Use the Web based "*Kinetics Mechanism Simulation*" applet or *MathCad* or *MatLab*.

(b) Similarly find the integrated time course for the consecutive first-order mechanism:

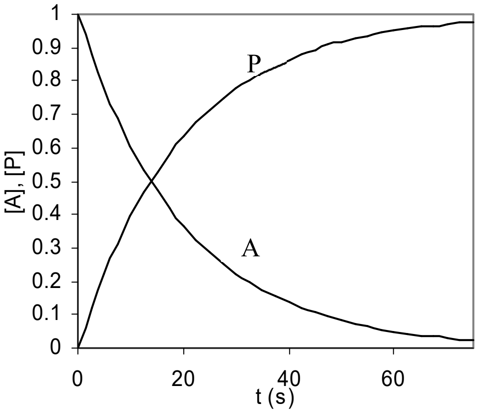
$$k_1 \qquad k_2$$

$$A \rightarrow X \rightarrow P$$

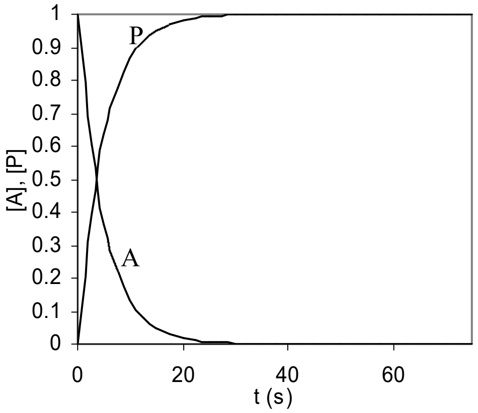
Use $k_1 = 0.2\ s^{-1}$ and $k_2 = 0.05\ s^{-1}$. Predict the step that will be the rate determining step. Plot the time course for A, X, and P. To which curve in part (a) does the disappearance of A correspond, $k=0.05$ or $k=0.20\ s^{-1}$? To which curve in part (a) does the appearance of product correspond? According to the plot, which step is the rate determining step? Is the intrinsically slow step the rate determining step?

Answer: Using the Web based "*Kinetics Mechanism Simulation*," the single-step first-order plots are:

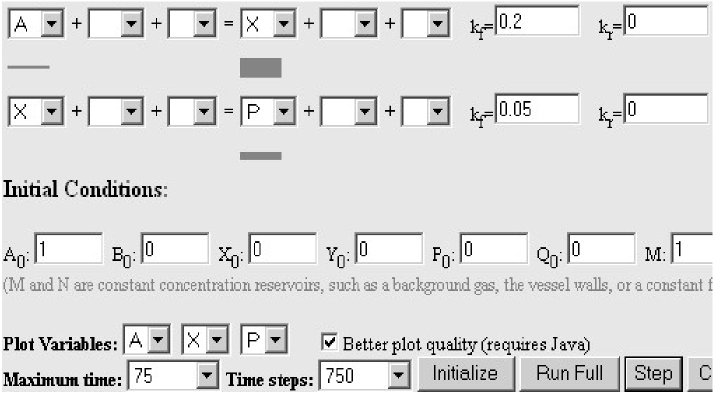
$k_1 = 0.05\ s^{-1}$



$k_1 = 0.20\ s^{-1}$



(b) The "*Kinetics Mechanism Simulation*" applet setup is:



A + + = X + + k_f= 0.2 k_r= 0

X + + = P + + k_f= 0.05 k_r= 0

Initial Conditions:

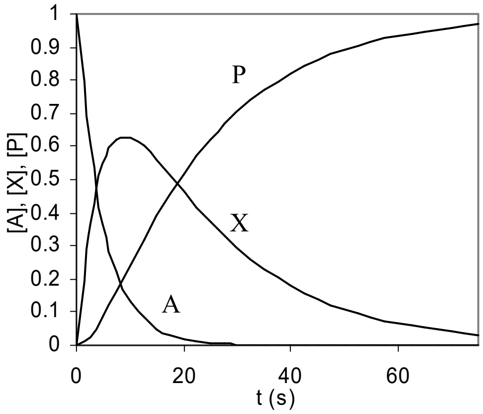
A_0: 1 B_0: 0 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1

(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant f

Plot Variables: A X P ☑ Better plot quality (requires Java)

Maximum time: 75 **Time steps:** 750

The "reservoirs" (green rectangles) are shown for t = 10 s, showing a significant concentration of the intermediate. The plot is shown below. The disappearance of A corresponds to the curve in part (a) for $k_a = 0.2\ s^{-1}$, that is, the faster rate constant. However, the appearance of product corresponds to the curve for $k_a = 0.05\ s^{-1}$, that is the slower rate constant. So the appearance of product is given by the slower second step. So, the rate determining step for the appearance of product is the intrinsically slower step. Since $k_1 >> k_2$, this is as we expected and the intermediate is a stable intermediate. The concentration of the intermediate builds to a significant fraction of the initial concentration of A. Note that the steady-state approximation would not be appropriate for this case.



8. Consider the reaction: $H_2O_2 + 2H^+ + 2\,I^- \rightarrow I_2 + 2\,H_2O$. The following mechanism has been proposed:

$H^+ + I^- \rightleftarrows HI$	rapid equilibrium
$HI + H_2O_2 \rightarrow H_2O + HOI$	slow
$HOI + I^- \rightarrow I_2 + OH^-$	fast
$OH^- + H^+ \rightarrow H_2O$	fast

Show that this mechanism is consistent with the experimentally determined rate law:

$$\upsilon = k\,[H^+][I^-][H_2O_2]$$

Answer: The rate law for the disappearance of H_2O_2 is:

$$-\frac{d[H_2O_2]}{dt} = k_2\,[HI][H_2O_2]$$

If the first step is a rapid pre-equilibrium, that is k_1 and $k_{-1} >> k_2$ then we can obtain the HI concentration from the equilibrium expression:

$$K_c = \left(\frac{[HI]}{[H^+][I^-]}\right)_{eq} \qquad \text{giving } [HI] = K_c\,[H^+][I^-]$$

Substituting this value for [HI] into the rate law for H_2O_2 gives:

$$-\frac{d[H_2O_2]}{dt} = k_2\,K_c\,[H^+][I^-][H_2O_2]$$

For the overall reaction, $H_2O_2 + 2H^+ + 2\,I^- \rightarrow I_2 + 2\,H_2O$: $\upsilon = -\frac{d[H_2O_2]}{dt}$. Fast steps after the rate determining step don't have an effect on the rate law for the disappearance of a reactant in the rate determining step.

9. A possible mechanism for 3rd order reactions is:

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AM$$

$$AM + A \xrightarrow{k_2} A_2 + M$$

Show that the rate law can be expressed as: $\frac{d[A_2]}{dt} = \frac{k_1k_2[A]^2[M]}{k_{-1} + k_2[A]}$

Answer: The plan is to use the steady-state approximation for the concentration of the reactive intermediate AM. Use the steps in the generalized scheme in Section 4.2. Step 1: The rate law for the formation of product is:

$$\frac{d[A_2]}{dt} = k_2\,[AM][A]$$

Step 2: The rate law for the formation of the reactive intermediate is equal to zero by the steady-state approximation:

$$\frac{d[AM]}{dt} = k_1[A][M] - k_{-1}\,[AM] - k_2\,[AM][A] \approx 0 \qquad (k_1 << k_2)$$

Step 3: Solving for the concentration of the reactive intermediate, AM, gives:

$$k_1[A][M] = k_{-1}\,[AM] + k_2\,[AM][A] \quad \text{giving} \quad [AM] = \frac{k_1[A][M]}{k_{-1} + k_2\,[A]}$$

Since there is only one reactive intermediate, we can skip step 4.
Step 5: Substituting the concentration of the reactive intermediate into the rate law for the formation of product gives the final desired result:

$$\frac{d[A_2]}{dt} = k_2\,\frac{k_1[A][M]}{k_{-1} + k_2\,[A]}\,[A] = \frac{k_1k_2[A]^2[M]}{k_{-1} + k_2[A]}$$

Step 6: If $k_{-1} >> k_2[A]$, then this mechanism is a pre-equilibrium mechanism and is third-order overall. On the other hand, if $k_2[A] >> k_{-1}$, this overall rate law reverts to a second-order process.

10. Use the steady-state approximation to determine the rate law for the following mechanism:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \qquad\qquad B + C \xrightarrow{k_3} D$$

Answer: The plan is to treat B as a reactive intermediate using the steady-state approximation.
Step 1: The rate law for the production of product is:

$$\frac{d[D]}{dt} = k_3\,[B][C]$$

Step 2: The rate law for the formation of the reactive intermediate is equal to zero by the steady-state approximation:

$$\frac{d[B]}{dt} = k_1[A] - k_2\,[B] - k_3\,[B][C] \approx 0 \qquad\qquad (k_1 << k_3)$$

Step 3: Solving this last equation for the steady-state concentration of B gives:

$$k_1[A] = k_2\,[B] + k_3\,[B][C] \;\text{ giving }\; [B] = \frac{k_1[A]}{k_2 + k_3\,[C]}$$

Since there is only one reactive intermediate, we can skip step 4.
Step 5: Substitution into the rate law for the formation of product gives:

$$\frac{d[D]}{dt} = \frac{k_1k_3[A][C]}{k_2 + k_3[C]}$$

Step 6: If $k_2 >> k_3[C]$, is a pre-equilibrium mechanism, with $K_{eq} = k_1/k_2$, and then the process is second order overall. If $k_3[C] >> k_2$, then the first step is the rate determining step making the reaction first-order overall.

11. Determine the overall rate law for the proposed $H_2 + I_2$ mechanism:

$$I_2\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,I\,(g)$$

$$H_2\,(g) + I\,(g) \xrightarrow{k_2} HI\,(g) + H\,(g)$$

$$H\,(g) + I_2\,(g) \xrightarrow{k_2'} HI\,(g) + I\,(g)$$

Answer: The plan is to use the steady-sate approximation on both H and I atoms, as reactive intermediates. Step 1 is to write the rate law for the formation of product:

$$\frac{d[HI]}{dt} = k_2\,[H_2][I] + k_2'\,[H][I_2] \qquad 1$$

Step 2 for the steady-state mechanistic scheme is to find the rate law for the formation of the reactive intermediates:

$$\frac{d[I]}{dt} = 2\,k_1\,[I_2] - 2\,k_{-1}\,[I]^2 - k_2\,[H_2][I] + k_{2'}\,[H][I_2] = 0 \qquad 2$$

$$\frac{d[H]}{dt} = k_2\,[H_2][I] - k_2'\,[H][I_2] = 0 \qquad 3$$

Step 3: To solve for the concentration of the reactive intermediate, I, add Eqs. 2 and 3:

$$(2 + 3): \qquad 2\,k_1\,[I_2] - 2\,k_{-1}\,[I]^2 = 0 \qquad 4$$

and solve for [I]:

$$[I] = \left(\frac{k_1}{k_{-1}}\right)^{½} [I_2]^{½} \qquad 5$$

We have two reactive intermediates in this problem. Note, however, if we add Eq. 3 to Eq. 1 that the rate law for formation of product becomes:

$$(1 + 3): \qquad \frac{d[HI]}{dt} = 2\ k_2\ [H_2][I] \qquad 6$$

So only [I] is needed, which eliminates one of the unknowns. We can now proceed to Step 5 and find the overall rate law by substituting the steady-state I concentration from Eq. 5 back into the rate law for the formation of product, Eq. 6:

$$\frac{d[HI]}{dt} = 2\ k_2 \left(\frac{k_1}{k_{-1}}\right)^{½} [H_2]\ [I_2]^{½} \qquad 7$$

This mechanism does not agree with the empirical rate law, and may contribute only at high temperatures.

12. The decomposition of HI is given by the reaction 2 HI → H_2+ I_2. One proposed mechanism is:

$$HI \xrightarrow{k_1} H + I$$

$$H + HI \xrightarrow{k_2} H_2 + I$$

$$2\ I + M \xrightarrow{k_3} I_2 + M$$

Use the steady-state approximation to find the rate law for this mechanism. Show that this mechanism does not agree with the experimentally determined rate law:

$$\frac{d[H_2]}{dt} = k\ [HI]^2$$

Answer: The rate law for the production of H_2 from the second elementary step is:

$$\frac{d[H_2]}{dt} = k_2\ [H][HI]$$

This rate law is dependent on a reactive intermediate, so it is not in a form that would be typically found from an experimental study. We need to use the steady-state approximation to find the concentration of the reactive intermediate. To do this we need to assume that $k_1 << k_2$. Step 1 in the general scheme for the steady-state approximation is to write the rate law for the formation of products, which we have already done, above. Step 2 is to write the rate laws for the formation of any reactive intermediates. For the H atom:

$$\frac{d[H]}{dt} = k_1[HI] - k_2\ [H][HI] = 0$$

This rate law will allow us to solve for the H atom concentration in terms of the reactant, so we don't need to consider the formation of the other reactive intermediate, which is the I atom. Step 3 is to apply the steady-state approximation to the last equation by setting the rate of formation of H atoms equal to zero. Then solving for [H] gives:

$$[\mathrm{H}] = k_1/k_2$$

Step 5 is to substitute this value for the reactive intermediate back into the rate law for the formation of products:

$$\frac{d[\mathrm{H_2}]}{dt} = k_2\,[\mathrm{H}][\mathrm{HI}] = k_1\,[\mathrm{HI}]$$

Notice that to apply the steady-state approximation, we assumed that the first step was slower than the second step. In other words, the slow step is the first step, which is unimolecular in HI. This result does not agree with the experimentally determined rate law.

13. (a) Determine the integrated rate law for the Michaelis-Menten mechanism. Note that during the portion of the reaction where the steady-state approximation applies, $-\,d[\mathrm{S}]/dt = d[\mathrm{P}]/dt$ so that Eq. 4.2.31 becomes:

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_1\,[\mathrm{E}]_o[\mathrm{S}]}{(k_M + [\mathrm{S}])}$$

(b) Show that for short times, [S] is a linear function of time: $[\mathrm{S}] - [\mathrm{S}]_o = -\frac{[\mathrm{E}]_o([\mathrm{S}]_o + 1)\,k_1}{k_M}\,t$

[Hint: you can approximate $\ln(x) \approx x - 1$, when x is close to 1.]

Answer: (a). Separating variables by cross multiplying:

$$\frac{k_M + [\mathrm{S}]}{[\mathrm{S}]}\,d[\mathrm{S}] = -\,[\mathrm{E}]_o\,k_1\,dt$$

which simplifies to:

$$\left(\frac{k_M}{[\mathrm{S}]} + 1\right) d[\mathrm{S}] = -\,[\mathrm{E}]_o\,k_1\,dt$$

The integration limits start at t= 0, $[\mathrm{S}] = [\mathrm{S}]_o$:

$$\int_{[\mathrm{S}]_o}^{[\mathrm{S}]} \left(\frac{k_M}{[\mathrm{S}]} + 1\right) d[\mathrm{S}] = -\int_0^t [\mathrm{E}]_o\,k_1\,dt$$

The sum in the first integral can be split into two terms:

$$k_M\ \ln([\mathrm{S}]\Big|_{[\mathrm{S}]_o}^{[\mathrm{S}]} + [\mathrm{S}]\Big|_{[\mathrm{S}]_o}^{[\mathrm{S}]} = -\,[\mathrm{E}]_o\,k_1\,t$$

$$k_M \ln\frac{[\mathrm{S}]}{[\mathrm{S}]_o} + ([\mathrm{S}] - [\mathrm{S}]_o) = -\,[\mathrm{E}]_o\,k_1\,t$$

(b). At the beginning of the reaction $[S] \approx [S]_o$ and $[S]/[S]_o \approx 1$ in the logarithmic term. Remembering that the Taylor series for $\ln x \approx x - 1$, expanded about $x = 1$, then:

$$k_M \left(\frac{[S]}{[S]_o} - 1 \right) + ([S] - [S]_o) = -[E]_o k_1 t$$

Factoring $1/[S]_o$ out of the first term in parentheses gives:

$$\frac{k_M}{[S]_o}([S] - [S]_o) + ([S] - [S]_o) = \left(\frac{k_M}{[S]_o} + 1 \right)([S] - [S]_o) = \ -[E]_o k_1 t$$

Solving for the concentration difference gives: $\quad [S] - [S]_o = -\dfrac{[E]_o[S]_o k_1}{k_M + [S]_o} t$

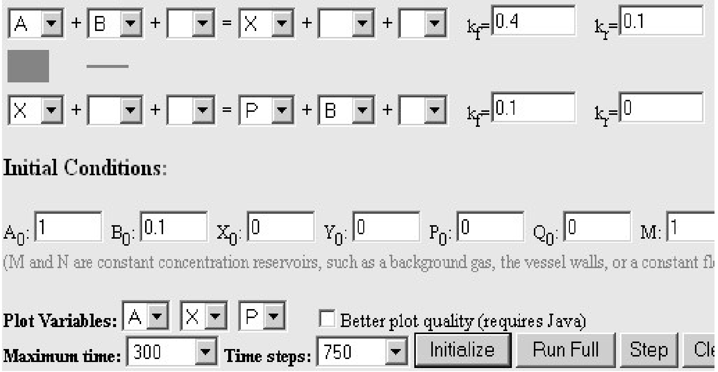
which is a linear function of time.

14. Use the "*Kinetic Mechanism Simulation*" applet to numerically integrate the rate laws for the Michaelis-Menten enzyme mechanism, Eq. 4.2.22. Set $k_2 = 0.40\ M^{-1}s^{-1}$, $k_{-1} = 0.1\ s^{-1}$, and $k_1 = 0.10\ s^{-1}$. Use the initial conditions $[S]_o = 1.0$ M and $[E]_o = 0.1$ M. Such a large enzyme concentration will make the plot scaling more convenient. (a). Plot [S], [ES], and [P] for a maximum of 300 s to verify the linear time course for short times. (b). To observe the pre-induction lag, using the same conditions, plot [ES] and [P] for a maximum time of 15 s.

Answer: In our Michaelis-Menten simulation, we will use the symbols:

$$A + B = X$$
$$X = P + B$$

where B is the enzyme, A is the substrate, X is the enzyme substrate complex, and P is the product. The set-up for the "*Kinetic Mechanism Simulation*" applet is:



A + B = X k_f= 0.4 k_r= 0.1

X = P + B k_f= 0.1 k_r= 0

Initial Conditions:

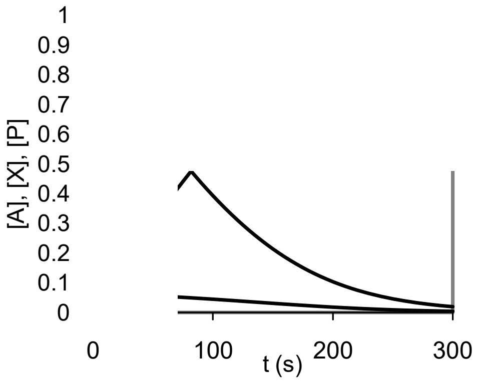
A_0: 1 B_0: 0.1 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1

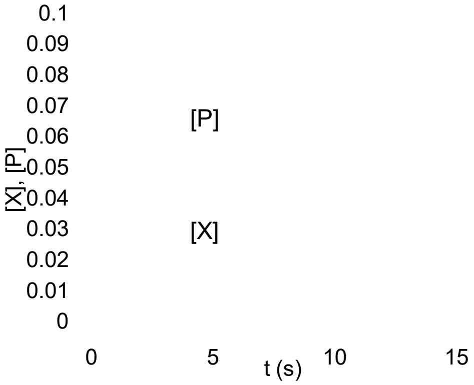
(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant fl

Plot Variables: A X P ☐ Better plot quality (requires Java)

Maximum time: 300 **Time steps:** 750

The requested plots are:





A straight line is included for the shorter time scale plot to show the pre-induction lag. The linear portion of the time course is offset from the origin.

15. Consider the Lindemann-Henshelwood Mechanism for first-order reactions. Compare the net rate of the pre-equilibrium step to the rate of the unimolecular step during the majority of the time course of the reaction. Look at the rate dependence after any induction period.

Answer: This portion of the time course is adequately approximated using the steady-state approximation. The rate law for the formation of the activated molecule is:

$$\frac{d[A^*]}{dt} = k_2[A]^2 - k_{-2}[A^*][A] - k_1[A^*] = 0$$

Applying the steady-state approximation corresponds to setting this rate equal to zero. We can rearrange this equation to place the rate terms for the appearance and disappearance of reactant on the left and the rate terms for the appearance of product from the activated molecule on the right:

$$\begin{array}{ccccc} k_2[A]^2 & - & k_{-2}[A^*][A] & = & k_1[A^*] \\ \upsilon_+ & - & \upsilon_- & = & \upsilon_2 \\ \textit{forward rate} & & \textit{reverse rate} & & \\ & \textit{first step} & & & \textit{second step} \end{array}$$

In accordance with the results from Eq. 4.2.19, the terms on the left give the net rate of the reversible first step and the term on the right gives the rate of the second step. As expected, these rates are equal during the majority of the time course for the reaction.

16. The following mechanism has been proposed for an enzyme reaction with two substrates, A and B:

$$E + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EA$$

$$EA + B \xrightarrow{k_2} EAB + Y$$

$$EAB \xrightarrow{k_3} E + P$$

where EA and EAB are enzyme substrate complexes. Assuming that k_2 and k_3 are large compared to k_1, show that the mechanism gives the rate law:

$$\frac{d[P]}{dt} = \frac{k_1\, k_2\, [E][A][B]}{k_{-1} + k_2\, [B]}$$

Answer: The plan is to use the steady state approximation for both reactive intermediates EA and EAB. Since the overall rate law is written in terms of the formation of product, we start with the rate law for the formation of products.

The rate law for the formation of products is a function of the reactive intermediate EAB:

$$\frac{dP}{dt} = k_3\, [EAB] \qquad 1$$

The rate laws for the formation of EA and EAB are equal to zero by the steady state approximation:

$$\frac{d[EA]}{dt} = k_1[E][A] - k_{-1}\, [EA] - k_2[EA][B] = 0 \qquad 2$$

$$\frac{d[EAB]}{dt} = k_2[EA][B] - k_3[EAB] = 0 \qquad 3$$

Solving Eq. 2 for [EA] gives: $[EA] = \dfrac{k_1[E][A]}{k_{-1} + k_2[B]}$ 4

Solving Eq. 3. for [EAB] gives: $[EAB] = \dfrac{k_2}{k_3}\, [EA][B]$ 5

Substituting Eq. 4 into EQ. 5 gives: $[EAB] = \dfrac{k_1 k_2}{k_3}\, \dfrac{[E][A][B]}{(k_{-1} + k_2[B])}$ 6

Substituting the concentration of the reactive intermediate from Eq. 6 into the rate law for the formation of product, Eq. 1, gives the final rate law:

$$\frac{dP}{dt} = \frac{k_1 k_2 [E][A][B]}{(k_{-1} + k_2[B])}$$

17. Consider the following proposed mechanism for the decomposition of ozone. M is an unreactive gas molecule that collides with the ozone to break the ozone apart:

$$O_3 + M \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} O_2 + O + M \qquad\qquad O + O_3 \xrightarrow{k'_2} 2\, O_2$$

Assume $k'_2 \gg k_2$. Show that the rate law that corresponds to this mechanism is:

$$\frac{d[O_2]}{dt} = \frac{3\,k'_2\,k_2\,[O_3]^2[M]}{k_{-2}[O_2][M] + k'_2[O_3]}$$

Answer: The plan is to use the steady state approximation for the reactive intermediate O atoms. Since the rate law is written in terms of the formation of the product O_2, we start with the rate law for the formation of O_2.

For the formation of product:

$$\frac{d[O_2]}{dt} = k_2\,[O_3][M] - k_{-2}\,[O_2][O][M] + 2\,k'_2\,[O][O_3] \qquad 1$$

Use the steady-state approximation for the reactive intermediate, [O]:

$$\frac{d[O]}{dt} = k_2\,[O_3][M] - k_{-2}\,[O_2][O][M] - k'_2\,[O][O_3] = 0 \qquad 2$$

Subtracting Eq. 2 from Eq. 1 cancels terms, eliminating the explicit dependence on [M]:

$$\frac{d[O_2]}{dt} = 3\,k'_2\,[O][O_3] \qquad 3$$

Solving Eq. 2 for the concentration of the reactive intermediate gives:

$$[O] = \frac{k_2\,[O_3][M]}{k_{-2}\,[O_2]\,[M] + k'_2\,[O_3]} \qquad 4$$

Substitute this result for [O] into Eq. 3: $$\frac{d[O_2]}{dt} = \frac{3\,k'_2\,k_2\,[O_3]^2[M]}{k_{-2}\,[O_2]\,[M] + k'_2\,[O_3]}$$

18. Report all six of the rate constants for the kinetics of proton exchange in aqueous solution of acetic acid, Figure 4.5.1. The reaction was studied at pH = 4.74 with the acetic acid and acetate concentrations both 0.100 M. The rate constants determined from temperature jump kinetics studies are $k_{31} = 4.5\text{x}10^{10}\ M^{-1}\ s^{-1}$ and $k_{23} = 1.8\text{x}10^{10}\ M^{-1}\ s^{-1}$.[1] Use the data from Example 3.6.1 for the auto-protolysis constants for water. The K_a for acetic acid is:

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]} = 1.75\text{x}10^{-5}\ M$$

Answer: Because of the cyclic mechanism, the number of independent rate constants is five. The specification of the acid dissociation constant, $K_a = k_{13}/k_{31}$, relates k_{13} and k_{31}. The auto-protolysis equilibrium constant for water is $K_c = k_{21}/k_{12}$, with water explicitly in the equilibrium expression, Example 3.6.1. The auto-protolysis equilibrium constant for water relates k_{12} and k_{21} giving three independent rate constants left to be to determined (Example 4.5.1). With the given rate constant for the recombination of the proton and the conjugate base of the weak acid, $k_{31} = 4.5\text{x}10^{10}\ M^{-1}\ s^{-1}$, and the K_a we can find the weak acid dissociation rate constant:

$$k_{13} = K_a\,k_{31} = 1.75\text{x}10^{-5}\ M\,(4.5\text{x}10^{10}\ M^{-1}\ s^{-1}) = 7.9\text{x}10^{5}\ s^{-1} \qquad 1$$

At equilibrium, the forward and reverse rates for the hydrolysis of acetate, (2)⇄(3), are equal and given by:

$$k_{32}\,[OAc^-][H_2O] = k_{23}\,[OH^-][HOAc] \qquad 2$$

with the concentration of water explicitly given in the rate law. Since pH = 4.74, $[H^+] = 10^{-4.74}$, giving $[OH^-] = 10^{-9.26} = 5.50\text{x}10^{-10}$ M. With the given rate constant for proton transfer from the weak acid to hydroxide, k_{23}:

$$k_{32}\,(0.100\text{ M})(55.33\text{ M}) = 1.8\text{x}10^{10}\text{ M}^{-1}\text{ s}^{-1}(5.50\text{x}10^{-10}\text{ M})(0.100\text{ M})$$
$$k_{32} = 0.181\text{ M}^{-1}\text{ s}^{-1} \qquad 3$$

with water explicitly in the rate expression. Alternatively, if the concentration of water is combined with the k_{32} rate constant then Eq. 2 is written:

$$k_{32}\,[OAc^-] = k_{23}\,[OH^-][HOAc]$$
$$k_{32}\,(0.100\text{ M}) = 1.8\text{x}10^{10}\text{ M}^{-1}\text{ s}^{-1}\,(5.50\text{x}10^{-10}\text{ M})(0.100\text{ M})$$
$$k_{32} = 9.9\text{ s}^{-1} \qquad 4$$

Instead of working with the rate laws directly, Eq. 2 and 4, we could have done this problem equivalently using the equilibrium constant for the hydrolysis. Remembering from General Chemistry that:

$$K_b = \frac{K_w}{K_a} = \frac{[OH^-][HOAc]}{[OAc^-]} = 5.76\text{x}10^{-10}\text{ M} \qquad 5$$

Then $K_b = k_{32}/k_{23}$ and from the given k_{23}:

$$k_{32} = 5.76\text{x}10^{-10}\text{ M}\,(1.8\text{x}10^{10}\text{ M}^{-1}\text{ s}^{-1}) = 10.\underline{4}\text{ s}^{-1} \qquad 6$$

where Eq. 4 and 6 differ because of round-off error.

Just a note on uncertainty; the relaxation times and rate constants are uncertain to about 30%, so the number of significant figures is really only 1 for each result. The rate constants for the auto-protolysis of water are given in Example 3.6.1:

$$k_{21} = 1.35\text{x}10^{11}\text{ M}^{-1}\text{s}^{-1}$$
$$k_{12} = k_{21}/K_c = 2.45\text{x}10^{-5}\text{ s}^{-1}$$

<u>19</u>. The following mechanism has been proposed for the oxidation of HBr to Br_2:

$$HBr + O_2 \xrightarrow{k_1} HOOBr$$

$$HOOBr + HBr \xrightarrow{k_2} 2\,HOBr$$

$$HOBr + HBr \xrightarrow{k_3} H_2O + Br_2$$

To give the proper overall stoichiometry, this last step must be doubled. All the steps are unidirectional. Show that the corresponding rate law can be expressed as:

$$\frac{d[Br_2]}{dt} = k_1\,[HBr][O_2]$$

Answer: There are two reactive intermediates in this mechanism, HOOBr and HOBr. The way to determine that these are reactive intermediates is to note that neither HOOBr nor HOBr are reactants or products. We will need to apply the steady-state approximation to both. Step 1: The rate law for the production of product is:

$$\frac{d[Br_2]}{dt} = k_3\,[HOBr][HBr] \qquad 1$$

Step 2: The rate laws for the formation of the reactive intermediates are equal to zero by the steady-state approximation:

$$\frac{d[HOOBr]}{dt} = k_1\,[HBr][O_2] - k_2\,[HOOBr][HBr] \approx 0 \qquad 2$$

$$\frac{d[HOBr]}{dt} = 2\,k_2\,[HOOBr][HBr] - 2\,k_3\,[HOBr][HBr] \approx 0 \qquad 3$$

The 2 k_3 is required to give the proper overall stoichiometry. Step 3: Multiplying Eq. 2 by two and adding to Eq. 3 gives:

$$2\,k_1\,[HBr][O_2] - 2\,k_3\,[HOBr][HBr] = 0 \qquad 4$$

and solving for [HOBr]:

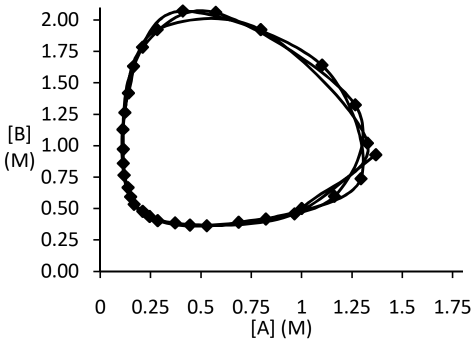
$$[HOBr] = \frac{k_1\,[HBr][O_2]}{k_3\,[HBr]} \qquad 5$$

Step 5: Substitution of this last equation into the rate law for the production of products, Eq. 1, gives:

$$\frac{d[Br_2]}{dt} = k_3\,\frac{k_1\,[HBr][O_2]}{k_3\,[HBr]}\,[HBr] = k_1\,[HBr][O_2] \qquad 6$$

20. For some oscillating mechanisms the same cycle results, after a short initial period, no matter the starting conditions. For such cases the plot of the oscillating concentrations is called a **limit cycle**. Does the Lotka-Volterra mechanism give a limit cycle? [Hint: repeat Example 4.4.1 but with initial conditions $[A]_o = 1$ M and $[B]_o = 0.5$ M. Does the same cycle result as in Figure 4.4.2b?]

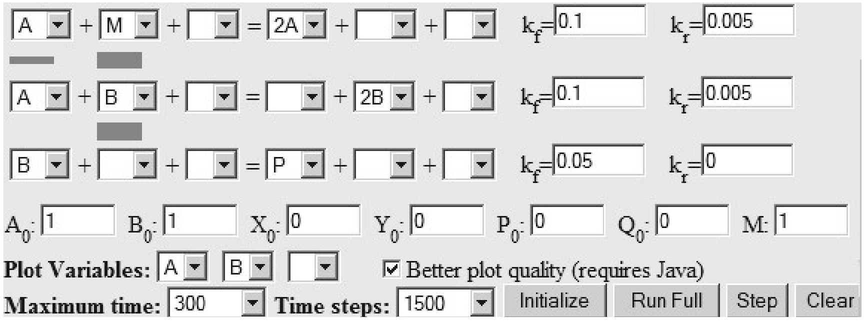
Answer: The settings specified in Example 4.4.1 were used for the "Kinetics Mechanism Simulation," except with the new starting conditions. The new starting conditions give the cycle shown below:



The cycle concentration ranges are larger than Example 4.4.2b. The Lotka-Volterra mechanism does not give a limit cycle. Similarly, Example 4.4.1 showed that no time dependence resulted when the steady state concentrations were used as the initial conditions.

21. The Lotka-Volterra mechanism with all irreversible steps, Eqs. 4.4.6, are unrealistic in several ways. One result is that oscillations occur for too wide a range of rate constants and starting conditions. In addition, the system does not evolve towards a steady state. Modify the mechanism to include reversible reactions for the formation of A and B (steps 1 and 2), but leave the formation of products as irreversible. Run a simulation with the same conditions as in Example 4.4.1, except set the equilibrium constants for the formation of A and of B at 20. Comment on the results.

Answer: The "Kinetic Mechanism Simulation" applet was set up as in Example 4.4.1, but with the reverse rate constants for steps 1 and 2 set to 0.005, since $K_{eq} = k_f/k_r = 0.1/0.005 = 20$.



A + M = 2A k_f=0.1 k_r=0.005

A + B = 2B k_f=0.1 k_r=0.005

B = P k_f=0.05 k_r=0

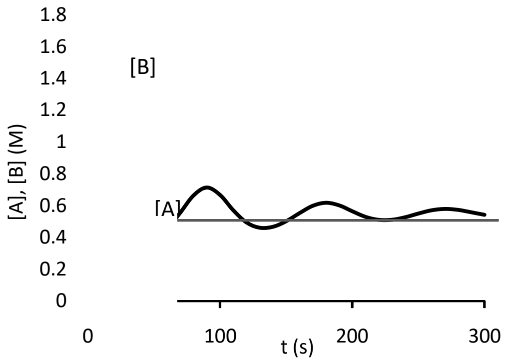
A_0: 1 B_0: 1 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1

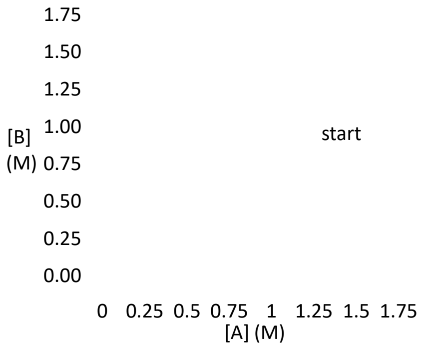
Plot Variables: A B

☑ Better plot quality (requires Java)

Maximum time: 300 **Time steps:** 1500

The resulting simulation is shown below.





The oscillations now last for a limited time and the system approaches the steady state. Choosing an even smaller equilibrium constant for the first two steps damps out the oscillations. One of the reasons that the reversible processes inhibit oscillations is that the initial conditions are not as far from equilibrium. Notice also that the steady-state shifts slightly for the case with irreversible reactions.

<u>22</u>. The "Brusselator" or "trimolecular" mechanism is a more realistic model for oscillating systems than the Lotka-Volterra mechanism. The Brusselator displays most of the complex phenomena associated with reactions far from equilibrium and is centrally important in the development of non-equilibrium thermodynamics. The mechanism is:[2]

$$\mathrm{M} \xrightarrow{k_1} \mathrm{A}$$

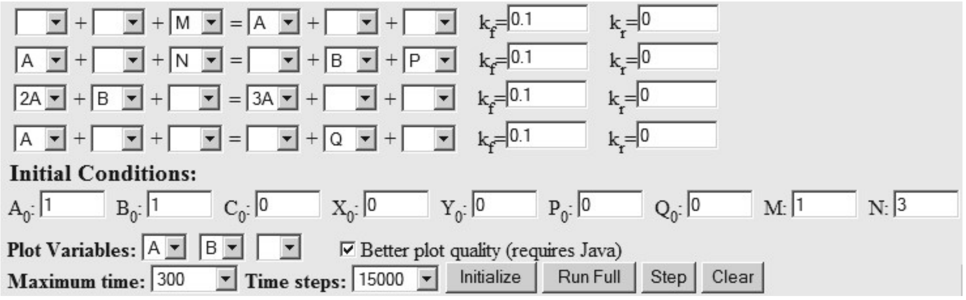
$$\mathrm{N} + \mathrm{A} \xrightarrow{k_2} \mathrm{B} + \mathrm{P}$$

$$2\,\mathrm{A} + \mathrm{B} \xrightarrow{k_3} 3\,\mathrm{A}$$

$$\mathrm{A} \xrightarrow{k_4} \mathrm{Q}$$

where M and N are held constant by running the reaction in a flowing system. A convenient set of conditions for simulation is to set all the rate constants to 0.10, $[\mathrm{M}]_o = 1.00$ M and $[\mathrm{N}]_o = 3.00$ M. Run kinetics simulations using *MatLab*, *Mathematica*, or the "*Kinetic Mechanism Simulation*" applet for three sets of initial conditions: (a) $[\mathrm{A}]_o = [\mathrm{B}]_o = 1.00$ M; (b) $[\mathrm{A}]_o = 1.00$ M, $[\mathrm{B}]_o = 2.00$ M; and (c) $[\mathrm{A}]_o = 1.00$ M, $[\mathrm{B}]_o = 3.00$ M, which are the steady state concentrations. Run the simulation for 300 s. Because the concentrations change rapidly over the time interval, you will need to choose a large number of time steps to ensure numerical accuracy, choose 15000 time steps. Plot the concentrations of A and B.

Answer: The set-up for the "Kinetics Mechanism Simulation" applet is shown below. Notice the large number of time steps to insure better accuracy for the numerical integration.



+ + M = A + + k_f=0.1 k_r=0
A + + N = + B + P k_f=0.1 k_r=0
2A + B + = 3A + + k_f=0.1 k_r=0
A + + = + Q + k_f=0.1 k_r=0

Initial Conditions:

A_0: 1 B_0: 1 C_0: 0 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1 N: 3

Plot Variables: A B ☑ Better plot quality (requires Java)

Maximum time: 300 **Time steps:** 15000

The output for the three runs is shown below:

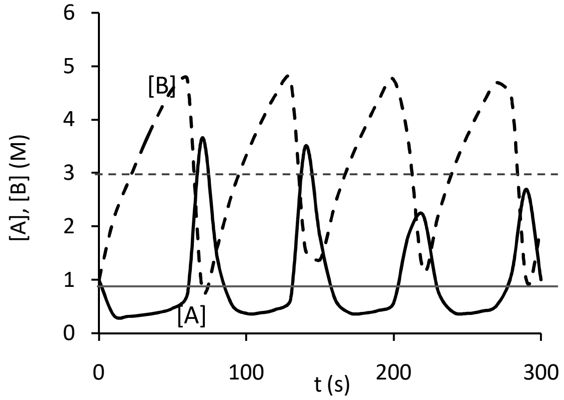


Figure P22.1: $[A]_o = [B]_o = 1.00$ M

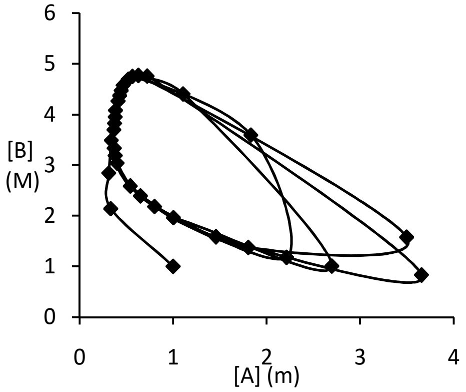


Figure P22.2: $[A]_o = [B]_o = 1.00$ M

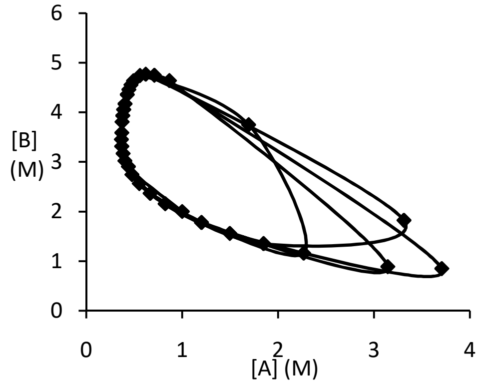


Figure P22.3: $[A]_o = 1.00$, $[B]_o = 2.00$ M

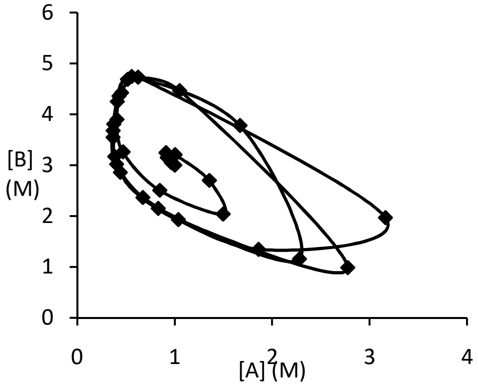


Figure P22.4: $[A]_o = 1.00$, $[B]_o = 3.00$ M

In Figure P22.1, the concentration maximum at 220 s should be comparable to the previous maxima; the appearance of the time course is distorted by the large time interval used for plotting. Notice the similarity between Figures P22.2 and P22.3 at long times. Notice also that when the reaction is started with the steady state conditions, $[A]_o = 1.00$ M, $[B]_o = 3.00$ M, the reactions also oscillate, Figure P22.4. When run for longer time intervals, all initial conditions result in the same cycle; the Brusselator gives a **limit cycle** (see Problem 20). See the next problem for the derivation of the steady-state conditions.

23. The Brusselator mechanism is given in the previous problem. (a). Find relationships for the steady state concentrations of A and B in terms of the rate constants. (b). Find the steady state concentrations for the conditions given in the previous problem: that is, all the rate constants equal to 0.10, $[M]_o = 1.00$ M, and $[N]_o = 3.00$ M.

Answer: The plan is to use the steady-state approximation for the intermediates A and B.
The rate laws for the appearance of A and B are set to zero, according to the steady-state approximation. For intermediate B:

$$\frac{d[B]}{dt} = k_2[N][A] - k_3[A]^2[B] = 0 \qquad 1$$

Solving for $[B]_{ss}$ gives: $[B]_{ss} = \dfrac{k_2[N][A]_{ss}}{k_3[A]_{ss}^2}$ 2

The rate law for the appearance of [A] is:

$$\frac{d[A]}{dt} = k_1[M] - k_2[N][A] - 2k_3[A]^2[B] + 3k_3[A]^2[B] - k_4[A] = 0 \qquad 3$$

$$= k_1[M] - k_2[N][A] + k_3[A]^2[B] - k_4[A] = 0 \qquad 4$$

Substituting the equation for $[B]_{ss}$ into this last equation gives:

$$k_1[M] - k_2[N][A] + k_2[N][A] - k_4[A] = k_1[M] - k_4[A] = 0 \qquad 5$$

Solving for $[A]_{ss}$ gives: $[A]_{ss} = \dfrac{k_1}{k_4}[M]$ 6

Substitution of Eq. 6 into Eq. 2 gives: $[B]_{ss} = \dfrac{k_2 k_4[N]}{k_1 k_3[M]}$ 7

(b). Eqs. 6 and 7 give the steady-state conditions as:

$$[A]_{ss} = \frac{0.1}{0.1}[1.00\text{ M}] = 1.00\text{ M} \qquad \text{and } [B]_{ss} = \frac{(0.1)(0.1)[3.00\text{ M}]}{(0.1)(0.1)[1.00\text{ M}]} = 3.00\text{ M}$$

as given in the previous problem.

24. The Belousov-Zhabotinsky reaction is an oscillating reaction based on the oxidation of malonic acid with $KBrO_3$, which is catalyzed by Ce(IV):

$$3\,CH_2(CO_2H)_2 + 4\,BrO_3^- \rightarrow 4\,Br^- + 9\,CO_2 + 6\,H_2O$$

The BZ reaction played a central role in the development of techniques to study oscillating reactions and in the theory of non-equilibrium thermodynamics.[2,3] The initiation step is the generation of $HBrO_2$, the key reactive intermediate, from BrO_3^-:

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \qquad 1$$

The bulk of the $HBrO_2$ is produced auto-catalytically:

$BrO_3^- + HBrO_2 + 2\,Ce^{3+} + 3\,H^+ \rightarrow 2\,HBrO_2 + 2\,Ce^{4+} + H_2O$ 2

The intermediate $HBrO_2$ is consumed in the reactions:

$HBrO_2 + Br^- + H^+ \rightarrow 2\,HOBr$ 3

$2\,HBrO_2 \rightarrow BrO_3^- + HBrO + H^+$ 4

The oxidation of malonic acid is complex, but a simplified version includes first the bromination of malonic acid:

$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$ 5
$Br_2 + CH_2(CO_2H)_2 \rightarrow BrCH(CO_2H)_2 + H^+ + Br^-$ 6

and the oxidation of malonic acid and bromomalonic acid by Ce^{4+}:

$Ce^{4+} + \tfrac{1}{2}\,[CH_2(CO_2H)_2 + BrCH(CO_2H)_2] \rightarrow \tfrac{1}{2}\,Br^- + Ce^{3+} + \text{products}$ 7

The products include CO_2, H_2O, and a mixture of organic acids. For modeling purposes, the oxidation of the malonic acid by Ce(IV) is represented by the net Ce(IV) to Br^- stoichiometry using:

$CH_2(CO_2H)_2 + Ce^{4+} + HOBr \rightarrow Ce^{3+} + Br^- + H^+ + \text{products}$ net 5-7

Field, Körös, and Noyes have developed a mechanism for the reaction that displays oscillations. With steps numbered according to the mechanistic steps listed above, the FKN mechanism is:[2,3]

$B + M \xrightarrow{k_1} A + P$ $k_1 = 1.28\ \text{mol L s}^{-1}$ 1

$A + M \xrightarrow{k_2} 2\,A + 2\,C$ $k_2 = 8.0\ \text{mol}^{-1}\ \text{L s}^{-1}$ 2

$A + B \xrightarrow{k_3} 2\,Q$ $k_3 = 8.0\text{x}10^5\ \text{mol}^{-1}\ \text{L s}^{-1}$ 3

$2\,A \xrightarrow{k_4} Q + M$ $k_4 = 2.0\text{x}10^3\ \text{mol}^{-1}\text{L s}^{-1}$ 4

$C + N \xrightarrow{k_5} B$ $k_5 = 1.0\ \text{mol}^{-1}\ \text{L s}^{-1}$ net 5-7

with A = $HBrO_2$, B = Br^-, C = Ce^{4+}, M = BrO_3^-, N = malonic acid, Q = HOBr

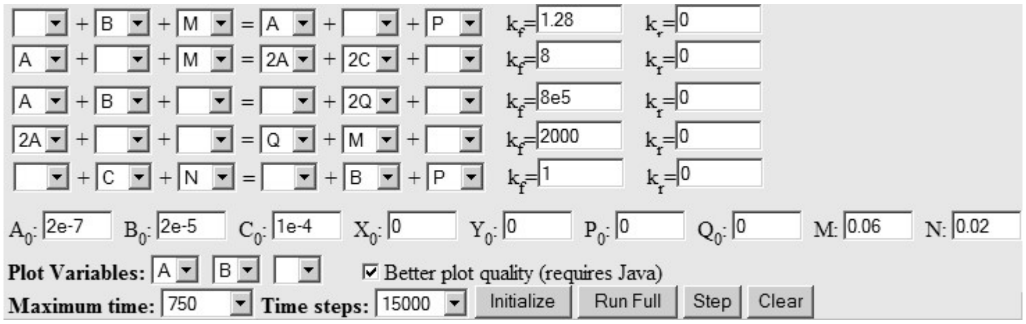
The H^+ and Ce^{3+} concentrations are roughly constant and are included through pseudo-rate constants. M and N are held constant by a flowing reactor. This mechanism is also called the "Oregonator."

Do a numerical simulation of the FKN mechanism using *MatLab*, *Mathematica*, or the "*Kinetics Mechanism Simulation*" applet on the companion CD or the textbook Web site with the following conditions:

$[M] = [BrO_3^-] = 0.06$ M, $[N] = [\text{malonic acid}] = 0.02$ M
$[A]_o = [HBrO_2] = 2.0\text{x}10^{-7}$M, $[B]_o = [Br^-] = 2.0\text{x}10^{-5}$ M, $[C]_o = [Ce^{4+}] = 1.0\text{x}10^{-4}$ M.

Run the simulation for 750 s. Because the rate constants span almost six orders of magnitude, you will need to choose a large number of time steps to ensure numerical accuracy, choose 7500 or more total time steps. Plot the concentrations of A and B.

Answer: The set-up for the "*Kinetics Mechanism Simulation*" applet is shown below. Notice the large number of time steps which insure better accuracy for the numerical integration.



+ B + M = A + + P k_f=1.28 k_r=0

A + + M = 2A + 2C + k_f=8 k_r=0

A + B + = + 2Q + k_f=8e5 k_r=0

2A + + = Q + M + k_f=2000 k_r=0

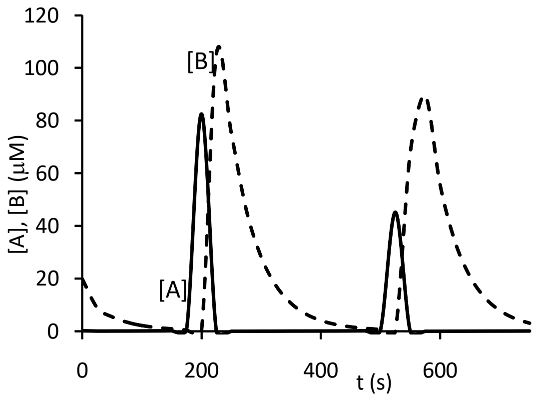
+ C + N = + B + P k_f=1 k_r=0

A_0: 2e-7 B_0: 2e-5 C_0: 1e-4 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 0.06 N: 0.02

Plot Variables: A B

☑ Better plot quality (requires Java)

Maximum time: 750 Time steps: 15000



25. Consider a reaction A ⇄ B at equilibrium that can occur via a catalyzed path and an uncatalyzed path, with C the catalyst:

$$A + C \underset{k_{BC}}{\overset{k_{AC}}{\rightleftarrows}} B + C \qquad \text{and} \qquad A \underset{k_B}{\overset{k_A}{\rightleftarrows}} B$$

Show that if 10% of the forward process at equilibrium occurs by the uncatalyzed path that 10% of the reverse process will also occur by the uncatalyzed path.

Answer: The overall rate law is given by:

$$\upsilon = \frac{d[A]}{dt} = -k_{AC}[A][C] - k_A[A] + k_{BC}[B][C] + k_B[B] \qquad 1$$

At equilibrium the rate with respect to A is zero and then the overall forward rate is equal to the overall reverse rate, $\upsilon_+ = \upsilon_-$:

$$k_{AC}\,[A][C] + k_A[A] = k_{BC}[B][C] + k_B[B] \qquad 2$$

By detailed balance, the forward rate must be equal to the reverse rate for each elementary step and then for the uncatalyzed path:

$$k_A\,[A] = k_B\,[B] \qquad 3$$

Dividing Eq. 3 by Eq. 2 gives the ratio of the uncatalyzed to the overall rate:

$$\frac{k_A\,[A]}{k_{AC}\,[A][C] + k_A[A]} = \frac{k_B\,[B]}{k_{BC}[B][C] + k_B[B]} \qquad 4$$

The term on the left of the equality is the fraction of the forward reaction that proceeds by the uncatalyzed path. The term on the right is the fraction of the reverse reaction that proceeds by the uncatalyzed path. The fractions are then shown to be equal.

<u>26</u>. A random bi-substrate enzyme mechanism requires two substrates, but the substrates can bind to the enzyme in either order. One example is an enzyme that phosphorylates a protein using ATP as the phosphate source; ATP and the protein target are the two substrates. The mechanistic steps are:

$$E + A \rightleftarrows [EA]$$

$$E + B \rightleftarrows [EB]$$

$$[EA] + B \rightleftarrows [EAB]$$

$$[EB] + A \rightleftarrows [EAB]$$

all of which are assumed to be in quasi-equilibrium (in the same sense as the pre-equilibrium mechanism). The production of product is assumed to be essentially irreversible:

$$[EAB] \rightarrow E + \text{products}$$

Draw the quasi-equilibrium mechanistic steps as a four-state cyclic process, and give the relationship among the corresponding rate constants.

Answer: The four states for the cycle are (1) E, (2) [EA], (3) [EAB], and (4) [EB]:

$$\begin{tikzcd}
\overset{(1)}{\boxed{E + A + B}} \arrow[r, shift left, "k_{12}"] \arrow[d, shift right, "k_{14}"'] & \overset{(2)}{\boxed{[EA] + B}} \arrow[l, shift left, "k_{21}"] \arrow[d, shift left, "k_{23}"] & \\
\underset{(4)}{\boxed{[EB] + A}} \arrow[u, shift right, "k_{41}"'] \arrow[r, shift left, "k_{43}"] & \underset{(3)}{\boxed{[EAB]}} \arrow[l, shift left, "k_{34}"] \arrow[u, shift left, "k_{32}"] \arrow[r, "k_p"] & \boxed{E + \text{products}}
\end{tikzcd}$$

$$\begin{tikzcd}
\begin{array}{c} E + A \\ +B \end{array} \arrow[r, shift left, "k_{12}"] \arrow[d, shift right, "k_{14}"'] & \begin{array}{c} [EA] \\ +B \end{array} \arrow[l, shift left, "k_{21}"] \arrow[d, shift left, "k_{23}"] & \\
{[EB] + A} \arrow[u, shift right, "k_{41}"'] \arrow[r, shift left, "k_{43}"] & {[EAB]} \arrow[l, shift left, "k_{34}"] \arrow[u, shift left, "k_{32}"] \arrow[r, "k_p"] & E + P
\end{tikzcd}$$

(a) Box model style (b) Conventional depiction

The relationship of the rate constants around the cycle is the product of all the forward rate constants divided by the product of all the reverse rate constants:

$$\frac{k_{12}\ k_{23}\ k_{34}\ k_{41}}{k_{21}\ k_{32}\ k_{43}\ k_{14}} = 1$$

<u>27</u>. Consider the bidirectional reaction:

$$A \rightleftarrows B \rightleftarrows C$$

The initial rate law for the reaction, starting with A only, is experimentally determined to be:

$$\frac{d[A]}{dt} = -\ k_{obs,f}\ [A]_o$$

If the reverse reaction is run starting with C only, the initial rate law is determined to be:

$$\frac{d[C]}{dt} = -\ k_{obs,r}\ [C]_o$$

Why <u>isn't</u> the equilibrium constant for the overall reaction given by the ratio of the initial forward to the initial reverse rate constants, $k_{obs,f}/k_{obs,r}$?

Answer: The given experimentally determined rate laws are for the system away from equilibrium. Detailed balance only applies to reactions at equilibrium. For the reaction at equilibrium, applying detailed balance:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C$$

Comparing to the given experimental initial rate laws we find that $k_{obs,f} = k_1$ and $k_{obs,r} = k_{-2}$. Rather, at equilibrium detailed balance gives:

$$K_c = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

See the next problem for a detailed analysis of the rate laws for the complete mechanism.

<u>28</u>. This problem is an example of finding the relationship among the rate constants in a mechanism and the overall equilibrium constant, based on detailed balance. For the mechanism:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C$$

determine the rate law for the overall forward process, υ_+, and the rate law for the overall reverse process, υ_-, at equilibrium. Show that the ratio of the resulting rate constants gives the overall equilibrium constant.

Answer: The plan is to note that this problem is essentially like a steady-state approximation derivation, but the steady state approximation is exact at equilibrium. The flow of the problem is to formulate the overall rate law for A and then determine the portion that applies for the forward reaction and the portion that applies for the reverse reaction.

The rate laws with respect to A, B, and C are:

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] \qquad 1$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_2[B] + k_{-2}[C] \qquad 2$$

$$\frac{d[C]}{dt} = k_2[B] - k_{-2}[C] \qquad 3$$

At equilibrium, the change of the concentration of B with time is zero and the second rate law equals zero:

$$k_1[A] - k_{-1}[B] - k_2[B] + k_{-2}[C] = 0 \qquad 4$$

Solving for [B] gives:

$$[B] = \frac{k_1[A] + k_{-2}[C]}{k_{-1} + k_2} \qquad 5$$

Substitution into the rate law for A and taking a common denominator gives:

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}\left(\frac{k_1[A] + k_{-2}[C]}{k_{-1} + k_2}\right) = -\left(\frac{k_1k_{-1} + k_1k_2}{k_{-1} + k_2}\right)[A] + \left(\frac{k_1k_{-1}[A] + k_{-1}k_{-2}[C]}{k_{-1} + k_2}\right) \qquad 6$$

Cancelling terms gives:

$$\frac{d[A]}{dt} = -\frac{k_1k_2}{k_{-1} + k_2}[A] + \frac{k_{-1}k_{-2}}{k_{-1} + k_2}[C] \qquad 7$$

The overall rate is given by:

$$\upsilon = \frac{1}{V}\frac{d\xi}{dt} = -\frac{d[A]}{dt} \qquad 8$$

In terms of the <u>overall</u> process A → C, near equilibrium we would write the <u>overall</u> rate law in terms of the initial reactant and the final product:

$$\upsilon = -\frac{d[A]}{dt} = k_f[A] - k_r[C] \qquad \text{with } K_{eq} = k_f/k_r \qquad \text{(overall)} \qquad 9$$

Comparing Eqs. 7 and 9, the first term in Eq. 7 is the rate law for the overall forward process and the second term is the rate law for the overall reverse process at equilibrium:

$$\upsilon_+ = \frac{k_1 k_2}{k_{-1} + k_2}[A] \qquad \upsilon_- = \frac{k_{-1} k_{-2}}{k_{-1} + k_2}[C] \qquad 10$$

The effective rate constants for the forward and reverse processes are:

$$k_f = \frac{k_1 k_2}{k_{-1} + k_2} \quad \text{and} \quad k_r = \frac{k_{-1} k_{-2}}{k_{-1} + k_2} \qquad 11$$

and the ratio should give the overall equilibrium constant:

$$K_c = \frac{k_f}{k_r} = \frac{k_1 k_2}{k_{-1} k_{-2}} \qquad 12$$

This result agrees with Eq. 4.5.12, which is required by detailed balance.

29. Using the Principle of Detailed Balance, show that the following mechanism generates the expected overall equilibrium ratio when the reaction is at equilibrium:

$$HI \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H + I$$

$$H + HI \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} H_2 + I$$

$$2\,I + M \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} I_2 + M$$

overall:

$$K_{eq} = \left(\frac{[H_2][I_2]}{[HI]^2}\right)_{eq}$$

Derive the relationship between the rate constants and the overall equilibrium constant, starting from the rate laws for each mechanistic step.

Answer: Detailed balance requires that each mechanistic step and its exact reverse must be at equilibrium:

$$HI \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H + I$$

$$\upsilon_1 = k_1\,[HI] - k_{-1}\,[H][I] = 0$$

$$K_{eq,1} = \frac{k_1}{k_{-1}} = \left(\frac{[H][I]}{[HI]}\right)_{eq}$$

$$H + HI \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} H_2 + I$$

$$\upsilon_2 = k_2\,[H][HI] - k_{-2}\,[H_2][I] = 0$$

$$K_{eq,2} = \frac{k_2}{k_{-2}} = \left(\frac{[H_2][I]}{[H][HI]}\right)_{eq}$$

$$2\,I + M \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} I_2 + M$$

$$\upsilon_3 = k_3\,[I]^2[M] - k_{-3}\,[I_2][M] = 0$$

$$K_{eq,3} = \frac{k_3}{k_{-3}} = \left(\frac{[I_2][M]}{[I]^2[M]}\right)_{eq}$$

The overall equilibrium constant is then

$$K_{eq} = K_{eq,1}\, K_{eq,2}\, K_{eq,3} = \left(\frac{[H][I]}{[HI]}\right)_{eq}\left(\frac{[H_2][I]}{[H][HI]}\right)_{eq}\left(\frac{[I_2][M]}{[I]^2[M]}\right)_{eq} = \left(\frac{[H_2][I_2]}{[HI]^2}\right)_{eq}$$

and the relationship to the rate constants give the ratio of the forward rate constants to the reverse rate constants:

$$K_{eq} = K_{eq,1}\, K_{eq,2}\, K_{eq,3} = \frac{k_1\, k_2\, k_3}{k_{-1} k_{-2} k_{-3}}$$

<u>30</u>. The reaction A + B ⇄ D is proposed to have the following mechanism:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C$$

$$C + M \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} D + M$$

where C is a reactive intermediate and M is an inert gas in large concentration. (a). Show that with appropriate approximations that the rate law is:

$$\frac{d[D]}{dt} = \left(\frac{k_1 k_2 [A][B][M] - k_{-1} k_{-2}\, [D][M]}{k_{-1} + k_2[M]}\right)$$

(b). In terms of the <u>overall</u> process, A + B → D, near equilibrium, the <u>overall</u> rate law in terms of the initial reactant and the final product is:

$$\upsilon = \frac{d[D]}{dt} = k_f\, [A][B] - k_r\, [D]$$

Show that the equation in part (a) reduces to this last overall equation and find the relationship between the overall equilibrium constant and the four rate constants for the mechanistic steps from <u>this</u> equation. Discuss any approximations that you make for parts (a) and (b).

Answer: (a). The rate law for the formation of D is given as:

$$\frac{d[D]}{dt} = k_2\, [C][M] - k_{-2}\, [D][M] \tag{1}$$

The rate law for the intermediate is:

$$\frac{d[C]}{dt} = k_1\, [A][B] - k_{-1}\, [C] - k_2\, [C][M] + k_{-2}\, [D][M] = 0 \tag{2}$$

We apply the steady-state approximation to find the steady-state concentration of C. Note that this approximation holds before the system reaches equilibrium, if C is a reactive intermediate:

$$[C] = \frac{k_1\, [A][B] + k_{-2}\, [D][M]}{k_{-1} + k_2\, [M]} \tag{3}$$

Substitution into Eq. 1 to gives:

$$\frac{d[D]}{dt} = \frac{k_1\, k_2\, [A][B][M] + k_2\, k_{-2}\, [D][M]^2}{k_{-1} + k_2[M]} - k_{-2}\, [D][M] \tag{4}$$

Taking a common denominator:

$$\frac{d[D]}{dt} = \frac{k_1\, k_2\, [A][B][M] + k_2\, k_{-2}\, [D][M]^2 - k_{-1}\, k_{-2}\, [D][M] - k_2\, k_{-2}\, [D][M]^2}{k_{-1} + k_2[M]} \tag{5}$$

Canceling common terms:

$$\frac{d[D]}{dt} = \frac{k_1\, k_2\, [A][B][M] - k_{-1}\, k_{-2}\, [D][M]}{k_{-1} + k_2[M]} \tag{6}$$

(b). If M is a buffer gas in large concentration, then $k_2[M] >> k_{-1}$ is reasonable in the denominator, which gives:

$$\frac{d[D]}{dt} = \frac{k_1\, k_2}{k_2}\, [A][B] - \frac{k_{-1}\, k_{-2}}{k_2}\, [D] \tag{7}$$

which is in the form:

$$\upsilon = \frac{d[D]}{dt} = \underbrace{k_f\, [A][B]}_{\textit{forward rate}} - \underbrace{k_r\, [D]}_{\textit{reverse rate}} \tag{8}$$

At equilibrium, Eq. 7 is equal to zero giving:

$$\frac{k_1\, k_2}{k_2}\, [A][B] - \frac{k_{-1}\, k_{-2}}{k_2}\, [D] = 0 \qquad \text{(equilibrium)} \tag{9}$$

and solving for the equilibrium concentration ratio gives:

$$K_{eq} = \left(\frac{[D]}{[A][B]}\right)_{eq} = \frac{k_1\, k_2}{k_{-1}\, k_{-2}} \tag{10}$$

as expected from detailed balance.

<u>31</u>. The reaction $2\,A \rightleftarrows C$ is proposed to have the following mechanism:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C$$

(a). Show that near equilibrium:

$$-\frac{1}{2}\,\frac{d[A]}{dt} = \frac{d[C]}{dt} = k_1[A] - \left(\frac{k_1 k_{-1}[A] + k_{-1} k_{-2}\, [C]}{k_{-1} + k_2[A]}\right)$$

(b). In terms of the <u>overall</u> process, $2A \rightarrow C$, <u>at equilibrium</u> we would write the <u>overall</u> rate law in terms of the initial reactant and the final product:

$$\upsilon = -\frac{1}{2}\frac{d[A]}{dt} = k_f\,[A]^2 - k_r\,[C]$$

Show that the equation in part (a) reduces to this last overall equation and find the relationship between the overall equilibrium constant and the four rate constants for the mechanistic steps.

Answer: This problem can be done in several ways. For this answer, we will make the least restrictive assumptions at each step to give the most general interpretation of the final result and to give intermediate results that are as broadly applicable as possible.
(a). The rate law for the formation of A is given as:

$$\frac{d[A]}{dt} = -\,k_1\,[A] + k_{-1}\,[B] - k_2\,[A][B] + k_{-2}\,[C] \qquad 1$$

The rate law for the intermediate is:

$$\frac{d[B]}{dt} = k_1\,[A] - k_{-1}\,[B] - k_2\,[A][B] + k_{-2}\,[C] = 0 \qquad 2$$

We will apply the steady-state approximation to find the steady-state concentration of B. Note that this approximation holds before the system reaches equilibrium. The steady-state approximation becomes exact when the system reaches equilibrium. Applying the steady-state approximation gives for [B]:

$$[B] = \frac{k_1\,[A] + k_{-2}\,[C]}{k_{-1} + k_2\,[A]} \qquad 3$$

At steady state we can simplify Eq. 1 by subtracting Eq. 2 from Eq. 1 to give:

$$\frac{d[A]}{dt} = -\,2\,k_1\,[A] + 2\,k_{-1}\,[B] \qquad 4$$

which holds away from equilibrium, as long as the steady-state approximation is valid. Substituting in the concentration of the reactive intermediate then gives:

$$\frac{d[A]}{dt} = -\,2\,k_1\,[A] + 2\,k_{-1}\frac{k_1\,[A] + k_{-2}\,[C]}{k_{-1} + k_2\,[A]} \qquad 5$$

rearrangement gives:

$$-\frac{1}{2}\frac{d[A]}{dt} = k_1[A] - \left(\frac{k_1k_{-1}[A] + k_{-1}k_{-2}\,[C]}{k_{-1} + k_2[A]}\right) \qquad 6$$

(b). Taking a common denominator gives:

$$-\frac{1}{2}\frac{d[A]}{dt} = \left(\frac{k_1k_{-1}[A] + k_1k_2[A]^2 - k_1k_{-1}[A] - k_{-1}k_{-2}\,[C]}{k_{-1} + k_2[A]}\right) \qquad 7$$

or cancelling terms:

$$-\frac{1}{2}\frac{d[A]}{dt} = \left(\frac{k_1k_2}{k_{-1} + k_2[A]}\right)[A]^2 - \left(\frac{k_{-1}k_{-2}}{k_{-1} + k_2[A]}\right)[C] \qquad 8$$

If B is a reactive intermediate, the equilibrium between A and B must favor A, such that $k_1 << k_{-1}$. In other words, the reverse reaction for step one is rapid, with k_{-1} a large number compared to k_1. As the reaction proceeds, the concentration of A drops. When $k_{-1} >> k_2[A]$ this last equation reduces to:

$$-\frac{1}{2}\frac{d[A]}{dt} = \left(\frac{k_1k_2}{k_{-1}}\right)[A]^2 - \left(\frac{k_{-1}k_{-2}}{k_{-1}}\right)[C] \qquad 9$$

which is in the form:

$$\upsilon = -\frac{1}{2}\frac{d[A]}{dt} = \underset{\textit{forward rate}}{k_f\,[A]^2} - \underset{\textit{reverse rate}}{k_r\,[C]} \qquad 10$$

At equilibrium, Eq. 9 is equal to zero giving:

$$\left(\frac{k_1k_2[A]^2}{k_{-1}}\right)[A]^2 - \left(\frac{k_{-1}k_{-2}}{k_{-1}}\right)[C] = 0 \qquad \text{(equilibrium)} \quad 11$$

and solving for the equilibrium concentration ratio gives:

$$K_{eq} = \left(\frac{[C]}{[A]^2}\right)_{eq} = \frac{k_1\,k_2}{k_{-1}\,k_{-2}} \qquad 12$$

as expected from detailed balance.

Notice also, that at equilibrium Eq. 8 would also be equal to zero giving the same equilibrium constant. In other words, the assumption that $k_{-1} >> k_2[A]$ is not necessary to find the thermodynamic equilibrium constant.

32. For the reaction:

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,I \qquad\qquad H_2 + 2\,I \xrightarrow{k_3} 2\,HI$$

find the relationship of the experimentally determined, overall activation energy to the activation energies for the individual mechanistic steps. Assume the rate law is:

$$\frac{d[HI]}{dt} = \frac{k_1\,k_3}{k_{-1}}[H_2][I_2]$$

Answer: The plan is to follow Example 4.4.2. However, we can also consider another method based directly on the Arrhenius Law in the form $k = A\,e^{-Ea/RT}$.

Method 1 (based on Eq. 4.5.25): Taking the logarithm of the effective rate constant $k = k_1k_3/k_{-1}$ gives:

$$\ln k = \ln k_1 + \ln k_3 - \ln k_{-1}$$

The terms in the derivatives, at constant volume, are given by the corresponding activation energies for each mechanistic step:

$$\frac{d\ln k}{dT} = \frac{d\ln k_1}{dT} + \frac{d\ln k_3}{dT} - \frac{d\ln k_{-1}}{dT} = \frac{E_{a1}}{RT} + \frac{E_{a3}}{RT} - \frac{E_{a-1}}{RT} = \frac{E_a}{RT}$$

Comparison with the overall activation energy gives: $E_a = E_{a1} + E_{a3} - E_{a-1}$

Method 2 (based on $k = A\ e^{-Ea/RT}$): The overall reaction rate constant with activation energy E_a is $k = A\ e^{-E_a/RT}$. This form of the Arrhenius equation can also be applied to each individual elementary step. For the individual elementary steps, for step 1: $k_1 = A_1\ e^{-E_{a1}/RT}$, for the reverse of step 1: $k_{-1} = A_{-1}\ e^{-E_{a-1}/RT}$, and for the formation of product: $k_3 = A_3\ e^{-E_{a3}/RT}$. Finding the ratio of the individual rate constants in Arrhenius form gives:

$$k = \frac{k_1\ k_3}{k_{-1}} = \frac{A_1\ e^{-E_{a1}/RT}\ A_3\ e^{-E_{a3}/RT}}{A_{-1}\ e^{-E_{a-1}/RT}} = \frac{A_1\ A_3}{A_{-1}}\ e^{-(E_{a1} + E_{a3} - E_{a-1})/RT}$$

The overall activation energy is again $E_a = E_{a1} + E_{a3} - E_{a-1}$. The method based on Eq. 4.5.25 is less susceptible to errors for complex rate laws if there are non-integer rate exponents.

33. Consider the S_N1 mechanism as a typical multi-step mechanism. For the case given in Eq. 4.2.17, the rate law has the form:

$$\frac{d[P]}{dt} = k\,\frac{[RX]\,[Nuc:^-]}{[X^-]} \qquad (k_{-1}\,[X^-] >> k_2[Nuc:^-])$$

with the effective rate constant, $k = k_2\ k_1/k_{-1}$. From Eq. 3.5.1, for the overall reaction with activation energy E_a: $k = A\ e^{-E_a/RT}$. This form of the Arrhenius equation can also be applied to each individual elementary step. For the individual elementary steps, for step 1: $k_1 = A_1\ e^{-E_{a1}/RT}$, for the reverse of step 1: $k_{-1} = A_{-1}\ e^{-E_{a-1}/RT}$, and for the formation of product: $k_2 = A_2\ e^{-E_{a2}/RT}$. Using these Arrhenius expressions, find the relationship between the overall pre-exponential factor and activation energy and the pre-exponential factors and activation energies for the individual elementary steps.

Answer: Finding the ratio of the individual rate constants in Arrhenius form gives:

$$k = \frac{k_2\ k_1}{k_{-1}} = \frac{A_2\ e^{-E_{a2}/RT}\ A_1\ e^{-E_{a1}/RT}}{A_{-1}\ e^{-E_{a-1}/RT}} = \frac{A_2\ A_1}{A_{-1}}\ e^{-(E_{a2} + E_{a1} - E_{a-1})/RT}$$

We could also use the method in Example 4.5.2, based on Eq. 4.5.25, but we wouldn't have gotten the expression for the overall pre-exponential factor. The method based on Eq. 4.5.25 is easier for complex rate laws.

34. The connection between detailed balance and forward and reverse reaction rates for a multi-step mechanism is illustrated in Eqs. 4.5.3-4.5.10. The rate laws are written for each individual step in the mechanism, rather than the rate of appearance or disappearance of a particular species. Symbolize the net rates of the individual mechanistic steps as υ_1, υ_2, and υ_3:

$$\upsilon_1 = \frac{1}{V}\frac{d\xi_1}{dt} \qquad \upsilon_2 = \frac{1}{V}\frac{d\xi_2}{dt} \qquad \text{and} \qquad \upsilon_3 = \frac{1}{V}\frac{d\xi_3}{dt}$$

(a). Write the rate law for the appearance of intermediate A_2, the rate law for the appearance of intermediate X, and the rate law for the appearance of product D in terms of υ_1, υ_2, and υ_3. The purpose is to show the relationship between the species specific and step specific methods of writing rate laws.
(b). For a multi-step mechanism at steady state, the rates of the individual steps are equal, Sec. 4.2. Use the results of part (a) for intermediates A_2 and X to prove this statement for this example mechanism. [Hint: apply the steady-state approximation].

Answer: (a). The rates of appearance for A_2, X, and D written in the conventional manner is:

$$\frac{d[A_2]}{dt} = k_{AM}[A]^2[M] - k_{MA}[A_2][M] - k_{AB}[A_2][B] + k_{XA}[A][X]$$

$$\frac{d[X]}{dt} = k_{AB}[A_2][B] - k_{XA}[A][X] - k_X[X] + k_{DC}[C][D]$$

$$\frac{d[D]}{dt} = k_X[X] - k_{DC}[C][D]$$

Comparing these conventional rate laws to Eqs. 4.5.7-4.5.9 gives:

$$\frac{d[A_2]}{dt} = \upsilon_1 - \upsilon_2 \qquad \frac{d[X]}{dt} = \upsilon_2 - \upsilon_3 \qquad \text{and} \qquad \frac{d[D]}{dt} = \upsilon_3$$

(b). At steady-state, the rate of formation of the reactive intermediates is zero:

$$\frac{d[A_2]}{dt} = \upsilon_1 - \upsilon_2 = 0 \qquad \frac{d[X]}{dt} = \upsilon_2 - \upsilon_3 = 0$$

Solving for the rates of the individual steps gives $\upsilon_1 = \upsilon_2 = \upsilon_3$. At steady-state the net rate of each mechanistic step is identical. There is no “slow” or “fast” step.

35. Consider the S_N1 mechanism, Eqs. 4.2.6-4.2.7. The first mechanistic step is reversible and the second is uni-directional. Symbolize the net rates of the two mechanistic steps as υ_1 and υ_2:

$$\upsilon_1 = \frac{1}{V}\frac{d\xi_1}{dt} \qquad \text{and} \qquad \upsilon_2 = \frac{1}{V}\frac{d\xi_2}{dt}$$

(a). Write the rate law for the appearance of intermediate R^+ and the rate law for the appearance of product R-Nuc in terms of υ_1 and υ_2. The purpose is to show the relationship between the species specific and step specific methods of writing rate laws.
(b). For a multi-step mechanism at steady state, the rates of the individual steps are equal. Use the result of part (a) for intermediate R^+ to prove this statement for this example mechanism. [Hint: apply the steady-state approximation].

Answer: The plan is to use Eqs. 4.5.3-4.5.9 as a template for writing the step-specific rate laws.
(a). The rates of appearance for R^+ and product R-Nuc written in the conventional manner is:

$$\frac{d[R^+]}{dt} = k_1[RX] - k_{-1}[R^+][X^-] - k_2[R^+][Nuc:^-] \qquad 1$$

$$\frac{d[P]}{dt} = k_2[R^+][Nuc:^-] \qquad 2$$

The step-specific rate laws are:

$$\upsilon_1 = \frac{1}{V}\frac{d\xi_1}{dt} = k_1[RX] - k_{-1}[R^+][X^-] \qquad 3$$

$$\upsilon_2 = \frac{1}{V}\frac{d\xi_2}{dt} = k_2[R^+][Nuc:^-] \qquad 4$$

Comparing the conventional rate laws, Eqs. 1-2, to the step specific rate laws, Eqs. 3-4, gives:

$$\frac{d[R^+]}{dt} = \upsilon_1 - \upsilon_2 \qquad \text{and} \qquad \frac{d[P]}{dt} = \upsilon_2$$

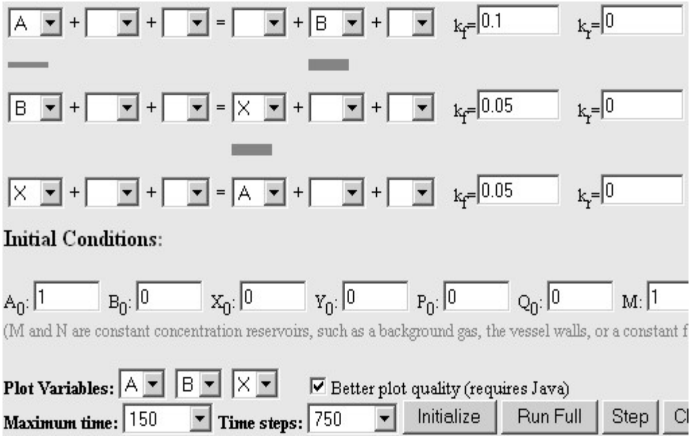
(b). At steady-state, the rate of formation of the reactive intermediate is zero:

$$\frac{d[R^+]}{dt} = \upsilon_1 - \upsilon_2 = 0 \qquad \text{or} \quad \upsilon_1 = \upsilon_2$$

At steady-state the net rate of each mechanistic step is equal. There is no "slow" or "fast" step. See also Eq. 4.2.19 for an alternate proof.

36. After a perturbation, the three unidirectional reactions in Eq. 4.5.1 approach a steady state very differently than a reversible process approaches equilibrium; the approach of the unidirectional steps to a steady state shows oscillatory behavior, but a reversible system approaches equilibrium in an exponential process.[4,5] (a) Use the Web based "*Kinetic Mechanism Simulation*" applet or *MatLab*, *Maple*, or *Mathematica* to numerically integrate the rate laws for the mechanism in Eq. 4.5.1. Set $k_{AB} = 0.1$, $k_{BC} = k_{CA} = 0.05$, and $[A]_o = 1$ while $[B]_o = [C]_o = 0$. Plot the approach to the steady state and verify the appearance of oscillations. (b) Change the rate law to match Eq. 4.5.2. Set the forward rate constants as in part (a) and the reverse rate constants to give the equilibrium constant for A $\rightleftarrows$ B as 2 and for B $\rightleftarrows$ C as 2. Compare the approach to equilibrium with part (a).

Answer: (a) Using the "*Kinetics Mechanism Simulation*," and [X] for [C], the model is set up as:



A + + = + B + k_f= 0.1 k_r= 0

B + + = X + + k_f= 0.05 k_r= 0

X + + = A + + k_f= 0.05 k_r= 0

Initial Conditions:

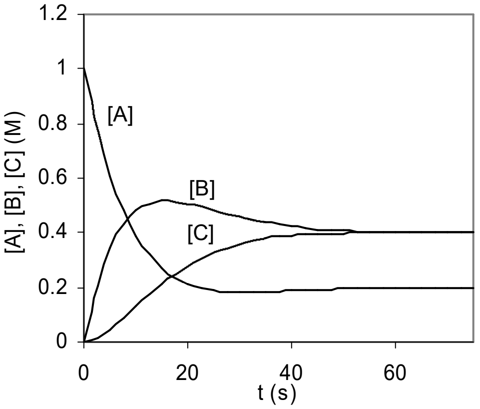
A_0: 1 B_0: 0 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1

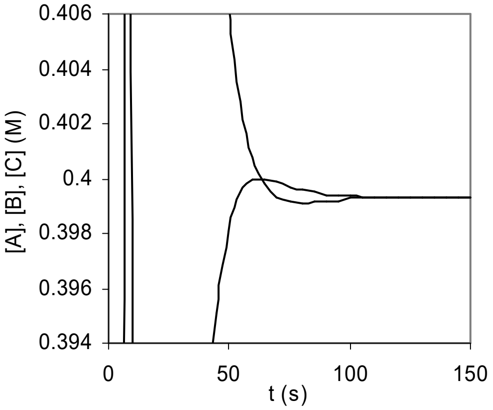
(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant f

Plot Variables: A B X ☑ Better plot quality (requires Java)

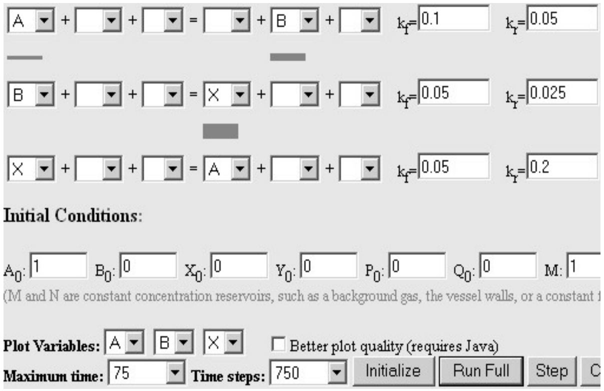
Maximum time: 150 **Time steps:** 750

The resulting plot and a plot with the scale expanded in the vertical direction to show the oscillations at longer times better are:





(b) For A $\rightleftarrows$ B, given $K_{AB} = k_f/k_r = 2$, then $k_r = 0.05$. For B $\rightleftarrows$ C, given $K_{BC} = k_f/k_r = 2$, then $k_r = 0.025$. Since this is a cyclic mechanism, from Eq. 4.5.16, with $k_{CA} = 0.05$, then $k_{AC} = 0.2$. The setup with reversible steps is:



A + + = + B + k_f= 0.1 k_r= 0.05

B + + = X + + k_f= 0.05 k_r= 0.025

X + + = A + + k_f= 0.05 k_r= 0.2

Initial Conditions:

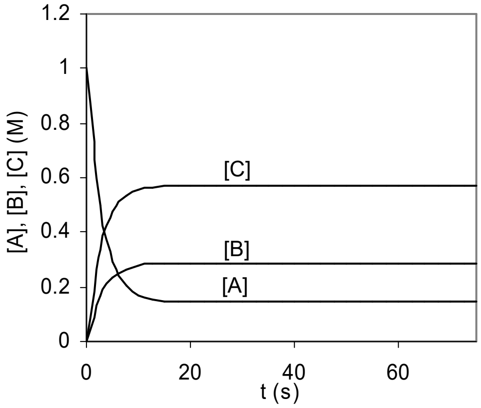
A_0: 1 B_0: 0 X_0: 0 Y_0: 0 P_0: 0 Q_0: 0 M: 1

(M and N are constant concentration reservoirs, such as a background gas, the vessel walls, or a constant f

Plot Variables: A B X ☐ Better plot quality (requires Java)

Maximum time: 75 **Time steps:** 750

The concentrations approach equilibrium smoothly, unlike the unphysical unidirectional case:



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Chapter 5 Problems: Photochemistry and Surface Chemistry

1. Show that the units are correct for Eq. 5.1.15 with ε in M^{-1} cm^{-1}, $\mathcal{A}$ in m^2, and V in liters in Eq. 5.1.6.

Answer: Substituting Eq. 5.1.6 into Eq. 5.1.15 gives:

$$\frac{d[B]}{dt} = 2.303\ J_o\Phi_B\ \varepsilon\ell\,[A] = \left(\frac{2.303\ J_o\ \varepsilon\ell\ \Phi_B}{N_A\ h\nu}\right)\left(\frac{\mathcal{A}}{V}\right)[A]$$

with J_o in J m^{-2} s^{-1}, ε in M^{-1} cm^{-1}, ℓ in cm, $\mathcal{A}$ in m^2, and V in L. The concentrations are in mol L^{-1}. Substituting in just the units:

$$\text{mol L}^{-1}\ \text{s}^{-1} = \left(\frac{\text{J m}^{-2}\ \text{s}^{-1}\ (\text{mol}^{-1}\ \text{L cm}^{-1})(\text{cm})}{\text{mol}^{-1}\ (\text{J s})(\text{s}^{-1})}\right)\left(\frac{\text{m}^2}{\text{L}}\right)[\text{mol L}^{-1}]$$

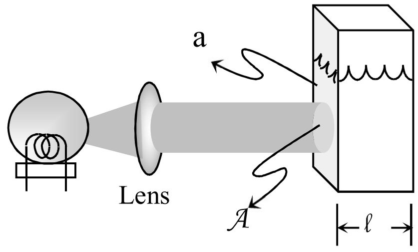
No other unit conversions are necessary.

2. Show that the photochemical rate constant for an optically thin solution is independent of path length for a cell with a uniform cross section. For example, a cell with uniform cross section includes cylindrical cells and rectangular cells where the volume is given by the area of the solution exposed on the face of the cell, a, multiplied by the path length, $V = a\ell$. Determine any unit conversion factors in the final result.

Answer: The photochemical rate constant for the formation of a secondary photoproduct from Eqs. 5.1.6 and 5.1.19 is:

$$j_B = \left(\frac{2.303\ J_o\ \varepsilon\ell\ \Phi_B}{N_A\ h\nu}\right)\left(\frac{\mathcal{A}}{V}\right) \qquad \text{with } \ell \text{ in cm, A in m}^2\text{, and V in L.}$$

The total volume of the solution is given by $V = a\ell$, where ℓ is the reaction cell path length.



Substituting $V = a\ell$ into Eqs. 5.1.6 and 5.1.19 gives:

$$j_B = \left(\frac{2.303\ J_o\ \varepsilon\ell\ \Phi_B}{N_A\ h\nu}\right)\left(\frac{\mathcal{A}}{a\ell}\right) = \left(\frac{2.303\ J_o\ \varepsilon\ \Phi_B}{N_A\ h\nu}\right)\left(\frac{\mathcal{A}}{a}\right)$$

which is independent of path length. In other words, as the path length increases, the volume of the solution also increases, keeping the increase in moles per unit volume per unit time constant.

However, now we need to be careful about units. With J_o in J m^{-2} s^{-1}, ε in M^{-1} cm^{-1}, and j_B in s^{-1} the conversions needed are:

$$j_B = \left(\frac{2.303\ J_o\ \varepsilon\ \Phi_B}{N_A\ h\nu}\right)(100\ \text{cm}/1\ \text{m})(1\ \text{m}^3/1000\ \text{L})$$

In other words, putting in just the units:

$$s^{-1} = \left(\frac{\text{J m}^{-2}\ \text{s}^{-1}\ (\text{mol}^{-1}\ \text{L cm}^{-1})}{\text{mol}^{-1}\ (\text{J s})(\text{s}^{-1})}\right)(100\ \text{cm}/1\ \text{m})(1\ \text{m}^3/1000\ \text{L})$$

3. A chemical actinometer is a solution with known quantum yield that can be used to find the incident intensity in photochemical experiments. The ferrioxalate actinometer uses the reaction:

$$2\ Fe^{3+} + (C_2O_4)^{2-} \overset{h\nu}{\rightarrow} 2\ Fe^{2+} + 2\ CO_2$$

A ferrioxalate concentration of 0.15 M is normally used for actinometry, which is optically thick. A common light source for photochemical reactions is the 366 nm emission line of a mercury lamp. The quantum yield for the ferrioxalate reaction at 366 nm is 1.18.[1] The progress of the reaction is monitored using the visible absorption of the *ortho*-phenanthroline complex of Fe^{2+} at 522 nm. The molar absorption coefficient of the Fe^{2+} complex at 522 nm is 8650. M^{-1} cm^{-1}. The *ortho*-phenanthroline complex for Fe^{3+} is very weak and transparent at 522 nm. The following experiment was used to determine the incident intensity for a photoreactor. A solution of 0.15 M ferrioxalate was irradiated for 10.0 min. A 1.00 mL aliquot was withdrawn and diluted with water to a total volume of 100.0 mL in a volumetric flask. The absorbance of this solution in a 1.00 cm pathlength cuvette at 522 nm was 0.410. Calculate the incident flux in mol L^{-1} s^{-1}.

Answer: The plan is to use the Beer-Lambert Law to calculate the concentration of Fe^{2+} in the aliquot. Then the dilution factor is used to calculate the Fe^{2+} concentration in the actinometer solution. Since the solution is optically thick, we assume a zeroth-order reaction and, using Eq. 5.1.14, we calculate the incident intensity.

Using the Beer-Lambert law: $A = \varepsilon \ell c$ the concentration of the aliquot is:

$$c = A/\varepsilon\ell = 0.410/(8650.\ M^{-1}\ cm^{-1}\ 1.00\ cm) = 4.74\text{x}10^{-5}M$$

The dilution factor for the absorbance sample is 1/100 giving the concentration of Fe^{2+} in the original actinometer as $[Fe^{2+}] = 4.74\text{x}10^{-3}$ M. Assuming zeroth-order kinetics, Eq. 5.1.14:

$$\frac{d[Fe^{2+}]}{dt} = \Phi_B\, J_a = \Phi_B\, J_o$$

which integrates to $[Fe^{2+}] = [Fe^{2+}]_o + \Phi_B\, J_o\, t$, where the initial concentration is zero, $[Fe^{2+}]_o = 0$. Using the known photochemical quantum yield, $\Phi_B = 1.18$, and the Fe^{2+} concentration at 10.0 min gives the incident intensity as:

$$[Fe^{2+}] = \Phi_B\, J_o\, t$$

or $J_o = [Fe^{2+}]/(\Phi_B\, t) = \dfrac{4.74\text{x}10^{-3}\ M}{1.18\ (10.0\ \text{min})(60\ \text{s}/1\ \text{min})} = 6.70\text{x}10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1}$

4. A high power mercury lamp produces 219.0 W m^{-2} at 366 nm at the surface of a photochemical reaction cell (see Problem 3). Assume the cross-section of the incident beam is 1.00 cm^2 and the solution volume is 10.0 mL. Calculate the incident flux in mol L^{-1} s^{-1}.

Answer: (a) The energy of 366 nm light in kJ mol^{-1} is:

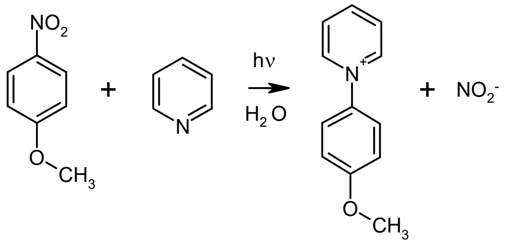
$$E = N_A h\nu = N_A hc/\lambda = 6.022\text{x}10^{23}\ \text{mol}^{-1}\ (6.626\text{x}10^{-34}\ \text{J s})(2.998\text{x}10^{8}\ \text{m s}^{-1})/366\text{x}10^{-9}\text{m} = = 3.268\ \text{x}10^{5}\ \text{J mol}^{-1} = 326.8\ \text{kJ mol}^{-1}$$

Using Eq. 5.1.6 gives the flux in mol L^{-1} s^{-1}:

$$J_o = \frac{J_o}{N_A h\nu}\left(\frac{\mathcal{A}}{V}\right) = \frac{219.0\ \text{J m}^{-2}\ \text{s}^{-1}}{3.268\ \text{x}10^{5}\ \text{J mol}^{-1}}\left(\frac{1\ \text{cm}^2\ (1\ \text{m}/100\ \text{cm})^2}{0.0100\ \text{L}}\right) = 6.70\text{x}10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

(which, by the way, corresponds to the answer from Problem 3).

5. When *p*-nitroanisole and pyridine are photolyzed in aqueous solution the reaction is:



The quantum yield for a solution containing 1.00x10^{-5}M *p*-nitroanisole and 0.0100 M pyridine in 1% acetonitrile is 4.65x10^{-3} at 366 nm.[2] The molar absorption coefficient at 366 nm of *p*-nitroanisole is 1990 M^{-1} cm^{-1}. Calculate the photochemical rate constant and write the rate law for an optically thin solution assuming the incident flux is 6.70x10^{-6} mol L^{-1} s^{-1} for a 10.00 cm path length reaction cell.

Answer: For an optically thin solution, using Eq. 5.1.19:

$$\begin{aligned} j_B &= 2.303\ J_o\Phi_B\ \varepsilon\ell \\ &= 2.303\ (6.70\text{x}10^{-6}\ \text{mol L}^{-1}\ \text{s}^{-1})(4.65\text{x}10^{-3})(1990\ \text{M}^{-1}\ \text{cm}^{-1})(10.0\ \text{cm}) \\ &= 1.43\text{x}10^{-3}\ \text{s}^{-1} \end{aligned}$$

The rate constants for environmental problems is often given in $days^{-1}$:

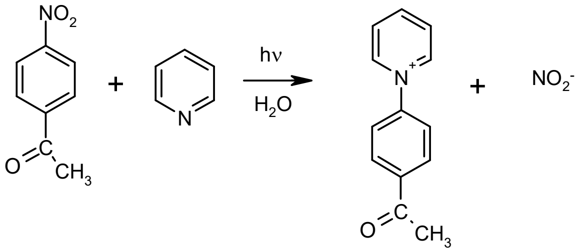
$$j_B = 1.43\text{x}10^{-3}\ \text{s}^{-1}\ (60\ \text{s}/1\ \text{min})(60\ \text{min}/1\ \text{hr})(24\ \text{hr}/1\ \text{day}) = 123\ \text{day}^{-1}$$

Using Eq. 5.1.17 gives the rate law:

$$\frac{d[B]}{dt} = j_B\,[A] = 1.43\text{x}10^{-3}\ \text{s}^{-1}\ [\text{PNA}]$$

where [PNA] is the concentration of *p*-nitroanisole. This reaction is commonly used as an actinometer for environmental studies.

6. A solution with a known photochemical quantum yield can be used to calculate the incident light flux during a photolytic reaction. Such solutions are called chemical actinometers (see Problems 3 and 5). Consider the reaction of *p*-nitroacetophenone and pyridine:



A chemical actinometer and a solution of *p*-nitroacetophenone and pyridine were simultaneously photolyzed at 366 nm in reaction cells with identical geometry. The path length of the reaction cell is 1.00 cm. The quantum yield for the actinometer is $4.65\text{x}10^{-3}$ with a molar absorption coefficient 1990 $\text{M}^{-1}\ \text{cm}^{-1}$. The photochemical rate constant for the actinometer is determined to be $1.43\text{x}10^{-3}\ \text{s}^{-1}$. The molar absorption coefficient of *p*-nitroacetophenone is 160. $\text{M}^{-1}\ \text{cm}^{-1}$.[2] The photochemical rate constant for $1.00\text{x}10^{-5}$ M *p*-nitroacetophenone and 0.100 M pyridine is $4.18\text{x}10^{-5}\ \text{s}^{-1}$. Calculate the quantum yield for the *p*-nitroacetophenone and pyridine reaction at 366 nm.

Answer: For an optically thin solution, using Eq. 5.1.19:

$$j_B = 2.303\ J_o \Phi_B\ \varepsilon\ell$$

The incident flux calculated from the actinometer is:

$$J_o = \frac{j_{act}}{2.303\ \Phi_{act}\ \varepsilon\ell} = \frac{1.43\text{x}10^{-3}\ \text{s}^{-1}}{2.303\ (4.65\text{x}10^{-3})(1990\ \text{M}^{-1}\ \text{cm}^{-1}\ 1\ \text{cm})}$$
$$= 6.71\text{x}10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Then applying Eq. 5.1.19 for the *p*-nitroacetophenone, PNAP, reaction gives:

$$\Phi_{PNAP} = \frac{j_{PNAP}}{2.303\ J_o\ \varepsilon\ell} = \frac{4.18\text{x}10^{-5}\ \text{s}^{-1}}{2.303\ (6.71\text{x}10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1})(160.\ \text{M}^{-1}\ \text{cm}^{-1}\ 1\ \text{cm})}$$
$$= 1.69\text{x}10^{-3}$$

This reaction is also commonly used as a chemical actinometer. This actinometer is appropriate with slower environmental reactions than are covered by the PNA actinometer in Problem 5.

7. Consider the following reversible first-step mechanism for a first-order photochemical reaction:

$$A + h\nu \underset{k_D}{\overset{j_{A^*}}{\rightleftarrows}} A^* \qquad\qquad A^* \xrightarrow{k_R} B$$

where k_D is the combined rate constant for all the non-photochemical deactivation processes, with $k_D = k_f + k_{ISC} + k_{nr}$. Derive Eq. 5.1.24 directly from this mechanism. [Hint: Express the rate law in the form of Eq. 5.1.17 and then use Eq. 5.1.19]

Answer: The plan is to use the steady-state approximation to find the overall rate law for the formation of products in the form of Eq. 5.1.17 and then find the photochemical quantum yield using Eq. 5.1.19. The reactive intermediate is the molecular excited state, A*. Step 1 is to write the rate law for the formation of product:

$$\frac{d[B]}{dt} = k_R\,[A^*]$$

Step 2 for the steady-state mechanistic scheme is to find the rate law for the formation of the reactive intermediate:

$$\frac{d[A^*]}{dt} = j_{A^*}\,[A] - k_D\,[A^*] - k_R\,[A^*] = 0$$

Step 3: Solving for the concentration of the reactive intermediate, A*:

$$[A^*] = \frac{j_{A^*}}{k_D + k_R}\,[A]$$

With only one unknown we can proceed to Step 5 and find the overall rate law by substituting the steady state A* concentration back into the rate law for the formation of product:

$$\frac{d[B]}{dt} = k_R\,\frac{j_{A^*}}{k_D + k_R}\,[A]$$

Comparing this last equation with Eq. 5.1.17 and 5.1.19, that is $j_B = \Phi_B\, j_{A^*}$, gives:

$$j_B = k_R\,\frac{j_{A^*}}{k_D + k_R} = \Phi_B\, j_{A^*}$$

which is an important equation in its own right. This equation shows the relationship between j_B, which is the rate constant for the overall production of the product while k_R is the rate constant for the formation of product from the molecular excited state. So solving for the photochemical quantum yield and using the definition of $k_D = k_f + k_{ISC} + k_{nr}$ gives:

$$\Phi_B = \frac{k_R}{k_f + k_{ISC} + k_{nr} + k_R}$$

8. Anthracene fluorescence is quenched by halogenated compounds like CCl_4. A Stern-Volmer quenching study was completed giving the fluorescence intensities, as a function of CCl_4

concentration, in the following table.[3] The intensities are in arbitrary units. The fluorescence lifetime in the absence of CCl_4 is 5.03 ns. Calculate the quenching rate constant.

$[CCl_4]$ (M)	0	0.02	0.04	0.08	0.12
Intensity	2437	1860	1490	1110	893

Answer: Using Eq. 5.1.31 in the absence of quencher, $k_R = k_q[Q] = 0$ gives:

$$k_f + k_{ISC} + k_{nr} = 1/\tau = 1/5.03\text{x}10^{-9}\text{ s} = 1.99\text{x}10^{8}\text{ s}^{-1}$$

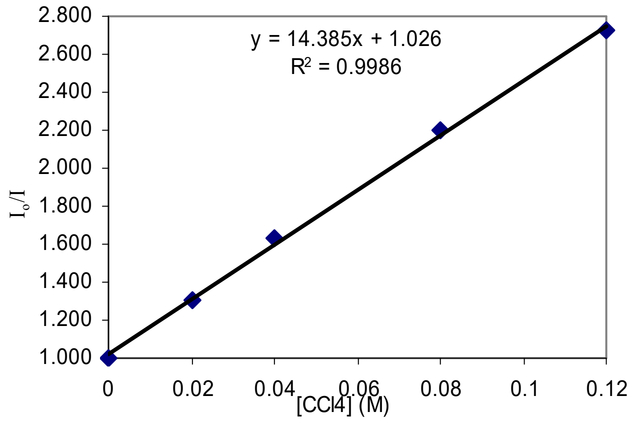
Using Eq. 5.1.28, in terms of the intensity ratio:

$$I_o/I = \Phi_o/\Phi_f = 1 + \frac{k_q[Q]}{k_f + k_{ISC} + k_{nr}}$$

a plot of I_o/I versus $[CCl_4]$ is constructed. The slope is determined by a least squares fit using the spreadsheet and linest():

[CCl]	Intensity	I_o/I
0	2437	1.000
0.02	1860	1.310
0.04	1490	1.636
0.08	1110	2.195
0.12	893	2.729

slope	14.3850	1.0260	intercept
±	0.3139	0.0212	±
r^2	0.9986	0.0302	s(y)
F	2099.9195	3.0000	df
$ss_{regression}$	1.9203	0.0027	$ss_{residual}$



From the slope the quenching rate constant is:

$$k_q = \text{slope } (k_f + k_{ISC} + k_{nr}) = 14.38\ (1.99\text{x}10^{8}\text{ s}^{-1}) = 2.86\text{x}10^{9} \pm 0.06\text{x}10^{9}\text{ s}^{-1}$$

9. Run a numerical simulation for the Chapman mechanism for the rate constants and concentrations appropriate at an altitude of 25 km. A table of appropriate constants is given below.[4,5S] Determine the steady-state concentration of ozone using Eq. 5.2.11 and by numerical simulation.

Altitude km	j_1 s^{-1}	k_2 cm^6 $molecule^{-2}s^{-1}$	j_3 s^{-1}	k_4 cm^3 $molecule^{-1}s^{-1}$	[M] molecule cm^{-3}	$[O_2]$ molecule cm^{-3}
25	$3.0\text{x}10^{-12}$	$1.2\text{x}10^{-33}$	$5.5\text{x}10^{-4}$	$6.9\text{x}10^{-16}$	$9\text{x}10^{17}$	$1.8\text{x}10^{17}$
40	$5.7\text{x}10^{-10}$	$9.1\text{x}10^{-34}$	$1.9\text{x}10^{-3}$	$2.2\text{x}10^{-15}$	$8.1\text{x}10^{16}$	$1.7\text{x}10^{16}$

Answer: We proceed by editing the *MatLab* files listed in Addendum 5.7. A longer maximum time is necessary to achieve a steady state. The changes necessary to the files listed in the Addendum define the rate constants:

```
% Constants for 25 km:
   j1=3.0e-12;
   k2=1.2e-33;
   j3=5.5e-4;
   k4=6.9e-16;
   M=9.0e17;
```

and the main file is changed to give:

```
% Set the initial values
    Xo = [0 1.8e17 0];
% Set the total integration time in seconds
    maxTime = 4.0e7;
```

The steady-state concentration of ozone that results is 1.645×10^{13} molecules cm^{-3}. A short Excel spread sheet was written to solve the quadratic equation for the steady-state ozone concentration from Eq. 5.2.11:

j1	3.00E-12	s^{-1}
k2	1.20E-33	cm^6 $molecule^{-2}$ s^{-1}
j3	5.50E-04	s^{-1}
k4	6.90E-16	cm^3 $molecue^{-1}$ s^{-1}
[M]	9.00E+17	molecule cm^{-3}
[O2]	1.80E+17	molecule cm^{-4}
a	7.59E-19	
b	7.45E-10	
c	-2.10E+08	
O3 (+root)	1.66E+13	molecule cm^{-6}
(-root)	-1.66E+13	molecule cm^{-7}

The listed a, b, and c cells are the normal coefficients for $ax^2 + bx + c = 0$. The analytical value, 1.66×10^{13} molecules cm^{-3}, is differs slightly from the limiting numerical value because of numerical error. Stiff methods are usually not as accurate as the much slower 4th order Runge-Kutta algorithm, ode45().

10. Nitrogen oxides catalyze the destruction of ozone and must be taken into account in accurate stratospheric models. The reactions and the rate constants appropriate for 25 km are:

$$NO + O_3 \xrightarrow{k_5} NO_2 + O_2 \qquad k_5 = 3.4 \times 10^{-15}\ cm^3\ molecules^{-1}\ s^{-1}$$

$$NO_2 + O \xrightarrow{k_6} NO + O_2 \qquad k_6 = 1.1 \times 10^{-11}\ cm^3\ molecules^{-1}\ s^{-1}$$

$$NO_2 + h\nu \xrightarrow{j_7} NO + O \qquad j_7 = 7 \times 10^{-3}\ s^{-1}$$

The values for the rate constants j_1-k_4 and [M] at 25 km are given in Problem 9. Guesses for the starting concentrations for NO and NO_2 that you can use are:

$$[NO]_o = 8.0\text{x}10^{8} \text{ molecules cm}^{3} \qquad \text{and} \quad [NO_2] = 1.0\text{x}10^{9} \text{ molecules cm}^{3}$$

Add these three reactions to the numerical simulation outlined in Addendum 5.7 to find the change of the ozone concentration with and without catalysis. You can use *MatLab* or *MathCad*, or any numerical routines that employ stiff methods.

Answer: The rate laws are:

$$\frac{d[O]}{dt} = 2\, j_1\, [O_2] - k_2\, [O][O_2][M] + j_3\, [O_3] - k_4\, [O][O_3] - k_6\, [NO_2][O] + j_7\, [NO_2] \tag{1}$$

$$\frac{d[O_2]}{dt} = -\, j_1\, [O_2] - k_2\, [O][O_2][M] + j_3\, [O_3] + 2\, k_4\, [O][O_3] + k_5\, [NO][O_3] + k_6\, [NO_2][O] \tag{2}$$

$$\frac{d[O_3]}{dt} = k_2\, [O][O_2][M] - j_3\, [O_3] - k_4\, [O][O_3] - k_5\, [NO][O_3] \tag{3}$$

$$\frac{d[NO]}{dt} = -\, k_5\, [NO][O_3] + k_6\, [NO_2][O] + j_7\, [NO_2] \tag{4}$$

$$\frac{d[NO_2]}{dt} = k_5\, [NO][O_3] - k_6\, [NO_2][O] - j_7\, [NO_2] \tag{5}$$

The rate of formation of odd oxygen species is obtained by adding Eqs. 1 and 3 to give:

$$\frac{d([O_3]+[O])}{dt} = 2\, j_1\, [O_2] - 2\, k_4\, [O][O_3] - k_5\, [NO][O_3] - k_6\, [NO_2][O] + j_7\, [NO_2] \tag{6}$$

The concentrations are set to X(4) = [NO] and X(5) = [NO$_2$]. The revised “chapman.m” method file for *MatLab* is called “chapmanNOx.m”:

```
function dX = chapmanNOx(t,X);
% Differintial equations for the Chapman Mechanism.
% Based on work by Farhan Akhtar, School of Earth and Atmospheric Sciences
% Georgia Institute of Technology:
%   http://www.prism.gatech.edu/~gte618p/chapman.html
% Constants for 25 km:
   j1=3.0e-12;
   k2=1.2e-33;
   j3=5.5e-4;
   k4=6.9e-16;
   k5=3.4e-15;
   k6=1.1e-11;
   j7=7.0e-3;
   M=9.0e17;
%Calculations
 dX = zeros(5,1) ;
 dX(1) = 2*j1*X(2)-k2*X(1)*X(2)*M+j3*X(3)-k4*X(1)*X(3)-k6*X(5)*X(1)+j7*X(5) ;
 dX(2) = -j1*X(2)-k2*X(1)*X(2)*M+j3*X(3)+2*k4*X(1)*X(3)+k5*X(5)*X(3)+k6*X(5)*X(1) ;
 dX(3) = k2*X(1)*X(2)*M-j3*X(3)-k4*X(1)*X(3)-k5*X(4)*X(3) ;
 dX(4) = -k5*X(4)*X(3)+k6*X(5)*X(1)+j7*X(5) ;
 dX(5) = -dX(4) ;
```

And the revised main program is:

```
% The differential equations are defined in the -m file: 'chapmanNOx.m'
%
clear
% Set the initial values
```

```
    Xo = [0 1.8e17 0 8e8 1e9];
% Set the total integration time in seconds
    maxTime = 4.0e7;
    trange = [0 maxTime];

% solve the differential equations
    [T,X] = ode15s(@chapmanNOx,trange,Xo);
```

These calculations give a steady-state ozone concentration of $8.74\text{x}10^{12}$ molecules cm^3, which is a factor of 0.53 smaller than the case without NO and NO_2. However, the exact change in ozone concentration is very dependent of the values of the rate constants and the total NO and NO_2 concentration. Hopefully, you noticed that the graph of $[O_2]$ shows a slow, constant increase for long times. This increase is from numerical errors that are caused by the use of the less accurate stiff differential equations solver. However, using the more accurate ode45(), a 4th order Runge-Kutta solver, requires many hours of computation time.

11. Problem 10 lists the three reactions that supplement the Chapman mechanism to account for the catalytic destruction of ozone caused by NO and NO_2. (a) At steady state, show that the rate law for odd oxygen species can be expressed as:

$$\frac{d([O_3]+[O])}{dt} = 2\,j_1\,[O_2] - 2\,k_4\,[O_3][O]\left(1 + \frac{k_6\,[NO_2]}{k_4\,[O_3]}\right)$$

The term in parentheses is called the enhancement factor, ρ:

$$\rho = \left(1 + \frac{k_6\,[NO_2]}{k_4\,[O_3]}\right)$$

which determines the extent of the catalysis of the destruction of ozone by NO and NO_2.Use the rate constants given in Problems 9 and 10 along with the following rough estimates for the steady-state concentrations to estimate the enhancement factor at 25 km. These concentrations are from the results of Problem 10 at 25 km:

$[O_3] = 8.74\text{x}10^{12}$ molecules cm^{-3} $\qquad$ $[NO_2] = 1.45\text{x}10^{9}$ molecules cm^{-3}

Answer: The rate laws are:

$$\frac{d[O]}{dt} = 2\,j_1\,[O_2] - k_2\,[O][O_2][M] + j_3\,[O_3] - k_4\,[O][O_3] - k_6\,[NO_2][O] + j_7\,[NO_2] \tag{1}$$

$$\frac{d[O_2]}{dt} = -\,j_1\,[O_2] - k_2\,[O][O_2][M] + j_3\,[O_3] + 2\,k_4\,[O][O_3] + k_5\,[NO][O_3] + k_6\,[NO_2][O] \tag{2}$$

$$\frac{d[O_3]}{dt} = k_2\,[O][O_2][M] - j_3\,[O_3] - k_4\,[O][O_3] - k_5\,[NO][O_3] \tag{3}$$

$$\frac{d[NO]}{dt} = -\,k_5\,[NO][O_3] + k_6\,[NO_2][O] + j_7\,[NO_2] \tag{4}$$

$$\frac{d[NO_2]}{dt} = k_5\,[NO][O_3] - k_6\,[NO_2][O] - j_7\,[NO_2] \tag{5}$$

The rate of formation of odd oxygen species is obtained by adding Eqs. 1 and 3 to give:

$$\frac{d([O_3]+[O])}{dt} = 2\,j_1\,[O_2] - 2\,k_4\,[O][O_3] - k_5\,[NO][O_3] - k_6\,[NO_2][O] + j_7\,[NO_2] \qquad 6$$

Eq. 6 involves both the NO and O atom concentrations. One of these intermediate concentrations can be eliminated using the steady-state approximation. Assume that the reactions are at steady state. The rate law for reaction 5 can then be set equal to zero. Adding Eqs. 5 and 6 eliminates [NO] as a variable and gives an additional destruction term:

$$\frac{d([O_3]+[O])}{dt} = \underset{\textit{production}}{2\,j_1\,[O_2]} - \underset{\textit{destruction}}{2\,k_4\,[O_3]\,[O]} - \underset{\textit{destruction}}{2\,k_6\,[NO_2][O]} \qquad 7$$

which can be rearranged to give:

$$\frac{d([O_3]+[O])}{dt} = \underset{\textit{production}}{2\,j_1\,[O_2]} - \underset{\textit{destruction}}{2\,k_4\,[O_3]\,[O]\left(1 + \frac{k_6\,[NO_2]}{k_4\,[O_3]}\right)} \qquad 8$$

with $\rho = \left(1 + \frac{k_6\,[NO_2]}{k_4\,[O_3]}\right)$ 9

Substituting in the values of the constants from Problems 9 and 10 and the steady-state concentrations of O_3 and NO_2 gives:

$$\rho = \left(1 + \frac{k_6\,[NO_2]}{k_4\,[O_3]}\right) = \left(1 + \frac{1.1\text{x}10^{-11}\text{ cm}^3\text{ molecules}^{-1}\text{ s}^{-1}\ (1.45\text{x}10^{9}\text{ molecules cm}^{-3})}{6.9\text{x}10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}\ (8.74\text{x}10^{12}\text{ molecules cm}^{-3})}\right)$$
$$= 3.6$$

The ozone destruction processes are accelerated by a factor of 3.6 by NO and NO_2 catalysis. This value is very sensitive to the values of the rate constants, especially the photolytic rate constant j_7, as shown in the next problem.

12. Nitrogen oxides catalyze the destruction of ozone and must be taken into account in accurate stratospheric models. The reactions and the rate constants appropriate for 25 km are:

$NO + O_3 \xrightarrow{k_5} NO_2 + O_2$ $k_5 = 3.4\text{x}10^{-15}\text{ cm}^3\text{ molecules}^{-1}\text{ s}^{-1}$

$NO_2 + O \xrightarrow{k_6} NO + O_2$ $k_6 = 1.1\text{x}10^{-11}\text{ cm}^3\text{ molecules}^{-1}\text{ s}^{-1}$

$NO_2 + h\nu \xrightarrow{j_7} NO + O$ $j_7 = 7\text{x}10^{-3}\text{ s}^{-1}$

Show that the ratio of the NO_2 and NO concentrations at steady-state are given by the relationship:

$$\frac{[NO_2]}{[NO]} = \frac{k_5\,[O_3]}{k_6\,[O] + j_7}$$

Calculate the steady-state ratio assuming that the O atom concentration is small enough that $k_6[O] << j_7$. Assume $[O_3] = 8.74\text{x}10^{12}$ molecules cm^{-3} (as in Problem 11).

Answer: The rate laws are:

$$\frac{d[NO]}{dt} = -k_5\,[NO][O_3] + k_6\,[NO_2][O] + j_7\,[NO_2] = 0 \qquad 1$$

$$\frac{d[NO_2]}{dt} = k_5\,[NO][O_3] - k_6\,[NO_2][O] - j_7\,[NO_2] = 0 \qquad 2$$

At steady-state both are equal to zero. Either Eq. 1 or 2 can be solved for the NO_2 to NO ratio:

$$k_5\,[NO][O_3] = k_6\,[NO_2][O] + j_7\,[NO_2] \qquad 3$$

$$\frac{[NO_2]}{[NO]} = \frac{k_5\,[O_3]}{k_6\,[O] + j_7} \qquad 4$$

This relationship can also be used to find the enhancement factor in Problem 11 in terms of the NO and O atom concentrations. Assuming $k_6[O] \ll j_7$ and substitution of the constants gives:

$$\frac{[NO_2]}{[NO]} = \frac{k_5\,[O_3]}{j_7} = \frac{3.4\text{x}10^{-15}\ \text{cm}^3\ \text{molecules}^{-1}\ \text{s}^{-1}\ (8.74\text{x}10^{12}\ \text{molecules cm}^{-3})}{7\text{x}10^{-3}\ \text{s}^{-1}}$$
$$= 4.2$$

This relationship shows that the ratio of NO_2 and NO and the O atom concentrations are sensitive to the rate constant for the photolytic decomposition of NO_2. Photolytic rate constants are dependent on time of day, time of year, and altitude and so are highly variable. The range of photolytically active wave lengths for the decomposition of NO_2 is 300-400 nm. Direct O_3 photolysis occurs in the ranges of 200-300 and 450-650 nm.

$$O_3 + h\nu(200\text{-}300,\ 450\text{-}650\ \text{nm}) \rightarrow O_2 + O$$
$$NO_2 + h\nu(300\text{-}400\ \text{nm}) \rightarrow NO + O$$

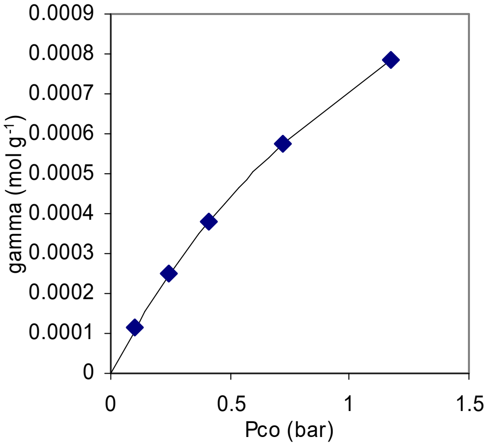
The UV-A range is 320–400 nm and the UV-B range is 280–320 nm.

13. The combustion of carbon sources, such as coal or charcoal, in limited amounts of oxygen produces carbon monoxide. Carbon monoxide is a commonly used reducing agent, especially in metallurgy. The reaction of carbon with high temperature steam produces carbon monoxide and hydrogen gas. Carbon monoxide and hydrogen are the feed stocks for industrial processes like the Fischer-Tropsch process, which can be used to produce transportation fuels from coal or biomass. Carbon monoxide readily adsorbs onto charcoal surfaces. The equilibrium surface loading of CO on charcoal at 0°C is given in the following table. Determine the Langmuir coefficient for this system.

Pco (bar)	0.0973	0.240	0.412	0.720	1.176
Γ (mmol g^{-1})	0.113	0.248	0.378	0.573	0.787

Answer: Based on Eq. 5.3.11 or 5.3.18, using the general form "abx/(1+bx)" in the "Nonlinear Least Squares Curve Fitting" applet gives the following results and corresponding curve-fit plot.

```
=======  Results  ============
 a= 0.001823 +- 0.000061
 b= 0.643 +- 0.033
--------------------------------------------
 sum of squared residuals= 8.473e-11
 stand. dev. y values= 0.000005315
 correlation between a & b= -0.989
```

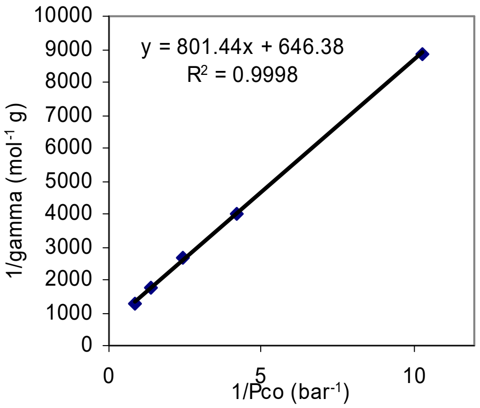


The fit gives b = 0.643± 0.033 bar^{-1}. A double reciprocal plot also works well, but again the nonlinear fit parameters are better because the uncertainties are handled better. Inverting Eq. 5.3.18:

$$\Gamma_{A\sigma} = \Gamma_{max\sigma}\frac{b\,P_A}{1 + b\,P_A} \qquad \text{gives} \qquad \frac{1}{\Gamma_{A\sigma}} = \frac{1}{\Gamma_{max\sigma}\,b\,P_A} + \frac{1}{\Gamma_{max\sigma}}$$

Pco (bar)	Γ (mol g^{-1})	1/Pco (bar^{-1})	1/Γ (mol^{-1} g)
0.0973	0.000113	10.27671	8859.907
0.240	0.000248	4.167778	4027.23
0.412	0.000378	2.427832	2647.382
0.720	0.000573	1.389259	1744.076
1.176	0.000787	0.850567	1270.541

The linear fit gives b = 0.81 bar^{-1}, which is outside the error bounds from the non-linear fit.



However, the double reciprocal plot does help verify Langmuir behavior. Notice the very high correlation coefficient between fit parameters in the non-linear fit, -0.989. The values of the maximum binding capacity and the Langmuir coefficient are highly correlated. To resolve this issue, to generate results that can be published, experimental points at higher P_{CO} are necessary.

14. Antibody-antigen interactions are very strong and very specific. The interaction between a protein, bovine serum albumin, and anti-BSA immunoglobulin G (IgG) was determined using SPR. BSA was attached to a gold surface and the IgG was flowed over the surface at constant concentration. The results for the observed association rate constant are given in the table below. The dissociation rate constants, from nonlinear curve fitting from the time courses, were averaged over each run and found to be 5.94x10^{-5} s^{-1}. Find k_a, the association equilibrium

constant, K_A, and the dissociation equilibrium constant, K_D. Convert K_D to picomolar units, pM, which is typical of the conventional choice of units in the medicinal chemistry literature.

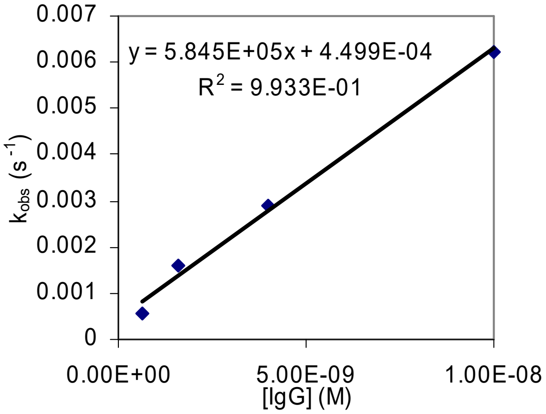
[IgG] (nM)	10.0	4.00	1.60	0.640
k_{obs} (s^{-1})	0.00623	0.002914	0.001578	0.00057

Answer: From Eq. 5.4.10, $k_{obs} = k_a [A]_o + k_d$, a plot of k_{obs} versus the concentration of IgG flowing over the surface, $[A]_o$, should yield a straight line. The linest() fit is for k_{obs} vs. [IgG] in units of nM, so the final slope must be multiplied by $1x10^9$ to convert to M^{-1} s^{-1}.

[IgG] nM	[IgG] (M)	k_{obs} (s^{-1})
10	1.00E-08	0.00623
4	4.00E-09	0.002914
1.6	1.60E-09	0.001578
0.64	6.40E-10	0.00057

In nM concentration units:

slope	0.00058452	0.00045	intercept
±	3.3891E-05	0.000185	±
r^2	0.9933	0.000247	s(y)
F	297.467	2	df
$ss_{regression}$	1.812E-05	1.22E-07	$ss_{residual}$



The resulting $k_a = 5.85x10^5 \pm 0.34x10^5$ M^{-1} s^{-1}, giving $K_A = 5.85x10^5$ M^{-1} s^{-1}/ $5.94x10^{-5}$ s^{-1} = $9.84x10^9$ M^{-1} and $K_D = 1/K_A = 1.02x10^{-10}$ M. In picomolar units:

$K_D = 1.02x10^{-10}$ M (1 pM/$1.0x10^{-12}$M) = 102. pM = 1. $x10^2$ pM

15. SPR is a commonly used technique in immunology. The interaction between a protein, porcine serum albumin, PSA, and anti-PSA immunoglobulin G (IgG) was determined using SPR. The anti-PSA IgG was attached to a gold surface and PSA was flowed over the surface at constant concentration. The results for the observed association rate constant are given in the table below.[6] The dissociation rate constants, from nonlinear curve fitting from the time courses, were averaged over each run and found to be $1.02x10^{-3}$ s^{-1}. Find k_a, the association equilibrium constant, K_A, and the dissociation equilibrium constant, K_D. Convert K_D to nanomolar units, nM, which is typical of the conventional choice of units in the medicinal chemistry literature.

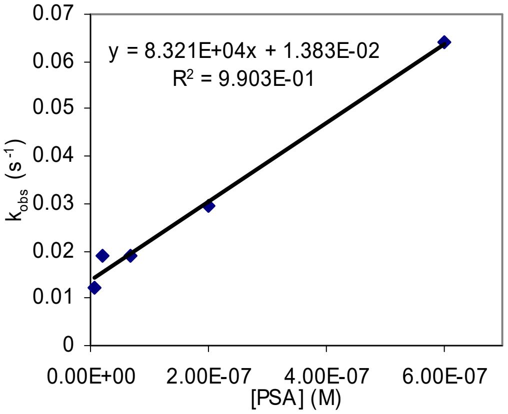
[PSA] (nM)	7.18	21.5	66.4	201.	601.
k_{obs} (s^{-1})	0.0122	0.00189	0.00189	0.0297	0.0641

Answer: From Eq. 5.4.10, $k_{obs} = k_a [A]_o + k_d$, a plot of k_{obs} versus the concentration of PSA flowing over the surface, $[A]_o$, should yield a straight line. The linest() fit is for k_{obs} vs. [PSA] in units of nM, so the final slope must be multiplied by $1x10^9$ to convert to M^{-1} s^{-1}.

[PSA] nM	[PSA] (M)	k_{obs} (s^{-1})
7.18E+00	7.18E-09	0.0122
2.15E+01	2.15E-08	0.0189
6.64E+01	6.64E-08	0.0189
2.01E+02	2.01E-07	0.0297

In nM concentration units:

slope	8.3207E-05	0.013825	intercept
±	4.7595E-06	0.001358	±
r^2	0.99028	0.00235969	s(y)
F	305.627	3	df
$ss_{regression}$	0.0017018	1.6704E-05	$ss_{residual}$



The resulting $k_a = 8.32\text{x}10^4 \pm 0.48\text{x}10^4$ M^{-1} s^{-1}, giving $K_A = 8.32\text{x}10^4$ M^{-1} s^{-1}/ $1.02\text{x}10^{-3}$ s^{-1} = $8.16\text{x}10^7$ M^{-1} and $K_D = 1/K_A = 1.23\text{x}10^{-8}$ M. In nanomolar units:

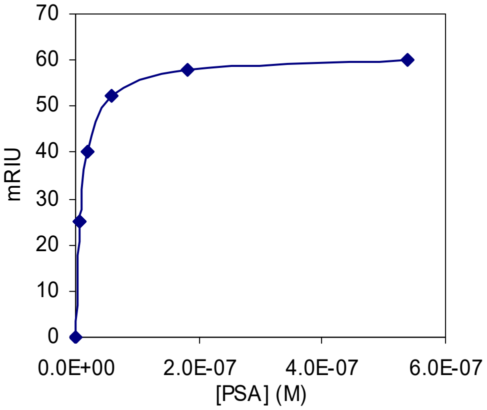
$K_D = 1.23\text{x}10^{-8}$ M (1 nM/$1.0\text{x}10^{-9}$M) = 12.3. nM = 1. $\text{x}10^1$ nM

16. It is not necessary in dynamic SPR measurements to wait for the surface adsorption to reach equilibrium. However, if the time course for the association does essentially reach equilibrium, the equilibrium values can be fit to the Langmuir adsorption isotherm. Such equilibrium SPR experiments provide an alternative method to determine the equilibrium dissociation constant that is complementary to dynamic measurements. Comparison between equilibrium and dynamic results helps to determine experimental uncertainties. The limiting refractive index values from the time course measurements for the system in Problem 15 are given below.[6] By fitting the results to a Langmuir adsorption isotherm, determine the equilibrium dissociation constant in nanomolar units. The units typical for SPR instrument output are micro-refractive index units, or µRIU.

[PSA] (nM)	0	7.18	7.18	19.7	59.2	181.3	538.5
R (µRIU)	0	23.6	26.5	38	55.6	57.6	58.8

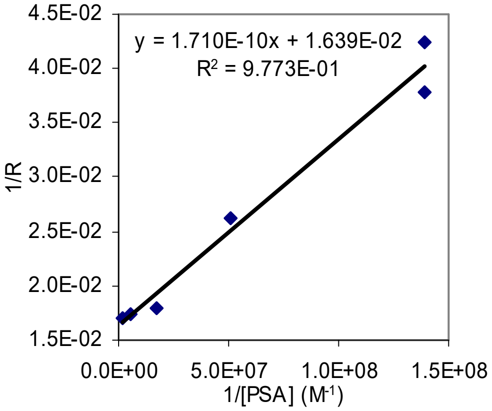
Answer: Based on Eq. 5.3.11 or 5.3.18, using the general form "abx/(1+bx)" in the "Nonlinear Least Squares Curve Fitting" applet gives the following results and corresponding curve-fit plot, below. The non-linear fit value for $K_A = 9.52\text{x}10^7 \pm 1.0\text{x}10^7$ M^{-1}. Then $K_D = 1/K_A = 1.05\text{x}10^{-8}$ M = 10.5 nM. The value from Problem 16 was ≈12 nM, which agrees within experimental uncertainty.

```
========  Results  =========
 a= 61.36 +- 1.55
 b= 95200000 +- 10000000
---------------------------------------------
 sum of squared residuals= 22.66
 stand. dev. y values= 2.129
 correlation between a & b= -0.6582
```



A double reciprocal plot also works well, but again the nonlinear fit parameters are better because the uncertainties are handled better:

[PSA] (M)	R (μRIU)	1/[PSA] (M^{-1})	1/R
0	0		
7.18E-09	23.6	1.39E+08	4.24E-02
7.18E-09	26.5	1.39E+08	3.77E-02
1.97E-08	38.0	5.06E+07	2.63E-02
5.92E-08	55.6	1.69E+07	1.80E-02
1.81E-07	57.6	5.52E+06	1.74E-02
5.38E-07	58.8	1.86E+06	1.70E-02



17. The rate of decomposition of NH_3 was determined as a function of the initial partial pressure of H_2 and is inhibited by product formation:[7]

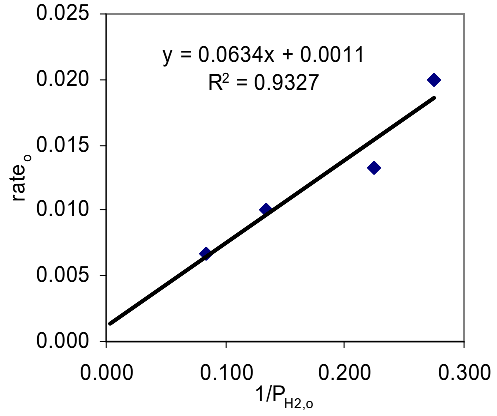
$$NH_3\,(g) \rightarrow \tfrac{1}{2}\,N_2(g) + {}^{3}/_{2}\,H_2\,(g)$$

The initial pressure of NH_3 in each run was 100 mm Hg, and varying amounts of H_2 gas were added to the reaction vessel at the beginning of the reaction. The catalyst was platinum and the reaction was run at 1138°C. The results are given below. Show that the dependence on the product, H_2, partial pressure is described by Eq. 5.5.17.

ΔP_{NH_3} in 120 s	P_{H_2} initially added
33	50
27	75
16	100
10	150

Answer: First we approximate the initial rate as $\upsilon_o = \Delta P_{NH3}/120$ s. Then a plot of the initial rate as a function of $1/P_{H2}$ should give a straight line in accordance with Eq. 5.5.17. A spreadsheet was set up and the plot was constructed:

ΔP_{NH3}	$P_{H2,o}$	υ_o (mm Hg s^{-1})	$1/P_{H2,o}$
33	50	0.275	0.020
27	75	0.225	0.013
16	100	0.133	0.010
10	150	0.083	0.007



The inverse dependence on P_{H2} is verified by the linear plot, to within experimental error.

18. Hydrogen is a clean burning substance that is being suggested as a transportation fuel. However, hydrogen is costly to produce. One proposal is to use solar thermal energy to provide the energy necessary to convert water into hydrogen gas. The Sulfur-Iodine cycle consists of three coupled reactions, which add to give the dissociation of water:

$H_2SO_4\ (l) \rightarrow SO_2\ (g) + H_2O\ (g) + \frac{1}{2}\ O_2\ (g)$ (>850°C)
$I_2 + SO_2 + 2\ H_2O \rightarrow 2\ HI + H_2SO_4$ (>120°C)
$2\ HI \rightarrow I_2 + H_2$ (>450°C)

net: $H_2O \rightarrow H_2\ (g) + \frac{1}{2}\ O_2\ (g)$

The first step is the most unfavorable thermodynamically and kinetically. The reaction occurs in two steps:

$H_2SO_4\ (l) \rightarrow SO_3\ (g) + H_2O\ (g)$
$SO_3\ (g) \rightarrow SO_2\ (g) + \frac{1}{2}\ O_2\ (g)$

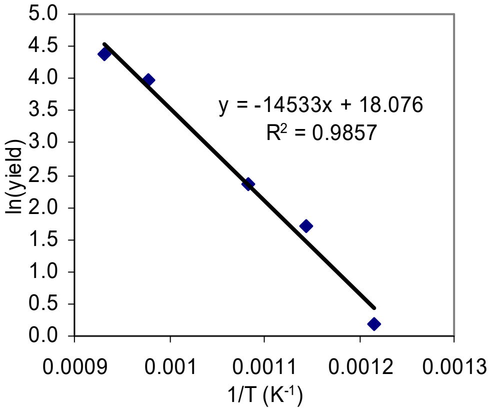
The decomposition of SO_3 has a negligible rate at 800°C without a catalyst. Mixed chromium-iron oxide catalysts have been proposed for the gas phase decomposition of SO_3.[8] The heterogeneous decomposition of SO_3 on $Fe_{1.6}Cr_{0.4}O_3$ in a constant flow reactor has been studied as a function of temperature. The percent yields at several temperatures are given in the table, below. The residence time of the reactant in a constant flow reactor is constant with temperature, so the percent yield is directly proportional to the reaction rate. Verify Arrhenius behavior and determine the activation energy.

T (°C)	550	600	650	750	800
SO_2 yield %	1.2	5.5	10.7	52.7	79.3

Answer: The ln(rate) and ln(yield) can be used interchangeably for this constant flow reactor data. A plot of ln(yield) versus 1/T will verify Arrhenius behavior with the slope = $-E_a/R$. A spreadsheet was set up, the plot was constructed, and the slope determined using linest():

T (°C)	SO_2 yield	T (K)	1/T (K^{-1})	ln(yield)
550	1.2	823.2	0.001215	0.182
600	5.5	873.2	0.001145	1.705
650	10.7	923.2	0.001083	2.370
750	62.7	1023.2	0.000977	4.138
800	79.3	1073.2	0.000932	4.373

slope	-14532.895	18.076	intercept
±	1011.114	1.087	±
r^2	0.986	0.236	st.dev. Y
F	206.588	3.000	df
ss_{reg}	11.506	0.167	ss_{resid}

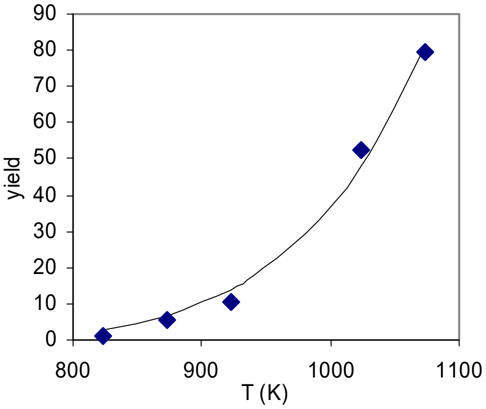


Given the experimental uncertainty, Arrhenius behavior may be justified. The lowest temperature point, which is the point with the largest absolute and relative uncertainty, deviates significantly from the line. Several additional data points at low temperatures would be necessary to judge if systematic curvature exists for the plot. Given Arrhenius behavior, the activation energy is:

$$E_a = -\text{slope } R = 148 \pm 23 \text{ kJ mol}^{-1}$$

The nonlinear fit using the "Nonlinear Least Squares Curve Fitting" applet, however, provides a very important lesson:

```
===========  Results  =============
 a= 4130000 +- 4750000
 b= -11630 +- 1200
---------------------------------------------------
 sum of squared residuals= 43.02
 stand. dev. y values= 3.787
 correlation between a & b= -0.9994
```



The activation energy from the non-linear fit is 97 ± 10 kJ mol^{-1}, which is outside the range of the experimental uncertainties. Why the large difference? The correlation coefficient between the fit values is very large at -0.9994, showing a very strong correlation between the fit values of A and E_A. You wouldn't have noticed this problem without the non-linear fit and you would have underestimated the uncertainty in the activation energy. In fact, using the linearized form of the data in the "Nonlinear Least Squares Curve Fitting" applet using the simple line option, "ax + b", also gives a very large correlation coefficient between the slope and the intercept of -0.9953. The results from this experiment are best given as $1.\text{x}10^2$ kJ mol^{-1} to avoid over-representing the uncertainty.

19. Derive the rate law for a bimolecular heterogeneous reaction with stoichiometry: A + C →P. Assume that reactant C is strongly adsorbed to the catalytic surface and A is weakly adsorbed.

Answer: The reaction mechanism can be approximated by:

$$\mathrm{A\,(g)} + \mathrm{B}_\sigma \underset{k_{Ad}}{\overset{k_{Aa}}{\rightleftarrows}} \mathrm{A}_\sigma + \mathrm{C}_\sigma \xrightarrow{k_\sigma} \mathrm{P}_\sigma + \mathrm{B}_\sigma \tag{1}$$

where the surface concentration of C is determined by the rapid pre-equilibrium:

$$\mathrm{C\,(g)} + \mathrm{B}_\sigma \underset{k_{Cd}}{\overset{k_{Ca}}{\rightleftarrows}} \mathrm{C}_\sigma \tag{2}$$

The rate law for the formation of products is constructed similarly to Eq. 5.5.2:

$$\frac{1}{\sigma}\frac{d\xi}{dt} = k_\sigma\,[A]_\sigma\,[C]_\sigma \tag{3}$$

with the pre-equilibrium concentration of free binding sites dominated by the fractional coverage for C, in analogy with Eq. 5.5.15 :

$$[C]_\sigma \approx [B]_{o\sigma} \tag{4}$$

and
$$[B]_\sigma \approx \frac{[B]_{o\sigma}}{b_C\,P_C} \tag{5}$$

with $b_C = k_{Ca}/k_{Cd}$ which is the equilibrium constant for the surface adsorption of C, and P_C the partial pressure for C. The rate law for the formation of A bound on the surface from Eq. 1 is:

$$\frac{d[A]_\sigma}{dt} = k_{Aa}\,[B]_\sigma\,P_A - k_{Ad}\,[A]_\sigma - k_\sigma[A]_\sigma[C]_\sigma = 0 \qquad \text{(steady-state)} \tag{6}$$

where $[B]_\sigma$ is given by Eq. 5. Solving for $[A]_\sigma$ using the steady-state approximation and substituting Eq. 5 gives:

$$[A]_\sigma = \frac{k_{Aa}}{k_{Ad} - k_\sigma[C]_\sigma}\,\frac{[B]_{o\sigma}}{b_C\,P_C}\,P_A \tag{7}$$

Substitution of Eq. 7 for the surface concentration for A into Eq. 3 and using Eq. 4 for the surface concentration of C gives:

$$\frac{1}{\sigma}\frac{d\xi}{dt} = k_\sigma\frac{k_{Aa}}{k_{Ad} - k_\sigma[B]_{o\sigma}}\,\frac{[B]_{o\sigma}}{b_C\,P_C}\,P_A\,[B]_{o\sigma} \tag{8}$$

For the rate law with respect to the disappearance of A, using Eq. 5.5.5:

$$-\frac{dP_A}{dt} = k_\sigma(RT)\frac{k_{Aa}}{k_{Ad} - k_\sigma[B]_{o\sigma}}\ \frac{\sigma/V\ [B]_{o\sigma}}{b_C\, P_C}\ P_A\ [B]_{o\sigma} \qquad 9$$

Gathering together all of the constants defines the observed rate constant:

$$k_{obs} = k_\sigma(RT)\frac{k_{Aa}}{k_{Ad} - k_\sigma[B]_{o\sigma}}\ \frac{\sigma/V\ [B]_{o\sigma}}{b_C}\ [B]_{o\sigma} \qquad 10$$

and then the final rate law is:

$$-\frac{dP_A}{dt} = k_{obs}\frac{P_A}{P_C} \qquad 11$$

In some cases the rate constant for the surface reaction, k_σ, is assumed to be very small so that the observed rate constant can be written:

$$k_{obs} = k_\sigma(RT)\frac{b_A}{b_C}\ \sigma/V\ [B]_{o\sigma}^2 \qquad 12$$

where $b_A = k_{Aa}/k_{Ad}$, which is the equilibrium constant for the surface adsorption of A.

20. Determine the integrated rate law for surface catalysis from an adsorbed monolayer using Eq. 5.5.7.

Answer: Starting with Eq. 5.5.7 and separating variables:

$$\frac{1 + b_A\, P_A}{b_A\, P_A}\, dP_A = \left(\frac{1}{b_A\, P_A} + 1\right) dP_A = -\, k\, dt$$

The integration limits start at t= 0, $P_A = P_{Ao}$:

$$\int_{P_{Ao}}^{P_A}\left(\frac{1}{b_A\, P_A} + 1\right) dP_A = -\int_0^t k\, dt$$

The sum in the first integral can be split into two terms:

$$\frac{1}{b_A}\ \ln(P_A\Big|_{P_{Ao}}^{P_A} + P_A\Big|_{P_{Ao}}^{P_A} = -\, kt$$

$$\frac{1}{b_A}\ \ln\frac{P_A}{P_{Ao}} + (P_A - P_{Ao}) = -\, kt$$

If A is weakly adsorbed, then b_A is small. Notice that if b_A is small, then the $(P_A - P_{Ao})$ is negligible compared to the logarithmic term and this last equation reduces to a simple first-order reaction, Eq. 5.5.8:

$$\frac{1}{b_A}\ln\frac{P_A}{P_{Ao}} \approx -\, kt \qquad \text{and} \qquad \ln\frac{P_A}{P_{Ao}} \approx -\, b_A\, kt$$

On the other hand, if b_A is large, the logarithmic term is negligible and the reaction is zeroth order, as expected from Eq. 5.5.9:

$$(P_A - P_{Ao}) \approx -kt$$

21. We assumed a pre-equilibrium mechanism to determine the rate for a heterogeneously catalyzed reaction according to Eq. 5.5.1:

$$A\,(g) + B_\sigma \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_\sigma \xrightarrow{k_\sigma} P\,(g) + B_\sigma$$

The rate law for the reaction, in terms of the products is then given by:

$$\frac{d[P]}{dt} = k_\sigma(RT)\,(\sigma/V)\,[A]_\sigma$$

To give a better approximation, use the steady-state approximation to determine the rate law. Then show that the more exact rate law reduces to Eq. 5.5.6 using a suitable approximation.

Answer: Eq. 5.5.1 is equivalent to the Michaelis-Menten mechanism, so the derivation for this rate law should be parallel to our previous derivation. The plan is to use the steady-state approximation on $[A]_\sigma$ and then use the mass balance for the total concentration of surface adsorption sites, $[B]_{o\sigma} = [B]_\sigma + [A]_\sigma$, Eq. 5.3.1.

The rate law for the appearance of surface bound A for this mechanism is identical to Eq. 5.5.11:

$$\frac{d[A]_\sigma}{dt} = k_{Aa}\,[B]_\sigma\,P_A - k_{Ad}\,[A]_\sigma - k_\sigma[A]_\sigma \qquad 1$$

In steady state, for $[A]_\sigma$ as the reactive intermediate:

$$k_a\,[B]_\sigma\,P_A - k_d\,[A]_\sigma - k_\sigma[A]_\sigma \approx 0 \qquad \text{or} \quad [A]_\sigma = \frac{k_a\,[B]_\sigma\,P_A}{k_d + k_\sigma} \qquad 2$$

Solving the mass balance equation, Eq. 5.3.1, for the concentration of free surface sites gives:

$$[B]_\sigma = [B]_{o\sigma} - [A]_\sigma \qquad 3$$

and substitution into Eq. 2 gives:

$$(k_d+k_\sigma)[A]_\sigma = k_aP_A([B]_{o\sigma} - [A]_\sigma) \qquad \text{or} \quad (k_d+k_\sigma+k_aP_A)[A]_\sigma = k_aP_A[B]_{o\sigma} \qquad 4$$

Solving for $[A]_\sigma$ gives:

$$[A]_\sigma = \frac{k_a\,P_A\,[B]_{o\sigma}}{k_d + k_\sigma + k_a\,P_A} \qquad 5$$

Dividing both numerator and denominator by k_d and using the definition of the Langmuir coefficient, $b_A = k_a/k_d$ gives:

$$[A]_\sigma = \frac{b_A\, P_A\, [B]_{o\sigma}}{1 + k_\sigma/k_d + b_A\, P_A} \qquad 6$$

Substitution of Eq. 6 into the rate law for appearance of product gives the final result:

$$\frac{d[P]}{dt} = k_\sigma(RT)\,(\sigma/V)\,[A]_\sigma = k_\sigma(RT)\,(\sigma/V)\,\frac{b_A\, P_A\, [B]_{o\sigma}}{1 + k_\sigma/k_d + b_A\, P_A} \qquad 7$$

If we assume that $k_d >> k_\sigma$ then the k_σ/k_d term is negligible and this last equation reduces to the pre-equilibrium mechanism result, Eq. 5.5.6.

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Chapter 6 Problems: Applications of Reaction Mechanisms

1. Qualitatively predict the effect of wind turbulence on the exchange of CO_2 across the air/sea interface.

Answer: Wind caused turbulence increases the mixing rate at the air/sea interface, thus decreasing the thickness of the stagnant boundary layer. Assuming a linear concentration gradient, using Eq. 6.1.29:

$$J_o = -\frac{D_{CO_2}}{\delta}\left([CO_2]^{bulk} - [CO_2]^{w/a}\right)$$

The thinner the boundary layer, the larger the concentration gradient and the larger the flux.

2. Find the second derivative with respect to x of a Gaussian distribution for a non-zero mean. Use explicit differentiation of the general form of the Gaussian distribution in Eq. 6.1.8.

Answer: Starting with Eq. 6.1.8:

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-(x-\mu)^2/2\sigma^2} \qquad 1$$

Taking the first derivative with respect to x of Eq. 6.1.8 gives:

$$\frac{dg}{dx} = \frac{1}{\sigma\sqrt{2\pi}}\,\frac{d\left(e^{-(x-\mu)^2/2\sigma^2}\right)}{dx} = \frac{1}{\sigma\sqrt{2\pi}}\left(\frac{-2(x-\mu)}{2\sigma^2}\right) e^{-(x-\mu)^2/2\sigma^2} \qquad 2$$

This last equation can be written more simply by substituting back in the definition of g(x):

$$\frac{dg}{dx} = \left(\frac{-(x-\mu)}{\sigma^2}\right) g \qquad 3$$

and then the derivative of this last equation gives the second derivative. Let f equal the first term: $f = (-(x-\mu)/\sigma^2)$. Using the product rule $d(fg)/dx = f\, dg/dx + g\, df/dx$:

$$\frac{d^2g}{dx^2} = \frac{d\left(\frac{-(x-\mu)}{\sigma^2}\, g\right)}{dx} = \left[\left(\frac{-(x-\mu)}{\sigma^2}\right)\left(\frac{dg}{dx}\right) + g\,\frac{d\left(\frac{-(x-\mu)}{\sigma^2}\right)}{dx}\right] \qquad 4$$

Using Eq. 3 for the first derivative of g gives:

$$\frac{d^2g}{dx^2} = \frac{d\left(\frac{-(x-\mu)}{\sigma^2}\, g\right)}{dx} = \left[\left(\frac{-(x-\mu)}{\sigma^2}\right)\left(\frac{-(x-\mu)}{\sigma^2}\right) g + \left(\frac{-1}{\sigma^2}\right) g\right] = \left[\left(\frac{(x-\mu)^2}{\sigma^4}\right) - \left(\frac{1}{\sigma^2}\right)\right] g$$

3. In deriving Eq. 6.1.24, we used Eq. 6.1.19 from *General Pattern* ***℘5***. Instead, derive Eq. 6.1.24 by explicit differentiation of Eq. 6.1.7.

Answer: Starting with the Gaussian concentration profile from Eq. 6.1.7:

$$c(x,t) = \frac{n_o}{A\sqrt{4\pi Dt}}\, e^{-x^2/4Dt}$$

Taking the first derivative of Eq. 6.1.7 with respect to distance while keeping t constant gives:

$$\left(\frac{\partial c}{\partial x}\right)_t = \frac{n_o}{A\sqrt{4\pi Dt}} \frac{d\left(e^{-x^2/4Dt}\right)}{dx} = \frac{n_o}{A\sqrt{4\pi Dt}}\left(\frac{-2x}{4Dt}\right) e^{-x^2/4Dt}$$

Using the definition of c(x,t) in this last equation gives:

$$\left(\frac{\partial c}{\partial x}\right)_t = \left(\frac{-2x}{4Dt}\right) c$$

and then the derivative of this last equation gives the second derivative. Let f equal the first term: f = (–2x/4Dt). Using the product rule d(fc)/dx = f dc/dx + c df/dx :

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_t = \frac{d\left(\frac{-2x\ c}{4Dt}\right)}{dx} = \left[\left(\frac{-2x}{4Dt}\right)\left(\frac{dc}{dx}\right) + c\left(\frac{-2}{4Dt}\right)\right]$$

Substitution of the first derivative gives:

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_t = \left[\left(\frac{-2x}{4Dt}\right)\left(\frac{-2x}{4Dt}\right) c + \left(\frac{-2}{4Dt}\right) c\right] = \left[\left(\frac{x^2}{4D^2t^2}\right) - \left(\frac{1}{2Dt}\right)\right] c$$

4. Write an Excel spreadsheet that uses the finite difference approximation to solve Eq. 6.1.6 for the one-dimensional planar diffusion problem. The analytical solution is Eq. 6.1.7. To do this, first assume finite differences for Eq. 6.1.6 to give:

$$\Delta c(x) = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t \Delta t$$

where this equation is applied at each point, x, on equally spaced intervals along the x-axis. We also need an approximation for the second derivative. Assume the concentrations along the x-axis are c_0, c_1, c_2, c_3, …., which are evaluated at points x = 0, dx, 2dx, 3dx,… The first derivative from c_0 to c_1 and the first derivative from c_1 to c_2 are:

$$\left(\frac{dc}{dx}\right)_{x=0.5\,dx} = \frac{c_1 - c_0}{dx} \qquad \text{and} \qquad \left(\frac{dc}{dx}\right)_{x=1.5\,dx} = \frac{c_2 - c_1}{dx}$$

The second derivative is the derivative of the first derivatives:

$$\left(\frac{d^2c}{dx^2}\right)_{x=dx} = \frac{\left(\frac{c_2 - c_1}{dx}\right) - \left(\frac{c_1 - c_0}{dx}\right)}{dx} = \frac{c_2 - 2\,c_1 + c_0}{dx^2}$$

This result is then used to find the new value for the concentration at c_1 in the next time interval using the finite difference formula. Assume the diffusion coefficient is $1.0\text{x}10^{-9}$ m^2s^{-1}. Assume a time interval of $\Delta t = 0.01$ s and integrate to 0.3 s. Assume an x spacing of $dx = 1.0\text{x}10^{-5}$m from 0 to $1\text{x}10^{-4}$m. (In other words, use a range from 0 to 100 μm.) Assume the initial conditions are a concentration of 1.00 mol m^{-3} in the first x interval and zero at larger distances. One problem arises however. The second derivative can't be calculated at the very first or very last spatial point. For this problem, just set the value of the concentration at the largest value of x at zero. For the value of the concentration at x = 0, that is c_0, we can use conservation of mass. In other words find the sum of the concentrations: $c_1+c_2+c_3+c_4$… and then subtract from the initial concentration, c_0 at t = 0. Here is a start on how you might lay out the first few rows of your spreadsheet. The concentrations at equally spaced x are arranged across the columns and successive time points correspond to successive rows:

A1	B	C	D	E	F	G	H	I	J	K	L	M	N
2			dt=	0.01	s								
3			dx=	1.E-05	m								
4			D=	1.E-09	$m^2 s^{-1}$								
5			c(0,0)=	1	mol m^{-3}								
6			x (m):										
7		t (s):	0	1.E-05	2.E-05	3.E-05	4.E-05	5.E-05	6.E-05	7.E-05	8.E-05	9.E-05	1.E-04
8		0	1.00	0	0	0	0	0	0	0	0	0	0
9		0.01											
10		0.02											

:

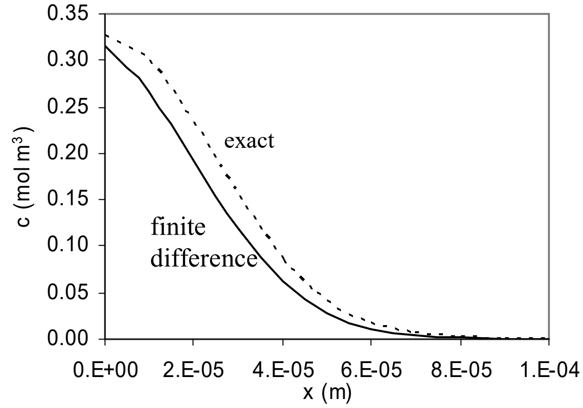
:

Answer: The formula in cell E9 is: "=E8+$E$4*(F8-2*E8+D8)/$E$3^2*$E$2". This formula can then be automatically filled across and down the spreadsheet to provide the formulas for all the other cells, except the first and last concentration points. The formula in the cell D9 is: "=$E$5-SUM(E9:N9)". This formula can then be filled down for all the other c_0 values. The last concentration at $x = 1.0\text{x}10^{-4}$ m is set to zero for each time.

A1	B	C	D	E	F	G	H	I	J	K	L	M	N
2			dt=	0.01	s								
3			dx=	1.E-05	m								
4			D=	1.E-09	$m^2 s^{-1}$								
5			c(0,0)=	1	mol m^{-3}								
6			x (m):										
7		t (s):	0	1E-05	2E-05	3E-05	4E-05	5E-05	6E-05	7E-05	8E-05	9E-05	1E-04
8		0	1.00	0	0	0	0	0	0	0	0	0	0
9		0.01	0.90	0.100	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10		0.02	0.82	0.170	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
11		0.03	0.76	0.219	0.025	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
12		0.04	0.70	0.253	0.042	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000
13		0.05	0.66	0.277	0.059	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000
14		0.06	0.62	0.293	0.076	0.011	0.001	0.000	0.000	0.000	0.000	0.000	0.000
15		0.07	0.59	0.304	0.091	0.017	0.002	0.000	0.000	0.000	0.000	0.000	0.000
16		0.08	0.56	0.311	0.105	0.023	0.003	0.000	0.000	0.000	0.000	0.000	0.000
17		0.09	0.53	0.315	0.117	0.029	0.005	0.001	0.000	0.000	0.000	0.000	0.000
18		0.1	0.51	0.317	0.128	0.035	0.007	0.001	0.000	0.000	0.000	0.000	0.000
19		0.11	0.49	0.318	0.138	0.042	0.009	0.001	0.000	0.000	0.000	0.000	0.000

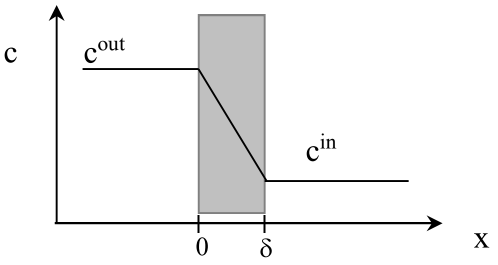
20		0.12	0.47	0.317	0.146	0.048	0.012	0.002	0.000	0.000	0.000	0.000	0.000
21		0.13	0.46	0.316	0.153	0.054	0.014	0.003	0.000	0.000	0.000	0.000	0.000
22		0.14	0.44	0.314	0.160	0.060	0.017	0.004	0.001	0.000	0.000	0.000	0.000
23		0.15	0.43	0.311	0.165	0.066	0.020	0.005	0.001	0.000	0.000	0.000	0.000
24		0.16	0.42	0.309	0.170	0.071	0.023	0.006	0.001	0.000	0.000	0.000	0.000
25		0.17	0.41	0.306	0.174	0.076	0.026	0.007	0.002	0.000	0.000	0.000	0.000
26		0.18	0.40	0.303	0.177	0.081	0.029	0.009	0.002	0.000	0.000	0.000	0.000
27		0.19	0.39	0.300	0.180	0.086	0.032	0.010	0.003	0.001	0.000	0.000	0.000
28		0.2	0.38	0.297	0.183	0.090	0.036	0.011	0.003	0.001	0.000	0.000	0.000
29		0.21	0.37	0.294	0.185	0.094	0.039	0.013	0.004	0.001	0.000	0.000	0.000
30		0.22	0.36	0.291	0.187	0.097	0.042	0.015	0.004	0.001	0.000	0.000	0.000
31		0.23	0.36	0.288	0.188	0.101	0.044	0.016	0.005	0.001	0.000	0.000	0.000
32		0.24	0.35	0.284	0.189	0.104	0.047	0.018	0.006	0.002	0.000	0.000	0.000
33		0.25	0.34	0.281	0.190	0.107	0.050	0.020	0.007	0.002	0.000	0.000	0.000
34		0.26	0.34	0.278	0.191	0.109	0.053	0.021	0.007	0.002	0.001	0.000	0.000
35		0.27	0.33	0.276	0.192	0.112	0.055	0.023	0.008	0.003	0.001	0.000	0.000
36		0.28	0.33	0.273	0.192	0.114	0.058	0.025	0.009	0.003	0.001	0.000	0.000
37		0.29	0.32	0.270	0.192	0.116	0.060	0.027	0.010	0.003	0.001	0.000	0.000
38		0.3	0.32	0.267	0.192	0.118	0.062	0.028	0.011	0.004	0.001	0.000	0.000

The plot of the last row at t = 0.3 s is shown below with the analytical solution from Eq. 6.1.7.



The agreement between the finite difference approach and the analytical solution is much better than you might expect from the coarse grid of x points and the large Δt that we used. Better agreement would be obtained for smaller Δt.

5. In this problem we will use Fick's Second Law to model diffusion through a membrane. Consider a membrane of thickness δ separating two well mixed solutions of concentration c^{out} and c^{in}. The origin of the x-axis is chosen to be at the interface between the membrane and the solution at concentration c^{out} as shown below:



(a.) Show that the concentration profile:

$$c(x) = \left(\frac{c^{in} - c^{out}}{\delta}\right) x + c^{out}$$

has the correct behavior at the surfaces of the membrane.
(b). Assume Fick's Second Law holds for diffusion within the membrane. Show that this linear concentration profile is a valid solution to Fick's Second Law at steady-state.
(c). Find the relationship for the flux across the membrane.

Answer: (a) At $x = 0$, $c(0) = c^{out}$ and at $x = \delta$:

$$c(\delta) = \left(\frac{c^{in} - c^{out}}{\delta}\right) \delta + c^{out} = c^{in} \qquad 1$$

This linear concentration profile has the correct concentrations at the edges of the membrane. In other words, it obeys the proper boundary conditions.
(b). At steady state, Eq. 6.1.6 is equal to zero and we no longer need to worry about time dependence:

$$D\frac{d^2c}{dx^2} = 0 \qquad 2$$

We need to show that the second derivative of the proposed solution is equal to zero. Starting with the first derivative gives the gradient:

$$\frac{dc}{dx} = \frac{d\,[(c^{in} - c^{out})\,x/\delta + c^{out}]}{dx} = \left(\frac{c^{in} - c^{out}}{\delta}\right) \qquad 3$$

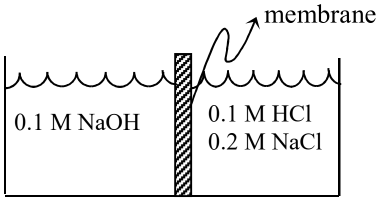
The second derivative is equal to zero, because the first derivative is a constant, as required by Eq. 2. Therefore, the proposed solution is a valid solution for $0 < x < \delta$.
(c). Fick's First Law of diffusion, Eq. 2.3.4, relates the molar flux of a substance to the concentration gradient, $J_m = -\,D\,dc/dx$. Eq. 3 is the gradient so that:

$$J_m = -\,D\left(\frac{c^{in} - c^{out}}{\delta}\right) \qquad 4$$

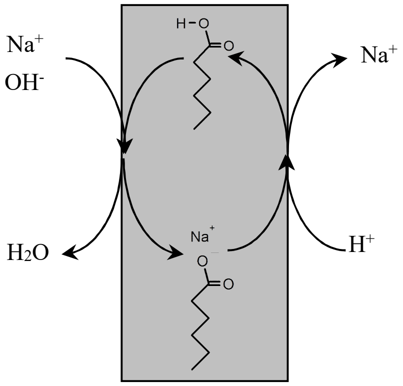
This final result is the same as for diffusion across an interface, Eq. 6.1.29, and also the general form from Eqs. 2.3.3 and 2.3.4. Therefore, all of the theory that we have developed for gas exchange across an interface is applicable to membrane diffusion.

6. A very simple model for active transport of Na^+ ions across a membrane is shown below, where the driving force for the transfer results from a H^+ gradient.[9] The key is the membrane soluble fatty acid that shuttles Na^+ and H^+ ions across the membrane in opposite directions. The

fatty acid is only soluble in the membrane. The reactions at the membrane surfaces are shown at right.



low $[Na^+]$ → high $[Na^+]$
low $[H^+]$ ← high $[H^+]$



The two forms of the fatty acid are HR and NaR. The reactions at the surfaces of the membrane are:

$$\text{Left:}\quad HR + Na^+(\text{left}) + OH^-(\text{left}) \xrightarrow{k_L} NaR + H_2O$$

$$\text{Right:}\quad \underline{NaR + H^+(\text{right}) \xrightarrow{k_R} HR + Na^+(\text{right})}$$

$$\text{Net:}\quad Na^+(\text{left}) + OH^-(\text{left}) + H^+(\text{right}) \rightarrow Na^+(\text{right}) + H_2O$$

The reactions don't occur within the membrane, so Eq. 6.1.26 applies just at each interface as a surface reaction. For the purposes of this problem, you can assume that the reactions are unidirectional. Assume that the solutions on the left and right are well mixed. Use Fick's Second Law to write the differential equations for the transport within the membrane. Indicate how you would find the steady-state for the fluxes. You don't need to solve the differential equations, but linear concentration gradients would be applicable at steady state if you did.

Answer: The rate of the reactions on the left-hand side are:

$$\upsilon_L = -\frac{d[HR]}{dt} = \frac{d[NaR]}{dt} = k_L\,[HR][Na^+(\text{left})][OH^-(\text{left})] \qquad (x = 0)$$

and for the right-hand side:

$$\upsilon_R = = -\frac{d[NaR]}{dt} = \frac{d[HR]}{dt} = k_R\,[NaR][H^+(\text{right})] \qquad (x = \delta)$$

at the left-hand interface using Eq. 6.1.26:

$$\left(\frac{\partial[HR]}{\partial t}\right)_x = D\left(\frac{\partial^2[HR]}{\partial x^2}\right)_t - k_L\,[HR][Na^+(\text{left})][OH^-] \qquad (x = 0)$$

$$\left(\frac{\partial[NaR]}{\partial t}\right)_x = D\left(\frac{\partial^2[NaR]}{\partial x^2}\right)_t + k_L\,[HR][Na^+(\text{left})][OH^-] \qquad (x = 0)$$

and at the right-hand interface:

$$\left(\frac{\partial[\mathrm{HR}]}{\partial t}\right)_x = D\left(\frac{\partial^2[\mathrm{HR}]}{\partial x^2}\right)_t + k_R\,[\mathrm{NaR}][\mathrm{H^+(right)}] \qquad (x = \delta)$$

$$\left(\frac{\partial[\mathrm{NaR}]}{\partial t}\right)_x = D\left(\frac{\partial^2[\mathrm{NaR}]}{\partial x^2}\right)_t - k_R\,[\mathrm{NaR}][\mathrm{H^+(right)}] \qquad (x = \delta)$$

and within the membrane with no chemical reactions:

$$\left(\frac{\partial[\mathrm{HR}]}{\partial t}\right)_x = D\left(\frac{\partial^2[\mathrm{HR}]}{\partial x^2}\right)_t \quad \text{and} \quad \left(\frac{\partial[\mathrm{NaR}]}{\partial t}\right)_x = D\left(\frac{\partial^2[\mathrm{NaR}]}{\partial x^2}\right)_t \qquad (0 < x < \delta)$$

For steady-state fluxes, the time derivatives in the six above equations would be set to zero.

Note that for a more realistic model, the chemical reactions at each interface should be reversible, which would add additional terms to the rate laws. At steady state for the fluxes, the reaction rate at both interfaces would be equal, $\upsilon_L = \upsilon_R$, which would help simplify the problem. Also note that H^+ gradients across membranes are used to drive many processes, including the primary events in photosynthesis.

7. Find the eigenvalue-eigenvector solution to the set of linear equations:

$$\begin{aligned} x + y \phantom{{}+z} &= 0 \\ x + y + z &= 0 \\ y + z &= 0 \end{aligned} \qquad \text{which give the coefficient matrix } \underset{\approx}{M} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix}$$

Calculate the eigenvalues by hand and the eigenvectors using *MatLab*, *MathCad*, *Maple*, or *Mathematica*. (For symmetric matrices, you can also use the "Matrix Diagonalization" applet on the textbook Web site and on the companion CD.) The *MatLab* command to use is [X,L] = eig(M), where X is the matrix of eigenvectors and L is the diagonal matrix of eigenvalues of the input matrix M.

Answer: Using the given coefficient matrix, the characteristic equation is:

$$(\underset{\approx}{M} - \lambda_i\, \underset{\approx}{I})\underset{\sim}{X_i} = \begin{pmatrix} 1-\lambda_i & 1 & 0 \\ 1 & 1-\lambda_i & 1 \\ 0 & 1 & 1-\lambda_i \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

This characteristic equation has the characteristic determinate $(\lambda - 1)(\lambda^2 - 2\lambda - 1) = 0$. The factor $(\lambda - 1) = 0$ gives the eigenvalue $\lambda = 1$. Solving the quadratic factor $(\lambda^2 - 2\lambda - 1) = 0$ gives the additional eigenvalues: $\lambda = -0.4142$ and 2.4142.

Here is the *MatLab* input (after the >>) and output:

```
>> M=[1,1,0;1,1,1;0,1,1]

  M =
       1     1     0
       1     1     1
       0     1     1

>> [X,L] =eig(M)
```

```
X =
    0.5000   -0.7071    0.5000
   -0.7071    0.0000    0.7071
    0.5000    0.7071    0.5000

L =
   -0.4142         0         0
         0    1.0000         0
         0         0    2.4142
```

Note that the L matrix lists the three eigenvalues along the diagonal. The X matrix lists the eigenvector as columns. The three sets of eigenvalues and eigenvectors are:

$$\lambda_1 = -0.4142 \qquad\qquad \lambda_2 = 1 \qquad\qquad \lambda_3 = 2.4142$$

$$\underset{\sim}{X}_1 = \begin{pmatrix} 0.5000 \\ -0.7071 \\ 0.5000 \end{pmatrix} \qquad \underset{\sim}{X}_2 = \begin{pmatrix} -0.7071 \\ 0 \\ 0.7071 \end{pmatrix} \qquad \underset{\sim}{X}_3 = \begin{pmatrix} 0.5000 \\ 0.7071 \\ 0.5000 \end{pmatrix}$$

To help you get used to eigenvectors, we can verify that $\underset{\sim}{X}_1$ is a valid solution. We need to prove that $\underset{\approx}{M}\underset{\sim}{X}_i = \lambda_i \underset{\sim}{X}_i$, for eigenvector 1:

$$\underset{\approx}{M}\underset{\sim}{X}_1 = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix}\begin{pmatrix} 0.5000 \\ -0.7071 \\ 0.5000 \end{pmatrix} = \begin{pmatrix} 1(0.5)+1(-0.7071)+0(0.5) \\ 1(0.5)+1(-0.7071)+1(0.5) \\ 0(0.5)+1(-0.7071)+1(0.5) \end{pmatrix} = \begin{pmatrix} -0.2071 \\ 0.2929 \\ -0.2071 \end{pmatrix} = -0.4142\ \underset{\sim}{X}_1$$

Notice that any constant multiple of the listed eigenvectors is also a solution, including the case where all the signs are reversed. Matrix techniques allow the solution of problems that would otherwise be exceedingly time consuming to solve.

8. A bi-exponential process is given by the form:

$$[A] = c_1\, e^{-k_1 t} + c_2\, e^{-k_2 t}$$

The logarithmic plot of a bi-exponential process produces two straight line segments and a transition region between. Bi-exponential decay curves are fit in two segments. First the long time behavior of the logarithmic plot is fit to a straight line to determine the slope, k_2, and intercept $\ln(c_2)$. The non-linear transition region is avoided when points are selected for this plot. Then, the long time behavior is "stripped" from the time course:

$$\ln[A]_{short} = \ln([A] - c_2\, e^{-k_2 t})$$

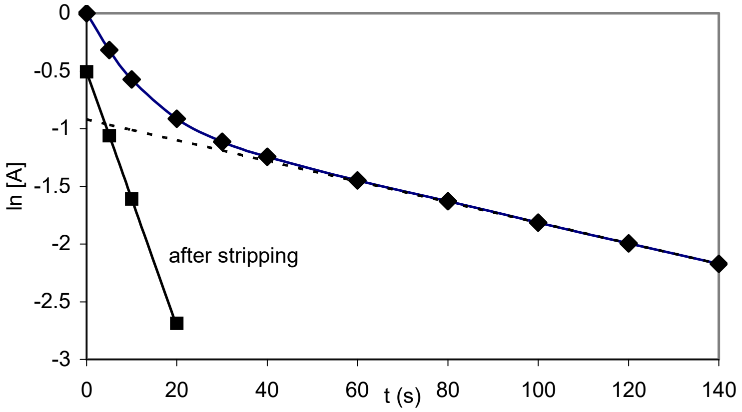
and a second logarithmic plot of the stripped data produces the short time k_1 and $\ln(c_1)$. These estimated constants are then used as guesses for non-linear curve fitting. Fit the following data to a bi-exponential function. For the non-linear fit, use the four-parameter version of the "Nonlinear Least Squares Curve Fit" applet on the textbook Web site and on the companion CD.

time	0	5	10	20	30	40	60	80	100	120	140
[A]	1	0.727	0.564	0.401	0.328	0.288	0.235	0.196	0.163	0.136	0.114

Answer: The spreadsheet to implement the stripping procedure is:

		original	original	stripped
time	[A]	ln [A]	ln [A]	ln([A]- $c_2$exp(k_2t))
0	1	0		-0.50777
5	0.727	-0.3188		-1.06062
10	0.564	-0.5727		-1.61001
20	0.401	-0.9138		-2.68794
30	0.328	-1.1147		
40	0.288	-1.2448		
60	0.235	-1.4482		
80	0.196	-1.6296		
100	0.163		-1.8140	
120	0.136		-1.995	
140	0.114		-2.1716	

The last few points are moved into a separate column so the curve fit can be done from the chart, directly. The stripped data is in the last column. The plot showing the stripped data is:



The linest() output for the long curve fit and the stripped, short-time curve fit are given below:

Long time fit				Short time fit after stripping			
slope	-0.00894	-0.9209	intercept	slope	-0.11022	-0.50834	intercept
±	6.7E-05	0.008109	±	±	0.000199	0.001288	±
r2	0.999944	0.001894	st.dev. y	r2	0.999997	0.001411	st.dev. y
F	17822.69	1	df	F	305307.4	1	df
ss$_{reg}$	0.063922	3.59E-06	ss$_{resid}$	ss$_{reg}$	0.607473	1.99E-06	ss$_{resid}$

The corresponding values for the constants are

$$c_2 = e^{-0.9209} = 0.3982 \qquad k_2 = 0.00894\ s^{-1}$$

$$c_1 = e^{-0.5083} = 0.6015 \qquad k_1 = 0.1102\ s^{-1}$$

www Using these fit values as guesses in the “Nonlinear Least Squares Curve Fit” applet with the “a exp(–bx) + c exp(–dx)” option and the above guesses gives:

```
===========   Results   ============
 a= 0.596731 +- 0.000631
 b= 0.111514 +- 0.00022
 c= 0.403231 +- 0.0006
 d= 0.0090422 +- 0.0000204
------------------------------------
 sum of squared residuals= 7.226e-7
 stand. dev. y values= 0.0003213
 correlation between a & b= -0.5727
```

```
correlation between b & c= 0.8166
correlation between a & c= -0.8726
correlation between c & d= 0.907
correlation between b & d= 0.6811
correlation between a & d= -0.8034
```

Notice that the correlation coefficient between c and d is high, but acceptible. If the long-time behavior were extended, the linear version of the fit could give good uncorrelated results for these parameters. Fitting bi-exponential curves is a difficult issue, and the corresponding fit coefficients are difficult to estimate accurately.

9. Draw the Chapman ozone mechanism, Section 5.2, as a box model.

Answer: The Chapman mechanism from Section 5.2 is comprised of four steps:

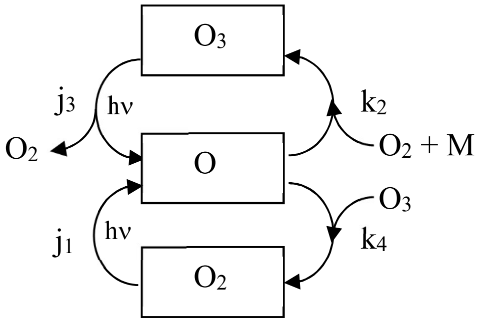
$$O_2 + h\nu \xrightarrow{j_1} 2\,{\bullet}O{\bullet}$$

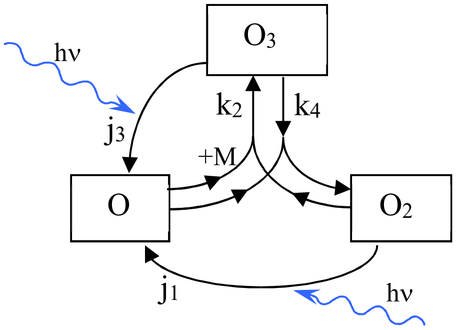
$${\bullet}O{\bullet} + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$O_3 + h\nu \xrightarrow{j_3} {\bullet}O{\bullet} + O_2$$

$${\bullet}O{\bullet} + O_3 \xrightarrow{k_4} 2\,O_2$$

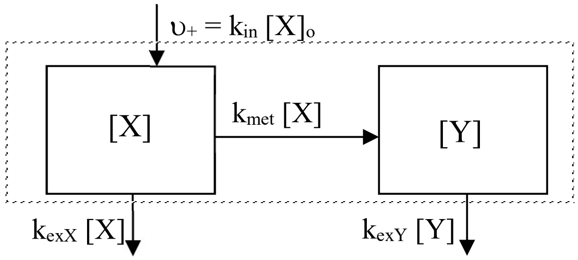
Common depictions of the Chapman model are:





Since steps 2 and 4 aren’t first order, the additional reactants must be shown with additional arrows, unlike purely first-order processes. There are many other possibilities, but all would have three boxes and at least four arrows that relate to the four elementary steps.

10. Would the residence time in the body for X be altered if an excretion pathway for Y was added to the model in Section 6.2, Figure 6.2.2? The added pathway is shown below.



Answer: The residence time for X would not be altered, because the new differential equation for X still does not involve the concentration for Y; Eq. 6.2.8 still holds:

$$\frac{d[X]}{dt} = k_{in}\,[X]_o - k_{ex}\,[X] - k_{met}\,[X]$$

Just as for any chemical reaction, the concentration of X does not depend on any unconnected "downstream" processes, if the mechanistic steps are uni-directional. However, if the metabolic process were reversible, then the concentration of X would depend on Y and the residence time would change (the effective rate of the metabolic removal would decrease).

11. Use *Maple* or *Mathematica* to solve for $X_1$and X_2 for the reversible two-box problem starting from the rate matrix, Eq. 6.3.3. Find the concentrations symbolically first. Then substitute in the specific constants: $k_1 = 0.3\ s^{-1}$, $k_{-1} = 0.15\ s^{-1}$, and $k_{ex} = 0.1\ s^{-1}$, with initial conditions $[X_1]_o = 1.0$ M and $[X_2]_o = 0$. Solve for the concentrations at t = 1 s. Note that in general Eqs. 6.3.8, 6.3.9, and 6.3.28 can be combined into:

$$\underset{\sim}{[X]} = \underset{\sim}{C}\,(\exp \underset{\sim}{\Lambda} t)\,\underset{\sim}{C}^{-1}\underset{\sim}{[X]}_o$$

where exp $\underset{\sim}{\Lambda}$t is the matrix with the exponential terms along the diagonal:

$$\exp \underset{\sim}{\Lambda} t = \begin{bmatrix} e^{\lambda_1 t} & 0 & 0 & \dots \\ 0 & e^{\lambda_2 t} & 0 & \dots \\ 0 & 0 & e^{\lambda_3 t} & \dots \\ \dots & \dots & \dots & \end{bmatrix}$$

Let K be the rate matrix, L be the vector of eigenvalues, C be the matrix of eigenvectors, and E be the diagonal matrix, exp $\underset{\sim}{\Lambda}$t. The set of initial conditions is given by the vector X_o. After defining the rate matrix, K, and initial values vector, X_o, the Maple commands to do these calculations symbolically are:

```
(L,C) := Eigenvectors(K) ;
E := DiagonalMatrix(Map(exp,L*t)) ;
X := C.E.MatrixInverse(C).Xo ;
```

Answer: The *Maple* input is:

```
with(LinearAlgebra) ;
K := Matrix([[ –kex–k1 , k-1 ], [ k1 ,–k-1 ]]) ;
Xo := Vector([1,0]) ;
(L,C) := Eigenvectors(K) ;
E := DiagonalMatrix(Map(exp,L*t)) ;
X := C.E.MatrixInverse(C).Xo ;
```

k_{ex} := 0.1 ;
k_1 := 0.3 ;
k_{-1} := 0.15 ;
t := 1.0 ;
eval(X) ;

which gives:

$$\begin{bmatrix} 0.68597 \\ 0.21308 \end{bmatrix}$$

The advantage of determining the result symbolically is that the concentrations can easily be calculated at any time. A finite difference numerical solution would need to start at t = 0 and integrate up to the desired time. The symbolic result is also exact.

12. Use *MatLab* to solve the two-box model in Figure 6.3.1 and Eq. 6.3.3. Plot [X_1] and [X_2] for t = 0 – 30 s. See Problem 11 for a hint on how to compactly write the solution. The corresponding *MatLab* commands are in the form:

```
[C,L] = eig(K) ;
```

to determine the eigenvalues, L, and eigenvectors, C. Then at time t, the vector of concentrations is given by:

```
E = diag(exp(diag(L)*t)) ;
X = C*E*inv(C)*X0 ;
```

[Note: You can create a matrix with concentrations as the rows and the time points indexed along the columns by using:

```
X(:,t+1) = C*E*inv(C)*X0 ;
```

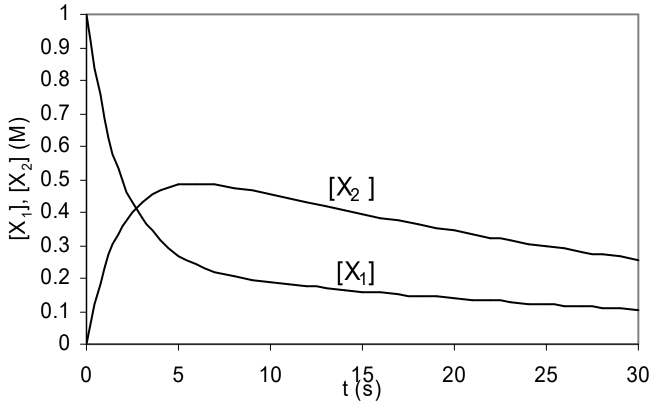
which makes plotting easier. The t values would be successive integers, so they can be used as array indices. The t+1 is necessary because we want to evaluate the concentrations at t = 0, but *MatLab* indexes vectors and matrices starting at 1.]

Answer: The MatLab –m file is:

```
kex = 0.1 ;
kf1 = 0.3 ;
kr1 = 0.15 ;
X0 = [1;0] ;
tmax = 30 ;

K(1,1) = -kex-kf1 ;
K(1,2) = kr1 ;
K(2,1) = kf1 ;
K(2,2) = -kr1 ;

[C,L] = eig(K) ;
```

```
for t = 0:1:tmax
    T(t+1) = t ;
    E = diag(exp(diag(L)*t)) ;
    X(:,t+1) = C*E*inv(C)*X0 ;
end

% Plot data
figure(1)
plot(T,X)
xlabel('Time (s)')
ylabel('[X1],[X2] (M)')
```

The plot is given below:



13. Use *Maple* or *Mathematica* to symbolically verify the solution to the reversible two-box problem, Eqs. 6.3.24-6.3.26, and also find the time course for X_2.

Answer: Refer to Example 6.3.3. Let K be the rate matrix, L be the vector of eigenvalues, and C be the matrix of eigenvectors with each eigenvector corresponding to a column. The set of initial conditions is given by the vector X_o and A is the vector of the α values. The *Maple* input is:

```
with(LinearAlgebra) ;
K := Matrix([[ –kex–k1,k-1], [ k1,–k-1]]) ;
Xo := Vector([1,0]) ;
(L,C) := Eigenvectors(K) ;
A := MatrixInverse(C).Xo ;
A[1] ·C[1..2,1] ;
A[2] ·C[1..2,2] ;
```

The eigenvectors are listed as:

$$\begin{bmatrix} -\tfrac{1}{2}k_{-1}-\tfrac{1}{2}k_{ex}-\tfrac{1}{2}k_1+\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \\ -\tfrac{1}{2}k_{-1}-\tfrac{1}{2}k_{ex}-\tfrac{1}{2}k_1-\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \end{bmatrix} = \begin{bmatrix} \lambda_1 \\ \lambda_2 \end{bmatrix} \qquad 1$$

The results for *A[1] ·C[1..2,1]* corresponding to the first eigenvalue, λ_1 :

$$\left(\frac{\left(-k_{-1}+k_{ex}+k_1+\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2}\right)\left(k_{-1}-k_{ex}-k_1+\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2}\right)X_o}{k_1\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2}}\right)\cdot$$

$$\begin{bmatrix} \frac{-1}{4}\,\frac{k_1}{-\frac{1}{2}k_{-1}+\frac{1}{2}k_{ex}+\frac{1}{2}k_1+\frac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2}} \\ \frac{-1}{4} \end{bmatrix} \tag{2}$$

This result can be simplified by noticing that:

$$\lambda_1-\lambda_2=\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \tag{3}$$

$$k_{-1}+\lambda_1=\tfrac{1}{2}k_{-1}-\tfrac{1}{2}k_{ex}-\tfrac{1}{2}k_1+\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \tag{4}$$

$$k_{-1}+\lambda_2=\tfrac{1}{2}k_{-1}-\tfrac{1}{2}k_{ex}-\tfrac{1}{2}k_1-\tfrac{1}{2}\sqrt{k_{-1}^2-2k_{-1}k_{ex}+2k_{-1}k_1+k_{ex}^2+2k_{ex}k_1+k_1^2} \tag{5}$$

Substitution of Eqs. 3-5 into Eq. 2 gives:

$$\begin{bmatrix} \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)\,k_{-1}}{-(k_{-1}+\lambda_2)\,k_{-1}\,(\lambda_1-\lambda_2)}X_o \\[2ex] \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix} = \begin{bmatrix} \frac{(k_{-1}+\lambda_1)}{(\lambda_1-\lambda_2)}X_o \\[2ex] \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}$$

Similarly for *A[2] ·C[1..2,2]* corresponding to the second eigenvalue, λ_2 :

$$\begin{bmatrix} \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)\,k_{-1}}{-(k_{-1}+\lambda_1)\,k_{-1}\,(\lambda_1-\lambda_2)}X_o \\[2ex] \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix} = \begin{bmatrix} -\frac{(k_{-1}+\lambda_2)}{(\lambda_1-\lambda_2)}X_o \\[2ex] \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix}$$

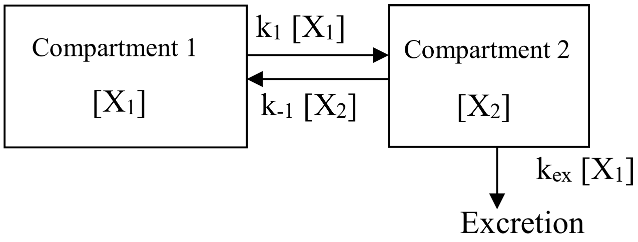
The final time profiles are:

$$\begin{array}{cc} \textit{coefficients for1st eigenvalue} & \textit{coefficients for2nd eigenvalue} \\ A[1]\cdot C[1..2,1]= & A[2]\cdot C[1..2,2]= \\ \begin{bmatrix} \frac{(k_{-1}+\lambda_1)}{(\lambda_1-\lambda_2)}X_o \\[2ex] \frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix} & \begin{bmatrix} -\frac{(k_{-1}+\lambda_2)}{(\lambda_1-\lambda_2)}X_o \\[2ex] \frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o \end{bmatrix} \\ \downarrow & \downarrow \end{array}$$

$$[X_1]=\frac{(k_{-1}+\lambda_1)}{(\lambda_1-\lambda_2)}X_o\ e^{-\lambda_1 t}\ -\ \frac{(k_{-1}+\lambda_2)}{(\lambda_1-\lambda_2)}X_o\ e^{-\lambda_2 t}$$

$$[X_2]=\frac{-(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o\,e^{-\lambda_1 t}+\frac{(k_{-1}+\lambda_2)(k_{-1}+\lambda_1)}{k_{-1}\,(\lambda_1-\lambda_2)}X_o\,e^{-\lambda_2 t}$$

14. The box model below corresponds to a reversible first-step mechanism, as in Section 4.1, with all first-order processes. Determine the eigenvalues and time constants. Compare the results with the model in Figure 6.3.1 and Eq. 6.3.3.



Answer: The rate laws for this model are:

$$\upsilon_1 = \frac{d[X_1]}{dt} = -k_1\,[X_1] + k_{-1}\,[X_2] \qquad 1$$

$$\upsilon_2 = \frac{d[X_2]}{dt} = k_1\,[X_1] - k_{-1}\,[X_2] - k_{ex}\,[X_1] \qquad 2$$

The rate matrix is:

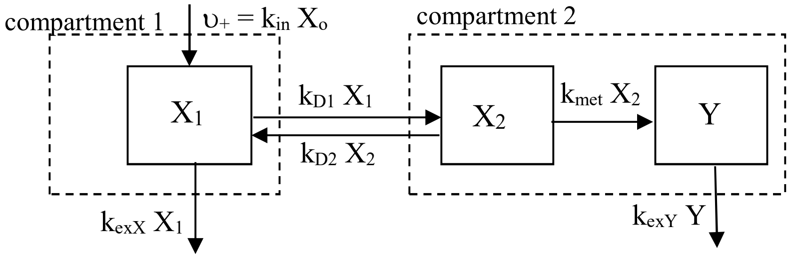
$$\underset{\approx}{K} = \begin{pmatrix} -k_1 & k_{-1} \\ k_1 & -(k_{-1} + k_{ex}) \end{pmatrix} \qquad 3$$

Using Eq. 6.3.23 gives the eigenvalues as:

$$\lambda_i = \frac{-(k_1 + k_{-1} + k_{ex}) \pm \sqrt{(-k_1 + k_{-1} + k_{ex})^2 + 4\,k_1\,k_{-1}}}{2} \qquad 4$$

The result is similar to, but not identical to, Eq. 6.3.24. For the same constant values as Example 6.3.1, the eigenvalues in this case are: $\lambda_i = -0.4886, -0.0614$.

15. The model in Section 6.2, Figure 6.2.2, considers the metabolic elimination of a drug in parallel with excretion. Since the liver is often the site for metabolic processes, this model would be more realistic if the drug is first transported by the blood plasma (bulk flow) to the liver where the drug is metabolized and excreted. (Compounds can be excreted from the liver in the bile.) The added pathways are shown below, including a constant flow input.



(a). Set up the differential equations for this model and write the rate matrix. (b). Find the relationship between k_{D1} and k_{D2}. The typical plasma volume of a 70 kg person is 3 L, and the volume of extracellular fluids, excluding plasma, is 12 L. The total body water is about 42 L, so most of the water volume is in the cellular cytoplasm, which is about 80% water. Assume compartment 1 is the blood plasma and compartment 2 is the liver. Assume the effective volume for this process in the liver is 0.5 L.

Answer: (a). Because this model uses more than one spatial compartment and mass transfer is occurring, the differential equations should be written in terms of moles instead of concentrations, for each process for consistency.
The rate laws are:

$$\frac{dX_o}{dt} = 0 \qquad\qquad (X_o \text{ is a constant flow input})$$

$$\frac{dX_1}{dt} = k_{in}X_o - k_{exX}\, X_1 - k_{D1}\, X_1 + k_{D2}\, X_2$$

$$\frac{dX_2}{dt} = k_{D1}\, X_1 - k_{D2}\, X_2 - k_{met}\, X_2$$

$$\frac{dY}{dt} = k_{met}\, X_2 - k_{exY}\, Y$$

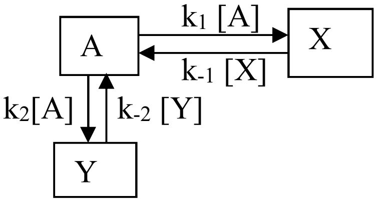
The rate matrix is given below with the rows and columns labeled to help you see the relationships:

$$\underset{\approx}{K} = \begin{array}{c@{}c} \begin{array}{cccc} X_o & X_1 & X_2 & Y \\ \downarrow & \downarrow & \downarrow & \downarrow \end{array} & \\ \begin{pmatrix} 0 & 0 & 0 & 0 \\ k_{in} & -k_{exX}-k_{D1} & k_{D2} & 0 \\ 0 & k_{D1} & -k_{D2}-k_{met} & 0 \\ 0 & 0 & k_{met} & -k_{exY} \end{pmatrix} & \begin{array}{l} \leftarrow dX_o/dt \\ \leftarrow dX_1/dt \\ \leftarrow dX_2/dt \\ \leftarrow dY/dt \end{array} \end{array}$$

The time course for this problem would be determined by numerical simulation.
(b). The ratio of the mass transport coefficients is given by Eq. 6.1.46: $k_{D2}/k_{D1} = V_1/V_2 = 3\,/0.5$.

This general model has many applications. For example, in atmospheric environmental chemistry, compartment 1 could be the gaseous atmosphere and compartment 2 an aerosol droplet where a reaction occurs. One specific example is the conversion of NaCl particles to $NaHSO_4$ (aq) by reaction with sulfuric acid. Another example is the reaction of dimethyl sulfide produced by bacteria in the ocean with ozone or hydroxyl radical in cloud droplets or on particle surfaces.

16. Show that the kinetic versus thermodynamic control mechanism in Example 4.1.2 gives two exponential time constants. Calculate the time constants using the rate constants given in Example 4.1.2, namely: $k_1 = 0.020\ s^{-1}$, $k_{-1} = 0.00050\ s^{-1}$, $k_2 = 0.50\ s^{-1}$, and $k_{-2} = 1.50\ s^{-1}$. The corresponding box model is shown below.



Answer: The rate matrix is:

$$\underset{\approx}{K} = \begin{pmatrix} -k_{-1}-k_{-2} & k_{-1} & k_{-2} \\ k_1 & -k_{-1} & 0 \\ k_2 & 0 & -k_{-2} \end{pmatrix}$$

The secular equation is:

$$(\underset{\approx}{M} - \lambda_i \underset{\approx}{I})\underset{\sim}{X_i} = 0 = \begin{pmatrix} -k_{-1}-k_{-2}-\lambda_i & k_{-1} & k_{-2} \\ k_1 & -k_{-1}-\lambda_i & 0 \\ k_2 & 0 & -k_{-2}-\lambda_i \end{pmatrix})$$

Expanding the determinant in terms of the first column gives:

$$(-k_{-1}-k_{-2}-\lambda_i)(-k_{-1}-\lambda_i)(-k_{-2}-\lambda_i) - k_1 k_{-1}(-k_{-2}-\lambda_i) - k_2 k_{-2}(-k_{-1}-\lambda_i) = 0$$

The multiplications give:

$$-\lambda_i^3 - \lambda_i^2(k_1 + k_2 + k_{-1} + k_{-2}) - \lambda_i(k_1k_{-2} + k_{-1}k_2 + k_{-1}k_{-2}) = 0$$

Since there is a common factor of λ_i, one of the eigenvalues is zero. A zero eigenvalue is expected because all the processes are reversible (℘ *7* point 14). Dividing the characteristic polynomial by $-\lambda_i$ gives:

$$\lambda_i^2 + \lambda_i(k_1 + k_2 + k_{-1} + k_{-2}) + (k_1k_{-2} + k_{-1}k_2 + k_{-1}k_{-2}) = 0$$

This equation can then be solved using the quadratic equation using Excel:

k_{f1}	0.02	s^{-1}
k_{r1}	0.0005	s^{-1}
k_{f2}	0.5	s^{-1}
k_{r2}	1.5	s^{-1}
a=	1	
b=	2.0205	
c=	0.031	
lamda(+)=	-0.015461	s^{-1}
lamda(-)=	-2.005039	s^{-1}
$\tau_1 = 1/\lambda 1$	64.6786759	s
$\tau_2 = 1/\lambda 2$	0.49874343	s

The listed a, b, and c cells are the normal coefficients for $ax^2 + bx + c = 0$. Notice that the two time constants differ by over two-orders of magnitude. That is the reason for the very quick rise and comparatively slow decay in Figure 4.1.2.

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Chapter 7 Problems: Heat and Work

1. The movie "On Golden Pond" (IPC Films, 1982, 3 Academy Awards) was based on a play that was written about a summer home on Great Pond in central Maine. The surface area of Great Pond is $3.383\text{x}10^7\ \text{m}^2$ and the volume is $2.130\text{x}10^8\ \text{m}^3$. Great Pond is a large lake. The solar insolation for the Boston area is given in Chapter 2, Problem 13 as $4.16\ \text{kWh m}^{-2}\ \text{day}^{-1}$. Calculate the total energy received by the lake per day on average and the corresponding change in temperature.

Answer: From Chapter 2 Problem 12 the conversion factor is given as:

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

The total energy received by the lake on an average day is given by:

$$q = JA\Delta t$$
$$= 4.16\ \text{kWh m}^{-2}\ \text{day}^{-1}(3.6\text{x}10^6\ \text{J}/1\ \text{kWh})(3.383\text{x}10^7\ \text{m}^2)(1\ \text{day}) = 5.066\text{x}10^{14}\ \text{J}$$

The molar heat capacity of water is $75.291\ \text{J K}^{-1}\ \text{mol}^{-1}$, Table 7.2.2. The specific heat capacity of water is:

$$C_s(H_2O) = C_{p,m}(H_2O)/\mathfrak{M}_{H_2O} = 75.291\ \text{J K}^{-1}\ \text{mol}^{-1}\ (1\ \text{mol}/18.02\ \text{g}) = 4.178\ \text{J K}^{-1}\ \text{g}^{-1}$$

The density of water at 20.0°C, Table 2.2.1, is $0.9982\ \text{g mL}^{-1}$, giving the heat capacity of the lake as:

$$C_p = (4.178\ \text{J K}^{-1}\ \text{g}^{-1})(2.130\text{x}10^8\ \text{m}^3)(0.9982\ \text{g mL}^{-1})(1\text{x}10^6\text{mL}/1\ \text{m}^3) = 8.902\text{x}10^{14}\ \text{J K}^{-1}$$

The corresponding change in temperature is obtained from $q_p = C_p\ \Delta T$:

$$\Delta T = q_p/C_p = 5.066\text{x}10^{14}\ \text{J}/8.902\text{x}10^{14}\ \text{J K}^{-1} = 0.57\ \text{K}$$

As the temperature of the lake rises, there will be significant loss of energy by radiation, convection at higher winds speeds, and evaporation. These losses will moderate the temperature rise. The predominant energy loss mechanism is radiative loss.

2. The specific heat capacity of stainless steel is $0.505\ \text{J K}^{-1}\ \text{g}^{-1}$. A typical spoon weighs 20.9 g. Calculate the change in temperature when you place a spoon at 21.5 °C into 250. mL of hot coffee at 58.5° C. Assume the heat capacity of coffee is $4.179\ \text{J K}^{-1}\ \text{g}^{-1}$ and the density is the density of water at 50°C from Table 2.2.1.

Answer: This problem is very similar to Example 7.2.1. The plan is to use the fact that: $q_{coffee} = -\ q_{spoon}$. The heat capacities are constant pressure heat capacities since the system is open to the atmosphere. The density of water at 50.0°C, Table 2.2.1, is $0.9880\ \text{g mL}^{-1}$.

The mass of the coffee solution is $w_{coffee} = d_{H_2O}\ V_{coffee} = 0.9880\ \text{g mL}^{-1}\ (250.0\ \text{mL}) = 247.0\ \text{g}$. The energy transfered as heat to the spoon is given by:

$$q_{spoon} = w_{spoon}\ C_s(\text{spoon})(T_2 - T_{1,spoon})$$

The energy transferred as heat from the coffee is:

$$q_{coffee} = w_{coffee}\, C_s(coffee)(T_2 - T_{1,coffee})$$

Using $q_{coffee} = - q_{spoon}$ gives:

$$w_{coffee}C_s(coffee)(T_2 - T_{1,coffee}) = - w_{spoon}\, C_s(spoon)(T_2 - T_{1,spoon})$$

Solving for T_2 gives:

$$247.0\ g(4.179\ J\ K^{-1}\ g^{-1})(T_2 - 58.5°C) = - 20.9\ g(0.505\ J\ K^{-1}\ g^{-1})(T_2 - 21.5°C)$$
$$1032.2\ T_2 - 60384. = -10.555\ T_2 + 227.$$
$$1042.\ 8\ T_2 = 60611.$$
$$T_2 = 58.13\ °C$$

The change in temperature of the coffee is only $\Delta T = -0.4$ °C. The result has only one significant figure since $\Delta T = 58.13\ °C - 58.5\ °C = -0.4\ °C$.

3. Calculate the work done as a gas expands from an initial volume of 1.00 L to a final volume of 10.00 L against a constant external pressure of 1.000 atm.

Answer: We need to convert to pascals and m^3 to find the work in joules. The conversions are:

$$1.000\ atm = 1.01325x10^5\ Pa \qquad \text{and} \qquad 1.00\ L = 1.00x10^{-3}\ m^3$$

Giving the work against a constant external pressure as:

$$w = -P_{ext}\, \Delta V = -(1.01325x10^5\ Pa)(9.00x10^{-3}\ m^3) = -912.\ J$$

The work is negative because the system loses energy pushing against the external pressure.

4. Calculate the work done by one mole of an ideal gas in a reversible isothermal expansion from an initial volume of 1.00 L to a final volume of 10.00 L at 298.2 K. Compare the work done to the constant pressure expansion given in Problem 3.

Answer: For a reversible isothermal expansion the work is given by Eq. 7.3.6°:

$$w = - nRT\ \ln\left(\frac{V_2}{V_1}\right) = - 1.00\ mol(8.314\ J\ K^{-1}\ mol^{-1})(298.15\ K)\ \ln\left(\frac{10.00}{1.00}\right) = -5708.\ J$$
$$= -5.71\ kJ$$

Reversible expansions do the maximum amount of work, in magnitude, for the given initial and final states of the system. The magnitude of the work for a reversible expansion is maximal because the system pressure is equal to the external opposing pressure, $P = P_{ext}$, so the system always pushes against the maximum external pressure.

5. Calculate the work done by one mole of an ideal gas in a reversible isothermal expansion from an initial pressure of 10.00 bar to a final pressure of 1.00 bar at 298.2 K. Compare the work done to the isothermal reversible expansion in Problem 4.

Answer: For an isothermal process in an ideal gas $P_1V_1 = P_2V_2$ or:

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Substitution into Eq. 7.3.6° gives:

$$w = -\,nRT\ln\left(\frac{V_2}{V_1}\right) = -\,nRT\ln\left(\frac{P_1}{P_2}\right)$$

$$= -\,1.00\text{ mol}(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})\ln\left(\frac{10.00}{1.00}\right) = -5708.\text{ J}$$

$$= -5.71\text{ kJ}$$

Comparing to Problem 4, if the volume increases by a factor of 10 for an isothermal expansion, the pressure will drop by a factor of 10. So this problem and Problem 4 are the same problem. This expansion is reversible, so the system does maximum work for the given initial and final states.

6. How ideal is water vapor? To answer this question, try the following problem: Assume a volume for a closed flask of 10.000 L, a temperature of 298.15K, and 0.01280 moles of water vapor. Calculate the pressure of water vapor in the flask using the ideal gas law and the Van der Waals equation of state and compare. (For comparison with the results of this problem, note that the vapor pressure of water at 298K is P_{vap}= 23.8 torr.)

Answer: From the Van der Waals equation, Eq. 7.5.1:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \qquad \text{as compared to the ideal gas} \quad P = nRT/V$$

with a = 5.536 bar L^2 mol^{-2} and b = 0.03049 L mol^{-1}, Table 7.5.1. The Van der Waals result is:

$$P = \frac{0.01280\text{ mol}(0.0831447\text{ bar L K}^{-1}\text{ mol}^{-1})(298.15\text{ K})}{10.0\text{ L} - 0.01280\text{ mol }(0.03049\text{ L mol}^{-1})} - \frac{5.536\text{ bar L}^2\text{ mol}^{-2}(0.01280\text{ mol})^2}{10.0^2}$$

$$P = 0.031732 - 9.07\times10^{-6}\text{ bar} = 0.031723\text{ bar}$$

or $$P = 0.031308\text{ atm} = 23.794\text{ torr}$$

The ideal gas result is:

$$P = \frac{0.01280\text{ mol}(0.0831447\text{ bar L K}^{-1}\text{ mol}^{-1})(298.15\text{ K})}{10.000\times10^{-3}\text{m}^3} = 0.031731\text{ bar}$$

$$P = 0.031316\text{ atm} = 23.800\text{ torr}$$

Water vapor at its equilibrium vapor pressure at room temperature is well described by the ideal gas law.

7. Find the formula for the work done in the reversible isothermal expansion of a Van der Waals gas. (i.e. derive the equation corresponding to the ideal gas result: $w = -\,nRT \ln(V_2/V_1)$)

Answer: For a reversible process $P = P_{ext}$ and then $w = -\int P\,dV$. From the Van der Waals equation, Eq. 7.5.1:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

which upon substitution into the formula for the work gives:

$$w = -\int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) dV$$

$$w = -\int_{V_1}^{V_2} \left(\frac{nRT}{V - nb}\right) dV + \int_{V_1}^{V_2} \frac{an^2}{V^2}\, dV$$

$$w = -\,nRT\,(\ln(V - nb))\Big|_{V_1}^{V_2} - \frac{an^2}{V}\Big|_{V_1}^{V_2}$$

$$w = -\,nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Notice the effect of the second term. The Van der Waals a-coefficient is proportional to the average intermolecular forces that exist between gas molecules. For an expansion, V_2 is bigger than V_1 making $(1/V_2 - 1/V_1) < 0$. The overall sign of the second term is then positive. The resulting work done will be less than an ideal gas expansion, since the intermolecular force term is opposite in sign to the main work term. One way of thinking about this effect is that some energy goes into separating the gas molecules against their intermolecular forces, thus decreasing the work that can be done by the gas.

8. Derive the relationships between the second and third virial coefficients and the Van der Waals coefficients, as listed in Eqs. 7.5.9. Assume that the virial equation is truncated after the cubic term. [Hint: use the Taylor series approximation that for small x: $1/(1 - x) \approx 1 + x + x^2$]

Answer: The plan is to rearrange the Van der Waals equation to find z and then arrange this expression into a power series in (n/V).

Starting with Eqs. 7.5.1 and solving for P gives:

$$P = \frac{nRT}{V - nb} - \left(a\,\frac{n^2}{V^2}\right)$$

Next solving for z by multiplying by (V/nRT) gives:

$$z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{a}{RT}\left(\frac{n}{V}\right)$$

$$z = \frac{1}{\left(1 - b\left(\frac{n}{V}\right)\right)} - \frac{a}{RT}\left(\frac{n}{V}\right)$$

The last term is already in the form expected for a term in a power series expansion. However, the first term is not. Using the Taylor series approximation, $1/(1 - x) \approx 1 + x + x^2$, for the first term gives:

$$z = 1 + b\left(\frac{n}{V}\right) + b^2\left(\frac{n}{V}\right)^2 - \frac{a}{RT}\left(\frac{n}{V}\right)$$

Gathering the terms in (n/V) and comparing this result to the virial expansion, Eq. 7.5.7, gives:

$$z = 1 + \left(b - \frac{a}{RT}\right)\left(\frac{n}{V}\right) + b^2\left(\frac{n}{V}\right)^2$$

$$z = 1 + B\left(\frac{n}{V}\right) + C\left(\frac{n}{V}\right)^2 \qquad (7.5.7)$$

$$B = b - \frac{a}{RT} \quad \text{and} \quad C = b^2$$

At this level of approximation, we see clearly why B is a function of temperature.

9. Show that the Van der Waals equation is a cubic equation in the volume. In other words, rearrange the Van der Waals equation to give a cubic polynomial in V.

Answer: Starting with Eq. 7.5.1, multiply both sides of the equation by V^2 and then take the product of the pressure and volume terms:

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT \qquad 7.5.1$$

$$(PV^2 + an^2)(V - nb) = nRT\, V^2$$

$$PV^3 + an^2V - nbPV^2 - abn^3 = nRT\, V^2$$

$$PV^3 - (nbP + nRT)V^2 + an^2V - abn^3 = 0$$

Luckily, we can usually avoid having to solve this equation for V. The cubic form explains the shape of the isotherms at temperatures below the critical point in Figure 7.5.3.

10. Use the virial equation to find the compressibility factor and the pressure for 10.00 mol of O_2 contained in a 1.000 L vessel at 298.15 K. Do attractive or repulsive forces dominate?

Answer: Using the virial expansion, Eq. 7.5.7 and the coefficients from Table 7.5.4 gives:

$$z = 1 + B(T)\left(\frac{n}{V}\right) + C(T)\left(\frac{n}{V}\right)^2$$

$$= 1 + (-0.0161 \text{ L mol}^{-1})\left(\frac{10.00 \text{ mol}}{1.000 \text{ L}}\right) + (0.001200 \text{ L}^2\text{mol}^{-2})\left(\frac{10.00 \text{ mol}}{1.000 \text{ L}}\right)^2$$
$$= 1 - 0.161 + 0.1200 = 0.959$$

Since $z < 1$, attractive forces dominate. Using $PV = z\,nRT$ gives:

$$P = z\,nRT/V = 0.959(10.00 \text{ mol})(0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/1.000 \text{ L} = 238. \text{ bar}$$

which is a factor of (1 – 0.959) or 4.1% less than the ideal value.

11. Integrate Eq. 7.6.9 for a small change in pressure during an isothermal process; that is, integrate $dV = -V\,\kappa_T\,dP$.

Answer: Integrating from V_o, P_o to V, P gives:

$$\int_{V_o}^{V} dV = -\int_{P_o}^{P} V\,\kappa_T\,dP$$

For small changes in pressure we can approximate the volume in the integrand as $V \approx V_o$. Then the factor of ($V_o\,\kappa_T$) is a constant, which factor out of the integral to give:

$$V - V_o = -\int_{P_o}^{P} V_o\,\kappa_T\,dP = -V_o\,\kappa_T\,(P - P_o)$$

or succinctly as $\Delta V = -V_o\,\kappa_T\,\Delta P$. We can also solve for the final volume as:

$$V = V_o - V_o\,\kappa_T\,(P - P_o)$$

12. If the isothermal compressibility of acetone is $111.\text{x}10^{-6}$ atm^{-1} at 14.2°C, what is the change in volume if the pressure is increased from 10.0 atm to 35.0 atm? Assume an initial volume of 1.00 L, the ΔP is small so that $V \approx V_o$, and the isothermal compressibility is constant.

Answer: From Eq. 7.6.9, for a constant temperature:

$$dV = -V\,\kappa_T\,dP$$

Assuming a small enough temperature change to give $V \approx V_o$ and a constant isothermal compressibility gives:

$$\Delta V = V_o\,\kappa_T\,\Delta P$$
$$= -(1.00 \text{ L})(111.\text{x}10^{-6} \text{ atm}^{-1})(35.0 - 10.0 \text{ atm}) = -2.78\text{x}10^{-3} \text{ L}$$
$$= -2.78 \text{ mL}$$

13. From the definition of κ_T prove that for moderate changes in pressure:

$$V = V_o - V_o\,\kappa_T\,(P - P_o) + \frac{V_o\,\kappa_T^2}{2}(P - P_o)^2.$$

Answer: Integrating from V_o, P_o to V, P gives:

$$\int_{V_o}^{V} dV = -\int_{P_o}^{P} V\,\kappa_T\,dP$$

For moderate changes in pressure we can approximate the volume in the integrand using the result of Problem 11 as $V = V_o - V_o\,\kappa_T\,(P - P_o)$. The integral is then:

$$\begin{aligned} V - V_o &= -\int_{P_o}^{P} [\,V_o - V_o\,\kappa_T\,(P - P_o)]\,\kappa_T\,dP \\ &= -\int_{P_o}^{P} V_o\,\kappa_T\,dP + \int_{P_o}^{P} V_o\,\kappa_T^2\,(P - P_o)\,dP \end{aligned}$$

Then the factors of $(V_o\,\kappa_T)$ and $(V_o\,\kappa_T^2)$ are constants, which factor out of the integrals to give:

$$V - V_o = -V_o\,\kappa_T\,(P - P_o) + \frac{V_o\,\kappa_T^2}{2}\,(P - P_o)^2\Big|_{P_o}^{P}$$

$$V - V_o = -V_o\,\kappa_T\,(P - P_o) + \frac{V_o\,\kappa_T^2}{2}\,(P - P_o)^2$$

<u>14</u>. Find the relationship between $\left(\frac{\partial T}{\partial P}\right)_V$ and α and κ_T. Use the Euler chain relationship in your proof.

Answer: Noting that $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, neither derivative is taken at constant volume. The key to finding the relationship is to focus on the constant volume constraint. For a constant volume process the total differential of the volume is zero; from Eq. 7.6.7:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = 0 \qquad 1$$

Subtracting the pressure dependent term from both sides of the equation gives:

$$\left(\frac{\partial V}{\partial T}\right)_P dT = -\left(\frac{\partial V}{\partial P}\right)_T dP \qquad 2$$

We can then solve for the differential of the temperature:

$$dT = \frac{-\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P}\,dP \qquad 3$$

To find the partial derivative $(\partial T/\partial P)_V$ "divide" by dP and specify constant volume conditions:

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{-\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_P} \qquad 4$$

We can relate these partial derivatives to α and κ_T by dividing the numerator and denominator of this expression by the volume:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{\kappa_T}{\alpha} \qquad 5$$

The result is that the behavior of the system can be expressed as a function of only α and κ_T.

15. Calculate the expansion work done by 1.00 L of water when the temperature is raised by 100.0°C. Assume the pressure is constant at 1.00 bar. This problem is an important issue when considering upwelling in the ocean.[1] The effect is small on the laboratory scale, but important on an oceanic scale.

Answer: The plan is to use Eq. 7.6.29 and the value of the thermal expansion coefficient from Table 7.6.1. We need to be careful about units, to get joules we need to work with volume in m^3 and pressures in Pa, 1 bar = 1×10^5 Pa:

$$w = -PV_o\, \alpha\, \Delta T = -(1.00\times10^5\ \text{Pa})(1.00\ \text{L})(1\ \text{m}^3/1000\ \text{L})(2.57\times10^{-4}\ \text{K}^{-1})(100.0\ \text{K})$$
$$= -2.57\ \text{J}$$

In the laboratory, we can neglect the work of expansion of liquids and solids under most circumstances.

16. The upwelling of deep-sea water is caused by large scale ocean currents such as the Atlantic current, which brings warm water north in the Atlantic. This current keeps western Europe warmer than other areas at similar latitude. As a packet of water rises, the pressure drops, the volume of the packet expands and the system does work.[1] The work is given by:
$\text{đ}w = PV\kappa_T\, dP$ at constant temperature. Derive this relationship.

Answer: The work is given by $\text{đ}w = -P_{ext}\, dV$. A packet of water is surrounded by and is in contact with its surroundings so that $P = -P_{ext}$, where P_{ext} is the pressure at the given depth for the packet of water. The process is reversible. The change in volume with pressure at constant temperature is given by the definition of the isothermal compressibility, Eq. 7.6.9 and Eq. 7.6.10:

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{with } dV = V\,\alpha\, dT - V\,\kappa_T\, dP$$

For constant temperature this last equation reduces to:

$$dV = - V\,\kappa_T\,dP \qquad \text{(cst. T)}$$

Substituting this last equation into the general equation for the work of the system gives:

$$\text{đ}w = - P\,dV = PV\kappa_T\,dP \qquad \text{(reversible, cst. T)}$$

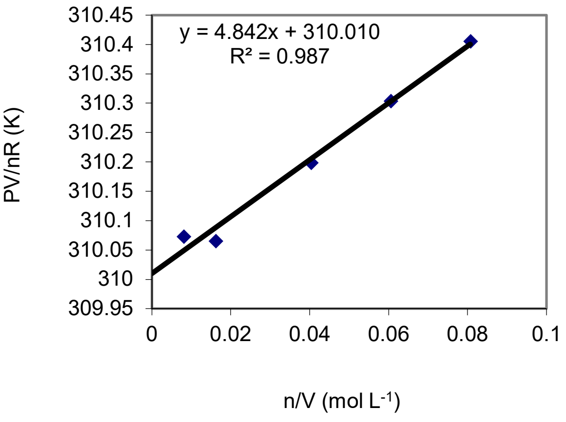
17. The empirical temperature scale is based on the ideal gas thermometer. However, how can you build an ideal gas thermometer when there is no such thing as an ideal gas? The answer is that the effective temperature based on the ideal gas law is measured for differing amounts of gas and the results are extrapolated to zero gas density. The ideal gas thermometer can then be used to calibrate more convenient thermometers. An ideal gas thermometer using helium is constructed with an internal volume for the gas of 0.500 L. The following table gives the number of moles of gas and the corresponding pressure at the fixed external temperature to be measured. Use the ideal gas law to calculate the effective temperature and then extrapolate the results to zero density.

n mol	0.040342	0.030256	0.020171	0.008068	0.004034
P (bar)	2.08225	1.56116	1.04042	0.41602	0.20797

Answer: A spreadsheet was set up to calculate the molar density of the gas and PV/nR from the measured parameters.

n	n/V	PV/nR
0.040342	0.080684	310.4108
0.030256	0.060513	310.3071
0.020171	0.040342	310.2017
0.008068	0.016137	310.0884
0.004034	0.008068	310.0306

slope	4.842429	310.0098	intercept
±	0.32278	0.015895	+-
r^2	0.986846	0.019524	s(y)
F	225.0679	3	df
ss_{reg}	0.085789	0.001144	ss_{resid}



The extrapolated temperature in the ideal gas limit is 310.01 ± 0.02 K.
[Note: Vacuum lines can be easily set up to include calibrated gas burets. Then Avagadro's Law can be used to meter out the required amounts of helium for each run. Using Avagadro's law avoids using the full, accurate equation of state, which was unknown when gas thermometry was first developed. The mole amounts need not be accurate since the intercept is the desired quantity, as long as the amounts are precise and proportional.]

18. The heat transfer at constant volume is the internal energy change and the heat transfer at constant pressure is the enthalpy change. Consider a constant volume process for an ideal gas. Even though the pressure isn't constant, you can still calculate ΔH. Calculate the change in enthalpy for a constant volume process given the temperature change, ΔT or dT. Assume a constant heat capacity over the temperature range. Give your answer in differential, derivative, and integrated (ΔH) form.

Answer: From the definition of the enthalpy, $H \equiv U + PV$, the change in enthalpy can be determined from the differential: $dH = dU + d(PV)$. For an ideal gas, $PV = nRT$ and for a closed system $d(PV) = nR\,dT$, giving dH as:

$$dH = dU + nR\,dT \qquad \text{(ideal gas)}$$

Then at constant volume for any system $dU = C_v dT$:

$$dH = C_v dT + nR\,dT \qquad \text{(ideal gas)}$$

Integrating this expression for a constant heat capacity gives:

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_v dT + \int_{T_1}^{T_2} nR\,dT \qquad \text{(ideal gas)}$$

or $$\Delta H = C_v\,\Delta T + nR\,\Delta T \qquad \text{(ideal gas)}$$

Notice that since $C_p = C_v + nR$ for an ideal gas this last equation is equivalent to $\Delta H = C_p\,\Delta T$. Now we need to get the derivative form $(\partial H/\partial T)_v$. Once again using the definition of the enthalpy, $H \equiv U + PV$:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V$$

The first derivative on the right is the constant volume heat capacity. For an ideal gas, $P = nRT/V$ giving:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \qquad \text{(ideal gas)}$$

Substitution then gives:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_v + nR \qquad \text{(ideal gas)}$$

which is consistent with our previous results.

19. Enthalpy is a state function. The heat transfer at constant pressure is the enthalpy change, $q_P = \Delta H$. Does this equality argue that q is a state function?

Answer: No, ΔH is a state function, but q is not. The heat transferred depends on the path. In the given expression, the path is specified as a constant pressure path. Only for the specific case of a constant pressure path is $q_P = \Delta H$.

20. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.[2]

(a). The work done by the system on the surroundings during a change in state is never greater than the decrease in the internal energy of the system.

(b). The enthalpy of a system cannot change during an adiabatic process.

(c). When a system undergoes a given isothermal change in state, the enthalpy change for the system does not depend upon the path of the process involved.

(d). When a change in state occurs, the increase in the enthalpy of the system must equal the decrease in the enthalpy of the surroundings.

(e). The equation $\Delta U = q + w$ is applicable to any macroscopic process, provided no electrical work is performed by the system on the surroundings.

(f). No change in state occurring in an isolated system can cause a change in the system's internal energy or enthalpy.

(g). For any constant pressure process, the increase in enthalpy equals the heat transferred whether or not electrical or chemical work is done during the process.

(h). A reversible process is one in which the internal energy lost by the system is just sufficient to restore the system to its original state.

(i). When a real gas expands into a vacuum, it does work because the molecules of the gas have been separated from one another against an attractive force.

Answers: (a). The work done by the system on the surroundings during a change in state is never greater than the decrease in the internal energy of the system.

False: Solving $\Delta U = q + w$ for the work gives $w = \Delta U - q$. The work done on the surroundings is $-w = -\Delta U + q$. The work done on the surroundings can be greater than $-\Delta U$ if heat is transferred into the system ($q>0$). In fact, the internal energy need not change at all for work to be done. The corrected statement is: "The work done by the system on the surroundings during a change in state is equal to the decrease in the internal energy of the system added to any heat transferred into the system."

(b). The enthalpy of a system cannot change during an adiabatic process.

False: For an adiabatic process $đq = 0$ giving $dU = đw = -P_{ext}\, dV$ and in general P, V, and T can all change. The definition of enthalpy then gives:

$$dH = dU + d(PV) = dU + PdV + VdP = -P_{ext}\, dV + PdV + VdP \qquad \text{(adiabatic)}$$

which can be non-zero. For example, consider a system in contact with the surroundings so that $P = P_{ext}$ in a reversible adiabatic expansion. During the expansion the pressure of the system decreases and the change in enthalpy is given by Eq. 7.8.31:

$$dH = -P\,dV + PdV + VdP = V\,dP \qquad \text{(reversible adiabatic)}$$

Then dH = 0 only for a reversible, <u>constant pressure</u>, adiabatic process, but not in general. The correct statement is: "The enthalpy of a system cannot change during a reversible adiabatic process at constant pressure." An example of such a process is the Joule-Thomson expansion.

(c). When a system undergoes a given isothermal change in state, the enthalpy change for the system does not depend upon the path of the process involved.

<u>True but too restrictive</u>: The statement is too restrictive because the process does not need to be isothermal to be path independent, since enthalpy is a state function. The correct statement is "For any given change in state, the enthalpy change is independent of the path."

(d). When a change in state occurs, the increase in the enthalpy of the system must equal the decrease in the enthalpy of the surroundings.

<u>False</u>: Both internal energy and enthalpy are state functions. However, while internal energy is conserved, enthalpy is not (see Section 7.8). Consider a reversible process. The change in the enthalpy is given by Eq. 7.8.30:

$$dH = đq + V\,dP \qquad \text{(reversible, PV work only)} \qquad 1$$

Now consider the surroundings. Assume that the surroundings are large in extent and uniform so that the pressure of the surroundings is constant. The enthalpy change for the surroundings is given by the heat transfer at the constant pressure of the surroundings:

$$dH_{surr} = dq_{p,surr} = -đq \qquad \text{(surroundings at cst. P, PV work only)} \qquad 2$$

Comparing Eq. 1 for the system and Eq. 2 for the surroundings shows that enthalpy is not in general conserved; the increase in the enthalpy of the system is not equal to the decrease in the enthalpy of the surroundings for a general reversible process.

However, the enthalpy change of the surroundings <u>is</u> equal in magnitude and opposite in sign to the system enthalpy change specifically for a constant pressure process. Then $dH = đq_p$ for the system from Eq. 1 (or Eq. 7.8.18) and $dH_{surr} = -đq_p$ for the surroundings. So the corrected wording is "the increase in the enthalpy of the system is equal to the decrease in the enthalpy of the surroundings for a constant pressure process."

(e). The equation $\Delta U = q + w$ is applicable to any macroscopic process, provided no electrical work is performed by the system on the surroundings.

<u>True but too restrictive</u>: The First Law, $\Delta U = q + w$, holds for any form of work. The work done in expansion and electrical work is given by:

$$đw = -P_{ext}\,dV + \phi\,dq_i \quad \text{giving} \quad dU = đq + đw = đq - P_{ext}\,dV + \phi\,dq_i$$

For another example of non-PV work, for an open system with one component i gives:

$$dU = đq - P_{ext}\,dV + \mu_i\,dn_i$$

The correct statement is “The equation $\Delta U = q + w$ is applicable to any macroscopic process for the system.”

(f). No change in state occurring in an isolated system can cause a change in the system’s internal energy or enthalpy.

False for the enthalpy but true for the internal energy: The statement is equivalent to the First Law in the case of the internal energy, but the enthalpy is not conserved. In general, $dH = dU + d(PV) = dU + PdV + VdP$. In an isolated system $dU = 0$ and $dV = 0$ and then:

$$dH = VdP \qquad \text{or since V is constant:}\ \ \Delta H = V\Delta P \qquad\qquad \text{(isolated)}$$

(See also Eq. 7.8.31) So the enthalpy is not necessarily constant for an isolated system. The point here is that the “P” in the definition of the enthalpy, $H \equiv U + PV$, is the system pressure. A process in an isolated system can cause a change in pressure. The correct statement is just “No change in state occurring in an isolated system can cause a change in the system’s internal energy.”

(g). For any constant pressure process, the increase in enthalpy equals the heat transferred whether or not electrical work is done during the process.

False: Consider a process with PV and electrical work, Eq. 7.9.7:

$$dU = đq + đw = đq - P_{ext}\, dV + \phi\, dq_i$$

From the definition of enthalpy, $dH = dU + d(PV)$, giving:

$$dH = đq - P_{ext}\, dV + \phi\, dq_i + d(PV)$$

For a constant pressure process in contact with the surroundings $P = P_{ext}$ and the last equation reduces to:

$$dH = đq_p - P\, dV + \phi\, dq_i + PdV = đq_p + \phi\, dq_i$$

Solving for the heat transfer at constant pressure gives:

$$đq_p = dH - \phi\, dq_i$$

The correct statement is “The heat transer at constant pressure is the change in enthalpy minus any non-PV work.”

(h). A reversible process is one in which the internal energy lost by the system is just sufficient to restore the system to its original state.

True but too restrictive: Internal energy is a state function, so the change in internal energy is independent of the path. For a given change in state, the change in internal energy for the forward and the reverse processes are always equal in magnitude and opposite in sign. This statement is true for any process, reversible and irreversible. The correct statement is something like “For any given change in state, the internal energy lost by the system is just sufficient to restore the system to its original state.” For a reversible process, specifically, the statement is “A reversible process is one in which the work transfer by the system is just sufficient to restore the system to its original state.”

(i). When a real gas expands into a vacuum, it does work because the molecules of the gas have been separated from one another against an attractive force.

False: The work is only a function of the external pressure: $đw = -P_{ext}\, dV$. For expansion into a vacuum $P_{ext} = 0$ and no work is done. The internal energy, however, does change for a real gas expansion against a vacuum. We will calculate the change of the internal energy in Chapter 9. The correct statement is "When a real or ideal gas expands into a vacuum, no work is done, because the external pressure is zero."

21. The Gibbs free energy is usually considered a function of the temperature and the pressure, G(T,P). Write the total differential of G with respect to changes in temperature and pressure.

Answer: The independent variables for G are given as T and P. So both T and P change: giving dT and dP. The form of the differential is then:

$$dG = \left(\frac{\partial}{\partial}\right) dT + \left(\frac{\partial}{\partial}\right) dP$$

Then the total differential is given as:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

22. Write the total differential of U considered as a function of T and P as independent variables.

Answer: The independent variables for U are given as T and P. So both T and P change, and these changes are dT and dP. The form of the differential is then:

$$dU = \left(\frac{\partial}{\partial}\right) dT + \left(\frac{\partial}{\partial}\right) dP$$

Then the total differential is given as:

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

23. (a). Integrate Eq. 7.6.10 for a constant temperature process using the total differential. Assume a narrow pressure range so that $V \approx V_o$ and κ_T is constant. (b). Integrate Eq. 7.6.9 using the "short-cut" method discussed in the Addendum, Sec. 7.11.

Answer: (a). For a constant temperature process, Eq. 7.6.10 reduces to: $dV = -V\, \kappa_T\, dP$. See problem 12 and 13 for the integration.
(b). From the definition of κ_T, Eq. 7.6.9, multiplying both sides of the equation by $-V$ gives:

$$\left(\frac{\partial V}{\partial P}\right)_T = -V\,\kappa_T$$

Multiply both sides of the equation by dP and "cancel" the ∂P and dP on the left:

$$\left(\frac{\partial V}{\partial P}\right)_T dP = -V\,\kappa_T\,dP \qquad \text{or} \qquad dV = -V\,\kappa_T\,dP$$

which is the same as the rigorous approach starting with the total differential.

24. Find $(\partial P/\partial T)_V$ for a Van der Waals gas in a closed system.

Answer: Rearranging the Van der Waals equation, Eq. 7.5.1, to isolate P as the dependent variable on the left side of the equation gives:

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

Only the first term on the right is temperature dependent:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$$

since n and R are constants, and V is the independent variable that is held constant for the partial derivative

25. The critical point is the point of inflection on the critical isotherm. The point of inflection corresponds to:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Assume the gas is described by the Van der Waals equation of state. The two equations for the inflection point, above, provide two equations in two unknowns. Show that, in terms of the Van der Waals a and b coefficients, the critical volume, temperature, and pressure are given by:

$$V_c = 3nb \qquad T_c = \frac{8a}{27bR} \qquad P_c = \frac{a}{27\,b^2}$$

Answer: Starting from Example 7.6.1: $$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT_c}{(V_c - nb)^2} + \frac{2an^2}{V_c^3} = 0 \qquad 1$$

The second derivative is: $$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2nRT_c}{(V_c - nb)^3} - \frac{6an^2}{V_c^4} = 0 \qquad 2$$

To solve for V_c multiply Eq. 1 by $2/(V_c - nb)$ to give:

$$-\frac{2nRT_c}{(V_c - nb)^3} + \frac{4an^2}{V_c^3(V_c - nb)} = 0 \qquad 3$$

Now add Eqs. 2 and 3:

$$2 + 3: \qquad -\frac{6an^2}{V_c^4} + \frac{4an^2}{V_c^3(V_c - nb)} = 0 \qquad 4$$

Dividing both sides of Eq. 4 by the common factor $2an^2/V_c^3$ gives:

$$-\frac{3}{V_c} + \frac{2}{(V_c - nb)} = 0 \qquad 5$$

and solving for V_c gives : $V_c = 3nb$ 6

Substituting Eq. 6 into Eq. 1 gives:

$$-\frac{nRT_c}{(3nb - nb)^2} + \frac{2an^2}{(3nb)^3} = 0 \qquad \text{or} \quad T_c = \frac{8a}{27bR} \qquad 7$$

Finally, substituting Eq. 6 and 7 into the original Van der Waals equation gives:

$$P_c = \frac{nRT_c}{V_c - nb} - \frac{an^2}{V_c^2} = \frac{nR\left(\frac{8a}{27bR}\right)}{3nb - nb} - \frac{an^2}{(3nb)^2} \qquad 8$$

$$P_c = \frac{a}{27\,b^2} \qquad 9$$

<u>26</u>. Calculate the change in internal energy for an adiabatic expansion of a gas for a change in volume from 1.00 L to 10.00 L against a constant external pressure of 1.00 bar.

Answer: Starting with Eq. 7.8.2, for the finite process $\Delta U = q + w$. However, for an adiabatic process, $q = 0$, giving $\Delta U = w$. The work done in the expansion is $w = -P_{ext}\,\Delta V$:

$$w = -1.00\text{x}10^5 \text{ Pa } (10.00 \text{ L} - 1.00 \text{ L})(1 \text{ m}^3/1000 \text{ L}) = -900. \text{ J}$$

which gives $\Delta U = -900.$ J

<u>27</u>. Calculate the internal energy and enthalpy change for a constant volume process for one mole of ideal gas with a change in temperature from 298.2 K to 323.2 K. Assume the gas is diatomic with a constant volume heat capacity of $^5/_2$ nR. Explain the relative sizes of the internal energy and the enthalpy changes.

Answer: The plan is to use $\Delta U = q_v = C_v\,\Delta T$, since the process is at constant volume. Then Eq. 7.8.29° can be used to calculate the enthalpy, since this system is an ideal gas.

From Eq. 7.8.10:

$$\Delta U = C_v\,\Delta T = {}^5\!/_2\, nR\,\Delta T = {}^5\!/_2\,(1.000\text{ mol})(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(323.2\text{ K} - 298.2\text{ K})$$
$$= 519.6\text{ J}$$

Using Eq. 7.8.29°:

$$\Delta H = \Delta U + nR\,\Delta T = 519.6\text{ J} + (1.00\text{ mol})(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(25.0\text{ K})$$
$$= 519.6\text{ J} + 207.9\text{ J} = 727.\text{ J}$$

So even though the pressure changes in this process, the change in enthalpy can still be calculated. Now, why is the enthalpy change bigger than the internal energy change? Since the pressure of the gas increases on heating, the PV-product increases: $d(PV) > 0$. No work is done, since the volume is constant, but the PV-product does increase. Then $dH = dU + d(PV)$ for a general process and $d(PV)$ adds to dU. So the enthalpy change is bigger than the internal energy change. Notice that the difference between ΔH and ΔU is <u>not</u> the work done by <u>this</u> process, because no expansion work is done at constant volume.

<u>28</u>. Find the enthalpy change for a constant volume process for a change in temperature ΔT of a Van der Waals gas, starting from the internal energy change, ΔU.

Answer: The plan is to use Eq. 7.8.16 and the Van der Waals equation of state to find $\Delta(PV)$.

From the Van der Waals equation, Eq. 7.5.1:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

The PV-product is then:

$$PV = \left(\frac{V}{V - nb}\right) nRT - \frac{an^2}{V}$$

and for a constant volume process for a change in temperature ΔT:

$$\Delta(PV) = \left(\frac{V}{V - nb}\right) nR\Delta T \qquad \text{(cst. V)}$$

Finally then from Eq. 7.8.16:

$$\Delta H = \Delta U + \left(\frac{V}{V - nb}\right) nR\Delta T \qquad \text{(cst. V)}$$

You can also use Eq. 7.8.10 if the heat capacity is constant over the temperature range:

$$\Delta H = C_v\,\Delta T + \left(\frac{V}{V - nb}\right) nR\Delta T \qquad \text{(cst. V)}$$

29. Heat capacities are often approximated by a power series: $C_{p,m} = a + b\,T + c\,T^2$. Find the change in molar enthalpy for a constant pressure process from T_1 to T_2.

Answer: The plan is to integrate the partial derivative relationship $(\partial H/\partial T)_P = C_p$. For a constant heat capacity, $\Delta H = C_p(T_2 - T_1) = C_p\Delta T$.

The integral is:

$$\begin{aligned}
\Delta H &= \int_{T_1}^{T_2} C_p\,dT = \int_{T_1}^{T_2} (a + b\,T + c\,T^2)\,dT \\
&= \int_{T_1}^{T_2} a\,dT + \int_{T_1}^{T_2} bT\,dT + \int_{T_1}^{T_2} cT^2\,dT \\
&= a\,[\,T\,|_{T_1}^{T_2} + \frac{b}{2}\,[\,T^2\,|_{T_1}^{T_2} + \frac{c}{3}\,[\,T^3\,|_{T_1}^{T_2} \\
&= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)
\end{aligned}$$

30. Consider the surroundings as a constant temperature and pressure reservoir. Show for a reversible adiabatic expansion of a gas from P_1 to P_2 that the enthalpy change of the system is not equal in magnitude and opposite in sign to the enthalpy change of the surroundings. In other words, enthalpy is not conserved.

Answer: The plan is to note that the surroundings are at constant pressure, which gives a simple relationship for the enthalpy change of the surroundings. The enthalpy change of the system is given by Eq. 7.8.31.

Since the surroundings are at constant pressure, the enthalpy change for the surroundings is the heat transfer to the surroundings. This transfer is at constant pressure, from the perspective of the surroundings, even if the system is not at constant pressure. The heat transferred to the surroundings is then the negative of the heat transfer of the system: $\Delta H_{surr} = -đq$. For an adiabatic process, $đq = 0$ giving no change in enthalpy for the surroundings. The enthalpy change of the system for a reversible adiabatic process is given by Eq. 7.8.31: $dH = VdP$, which is non-zero. Because the enthalpy change of the system is not equal in magnitude and opposite in sign to the enthalpy change of the surroundings, enthalpy is not conserved.

31. Consider the surroundings as a constant temperature and pressure reservoir. Show for a constant pressure process that the enthalpy change of the system is equal in magnitude and opposite in sign to the enthalpy change of the surroundings.

Answer: The plan is to note that the surroundings are at constant pressure, which gives a simple relationship for the enthalpy change of the surroundings.

Since the surroundings are at constant pressure, the enthalpy change for the surroundings is the heat transfer to the surroundings. This transfer is at constant pressure, from the perspective of the surroundings, even if the system is not at constant pressure. The heat transferred to the surroundings is then the negative of the heat transfer of the system: $\Delta H_{surr} = -đq$.

The process is at constant pressure for the system, giving $\Delta H = đq = đq_P$. As a consequence, $\Delta H = -\Delta H_{surr}$ for the special case of a constant pressure process, for the system. Note that the pressure of the system and the pressure of the surroundings do not necessarily need to be the same. For example, a gas can be confined in a cylinder with a weight on the piston, giving $P > P_{surr.}$ However, if the system is held at constant pressure by contact with the surroundings, then $\Delta H = -\Delta H_{surr}$ is guaranteed since $P = P_{surr}$. This holds for example, for a solution in a beaker at ambient pressure.

For a constant pressure process, enthalpy is conserved. However, enthalpy is not conserved in general (see the previous problem for an example).

Literature Cited:

1. T. J. McDougall, R. Feistel, “What causes the adiabatic lapse rate?” *Deep-Sea Research I*, **2003**, *50*, 1523-1535.
2. J. Waser, K. N. Trueblood, C. M. Knobler, *Chem One,2nd.Ed.,* McGraw Hill, New York, NY, 1980. pp. 414-415.

Chapter 8 Problems: Thermochemistry

1. Verify the statement from Sec. 8.2 that the difference between Eqs. 8.2.3 and 8.2.4 is the enthalpy of vaporization of water, Eq. 8.1.1.

Answer: Reversing Eq. 8.1.1 and adding to 8.2.3 gives Eq. 8.2.4:

$$3\ NO_2\,(g,\ 1bar) + H_2O\,(l) \rightarrow 2\ HNO_3\,(l) + NO\,(g,\ 1bar) \qquad \Delta_rH° = -71.66\ kJ\ mol^{-1} \qquad (8.2.3)$$

$$H_2O\ (g) \rightarrow H_2O\ (l) \qquad -\Delta_{vap}H = -44.01\ kJ\ mol^{-1} \qquad -(8.1.1)$$

$$3\ NO_2\,(g,\ 1bar) + H_2O\,(g) \rightarrow 2\ HNO_3\,(l) + NO\,(g,\ 1bar) \qquad (8.2.4)$$

By Hess's Law the sum of the reaction enthalpies for the two reactions as written should give the reaction enthalpy for Eq. 8.2.4:

$$\begin{aligned} \Delta_rH°(\text{Eq. } 8.2.4) &= \Delta_rH°(\text{Eq. } 8.2.3) - \Delta_{vap}H(H_2O) \\ &= -71.66\ kJ\ mol^{-1} - 44.01\ kJ\ mol^{-1} = -115.67\ kJ\ mol^{-1} \end{aligned}$$

as listed for Eq. 8.2.4. Rearranging then, $\Delta_rH°(\text{Eq. } 8.2.3) - \Delta_rH°(\text{Eq. } 8.2.4) = \Delta_{vap}H(H_2O)$.

2.(a). Write the chemical reaction that corresponds to the enthalpy of formation of urea, $(NH_2)_2CO$. (b). The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide. Using the data in the appendix, calculate the reaction enthalpy for the hydrolysis of urea to give gaseous ammonia and carbon dioxide, at standard state and at 298.15 K.

Answer: (a). The formation reaction is the production of one mole of substance from the constituent elements in their standard states:

$$C\ (graph) + 2\ H_2\ (g,\ 1\ bar) + N_2\ (g,\ 1bar) \rightarrow (NH_2)_2CO\ (s) \qquad \Delta_fH° = -333.1\ kJ\ mol^{-1}$$

(b). The hydrolysis reaction and enthalpies of formation, from Tables 8.4.1 and 8.4.2, are:

	$(NH_2)_2CO\ (s)$ +	$H_2O\ (l)$ →	$2\ NH_3\ (g,\ 1\ bar)$ +	$CO_2\ (g,\ 1bar)$	units
$\Delta_fH°$	-333.1	-285.830	-46.11	-393.509	$kJ\ mol^{-1}$

Remember that the enthalpy is an extensive function, so the stoichiometric coefficients are important. The reaction enthalpy change is given by Eq. 8.4.9:

$$\Delta_rH° = [\Sigma products] - [\Sigma reactants] = \sum \nu_i\, \Delta_fH°$$

$$\Delta_rH° = [2(-46.11) + (-393.509)] - [(-333.1) + (-285.83)]\ kJ\ mol^{-1} = 133.2\ kJ\ mol^{-1}$$

3. NaCl aerosols are created when bubbles burst at the surface of the ocean. However, NaCl in marine aerosols has a short lifetime. A natural source of sulfur in the atmosphere above the ocean is the production of H_2S (g) from bacteria. H_2S is oxidized by atmospheric oxygen to give sulfur trioxide, which then dissolves in water droplets to form highly concentrated sulfuric acid. The sulfuric acid reacts with NaCl to give HCl gas and aqueous $NaHSO_4$. (a). Using the data in the appendix, calculate the reaction enthalpy for the reaction of NaCl (s), H_2S (g), and atmospheric O_2 through the following reactions, under standard conditions and at 298.15 K.

H_2S (g, 1bar) + 2 O_2 (g, 1bar) → SO_3 (g, 1bar) + H_2O (g, 1bar)
SO_3 (g, 1 bar) + H_2O (l) → H_2SO_4 (l)
NaCl (s) + H_2SO_4 (l) → HCl (g, 1bar) + Na^+ (ao) + HSO_4^- (ao)

(b). Combine the three reactions to show the overall process. Use the combined reaction to calculate the overall reaction enthalpy. Compare with the result in part (a).

Answer: The plan is to use Hess's Law for each reaction and then the three reactions in sequence. Note that both gaseous and liquid water are involved in the reactions. Use the enthalpy of formation for pure liquid H_2SO_4.

(a). The enthalpies of formation, from Table 8.4.1, combine to give the reaction enthalpies:

	H_2S (g, 1bar) +	2 O_2 (g, 1bar) →	SO_3 (g, 1bar) +	H_2O (g, 1bar)	units	1
$\Delta_fH°$:	-20.63	0	-395.72	-241.818	kJ mol^{-1}	

	SO_3 (g, 1 bar) +	H_2O (l) →	H_2SO_4 (l)		2
$\Delta_fH°$:	-395.72	-285.83	-813.989	kJ mol^{-1}	

	NaCl (s) +	H_2SO_4 (l) →	HCl (g, 1bar) +	Na^+ (ao) +	HSO_4^- (ao)		3
$\Delta_fH°$:	-411.003	-813.989	-92.307	-240.12	-887.34	kJ mol^{-1}	

Each reaction enthalpy change is given by Eq. 8.4.9:

$$\Delta_rH° = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \sum \nu_i \, \Delta_fH°$$

For reaction 1:

$$\Delta_rH° = [(-395.72) + (-241.818)] - [(-20.63) + 0] \text{ kJ mol}^{-1} = -616.91 \text{ kJ mol}^{-1}$$

For reaction 2:

$$\Delta_rH° = [(-813.989)] - [(-395.72) + (-285.83)] \text{ kJ mol}^{-1} = -132.44 \text{ kJ mol}^{-1}$$

For reaction 3:

$$\Delta_rH° = [(-92.307) + (-240.12) + (-887.34)] - [(-411.003) + (-813.989)] \text{ kJ mol}^{-1} = 5.23 \text{ kJ mol}^{-1}$$

The overall sequence gives $\Delta_rH° = (-616.91) + (-132.44) + (5.23) \text{ kJ mol}^{-1} = -744.12 \text{ kJ mol}^{-1}$

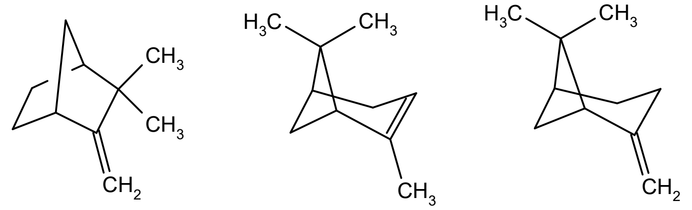
(b). We can check the results by working directly with the overall reaction. The sum of the three steps gives:

	H_2S (g) +	$2O_2$ (g) +	NaCl (s) +	H_2O (l) →	HCl (g) +	Na^+(ao) +	HSO_4^- (ao) +	H_2O (g)	
$\Delta_fH°$:	-20.63	0	-411.003	-285.83	-92.307	-240.12	-887.34	-241.818	kJ mol^{-1}

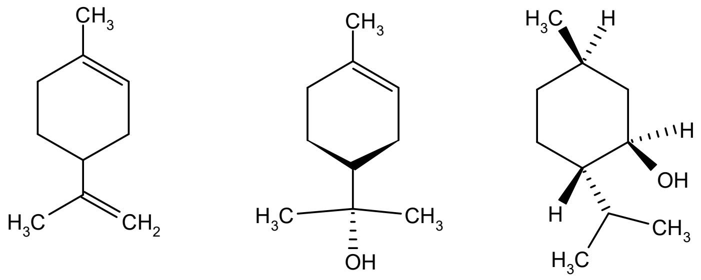
$$\begin{aligned}\Delta_rH° &= [(-92.307)+(-240.12)+(-887.34)+(-241.818)] - \\ &\qquad [(-20.63)+(0)+(-411.003)+(-285.83)] \text{ kJ mol}^{-1} \\ &= -744.12 \text{ kJ mol}^{-1}\end{aligned}$$

The results are identical to the sum of the three sequential reactions; enthalpy is a state function, which is independent of the path. Notice that the combined process includes the enthalpy of vaporization of water. The actual aerosols are probably best thought of as "slush balls" with NaCl in the solid and aqueous phase, the ratios of which depend on the humidity. The standard state for the aqueous electrolytes is totally dissociated at a concentration of 1.000 m.

4. Components of perfumes must be in the gas phase to be smelled. Monoterpines are common ingredients in perfumes and “essential oils,” Figure P8.1. Monoterpines are also found in health-care products and the air in forests. Determine the enthalpy of formation for each listed monoterpine in the gas phase. The literature values for the enthalpy of formation of the solids or liquids are available from Lange's Handbook, the CRC, or Data Section Table 8.4.2. The enthalpies of vaporization or sublimation are in Data Section Table 8.1.1.



camphene α-pinene β-pinene



limonene, α-terpineol menthol

Figure P8.1: Some monoterpine natural products.

Answer: The enthalpies of vaporization or sublimation in kJ mol^{-1} are: camphene, 43.5; α-pinene, 44.7; β-pinene, 46.4; limonene, 43.9; α-terpineol, 52.3; menthol, 56.5 kJ/mol, Table 8.1.1. The enthalpy of vaporization or sublimation must be added to the liquid or solid enthalpy of formation:

	$\Delta_f H°$ (s or l) kJ mol^{-1} (kcal mol^{-1})	$\Delta_{sub}H°$ or $\Delta_{vap}H°$ kJ mol^{-1} (kcal mol^{-1})	$\Delta_f H°$(g) kJ mol^{-1} (kcal mol^{-1})
camphene (s)	-76.23 (-18.22)	43.5 (10.40)	-32.7 (-7.82)
α-pinene (l)	-16.4 (-4.04)	44.7 (10.68)	28.3 (6.76)
β-pinene (l)	-7.70 (-1.84)	46.4 (11.09)	38.7 (9.25)
limonene (l)	-54.5 (-23.51)	43.9 (10.49)	-10.6 (-2.53)
α-terpineol (l)	-359.2 (-85.84)	52.3 (12.50)	-306.9 (-73.34)
menthol (s)	-480.57 (-114.86)	56.5 (13.50)	-424.07 (-101.36)

We will use these values for a later problem using molecular mechanics.

5. Calculate the standard internal energy of formation at 298.2 K of liquid methyl acetate, $C_3H_6O_2$, from its standard enthalpy of formation, which is -442.0 kJ mol^{-1} at 298.2 K.

Answer: The plan is to write the balanced chemical reaction that corresponds to the process and then use $\Delta_r H = \Delta_r U + \Delta_r n_g RT$. The balanced reaction is:

$$3\ C\ (graph) + 3\ H_2\ (g) + O_2\ (g) \rightarrow C_3H_6O_2\ (l)$$

and $\Delta_r n_g$ = [Σproducts] – [Σreactants] = [0] – [4 mol] = -4 mol

$$\Delta_r H = \Delta_r U + \Delta_r n_g RT$$
$$(1\ mol)(-442.0\ kJ\ mol^{-1}) = \Delta_r U + (-4\ mol)(8.314\ J\ K^{-1}\ mol^{-1})(1\ kJ/1000\ J)(298.2\ K)$$
$$\Delta_f U° = \Delta_r U = -442.0\ kJ + 9.92\ kJ = -432.1\ kJ$$

Since the internal energy of formation is for one mole, the final value may also be written as $\Delta_f U° = -432.1$ kJ mol^{-1}. Alternatively, $\Delta_r n_g$ is usually taken as unitless.

6. The enthalpy of combustion of cyclopropane, C_3H_6, is -2091. kJ mol^{-1} at 298.2 K and 1.00 bar. Given that $\Delta_f H^\circ$ for CO_2= -393.509 kJ mol^{-1} and $\Delta_f H^\circ$ for $H_2O(l)$= -285.830 kJ mol^{-1}, calculate the enthalpy of formation of cyclopropane.

Answer: The pressure given is 1 bar, so the system is in the standard state. The first step to write the balanced chemical reaction for the combustion process and to note the literature values for the known enthalpies of formation:

$$\begin{array}{lcccc} & C_3H_6\ (g) + {}^9/_2\ O_2\ (g) & \rightarrow & 3\ CO_2\ (g) & + \quad 3\ H_2O\ (l) \\ \Delta_f H°: & x \qquad\qquad 0 & & -393.509\ kJ\ mol^{-1} & -285.830\ kJ\ mol^{-1} \end{array}$$

Remember that the enthalpy is an extensive function, so the stoichiometric coefficients are important. The reaction enthalpy change is given by Eq. 8.4.9:

$$\Delta_r H° = \Delta_{comb} H° = [\Sigma products] - [\Sigma reactants] = \sum \nu_i\, \Delta_f H°$$

$$\Delta_{comb} H° = [3\ (-393.509\ kJ\ mol^{-1}) + 3\ (-285.830\ kJ\ mol^{-1})] - [x + 0]$$
$$-2091.\ kJ\ mol^{-1} = -2038.017\ kJ\ mol^{-1} - x$$

where:

$$x = \Delta_f H°(cyclopropane) = -2038.017 + 2091.\ kJ\ mol^{-1} = 53.\ kJ\ mol^{-1}$$

7. The enthalpy of combustion at 298.2 K and 1.000 bar pressure for cyclohexane is -3953.0 kJ mol^{-1}. Calculate the standard state enthalpy of formation at 298.2 K.

Answer: The pressure given is 1 bar, so the system is in the standard state. The first step is to write the balanced chemical reaction for the combustion process and to note the literature values for the known enthalpies of formation:

$$\begin{array}{lllll} & C_6H_{12}\,(l) + 9\,O_2\,(g) & \rightarrow\; 6\,CO_2\,(g) & + & 6\,H_2O\,(l) \\ \Delta_f H°: & x \qquad\qquad 0 & -393.509\text{ kJ mol}^{-1} & & -285.830\text{ kJ mol}^{-1} \end{array}$$

Remember that the enthalpy is an extensive function, so the stoichiometric coefficients are important. The reaction enthalpy change is given by Eq. 8.4.9:

$$\Delta_r H° = \Delta_{comb} H° = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \sum \nu_i\, \Delta_f H°$$

$$\Delta_{comb} H° = [6(-393.509\text{ kJ mol}^{-1}) + 6(-285.830\text{ kJ mol}^{-1})] - [x + 0]$$
$$-3953.0\text{ kJ mol}^{-1} = -4076.034\text{ kJ mol}^{-1} - x$$

where:

$$x = \Delta_f H°(\text{cyclohexane}) = -4076.034 + 3953.0\text{ kJ mol}^{-1} = -123.0\text{ kJ mol}^{-1}$$

8. The Haber process is central to the production of fertilizers and many commodity chemicals:

$$½\,N_2\,(g) + {}^3/_2\,H_2\,(g) \rightarrow NH_3\,(g)$$

The kinetics for the reaction are unfavorable at room temperature. Calculate the enthalpy change for the reaction at 500. K. Use Table 7.2.3 to express the heat capacities as a cubic polynomial.

Answer: The enthalpy change for the reaction is just the enthalpy of formation of NH_3 (g), -46.11 kJ mol^{-1}. For constant heat capacities, $\Delta_r H_{T2} = \Delta_r H_{T1} + \Delta_r C_p\, \Delta T$. However, in this case we need to take the temperature dependence of the heat capacities into account. The difference for the heat capacities for the reaction is:

Substance	a J K^{-1} mol^{-1}	b 10^{-2} J K^{-2} mol^{-1}	c 10^{-5} J K^{-3} mol^{-1}	d 10^{-9} J K^{-4} mol^{-1}
N_2 (g)	28.883	-0.157	0.808	-2.871
H_2 (g)	29.088	-0.192	0.400	-0.870
NH_3 (g)	24.619	3.75	-0.138	
Δ_r	-33.454	4.116	-1.142	2.740

$$\Delta_r C_p = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \Delta_r a + \Delta_r b\, T + \Delta_r c\, T^2 + \Delta_r d\, T^3$$
$$= -33.454 + 0.04116\, T + (-1.142\text{x}10^{-5})\, T^2 + 2.740\text{x}10^{-9}\, T^3 \quad \text{J K}^{-1}$$

Then using this cubic polynomial:

$$\Delta_r H_{T2} = \Delta_r H_{T1} + \Delta_r a\,(T_2 - T_1) + \frac{\Delta_r b}{2}(T_2^2 - T_1^2) + \frac{\Delta_r c}{3}(T_2^3 - T_1^3) + \frac{\Delta_r d}{4}(T_2^4 - T_1^4)$$

The enthalpy at 500.0°C is then:

$$\Delta_r H_{T2} = -46.11\text{ kJ mol}^{-1} - 3.77\text{ kJ mol}^{-1} = -49.88\text{ kJ mol}^{-1}$$

9. Yeasts convert glucose to ethanol. Calculate the change in enthalpy if one mole of glucose is converted to ethanol at 298.2 K:

$$C_6H_{12}O_6\ (s) \rightarrow 2\ CH_3CH_2OH\ (l) + 2\ CO_2\ (g)$$

[$\Delta_f H°$(glucose) = -1274. kJ mol^{-1}, $\Delta_f H°$(ethanol) = -277.69 kJ mol^{-1}, $\Delta_f H°(CO_2)$ = -393.51 kJ mol^{-1}] (For comparison the oxidation all the way to CO_2 and H_2O provides much more energy for the organism, but requires O_2.)

Answer: The reaction enthalpy change is given by Eq. 8.4.9:

$$\Delta_r H° = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \sum \nu_i\, \Delta_f H°$$

$$\Delta_r H° = [2(-277.69\text{ kJ mol}^{-1}) + 2\,(-393.51\text{ kJ mol}^{-1})] - [1\,(-1274.\text{ kJ mol}^{-1})]$$
$$= -68.4\text{ kJ mol}^{-1}$$

10. The molar enthalpy of vaporization of water at 298.2 K is $\Delta_{vap}H° = 44.01$ kJ mol^{-1}. Calculate the molar enthalpy of vaporization of water at the boiling point of water, 373.2 K. The $C_{p,m}$ of water liquid is 75.29 J K^{-1} mol^{-1} and of water vapor is 33.58 J K^{-1} mol^{-1}.

Answer: The transition is H_2O (l) → H_2O (g). The difference in heat capacity for the phase transition is:

$$\Delta_{tr}C_p = 33.58\text{ J K}^{-1}\text{ mol}^{-1} - 75.29\text{ J K}^{-1}\text{ mol}^{-1} = -41.71\text{ J K}^{-1}\text{ mol}^{-1}$$

Eq. 8.5.5 gives:

$$\Delta_{tr}H_{T2} = \Delta_{tr}H_{T1} + \Delta_{tr}C_p\,\Delta T$$
$$\Delta_{tr}H_{T2} = 44.01\text{ kJ mol}^{-1} + (-41.71\text{ J K}^{-1}\text{ mol}^{-1})(1\text{ kJ}/1000\text{ J})(373.15\text{ K} - 298.15\text{ K})$$
$$\Delta_{tr}H_{T2} = 44.01\text{ kJ mol}^{-1} - 3.128\text{ kJ mol}^{-1} = 40.88\text{ kJ mol}^{-1}$$

A significant amount of energy in our society is used to produce steam for space heating and drying. For example, the hot metal rollers used to dry paper are heated by steam. Papermaking is one of the top energy consuming industries for this reason.

11. Thermophilic bacteria operate at 80.0°C. Calculate the change in enthalpy for the reaction in the Problem 9 at 80.0°C. C_p for glucose is 209. J K^{-1}mol^{-1}, C_p for ethanol is 111.5 J K^{-1}mol^{-1}, and C_p for CO_2 is 37.11 J K^{-1} mol^{-1}.

Answer: Assuming constant heat capacities, $\Delta_r H_{T2} = \Delta_r H_{T1} + \Delta_r C_p\,\Delta T$. The difference for the heat capacities for the reaction is:

$$\Delta_r C_p = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \sum \nu_i\, C_{p,i}$$
$$= [2\,(111.5\text{ J K}^{-1}\text{mol}^{-1}) + 2\,(37.11\text{ J K}^{-1}\text{mol}^{-1})] - [1(209.\text{ J K}^{-1}\text{mol}^{-1})]$$

$$= 88.2\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The enthalpy at 80.0°C is then:

$$\Delta_rH_{T2} = -68.4\ \mathrm{kJ\ mol^{-1}} + 88.2\ \mathrm{J\ K^{-1}\ mol^{-1}}(55.0\ \mathrm{K})(1\ \mathrm{kJ}/1000\ \mathrm{J})$$
$$= -68.4 + 4.9\ \mathrm{kJ\ mol^{-1}} = -63.5\ \mathrm{kJ\ mol^{-1}} = -64.\ \mathrm{kJ\ mol^{-1}}$$

12. Show that the temperature drift in a calorimetry experiment, before and after the reaction is complete, for short times and small temperature differences with the surroundings, is approximately linear. [Hint use Newton's Law of Cooling.]

Answer: Newton's Law of Cooling, Eq. 7.2.18, gives:

$$(T - T_{surr}) = (T_o - T_{surr})\, e^{-r\,t} \qquad \text{with } r = \frac{\mathcal{K}\mathcal{A}}{\delta\, C_P} \qquad \text{(linear gradient)}$$

Expanding the exponential term in a Taylor series for short times, Eq. 1.4.20, and keeping only the first two terms gives $e^{-r\,t} \approx 1 - r\,t$:

$$(T - T_{surr}) = (T_o - T_{surr})\,(1 - r\,t)$$

Solving for the temperature as a function of time gives:

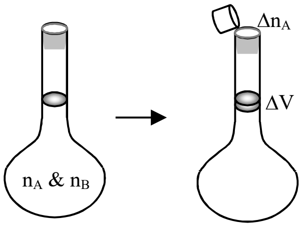
$$T = T_{surr} + T_o - T_{surr} - (T_o - T_{surr})\, r\,t = T_o - (T_o - T_{surr})\, r\,t$$

defining $\Delta T_o \equiv (T_o - T_{surr})$ gives a linear temperature drift:

$$T = T_o - \Delta T_o\, r\,t$$

13. In Sec. 8.4 we used two different perspectives for envisioning a partial derivative. The first was based on making a very small change in the extent of a reaction and then normalizing the change in enthalpy to place the result on a per mole basis, $\Delta_rH = (\partial H/\partial\xi)_P = \Delta H/\Delta\xi$. The second model was to make a one mole change in the extent of the reaction, but in such a large quantity of reactants and products that the partial pressures remained essentially constant, Figure 8.4.3. In either perspective the constancy of the pressures was maintained for the partial derivative. Consider a solution containing n_A moles of A and n_B moles of B. The partial molar volume with respect to changes in the number of moles of A while keeping the number of moles of B constant is given as $(\partial V/\partial n_A)_{n_B}$. The resulting partial derivative is at constant concentration in the same way that the reaction enthalpy is at constant pressure for each reactant and product. Use both of the perspectives for envisioning partial derivatives to describe the meaning of the partial molar volume.

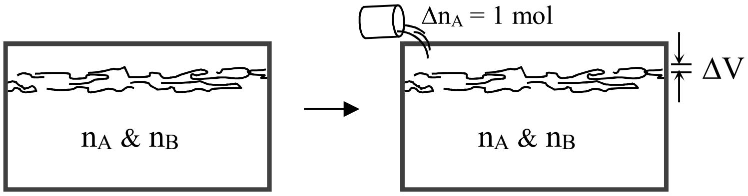
Answer: Consider the perspective of making a very small change and then normalizing to a per mole quantity. Start with n_A and n_B moles of the substances with a total volume V in a volumetric flask:



Add so small an amount of A, Δn_A, that the concentration of the solution remains essentially unchanged. Then the volume change per mole of added A is the partial molar volume:

$$\left(\frac{\partial V}{\partial n_A}\right)_{n_B} = \frac{\Delta V}{\Delta n_A} \qquad \text{limit as } \Delta n_A \rightarrow 0$$

This partial molar volume is the derivative of the solution volume with respect to changes in the amount of A. Now consider the perspective of making a one mole change in a very large amount of solution. Start with n_A and n_B moles of the substances with a total volume V in a swimming pool:



The amount of A and B in the pool is so large that the concentration of A remains essentially unchanged upon the addition of one mole of A. Then the change in volume is already for one mole of A and:

$$\left(\frac{\partial V}{\partial n_A}\right)_{n_B} = \Delta V \qquad \text{for } \Delta n_A = 1 \text{ mol}$$

The partial molar volume is the change in volume upon addition of one mole of A to so large a volume of solution that the concentration remains essentially unchanged.

14. In Sec. 8.4 we used two different perspectives for envisioning a partial derivative. The first was based on making a very small change in the extent of a reaction and then normalizing the change in enthalpy to place the result on a per mole basis, $\Delta_r H = (\partial H/\partial \xi)_P = \Delta H/\Delta \xi$. The second model was to make a one mole change in the extent of the reaction, but in such a large quantity of reactants and products that the partial pressures remained essentially constant, Figure 8.4.3. In either perspective the constancy of the pressures was maintained for the partial derivative. Use both of the perspectives for envisioning partial derivatives to describe the meaning of the reaction heat capacity $\Delta_r C_p$.

Answer: The change in heat capacity for the reactions is given by the analog of Eq. 8.5.26:

$$\Delta_r C_p = \sum_{i=1}^{n_s} \nu_i \, C_{pi} \qquad 1$$

where the C_{pi} are the molar heat capacities for each reactant and product. Consider the perspective of making a very small change and then normalizing to a per mole quantity. The reasoning follows Eqs. 8.4.17-8.4.19. Consider the change in heat capacity for a small change in extent of the reaction, say 0.0001 mole, and then divide the resulting change in C_p by the number of moles, $\Delta C_p/0.0001\text{ mol} = \Delta_r C_p$. The result is a per mole quantity, and since the change in extent of the reaction is so small, the partial pressures of the constituents remain essentially constant. The change in C_p for infinitesimal changes in the amounts of reactants and products is:

$$dC_p = \sum_{i=1}^{n_s} C_{pi}\, dn_i \qquad \text{(cst. T\&P)} \qquad 2$$

or in terms of the extent of the reaction, Eq. 3.1.4, with $dn_i = \nu_i\, d\xi$:

$$dC_p = \sum_{i=1}^{n_s} \nu_i\, C_{pi}\, d\xi \qquad \text{(cst. T\&P)} \qquad 3$$

Dividing both sides of the equation by $d\xi$ gives:

$$\left(\frac{\partial C_p}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{n_s} \nu_i\, C_{pi} = \Delta_r C_p \qquad \text{(cst. T\&P)} \qquad 4$$

where the last equality is from Eq. 1. Dividing dC_p by $d\xi$ puts the reaction heat capacity on a per mole basis, even though the change in extent of the reaction is infinitesimal. The reaction heat capacity is the derivative of the heat capacity with respect to the extent of the reaction.

Now consider the perspective of making a one mole change in extent in a very large amount of reactants and products, Figure 8.4.3. The reaction heat capacity, $\Delta_r C_p$, corresponds to the change in heat capacity for a change in reaction extent of one mole. However, since the mole change is such a small fraction of the total amounts, the partial pressure of each constituent remains constant. Then the change in heat capacity is already for $\Delta\xi$ = one mole and:

$$\left(\frac{\partial C_p}{\partial \xi}\right)_{T,P} = \Delta C_p \text{ for one mole}$$

The reaction heat capacity is the change in heat capacity for one mole of reaction for so large an amount of reactants and products that the partial pressures remain essentially unchanged.

15. Octane is often taken as being representative of the fuel value for gasoline. When 0.7908 g of benzoic acid was burned in a bomb calorimeter the temperature of the calorimeter increased 2.0252°C. When 0.5458 g of octane was burned in the same calorimeter under the same conditions, the temperature increase was 2.5272°C. Assume the calorimeter was at an average temperature of 298.15 K. Calculate the enthalpy of combustion and the enthalpy of formation of octane at 298.15 K.

Answer: The steps are outlined in Sec. 8.6. 1. Bomb calorimeters are at constant volume. The molar mass of octane is 114.23 g mol^{-1}. The amount of octane burned was $n_{oct} = 4.77808\text{x}10^{-3}$ mol.

1. Determine the heat capacity of the calorimeter:
   with q_{cal} from a known reaction: $q_{cal} = –q_v = 26.436 \text{ J g}^{-1} (0.7908 \text{ g}) = 20.9056 \text{ kJ}$
   $C_{cal} = q_{cal}/\Delta T_{cal} = 10.3227 \text{ kJ K}^{-1}$
2. Determine the internal energy change for the reaction in the calorimeter:
   a. with $q_{cal} = C_{cal}\ \Delta T_{react} = 10.3227 \text{ kJ K}^{-1}(2.5272 \text{ K}) = 26.0876 \text{ kJ}$
   and $q_{react} = – q_{cal} = -26.0876 \text{ kJ}$
   b. giving $q_{react} = q_v = \Delta U = -26.0876 \text{ kJ}$
3. Convert to molar terms for unit extent: $\Delta_{comb}U = \Delta U/n = -26.0876 \text{ kJ}/4.77808\text{x}10^{-3} \text{ mol}$
   $\Delta_{comb}U = -5459.85 \text{ kJ mol}^{-1}$

   Notice that once the value is on a per mole basis, you no longer need to know the actual amount used in the experiment.
4. Relate Δ_rU and Δ_rH: the balanced combustion reaction is:
   $C_8H_{18}\ (l) + {}^{25}/_2\ O_2\ (g) \rightarrow 8\ CO_2\ (g) + 9\ H_2O\ (l)$
   giving $\Delta_rn_g = 8 – {}^{25}/_2 = -{}^{9}/_2 = -4.5$ mol of gas per mol of reaction and then
   $\Delta_{comb}H = \Delta_{comb}U + \Delta_rn_g\ RT$
   $= -5459.85 \text{ kJ mol}^{-1} + (-4.5)(8.31447 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})$
   $= -5471.01 \text{ kJ mol}^{-1}$
5. Calculate $\Delta_fH°$ from Δ_rH: Use the table, below, and

   $\Delta_rH° = \Delta_{comb}H° = [\Sigma\text{products}] – [\Sigma\text{reactants}] = \sum \nu_i\ \Delta_fH°$

	C_8H_{18} (l) +	${}^{25}/_2\ O_2$ (g) →	8 CO_2 (g) +	9 H_2O (l)	units
$\Delta_fH°$:	x	0	-393.51	-285.83	kJ mol^{-1}

   $-5471.01 \text{ kJ mol}^{-1} = [8(-393.51 \text{ kJ mol}^{-1}) + 9(-285.83 \text{ kJ mol}^{-1})] – [\ x + {}^{25}/_2(0)]$
   $\Delta_fH° = x = -249.54 \text{ kJ mol}^{-1}$

<u>16</u>. This problem explores the difference between bond enthalpies, Table 8.8.1, and bond increments, Table 8.8.2. Use the bond enthalpies in Table 8.8.1 to estimate the enthalpy of formation for methane. Calculate the bond increment for the C–H bond as ¼ of the estimated enthalpy of formation of methane. Compare your results with the bond increments in Table 8.8.2.

Answer: The enthalpy of formation for methane can be estimated using bond enthalpies and the formation reaction:

$C(graph) + 4\ H_2\ (g) \rightarrow\ CH_4\ (g)$

# Bonds Broken			# Bonds Formed		
1 C (graph)	716.7 kJ mol^{-1}		4 C-H	4(412 kJ mol^{-1})	
2 H-H	2 (436 kJ mol^{-1})				
total	1588.7 kJ mol^{-1}	–	total	1648 kJ mol^{-1}	= -59.3. kJ mol^{-1}

bond increment(C–H Aliphatic) ≈ ¼ (-59.3 kJ mol^{-1}) ≈ -14.8 kJ mol^{-1}

The bond increment listed in Table 8.8.2 for C–H bonds differs from this result because the final parameters are optimized to reproduce the enthalpy of formation for a wide variety of aliphatic hydrocarbons in conjunction with steric energy calculations.

17. In Table 8.9.1 note that the constant volume heat capacity for CO_2 exceeds the prediction based on translation and rotation alone by a larger margin that does O_3. (a). Why? Answer qualitatively, no calculations are needed. (b). Why does rotation contribute only $^2/_2$ RT to the heat capacity for CO_2, while the contribution for O_3 and H_2O is $^3/_2$ RT?

Answer: (a). The heat capacity for CO_2 exceeds the prediction based on translation and rotation alone by a larger margin because CO_2 has two low frequency bending modes, while O_3 has only one, see Figures 8.9.2 and 8.11.1. Bending normal modes are typically at much lower frequency than stretching modes. (b). CO_2 is linear so it has only two degrees of freedom for rotation.

18. The general form for the Coulomb potential is:

$$\varepsilon_{ele} = \frac{q_i\, q_j}{4\pi\varepsilon_o\varepsilon_r\, r_{ij}}$$

where q_i and q_j are the charges on the two atoms in coulombs, ε_o is the vacuum permittivity, ε_r is the relative dielectric constant, and r_{ij} is the distance between the two charges in meters. Eq. 8.8.18 is written in terms of the partial charges Q_i, where $q_i = Q_i\, e$, with e the fundamental unit of charge in coulombs. For example, for an electron, $Q_i = -1$ and for a proton $Q_i = 1$. If the partial charge on an atom is given as $Q_i = 0.210$ then the charge in coulombs is $q_i = 0.210$ e. Q_i and ε_r are unitless. The vacuum permittivity is the dielectric constant of vacuum, $\varepsilon_o = 8.85419\text{x}10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1}$. Verify the units conversion constant in Eq. 8.8.18.

Answer: Assuming one mole of interacting charges, substituting $q_i = Q_i\, e$ for the charge, and r_{ij} in Angstroms gives:

$$\varepsilon_{ele} = \frac{N_A\, e^2\, Q_i\, Q_j}{4\pi\varepsilon_o\varepsilon_r\, r_{ij}\ 1\text{x}10^{-10}\ \text{m Å}^{-1}} = \left(\frac{N_A\, e^2}{1\text{x}10^{-10}\ \text{m Å}^{-1}\varepsilon_o}\right)\frac{Q_i\, Q_j}{4\pi\varepsilon_r\, r_{ij}}$$

$$= \left(\frac{6.02214\text{x}10^{23}\ \text{mol}^{-1}(1.60217733\text{x}10^{-19}\ \text{C})^2}{1\text{x}10^{-10}\ \text{m Å}^{-1}(8.85419\text{x}10^{-12}\ \text{J}^{-1}\ \text{C}^2\ \text{m}^{-1})}\right)\frac{Q_i\, Q_j}{4\pi\varepsilon_r\, r_{ij}}$$

$$= (1.74591\text{x}10^{7}\ \text{J mol}^{-1}\ \text{Å})\frac{Q_i\, Q_j}{4\pi\varepsilon_r\, r_{ij}} = (17459.1\ \text{J mol}^{-1}\ \text{Å})\frac{Q_i\, Q_j}{4\pi\varepsilon_r\, r_{ij}}$$

19. Calculate the electrostatic potential energy of two partial charges with $Q_i = Q_j = 0.40$ at a distance corresponding to the H atom distance in H_2O_2 assuming the relative dielectric constant for vacuum and also the relative dielectric constant for water. The dihedral angle for H_2O_2 is near 118° giving the H atom distance as 2.37 Å. Does the higher dielectric constant of water increase or decrease the magnitude of the electrostatic interaction?

Answer: Using Eq. 8.8.18 with the given parameters in vacuum gives:

$$\varepsilon_{\text{ele}} = (17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{Q_i\, Q_j}{4\pi\varepsilon_r\, r_{ij}} = (17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{(0.40)\,(0.40)}{4\pi(1)\; 2.37 \text{ Å}} = 93.80 \text{ kJ mol}^{-1}$$

or 22.42 kcal mol^{-1}. Assuming a uniform dielectric constant equal to that for water:

$$\varepsilon_{\text{ele}} = (17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{Q_i\, Q_j}{4\pi\varepsilon_r\, r_{ij}} = (17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{(0.40)\,(0.40)}{4\pi(78.54)\; 2.37 \text{ Å}} = 1.19 \text{ kJ mol}^{-1}$$

The effect of the higher dielectric constant for water is to decrease the magnitude of the electrostatic interaction. This effect is called dielectric screening. We will return to this issue in the chapter on solutions.

20. The Merck Molecular Force Field, MMFF, uses a "buffered" electrostatic interaction. MMFF is optimized for work on small molecules and proteins in aqueous solution, for use in medicinal chemisty. In addition, MMFF and some other force fields scale electrostatic interactions for atoms that are separated by three bonds by a factor of 0.75. Interactions for atoms separated by more than three bonds and atoms in different molecules are not scaled. The buffered Coulomb potential is:[1]

$$\varepsilon_{\text{ele}} = \frac{c\, Q_i\, Q_j}{4\pi\varepsilon_r\,(r_{ij} + 0.05 \text{ Å})}$$

The distance between the two oxygen atoms in hydrogen peroxide, H_2O_2, is near 2.37 Å and the partial charges are 0.40. The H-atoms are three bonds apart, H–O–O–H. Calculate the electrostatic potential energy term using Eq. 8.8.18 and also the buffered and scaled version.

Answer: The unbuffered and unscaled value using Eq. 8.8.18 is:

$$\varepsilon_{\text{ele}} = (17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{Q_i\, Q_j}{4\pi\varepsilon_r\, r_{ij}} = (17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{(0.40)\,(0.40)}{4\pi(1)\; 2.37 \text{ Å}} = 93.80 \text{ kJ mol}^{-1}$$

or 22.42 kcal mol^{-1}. The buffered and scaled version gives:

$$\varepsilon_{\text{ele}} = 0.75\,(17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{Q_i\, Q_j}{4\pi\varepsilon_r\,(r_{ij} + 0.05 \text{ Å})} =$$

$$= 0.75\,(17459.1 \text{ J mol}^{-1} \text{ Å}) \frac{(0.40)(0.40)}{4\pi(1)\,(2.37 + 0.05 \text{ Å})} = 68.89 \text{ kJ mol}^{-1}$$

or 16.47 kcal mol^{-1}. The difference in the two approaches is large. The justification for scaling and buffering is simply that the scaled and buffered potential works better in actual practice within the complete force field. The approach does seem arbitrary, and many physical chemists prefer to take a more fundamental approach using *ab initio* molecular orbital calculations with carefully defined solvation models. Such calculations, however, are currently impractical for large molecules.

21. The calculated equilibrium bond length for the C-H bond in ethane is $r_e = 1.0856$ Å. The potential energy for the C–H stretch is 0.1917 kJ mol^{-1} higher when the bond is compressed to 1.0750 Å. Calculate the stretching force constant.

Answer: The compressed bond length gives $(r - r_e) = (1.0750 - 1.0856 \text{ Å}) = -0.0106$ Å. Eq. 8.8.10 relates the potential energy for stretching a bond to the displacement:

$$\varepsilon_{str} = \tfrac{1}{2}\, k_{str,ij}\, (r_{ij} - r_o)^2$$

Solving for the stretching force constant results in:

$$\tfrac{1}{2}\, k_{str,CH} = \varepsilon_{str}/(r_{ij} - r_o)^2 = 0.1917 \text{ kJ mol}^{-1}/(-0.0106 \text{ Å})^2 = 1706. \text{ kJ mol}^{-1} \text{ Å}^{-2}$$

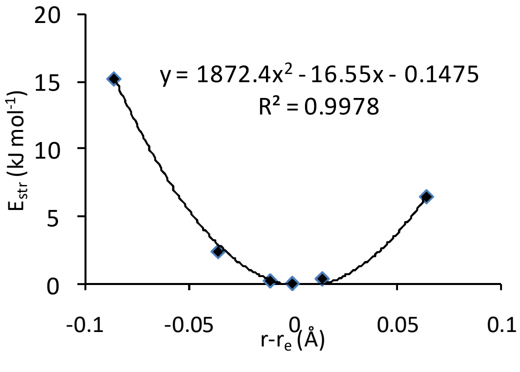
The value used in MM3 is 1384. kJ mol^{-1} Å^{-2}, however, this value was optimized with the cubic anharmonicity term, so differences are expected. The data for this problem are from molecular orbital calculations at the HF 6-31G* level, with the geometry frozen at the geometry optimized values, except for the one C–H bond.

22. The calculated equilibrium bond length for the C-H bond in ethane is $r_e = 1.0856$ Å. The potential energy for the C–H stretch is listed as a function of bond length in the following table. Calculate the stretching force constant. Assume a quadratic potential. (Don't bother to calculate uncertainties.)

$r_{C\text{-}H}$ (Å)	ε_{str} (kJ mol^{-1})
1	15.136
1.05	2.3630
1.075	0.1917
1.0856	0
1.1	0.3439
1.15	6.414

Answer: The plan is to use a quadratic curve fit and then compare with Eq. 8.8.10. The following Excel worksheet and plot were constructed.

$r_{C\text{-}H}$ (Å)	$r - r_e$ (Å)	ε_{str} (kJ mol^{-1})
1	-0.0856	15.13601
1.05	-0.0356	2.36295
1.075	-0.0106	0.191662
1.0856	0	0
1.1	0.0144	0.34394
1.15	0.0644	6.414096

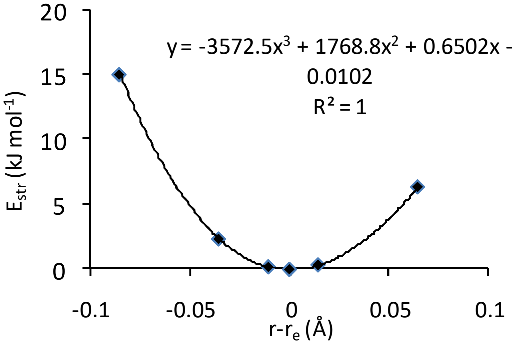


Comparison with Eq. 8.8.10, $\varepsilon_{str} = \tfrac{1}{2}\, k_{str,ij}\, (r_{ij} - r_o)^2$, gives $\tfrac{1}{2}\, k_{str,CH} = 1870$ kJ mol^{-1} Å^{-2}. For an exact fit to the model, the linear and constant terms in the quadratic polynomial should be zero. The fact that these terms are not zero shows that the purely quadratic potential is only an approximation. Terms for the anharmonicity need to be introduced for a better fit to the data. The value for ½ $k_{str,CH}$ in MM3 is 1384. kJ mol^{-1} Å^{-2}, however, this value was optimized with the cubic anharmonicity term, so differences are expected. The data for this problem are from molecular orbital calculations at the HF 6-31G* level, with the geometry frozen at the geometry optimized values, except for the one C–H bond.

23. Use the data in the last problem to determine the C–H stretching force constant and the cubic stretch constant.

Answer: The plan is to use a cubic curve fit and then compare with Eq. 8.8.20. The following Excel worksheet and plot were constructed.

$r_{C\text{-}H}$ (Å)	$r\text{-}r_e$ (Å)	ε_{str} (kJ mol^{-1})
1	-0.0856	15.13601
1.05	-0.0356	2.36295
1.075	-0.0106	0.191662
1.0856	0	0
1.1	0.0144	0.34394
1.15	0.0644	6.414096



Comparison with Eq. 8.8.20, $\varepsilon_{str} = ½\, k_{str,ij}\, (r_{ij} - r_o)^2 - ½\, k_{str,ij}\, C_s\, (r_{ij} - r_o)^3$, gives:

$½\, k_{str,CH} = 1769$ kJ mol^{-1} Å^{-2}

The cubic stretch constant is given by the coefficient for the cubic term:

$- ½\, k_{str,ij}\, C_s = -3572.5$ kJ mol^{-1} Å^{-3}

and then:

$C_s = 3572.5$ kJ mol^{-1} Å^{-3}/1769 kJ mol^{-1} Å^{-2} = 2.02 Å^{-1}

Please see the previous problem for a note about the source of the data for this problem. The fit to the data is seen to be a considerable improvement over the quadratic fit, as is expected since there is one more variable coefficient. The residual linear and constant terms in this cubic fit, however, are quite small, indicating that the cubic equation is sufficient for small deviations in bond length. The value of C_s = 2 Å^{-1} is the normal value for most force fields.

24. The geometry optimized bond angle for water is 105.50°. The potential energy for the bend is 0.305 kJ mol^{-1} higher when the bond angle is expanded to 107.50°, keeping the same bond lengths. Calculate the bending force constant.

Answer: Using the purely quadratic, Hookean potential in Eq. 8.8.11: $\varepsilon_{bend} = ½\, k_{bend,ijk}\, (\theta_{ijk} - \theta_o)^2$ Solving for ½ $k_{bend,HOH}$:

$$\tfrac{1}{2}\, k_{bend,HOH} = 0.305 \text{ kJ mol}^{-1}/(2.00^{\circ})^2 = 0.0762 \text{ kJ mol}^{-1}\, (^{\circ})^{-2}$$

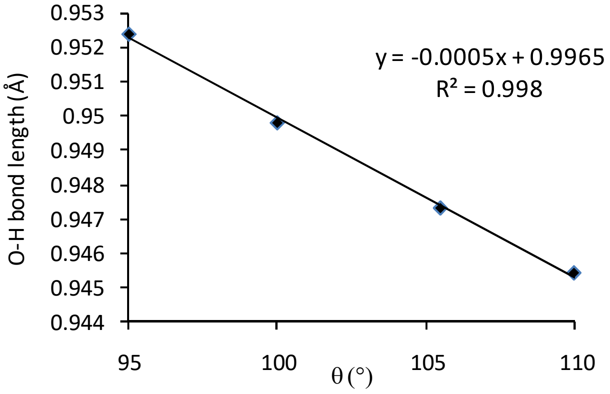
The value used by MMFF is 0.06035 kJ mol^{-1} $(^{\circ})^{-2}$, but in conjunction with a cubic bend anharmonicity correction ($C_b = -0.007(^{\circ})^{-1}$). The data for this problem are from molecular orbital calculations at the HF 6-31G* level, with the bond lengths frozen at the geometry optimized values.

25. Build and geometry optimize water using a molecular orbital calculation at the HF 6-31G* level (a fairly quick level with only moderate accuracy). Determine the equilibrium bond length. Then constrain the bond angle in several steps between 95° and 110° and geometry optimize at each new bond angle. (Make sure to measure the bond angle each time to verify that you constrained the bond angle properly.) Plot the geometry optimum bond length versus the bond angle. In our discussion of the stretch-bend interaction, Eq. 8.8.12, we argued that when a bond is bent to smaller angles, the two associated lowest energy bond lengths increase. Does your plot agree with this observation?

Answer: The following data was obtained at HF 6-31G* at constrained bond angles:

theta	E (H)	r (Å)
95	-76.007407	0.9524
100	-76.009851	0.9498
105.4971	-76.010747	0.9473
110	-76.010179	0.9454

1 H = 1 AU = 2625.5 kJ mol^{-1}



The data shows the stretch-bend interaction clearly. As the bond is bent to smaller angles, the optimum bond length does increase.

26. Determine the enthalpy of formation for the monoterpines listed in Problem 4 using the MM2, MM3, or MM4 molecular mechanics program. Compare the results with the literature values from Problem 4.

Answer: The literature $\Delta_f H^{\circ}(g)$ values are taken from Problem 4 and are listed in the first column of the following table. The values using the MM2 and MM3 programs are:

	$\Delta_f H^{\circ}(g)$ kcal mol^{-1}	$\Delta_f H^{\circ}$ MM2 kcal mol^{-1}	difference kcal mol^{-1}	$\Delta_f H^{\circ}$ MM3 kcal mol^{-1}	difference kcal mol^{-1}
camphene	-7.82	-3.07	4.75	-3.00	4.82

α-pinene	6.76	6.82	0.06	8.70	1.94
β-pinene	9.25	12.95	3.70	14.59	5.34
limonene	-2.53	-1.94	0.59	-0.50	2.03
α-terpineol	-73.34	-71.48	1.86	-69.64	3.7
menthol	-101.36	-104.84	-3.38	-93.44	7.92

The agreement with the literature values is quite good, given the experimental uncertainties and given the possible range of enthalpies of formation for molecule in this size range.

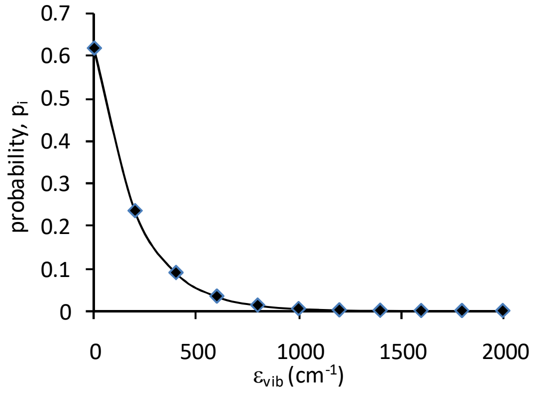
27. Estimate the contribution of vibration to the enthalpy of formation for the monoterpines in Problem 4. Use the approximate torsional increments described in Sec. 8.10.

Answer: The number of non-methyl group internal rotations for the monoterpines are: camphene, 0; α-pinene, 0; β-pinene, 0; limonene, 1; α-terpineol, 2; menthol 2. The contribution to the enthalpy of formation is estimated as 1.51 kJ mol^{-1} for each internal rotation.

28. Calculate the partition function for a harmonic oscillator with fundamental vibration frequency 200 cm^{-1} at 298.2 K, by explicit summation. (Use the lowest energy state as the reference energy, $\varepsilon_o = 0$). Then calculate the probability of occupation for the vibrational states with population greater than ~1%. Plot the probability as a function of the energy of the vibrational state.

Answer: The plan is to calculate the Boltzmann weighting factors for the states with significant population and sum, as given by Eq. 8.10.7. The probability for each state is then given by the Boltzmann distribution, Eq. 8.10.5. A spreadsheet was set-up with the appropriate factors:

i	ε_{vib} (cm^{-1})	$\exp(-\varepsilon_{vib}/kT)$	p_i
0	0	1	0.6191
1	200	0.380888	0.2358
2	400	0.1450754	0.090
3	600	0.0552574	0.0342
4	800	0.0210469	0.0130
5	1000	0.0080165	0.0050
6	1200	0.0030534	0.0019
7	1400	0.0011630	0.0007
8	1600	0.0004430	0.0003
9	1800	0.0001687	0.0001
10	2000	6.426E-05	3.98E-05
	q =	1.61517605	



The plot shows the exponential decrease in probability with increasing energy. The partition function can be interpreted as the number of accessible states for the system. Since Δε ≈ RT in this problem, most molecules are in the lowest energy state. The number of accessible states on average is 1.615.

29. A good example of the use of the Boltzmann distribution is the derivation of the barometric formula, Eq. 1.3.16°. The potential energy of a molecule of mass m at an elevation h is $\varepsilon = mgh$, with g the acceleration of gravity. The ratio of the number of molecules at height h to height h_o is then given by Eq. 8.10.8 with $\Delta\varepsilon = mg(h - h_o)$. Let the number of molecules at sea level, $h_o = 0$, be n_o. Then note that the molar mass is given by $\mathfrak{M} = N_A\, m$, and the pressure of the gas is $P = nRT/V$ for a given fixed volume of gas. In other words the pressure is proportional to the number of molecules. Derive the barometric formula from the Boltzmann distribution assuming a constant temperature.

Answer: The plan is to start with Eq. 8.10.8 and then do the units conversion to give pressures. The ratio of the number of molecules at the two elevations is given by Eq. 8.10.8:

$$\frac{n}{n_o} = e^{\frac{-\Delta\varepsilon}{kT}} = e^{\frac{-mg(h-h_o)}{kT}} \tag{1}$$

Multiply the numerator and denominator of the argument of the exponential term by Avogadro's number and then use $\mathfrak{M} = N_A\, m$ and $R = N_A k$:

$$\frac{-mg(h-h_o)}{kT} = \frac{-N_A\, mg(h-h_o)}{N_A\, kT} = \frac{-\mathfrak{M}\, g(h-h_o)}{RT} \tag{2}$$

Next note that for a given volume of air V at the two altidudes:

$$\frac{n}{n_o} = \frac{nRT/V}{n_oRT/V} = \frac{P}{P_o} \tag{3}$$

and then substituting Eqs. 2 and 3 into Eq. 1 with $h_o = 0$:

$$\frac{P}{P_o} = e^{\left(\frac{-\mathfrak{M}\, g\, h}{RT}\right)} \tag{4}$$

and multiplying through by P_o gives:

$$P = P_o\, e^{\left(\frac{-\mathfrak{M}\, g\, h}{RT}\right)} \qquad \text{(ideal gas, cst. T)} \tag{1.3.16°}$$

30. The energy between the ground electronic state and the first excited state in typical molecules is on the order of 30,000. cm^{-1}. Find the ratio of the number of molecules in the first excited state and the ground state at 298.2 K. Find the temperature that gives a ratio of 0.001. (Assume the ground and excited states are non-degenerate.)

Answer: Using Eq. 8.10.8 and RT in cm^{-1} as 207.23 cm^{-1}:

$$\frac{n_j}{n_i} = e^{\frac{-30000.\ \mathrm{cm^{-1}}}{207.23\ \mathrm{cm^{-1}}}} = 1.345\mathrm{x}10^{-63}$$

For all intents and purposes, all the molecules are in the ground electronic state. Converting 30,000. $\mathrm{cm^{-1}}$ into kJ $\mathrm{mol^{-1}}$gives:

$$\begin{aligned}\Delta E &= N_A\, hc/\lambda\ (1\ \mathrm{kJ/1000J}) = N_A\, hc\, \tilde{\nu}\ (1\ \mathrm{kJ/1000J})\\ &= 6.0223\mathrm{x}10^{23}\ \mathrm{mol^{-1}}(6.626\mathrm{x}10^{-34}\ \mathrm{J\ s})(2.998\mathrm{x}10^{10}\ \mathrm{cm\ s^{-1}})(30{,}000.\ \mathrm{cm^{-1}})(1\ \mathrm{kJ/1000J})\\ &= 358.9\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

For a ratio of 0.001 in the excited state, taking the logarithm of Eq. 8.10.8 gives:

$$\ln(0.001) = -\frac{\Delta\varepsilon}{RT} = -\frac{358.9\ \mathrm{kJ\ mol^{-1}}}{8.314\mathrm{x}10^{-3}\ \mathrm{kJ\ K^{-1}\ mol^{-1}}\ T}$$

Solving for T gives 6250 K. Only refractory oxides could survive at this temperature.

<u>31</u>. Calculate the energy difference in J, kJ $\mathrm{mol^{-1}}$, and $\mathrm{cm^{-1}}$ for transitions with the wavelength of maximum absorbance at 500.00 nm and 50,000. nm. The transition at 500 nm corresponds to the blue-green portion of the visible spectrum. The transition at 50,000 nm or equivalently 50 μm is in the infrared. Calculate the ratio of the number of molecules in two states separated by these energy differences at 298.2 K. Do this calculation with Δε/kT or Δε/RT with the energy in J, kJ $\mathrm{mol^{-1}}$, and $\mathrm{cm^{-1}}$ (three separate calculations).

Answer: Given $\Delta E = h\nu = hc/\lambda$, at 500 nm:

$$\Delta E = hc/\lambda = 6.626\mathrm{x}10^{-34}\ \mathrm{J\ s}\ (2.998\mathrm{x}10^{8}\ \mathrm{m\ s^{-1}})/500.\mathrm{x}10^{-9}\ \mathrm{m} = 3.9729\mathrm{x}10^{-17}\ \mathrm{J}$$

$$\Delta E = N_A\, hc/\lambda\ (1\ \mathrm{kJ/1000J}) = 23925.\ \mathrm{kJ\ mol^{-1}}$$

$$\tilde{\nu} = c/\lambda = 2.998\mathrm{x}10^{8}\ \mathrm{m\ s^{-1}}/500.\mathrm{x}10^{-9}\ \mathrm{m}\ (100\ \mathrm{cm/1\ m}) = 20000.\ \mathrm{cm^{-1}}$$

Using Eq. 8.10.8 for the population ratio gives:

$$\frac{n_j}{n_i} = e^{\frac{-\Delta\varepsilon}{kT}} = e^{\frac{-\Delta\varepsilon}{RT}} = e^{\frac{-\tilde{\nu}}{207.23\ \mathrm{cm^{-1}}}} \quad \text{at 298.2 K}$$

$$\frac{n_j}{n_i} = e^{\frac{-3.9729\mathrm{x}10^{-17}\ \mathrm{J}}{1.38066\mathrm{x}10^{-23}\ \mathrm{J\ K^{-1}}\ 298.2\ \mathrm{K}}} = e^{\frac{-23925.\ \mathrm{kJ\ mol^{-1}}}{8.3145\mathrm{x}10^{-3}\ \mathrm{kJ\ K^{-1}\ mol^{-1}}\ 298.2\ \mathrm{K}}} = e^{\frac{-20000.\ \mathrm{cm^{-1}}}{207.23\ \mathrm{cm^{-1}}}} \quad \text{at 298.2 K}$$

The results for several transition wavelengths are given in the table below.

nm	J	kJ $\mathrm{mol^{-1}}$	$\mathrm{cm^{-1}}$	Δε/kT	n_j/n_i
500	$3.9729\mathrm{x}10^{-19}$	239.253	20000	96.5	$1.216\mathrm{x}10^{-42}$
5000	$3.9729\mathrm{x}10^{-20}$	23.9253	2000	9.65	$6.434\mathrm{x}10^{-5}$
50000	$3.9729\mathrm{x}10^{-21}$	2.39253	200	0.965	0.381
500000	$3.9729\mathrm{x}10^{-22}$	0.23925	20	0.0965	0.908

<u>32</u>. Use the Equipartition theorem to predict the heat capacity of N_2O and HCN. Constant pressure heat capacities are more commonly tabulated than constant volume heat capacities. For an ideal gas $C_p = C_v + nR$. Compare your predictions to literature values for C_p.

Answer: Given that both N_2O and HCN are linear, without vibrations:

$$C_{v,m} = \underset{\text{translation}}{{}^{3}/_{2}\,R} + \underset{\text{rotation}}{{}^{2}/_{2}\,R} = {}^{5}/_{2}\,R$$

and $C_{p,m} = C_{v,m} + R = {}^{7}/_{2}\,R = 29.1\ J\ K^{-1}\ mol^{-1}$, which is the same as predicted for carbon dioxide. The literature values are $C_{p,m}(N_2O) = 38.45\ J\ K^{-1}\ mol^{-1}$ and $C_{p,m}(HCN) = 35.86\ J\ K^{-1}mol^{-1}$, which both exceed the prediction. Vibrations must contribute to the heat capacity. A linear triatomic molecule has 3(3)-5 = 4 normal modes. Two normal modes are the low frequency degenerate bending vibrations, Figure 8.11.1. With <u>just</u> the bending vibrations:

$$C_{v,m} = \underset{\text{translation}}{{}^{3}/_{2}\,R} + \underset{\text{rotation}}{{}^{2}/_{2}\,R} + \underset{\text{bending vibrations}}{2({}^{2}/_{2}\,R)} = {}^{9}/_{2}\,R$$

and $C_{p,m} = C_{v,m} + R = {}^{11}/_{2}\,R = 45.7\ J\ K^{-1}\ mol^{-1}$. The bending vibrations contribute, but not fully.

<u>33</u>. Molecular shape plays an important role in determining the properties of a substance. Of sulfur dioxide and carbon dioxide, which molecule is predicted to have the greater heat capacity? Constant pressure heat capacities are more commonly tabulated than constant volume heat capacities. For an ideal gas $C_p = C_v + nR$. Compare your predictions to literature values for C_p.

Answer: Note that CO_2 is linear and SO_2 is bent. For CO_2 with two moments of inertia, neglecting vibrations, Table 8.9.1:

$$C_{v,m}(CO_2) = \underset{\text{translation}}{{}^{3}/_{2}\,R} + \underset{\text{rotation}}{{}^{2}/_{2}\,R} = {}^{5}/_{2}\,R$$

and $C_{p,m} = C_{v,m} + R = {}^{7}/_{2}\,R = 29.1\ J\ K^{-1}\ mol^{-1}$. For SO_2 with three rotational moments of inertia:

$$C_{v,m}(CO_2) = \underset{\text{translation}}{{}^{3}/_{2}\,R} + \underset{\text{rotation}}{{}^{3}/_{2}\,R} = {}^{6}/_{2}\,R$$

and $C_{p,m} = C_{v,m} + R = {}^{8}/_{2}\,R = 33.3\ J\ K^{-1}\ mol^{-1}$. Neglecting vibrations, SO_2 is predicted to have the larger constant pressure heat capacity. The literature values agree, with $C_{p,m}(CO_2) = 37.11\ J\ K^{-1}\ mol^{-1}$ exceeded by $C_{p,m}(SO_2) = 39.87\ J\ K^{-1}$. Some caution is required, however, because CO_2 has two bending modes, while SO_2 has only one, but the bending mode in SO_2 will be lowered in frequency because of the greater mass of the central sulfur atom. So the vibrational contributions will not be the same for both molecules.

<u>34</u>. The amino acid valine has three possible conformations for the side chain $–CH(CH_3)_2$ group. Calculate the probabilities of the side chain being in each of these three conformations at 298.2 K. Use molecular mechanics with the MMFF force field in the gas phase for the zwitter-ionic form to determine the low energy side chain conformations and the corresponding energies.

Answer: The low energy conformations for zwitter-ionic valine in the gas phase using the MMFF94x force field are -3.0881, -5.3433, -4.4024 kcal mol^{-1} at -51.8°, 57.6°, -168.7° respectively. The dihedral angle was measured from the carbonyl carbon to the side chain methine-hydrogen, O=C–C$_\alpha$–C–H. Using the lowest energy conformer as the reference, the energies in kJ mol^{-1} in increasing order are then: 0, 3.937, 9.436 kJ mol^{-1}.

The Boltzmann weighting factor for the lowest energy conformer is 1, since $e^0 = 1$. The Boltzmann weighting factors for the higher energy conformers are:

$$e^{-\varepsilon_2/RT} = e^{-9.436\text{x}10^3 \text{J}/(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ } 298.2 \text{ K})} = 0.0222$$

$$e^{-\varepsilon_1/RT} = e^{-3.937\text{x}10^3 \text{J}/(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ } 298.2 \text{ K})} = 0.2043$$

The partition function, Eq. 8.10.7, is the normalization for the probability distribution:

$$q = \sum_i e^{-\varepsilon_i/kT} = 1 + 0.2043 + 0.0222 = 1.2265$$

The probabilities for each conformational state are then:

$$p_2 = e^{-\varepsilon_2/RT}/q = 0.0222/1.2265 = 0.0181$$

$$p_1 = e^{-\varepsilon_1/RT}/q = 0.2043/1.2265 = 0.1666$$

$$p_0 = e^{-\varepsilon_o/RT}/q = 1/q = 1/1.2265 = 0.8153$$

35. Nitrous oxide, N_2O, can act as a ligand in transition metal complexes. The infrared stretching frequencies for N_2O are used to judge the strength of coordination to the metal.[2] Nitrous oxide is also an important component of the atmosphere.[3] The isotopic composition of nitrous oxide is a useful marker in atmospheric photochemistry.[4] Nitrous oxide can be thought of as a resonance hybrid among: $N^-{=}N^+{=}O \leftrightarrow N{\equiv}N^+{-}O^- \leftrightarrow N{-}N^-{\equiv}O^+$. N_2O is isoelectronic with carbon dioxide. As such N_2O is linear and has a symmetric ($\tilde{\nu}_1 = 1285$ cm^{-1}) and an asymmetric ($\tilde{\nu}_3 = 2223.5$ cm^{-1}) stretching mode and two degenerate bending modes ($\tilde{\nu}_2 = 588$ cm^{-1}). Using valence force field techniques, the force constants for the NN and NO bonds in nitrous oxide have been estimated to be 1790 N m^{-1} and 1140 N m^{-1}, respectively.[5] (a). Use these bond force constant estimates and MatLab, Mathematica, or the "eigen" Web applet from the companion CD or the text Web site to calculate the frequencies for the symmetric and asymmetric stretches for nitrous oxide. Your calculation will be very similar to the CO_2 example in Sec. 8.11. For example, restrict the motions to just the x-axis (e.g. neglect the bending vibrations) and estimate the force constants in a similar way. You should end up, again, with a 3x3 mass weighted force constant matrix. [Hint: k_{xx}^{22} won't be equal to 2 k_{xx}^{11} in this case because there is a nitrogen on one side and an oxygen on the other side of the central atom, atom 2] (b). Which of the three resonance structures is most representative of the true bonding in N_2O, based on the NN and NO force constants?

Answer: (a). Assume that $k_{xx}^{22} = k(\text{NN}) + k(\text{NO})$, since moving the central N simultaneously stretches the NN bond and compresses the NO bond. The mass weighted force constant matrix is:

$$-\begin{array}{c|ccc} & N_1 & N_2 & O_3 \\ \hline N_1 & \frac{1790}{\sqrt{14}\sqrt{14}} & -\frac{1790}{\sqrt{14}\sqrt{14}} & 0 \\ N_2 & -\frac{1790}{\sqrt{14}\sqrt{14}} & \frac{2930}{\sqrt{14}\sqrt{14}} & -\frac{1140}{\sqrt{14}\sqrt{16}} \\ O_3 & 0 & -\frac{1140}{\sqrt{16}\sqrt{14}} & \frac{1140}{\sqrt{16}\sqrt{16}} \end{array} = \begin{pmatrix} -127.86 & 127.86 & 0 \\ 127.86 & -209.29 & 76.17 \\ 0 & 76.17 & -71.25 \end{pmatrix}$$

The output from the "eigen" applet with units conversion using Eq. 8.11.24 is:

```
Eigenvector 1: E=318.506
-0.539616
0.804598
-0.247865
-------------
```

or $\tilde{\nu}$ =2325. cm^{-1} (or 4.6% high)

```
Eigenvector 2: E=89.8936
-0.625007
-0.185588
0.758237
-------------
```

or $\tilde{\nu}$ = 1235.2 cm^{-1} (or 3.9% low)

```
Eigenvector 3: E=0.0000830617
0.564075
0.564074
0.603026
```

center of mass translation

The agreement is amazing given the approximations. (b). The resonance structure $N{\equiv}N^{+}{-}O^{-}$ is most representative of the bonding , because the NN force constant is larger than the NO force constant.

36. Acetylene is a linear hydrocarbon with a carbon-carbon triple bond, H-C≡C-H, with stretching modes at 1973.8 cm^{-1}, 3287.0 cm^{-1}, and 3373.7 cm^{-1}. Using valence force field techniques, the force constants for the C-H and C≡C bonds in acetylene have been estimated to be 592. N m^{-1} and 1580. N m^{-1}, respectively. Use these bond force constant estimates and MatLab, Mathematica, or the "eigen" Web applet, from the text Web site, to calculate the frequencies for the three linear stretch normal modes for acetylene. Your calculation will be similar to the CO_2 example in Sec. 8.11. For example, restrict the motions to just the x-axis (e.g. neglect the bending vibrations) and estimate the force constants in a similar way. You should end up with a 4x4 mass weighted force constant matrix. [Hint: k^{22}_{xx} won't be equal to 2 k^{11}_{xx} in this case because there is a hydrogen on one side and a carbon on the other side of atom 2]. Sketch the normal modes.

Answer: The plan is to number the H-C≡C-H atoms in the order 1-2≡3-4 and then note that k^{22}_{xx} involves stretching a C-H and a C≡C bond. By symmetry, $k^{22}_{xx} = k^{33}_{xx}$. The force constant k^{23}_{xx} involves moving atom 3 and noting the force on atom 2. The force on atom 2 for k^{23}_{xx} is only determined by the C≡C bond, because the C-H bond remains at equilibrium. By symmetry k^{23}_{xx} =

k_{xx}^{32}. A good test of the self-consistency of the Hessian is the small value of the eigenvalue that represents the motion of the center of mass.

The estimate for k_{xx}^{22} is 592. N m^{-1} + 1580. N m^{-1}, since moving atom 2 changes the extension of the C-H and C≡C bonds. The estimate for k_{xx}^{23} is -1580 N m^{-1}, because moving atom 3 in the positive x-direction gives a negative potential gradient for motion of atom 2 in the positive x-direction, based on just the C≡C bond extension. The mass weighted force constant matrix is:

$$\begin{array}{cc} & \begin{array}{cccc} \mathrm{H_1} & \mathrm{C_2} & \mathrm{C_3} & \mathrm{H_4} \end{array} \\ \begin{array}{c} \mathrm{H_1} \\ \mathrm{C_2} \\ \mathrm{C_3} \\ \mathrm{H_4} \end{array} & -\begin{pmatrix} \frac{592}{\sqrt{1}\sqrt{1}} & -\frac{592}{\sqrt{1}\sqrt{12}} & 0 & 0 \\ -\frac{592}{\sqrt{12}\sqrt{1}} & \frac{2172}{\sqrt{12}\sqrt{12}} & -\frac{1580}{\sqrt{12}\sqrt{12}} & 0 \\ 0 & -\frac{1580}{\sqrt{12}\sqrt{12}} & \frac{2172}{\sqrt{12}\sqrt{12}} & -\frac{592}{\sqrt{12}\sqrt{1}} \\ 0 & 0 & -\frac{592}{\sqrt{1}\sqrt{12}} & \frac{592}{\sqrt{1}\sqrt{1}} \end{pmatrix} = \begin{pmatrix} -592.0 & 170.90 & 0 & 0 \\ 170.90 & -181.0 & 131.67 & 0 \\ 0 & 131.67 & -181.0 & 170.90 \\ 0 & 0 & 170.90 & -592.0 \end{pmatrix} \end{array}$$

The output from the "eigen" applet with units conversion using Eq. 8.11.24 is:

```
Eigenvector 1: E=0.0000415985
0.196116
0.679366
0.679366
0.196116
-------------
```

center of mass translation

```
Eigenvector 2: E=-231.625
0.30298
0.638908
-0.638908
-0.30298
-------------
```

$\tilde{\nu} = (232.625/5.8921\text{x}10^{-5})^{1/2} = 1982.7$ cm^{-1} (0.46% high)

→ → ← ←
H-C≡C-H

```
Eigenvector 3: E=-641.333
0.679366
-0.196116
-0.196116
0.679366
-------------
```

$\tilde{\nu} = (641.333/5.8921\text{x}10^{-5})^{1/2} = 3299.2$ cm^{-1} (0.37% high)

→ ← ← →
H-C≡C-H

```
Eigenvector 4: E=-673.042
0.638908
-0.30298
0.30298
-0.638908
-------------
```

$\tilde{\nu} = (673.042/5.8921\text{x}10^{-5})^{1/2} = 3379.8.$ cm^{-1} (0.18% high)

→ ← → ←
H-C≡C-H

37. Infrared spectroscopy is a useful tool for functional group determination in organic molecules. The correlation chart from your Organic Chemistry text lists typical values for infrared frequencies for different functional groups.[6] Do a normal mode analysis for acetone and dimethylether using molecular mechanics or molecular orbital methods and compare the C–H, C=O, and C–O stretching frequencies to the typical values. These absorptions are typically easy to find because they are intense or in uncluttered regions of the spectrum.

Characteristic Infrared Absorption Frequencies[7]

bond	Compound type	Frequency range (cm^{-1})
C–H	Alkanes	2850-2960
C–H	Alkenes	3020-3080(*m*)
C–H	Aromatic	3000-3100(*m*)
C=C	Alkenes	1640-1680(*v*)
C$\overset{\cdots}{-}$C	Aromatic	1500, 1600(*v*)
C–O	Alcohols, ethers,carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
C≡N	Nitriles	2210-2260(*v*)
–NO_2	Nitro	1515-1560, 1345-1385

All absorptions are strong except: *m* moderate, *v* variable

Answer: The MM3 (left) and HF 6-31G* (right) output for acetone and dimethylether are given below. The molecular orbital frequencies are also tabulated as scaled by 0.9, to correct for anharmonicity. For acetone, the MM3 C–H stretches are from 3019-2901 cm^{-1}, modes 1-6, followed by a region with no vibrations and then the very strong 1727 cm^{-1} carbonyl-dominated normal mode 7, as expected from correlation tables. For dimethylether, the MM3 C-H stretches are from 2995-2850 cm^{-1}, modes 1-6, and the strong C-O dominated stretch is at 1172 cm^{-1}, mode 13, as expected from correlation tables. Notice the six eigenvalues that the MM3 program rounds to 0 cm^{-1} that account for the motion of the center of mass and the rotation of the molecule are not listed, to save space. The molecular orbital program did not list the translation/rotation eigenvalues.

If you do not have a visualization application that draws the normal mode displacements or animates the vibrations, you can identify the vibrations from their position in the spectrum and by looking at the numerical printout of the normal coordinate displacements. The acetone HF 6-31G* normal coordinate displacements for the C=O stretch show large displacements for the bonded C and O atoms:

```
      2021.60
        A1
      X      Y      Z
  C2 0.000  0.000  0.228
  O1 0.000  0.000 -0.148
```

The dimethylether HF 6-31G* normal coordinate displacements for the C–O stretch again show large displacements for the bonded C and O atoms:

```
      1045.33
        A1
      X      Y      Z
C1 -0.139  0.000 -0.057
O1  0.000  0.000  0.124
C2  0.139  0.000 -0.057
```

Acetone:

```
FUNDAMENTAL NORMAL VIBRATIONAL FREQUENCIES    HF 6-31G*
       ( THEORETICALLY  24 VALUES )

  Frequency : in 1/cm
  A(i)      : IR intensity (vs,s,m,w,vw,--)
  A(i) = -- : IR inactive

no  Frequency Symmetry  A(i)                  Frequency  Symm    x0.9
 1.  3018.9   (A1  )     m                    3323.89    A1      2992
 2.  3015.7   (B1  )     m                    3322.68    B2      2990
 3.  2989.6   (B2  )     s                    3265.39    B1      2939
 4.  2988.7   (A2  )    --                    3256.83    A2      2931
 5.  2901.5   (B1  )     m                    3210.29    A1      2889
 6.  2901.4   (A2  )     m                    3202.57    B2      2882
 7.  1727.1   (A1  )    vs                    2021.60    A1      1819
 8.  1439.3   (B2  )     w                    1632.50    B1      1469
 9.  1432.2   (A2  )    --                    1614.02    A1      1453
10.  1425.5   (A1  )     w                    1610.61    A2      1450
11.  1423.6   (B1  )    vw                    1607.68    B2      1447
12.  1410.9   (B1  )    vs                    1554.76    B2      1399
13.  1329.7   (A1  )     w                    1546.42    A1      1392
14.  1211.0   (B1  )     m                    1351.79    B2      1217
15.  980.1    (B2  )     w                    1239.41    B1      1115
16.  950.5    (A1  )     w                    1190.63    A1      1072
17.  905.5    (B1  )     w                    983.25     B2      885
18.  904.2    (A2  )    --                    980.71     A2      883
19.  776.9    (A1  )     w                    846.16     A1      762
20.  529.0    (B1  )     w                    574.74     B2      517
21.  479.6    (A1  )     w                    531.87     B1      479
22.  396.6    (B2  )    vw                    400.84     A1      361
23.  126.7    (B2  )     w                    146.20     B1      132
24.  102.8    (A2  )    --                    59.09      A2      53
```

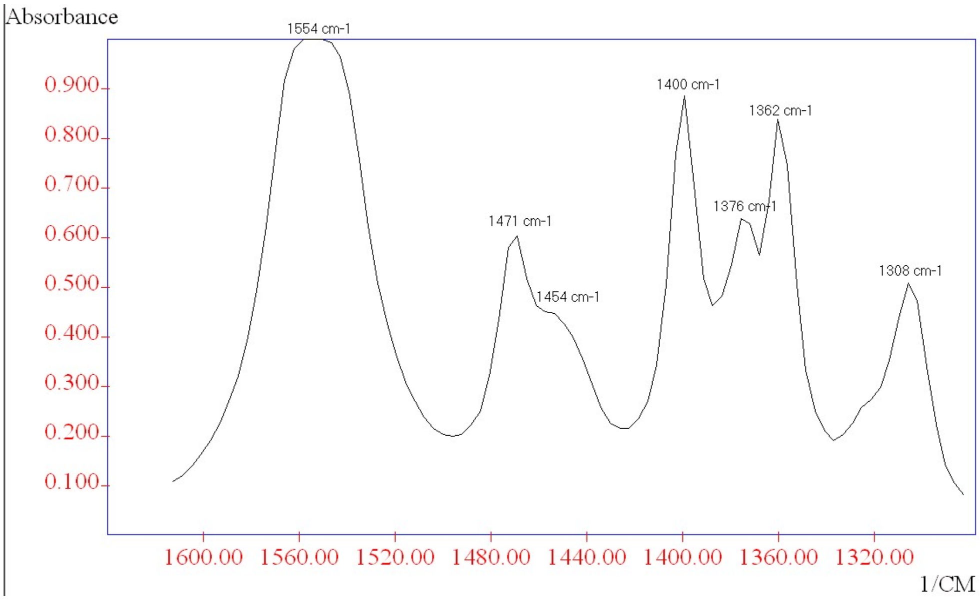
Dimethylether:

```
FUNDAMENTAL NORMAL VIBRATIONAL FREQUENCIES    HF 6-31G*
       ( THEORETICALLY  24 VALUES )

  Frequency : in 1/cm
  A(i)      : IR intensity (vs,s,m,w,vw,--)
  A(i) = -- :  IR inactive

no  Frequency Symmetry  A(i)                  Frequency  Symm    x0.9
 1.  2995.2   (A1  )     m                      3304.91  A1      2974
 2.  2993.1   (B1  )     m                      3302.37  B2      2972
 3.  2934.5   (B2  )     s                      3218.00  B1      2896
 4.  2933.3   (A2  )    --                      3215.44  A2      2894
 5.  2850.5   (A1  )     w                      3179.74  A1      2862
 6.  2849.8   (B1  )     w                      3163.77  B2      2847
 7.  1492.8   (B1  )     m                      1650.75  B1      1486
 8.  1485.1   (A1  )     w                      1670.72  A1      1504
 9.  1472.3   (B2  )     w                      1652.21  B2      1487
10.  1450.4   (A2  )    --                      1650.05  A1      1485
11.  1429.1   (B1  )     w                      1639.42  A2      1475
12.  1424.0   (A1  )     w                      1612.32  B2      1451
13.  1172.1   (B1  )     s                      1402.47  A1      1262
14.  1170.9   (A1  )     w                      1349.94  B2      1215
15.  1135.9   (B2  )     w                      1316.28  B1      1185
16.  1080.4   (A2  )    --                      1280.63  A2      1153
17.  1041.4   (B1  )     m                      1234.60  B2      1111
18.   924.6   (A1  )     m                      1045.33  A1      941
19.   399.4   (A1  )     w                       443.75  A1      399
20.   273.3   (B2  )     w                       265.81  B1      239
21.   187.6   (A2  )    --                       215.54  A2      194
```

Organic texts often imply the absorptions in a vibrational spectrum are individual bond stretches. However, the absorptions are actually normal modes that involve the concerted motion of many atoms in the molecule. However, for some normal modes, those involving C=O for example, the normal mode vibration is dominated by a particular functional group and occurs in a predictable range.

Your instructor may stress that molecular mechanics is insufficiently accurate for normal mode calculations, which is correct. However, for very large molecules molecular orbital based methods are too slow. MM3 was parameterized and designed to predict enthalpies of formation and normal mode frequencies, as accurately as possible within the classical perspective. MM3 often does better than low level molecular orbital methods. Very time intensive methods like B3LYP/6-31G* or MP2/6-311G* are usually necessary for accurate predictions from the quantum mechanical perspective (see the next problem).

38. The infrared spectrum for 2-nitropropane is shown below. Do a normal mode analysis using B3LYP/6-31G* molecular orbital calculations to assign the –NO_2 asymmetric and symmetric stretches. You will need to use a visualization environment that displays the normal mode displacements or animates the vibrations.



P 8.2: The infrared spectrum of 2-nitropropane.

Answer: The B3LYP/6-31B* normal modes in this region are 1668, 1541, 1525, 1518, 1511, 1460, and 1418 cm^{-1}, with the –NO_2 asymmetric stretch at 1668 and the symmetric stretch at 1460 cm^{-1}. Using the approximate scaling factor of ~0.9 to adjust for anharmonicity, the asymmetric stretch is predicted to be at 1500 cm^{-1}, which is close to the major peak at 1554 cm^{-1}. The ratio of the experimental to predicted peak positions is actually 1554 cm^{-1}/1668 cm^{-1} = 0.93. Using this new scaling factor for the predicted symmetric stretch gives 1460*0.93 = 1358 cm^{-1}, which matches well with the experimental peak at 1362 cm^{-1}. There are four vibrations that fall between the two –NO_2 stretches in both the predicted and experimental spectra, which is additional evidence for the assignment, however these intervening band positions don't match up well. In addition, experimental spectra often display overtones, sum, and difference bands, so simply noting the number of experimental peaks can be misleading.

The relatively high computational level of B3LYP/6-31G* is necessary for this example to find reasonable predictions. We will cover many of the issues surrounding molecular orbital calculations and the meaning of the acronyms in the later chapter on computational methods.

39. The energy density of fuels differs greatly. At times optimizing the energy density per unit weight is most important. For practical purposes the low energy density per unit volume for gases or biomass are an issue. Calculate the enthalpy of combustion on a kJ kg^{-1} and a kJ L^{-1} basis for the following fuels, and plot the enthalpy of combustion in kJ L^{-1} versus kJ kg^{-1}. Note that 1 Btu lb^{-1} = 2.326 kJ kg^{-1}. For the gases, assume ideal gas behavior at a pressure of 10 bar at 298 K. The octanes are commonly used to represent gasoline and methane is the major component in natural gas.

Enthalpy of formation or combustion for common fuels.[8-10]

Fuels	$\Delta_f H°$	$\Delta_{comb}H$	$\Delta_{comb}H$	density
	kJ mol^{-1}	kJ g^{-1}	Btu lb^{-1}	g mL^{-1}
graphite	0			2.25
methanol (l)	-238.66			0.7914
ethanol (l)	-277.69			0.7893
octane	-249.9			0.7025
isooctane	-255.1			0.6918
glucose	-1274			1.526
wood			-4480	0.55
biodeisel		-41.2		0.87
coal (lignite)			-8000	0.75
coal (anthracite)			-14000	0.88
H_2 (g)	0			
CH_4 (g)	-74.81			

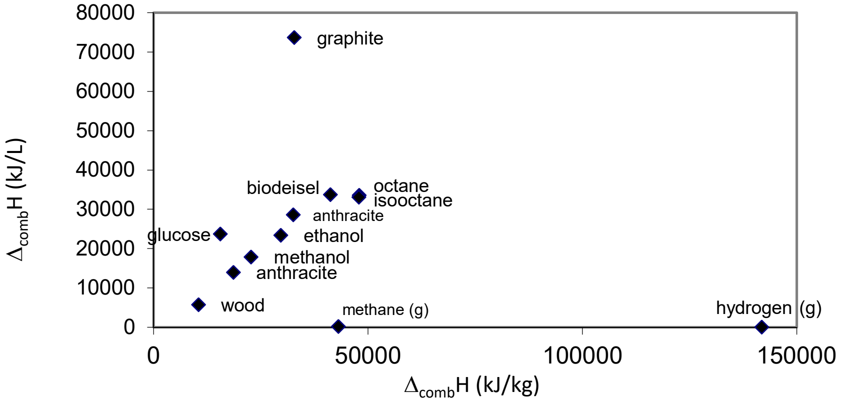
Answer: The following spreadsheet was developed:

Fuel	Formula			$\Delta_f H°$	$\Delta_{comb}H$	$\Delta_{comb}H$	$\mathfrak{M}$	$\Delta_{comb}H$	$-\Delta_{comb}H$	density	$-\Delta_{comb}H$
	C	H	O	kJ mol^{-1}	Btu lb^{-1}	kJ mol^{-1}	g mol^{-1}	kJ g^{-1}	kJ kg^{-1}	g mL^{-1}	kJ L^{-1}
graphite	1	0		0		-393.51	12.01	-32.77	32765	2.25	73722
methanol (l)	1	4	1	-238.66		-726.51	32.04	-22.67	22674	0.7914	17944
ethanol (l)	2	6	1	-277.69		-1366.82	46.07	-29.67	29670	0.7893	23419
octane	8	18		-249.9		-5470.65	114.22	-47.89	47895	0.7025	33646
isooctane	8	18		-255.1		-5465.45	114.22	-47.85	47849	0.6918	33102
glucose	6	12	6	-1274		-2802.04	180.15	-15.55	15554	1.526	23735
wood					-4480			-10.42	10420	0.551	5743
biodeisel								-41.2	41200	0.82	33784
coal lignite					-8000			-18.61	18608	0.753	14011
coal anthracite					-14000			-32.56	32564	0.881	28692
H_2 (g)		2		0		-285.83	2.02	-141.79	141795	0.000813	117
CH_4 (g)	1	2		-74.81		-604.53	14.03	-43.10	43101	0.00565	247

The enthalpy of combustion of graphite and H_2 were calculated using $\Delta_f H^{\circ}$ for CO_2= -393.509 kJ mol^{-1} and $\Delta_f H^{\circ}$ for $H_2O(l)$= -285.830 kJ mol^{-1}. The densities of the gases were calculated using:

$$d = \frac{\mathfrak{M}n}{V} = \frac{\mathfrak{M}P}{RT} \text{ with } P = 10 \text{ bar, } R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}\text{, } T = 298.2 \text{ K}$$

where $\mathfrak{M}$ is the molar mass. The corresponding plot shows H_2 to be the best fuel on a per weight basis, but difficult to transport because of its low density. Working with liquefied gases solves some of the density issues, but raises technological issues. Some interstitial metallic hydrides have higher effective H_2 energy density than liquid H_2.



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Chapter 9 Problems: Using the First Law

1. Write the total differential for V given as a function of the independent variables U and T.

Answer: Given V(U,T) then from Addendum Sec. 7.11, Eq. 7.11.13:

$$dV = \left(\frac{\partial V}{\partial U}\right)_T dU + \left(\frac{\partial V}{\partial T}\right)_U dT$$

These partial derivatives are not so strange as they may first appear. The first can simply be inverted to give the fundamental derivative: $(\partial V/\partial U)_T = 1/(\partial U/\partial V)_T$. For the second, a process at constant energy corresponds to a process in an isolated system.

2. Write the total differential for the new function G with independent variables T and P.

Answer: Given G(T,P) then from Addendum Sec. 7.11, Eq. 7.11.13:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

We will use this equation often where G is the Gibbs Energy.

3. Determine if the following total differential is exact: $dF = 3y^2\,dx + 6xy\,dy$

Answer: The general form of the total differential of F(x,y) is given by Eq. 9.1.5. Matching the terms in dx and dy identifies the coefficients:

$$\left(\frac{\partial F}{\partial x}\right)_y = 3y^2 \qquad \text{and} \qquad \left(\frac{\partial F}{\partial y}\right)_x = 6xy$$

The mixed partials are:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right)_x = \left(\frac{\partial(3y^2)}{\partial y}\right)_x \qquad \text{and} \qquad \left(\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right)_y = \left(\frac{\partial(6xy)}{\partial x}\right)_y$$

Completing the indicated derivatives gives:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right)_x = 6y \qquad \text{and} \qquad \left(\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right)_y = 6y$$

The mixed partials are equal, so the differential is exact and F(x,y) is a state function. Integrating <u>either</u> of these partial derivatives gives: $F = 3xy^2 + c$, where c is a constant. Compare the differential given in this problem with Example 9.1.2.

4. We showed that the differential in Example 9.1.1 is exact:

$$dV = \frac{nR}{P}\,dT - \frac{nRT}{P^2}\,dP \qquad \text{with} \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = \frac{-nRT}{P^2}$$

Separately integrate these partial derivatives to find V. Do indefinite integrals.

Answer: From $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$ $\qquad V = \int dV = \int \frac{nR}{P}\,dT = \frac{nRT}{P} + \text{constant}$

and from $\left(\frac{\partial V}{\partial P}\right)_T = \frac{-nRT}{P^2}$ $\qquad V = \int dV = \int \frac{-nRT}{P^2}\,dP = \frac{nRT}{P} + \text{constant}$

Both coefficients in the differential are consistent with the same function of V, which is the ideal gas law to within a constant. In this sense the differential is “complete.” The same information about the original function is available from either partial derivative. Integrating either gives the original function. You couldn’t get the same result for an inexact differential. An inexact differential is incomplete without the specification of the path of integration.

5. Find the partial derivative of the enthalpy with respect to volume at constant temperature from dH = dU + PdV + VdP. Express the result in terms of C_v, C_p, α, κ_T, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$.

Answer: From H ≡ U + PV, dH = dU + PdV + VdP. Now, take the derivative with respect to V at constant T:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P\left(\frac{\partial V}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

Note that $\left(\frac{\partial U}{\partial V}\right)_T$ = internal pressure and since $\left(\frac{\partial V}{\partial V}\right)_T = 1$:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P + V\left(\frac{\partial P}{\partial V}\right)_T$$

Also remember that $\left(\frac{\partial P}{\partial V}\right)_T = \frac{-1}{V\kappa_T}$ where κ_T is the isothermal compressibility.

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P - \frac{1}{\kappa_T}$$

This equation shows the relationship of the partial derivative to fundamental properties of the system.

6. Show that Eq. 9.4.12°, dH = dU + nR dT or $\Delta H = \Delta U + nR\Delta T$, is consistent with $C_P = C_V + nR$, which is true for an ideal gas.

Answer: Remember the definitions of the heat capacities: $\left(\frac{\partial U}{\partial T}\right)_V = C_v$ and $\left(\frac{\partial H}{\partial T}\right)_P = C_p$. To find $(\partial H/\partial T)_P$, "divide" $dH = dU + nRdT$ by dT at constant P:

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + nR\left(\frac{\partial T}{\partial T}\right)_P \qquad 1°$$

Substituting the definition of C_p, and using $(\partial T/\partial T)_P = 1$ in Eq. 1° gives:

$$C_p = \left(\frac{\partial U}{\partial T}\right)_P + nR \qquad 2°$$

To find $(\partial U/\partial T)_P$, identify P as the "misplaced" variable and work through the total differential of dU, U(V,T):

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad 3$$

Divide both sides of the equation by dT and specify constant P:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \qquad 4$$

(Remember that we derived this equation in our derivation of C_p–C_v, Eq. 9.4.5). Since $(\partial U/\partial V)_T = 0$ for an ideal gas, substitution into Eq. 4 and the definition of C_v gives:

$$\left(\frac{\partial U}{\partial T}\right)_P = C_v \qquad 5°$$

Then substitution of Eq. 5° into Eq. 2° gives:

$$C_p = C_v + nR \qquad 6°$$

Alternative Answer: Starting with $\Delta H = \Delta U + nR\Delta T$, remember that for an ideal gas for any process, $\Delta H = C_p\,\Delta T$ and $\Delta U = C_v\,\Delta T$. Substituting gives $C_p\,\Delta T = C_v\,\Delta T + nR\Delta T$. Division by ΔT gives $C_p = C_v + nR$.

7. Show that $\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas in a closed system.

Answer: Using the results of Problem 5:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P + V\left(\frac{\partial P}{\partial V}\right)_T$$

Note that for an ideal gas, $P = nRT/V$ and:

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-nRT}{V^2}$$

Substitution gives:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P + V\left(\frac{-nRT}{V^2}\right)$$

The V cancels in the last term to give –nRT/V, which is –P:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P + -P = \left(\frac{\partial U}{\partial V}\right)_T$$

8. Show that $\left(\frac{\partial H}{\partial P}\right)_T = (-nRT/P^2)\left(\frac{\partial U}{\partial V}\right)_T$ for an ideal gas in a closed system.

Answer: Substituting the definition of enthalpy, $H \equiv U + PV$, into $(\partial H/\partial P)_T$ gives:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T$$

From the ideal gas law PV = nRT, with n a constant for a closed system:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (nRT)}{\partial P}\right)_T$$

However, for an isothermal process T is constant and the second term is zero. We can use the chain rule to relate $(\partial U/\partial P)_T$ to $(\partial U/\partial V)_T$:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T$$

Using the ideal gas law in the form V = nRT/P gives $(\partial V/\partial P)_T = -nRT/P^2$ and then substitution into the last equation gives:

$$\left(\frac{\partial H}{\partial P}\right)_T = (-nRT/P^2)\left(\frac{\partial U}{\partial V}\right)_T$$

9. Find ΔH in terms of ΔU for a gas that obeys the Virial-type equation of state at constant volume:

$$PV = nRT(1 + B\frac{n}{V})$$

We will assume that B is a constant (the second Virial coefficient is actually temperature dependent). Use this result to find the change in enthalpy for heating one mole of water vapor starting at a pressure of 23.8 torr from an initial temperature of 298.2K to a final temperature of 373.2 K. Assume the volume is constant for the process. Assume $C_V = 6/2\ nR$ and $B = -425\ cm^3\ mol^{-1}$ (roughly the value for water at 373 K).[1] Compare with Example 9.3.2.

Answer: The plan is to use Eq. 9.3.10 and the Virial Equation in terms of the density:

$$PV = nRT(1 + B\frac{n}{V}) \qquad 1$$

Since V is constant, substitution of Eq. 1 into Eq. 9.4.10 gives:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T + (n^2RB/V)\Delta T \qquad 2$$

Next we need to find the volume of the gas. As a first approximation we can use the ideal gas law and the initial state to get the volume. Converting pressure units gives:

$$P = 23.8 \text{ torr} = 0.03132 \text{ atm} = 3.173\text{x}10^3 \text{ Pa} \qquad 3$$

and then:

$$V = 1.00 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})/3.173\text{x}10^3 \text{ Pa} = 0.7814 \text{ m}^3 \qquad 4°$$

Is this ideal value close enough or do we need to use the Virial equation to get the volume? How big is the correction to the volume from the Virial equation? We can use a successive approximations approach. We can substitute the V from the ideal gas law into the right-hand side of Eq. 1 and then solve for the corrected volume. Solving for V with:

$$B = –425. \text{ cm}^3 \text{ mol}^{-1} = –0.425 \text{ L mol}^{-1} = –4.25\text{x}10^{-4} \text{ m}^3 \text{ mol}^{-1} \qquad 5$$

$$V \approx nRT(1 + B\frac{n}{V})/P \qquad 6$$

but $B\frac{n}{V} = –4.25\text{x}10^{-4} \text{ m}^3 \text{ mol}^{-1}(1 \text{ mol})/0.7814 \text{ m}^3 = 5.4\text{x}10^{-4}$ 7

is negligible compared to 1. So the ideal gas equation of state will do fine for calculating the volume.

Then as in Example 9.3.2:

$$\Delta U = C_v\Delta T = 6/2 \text{ nR } \Delta T = 6/2 \text{ (1.00 mol)(8.314 J mol}^{-1}\text{K}^{-1})(373.2\text{-}298.2\text{K})$$

$$\Delta U = 1.871 \text{ kJ} \qquad 8$$

Substitution of this value of the internal energy change into Eq 2. gives:

$$\Delta H = 1.87 \text{ kJ} + (1.00 \text{ mol})(8.314\text{x}10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) (373.2\text{-}298.2\text{K})$$
$$+ (1.00 \text{ mol})^2(8.314 \text{ x}10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(-4.25\text{x}10^{-4} \text{ m}^3 \text{ mol}^{-1})(373.2\text{-}298.2\text{K})/0.7814 \text{ m}^3$$
$$\Delta H = 1.871 \text{ kJ} + 0.624 \text{ kJ} – 0.000339 \text{ kJ} = 2.495 \text{ kJ}$$

So for water vapor under these circumstances, the correction for non-ideality is negligible. We did assume that B was a constant, however. At 298.2 K, B is significantly more negative than the given value, which would make this correction larger. Eq. 2 is useful in geological circumstances where water vapor pressures are much higher and have a decisive effect on the types of minerals that are formed. Constant volume conditions are often appropriate for geological processes and computer simulations.

10. Show that:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_v + nR + \frac{n^2RB}{V}$$

for a gas that obeys the Virial-type equation of state:

$$PV = nRT(1 + B\frac{n}{V})$$

Assume that B is a constant (the second Virial coefficient is actually temperature dependent). Compare the result to the last problem.

Answer: Using the definition of the enthalpy: $H \equiv U + PV$:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial (PV)}{\partial T}\right)_V$$

with $PV = nRT(1 + B\frac{n}{V})$ gives:

$$\left(\frac{\partial (PV)}{\partial T}\right)_V = nR(1 + B\frac{n}{V}) = nR + \frac{n^2RB}{V}$$

Substitution back into $(\partial H/\partial T)_V$ gives the final result:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_v + nR + \frac{n^2RB}{V}$$

since $(\partial U/\partial T)_V = C_v$. For a constant volume process and assuming B is a constant over the temperature range gives the integrated result:

$$\Delta H = C_v\Delta T + nR\Delta T + (n^2RB/V)\Delta T$$

as we saw in the last problem.

11. In Section 9.3 for the isothermal reversible expansion of an ideal gas, which is Path 1 in Figure 9.3.1, we integrated $dH = dU + d(PV)$ to prove that $\Delta H = \Delta U$. Integrate:

$$dH = dU + P\,dV + V\,dP \qquad (9.2.5)$$

directly for an isothermal reversible process and show the result also gives $\Delta H = \Delta U$. In other words, assuming an ideal gas at constant temperature, substitute $P = nRT/V$ and $V = nRT/P$ and then integrate. Compare the integral to Eq. 9.3.10.

Answer: Integrating Eq. 9.2.5:

$$\int_{H_1}^{H_2} dH = \int_{U_1}^{U_2} dU + \int_{V_1}^{V_2} PdV + \int_{P_1}^{P_2} VdP \qquad \text{(closed)} \qquad 1$$

We need to be very careful about the P in PdV and the V in VdP. The P and V are not constant, as they are in Eq. 9.3.18. Assuming an ideal gas, at constant temperature $P = nRT/V$ and $V = nRT/P$. Substituting into Eq. 1 and integrating:

$$\Delta H = \Delta U + \int_{V_1}^{V_2} \frac{nRT}{V} dV + \int_{P_1}^{P_2} \frac{nRT}{P} dP \qquad \text{(closed, ideal gas, cst. T)} \qquad 2°$$

First note that since the process is isothermal, T is a constant, factors out of the integrals, and gives:

$$\Delta H = \Delta U + nRT\int_{V_1}^{V_2}\frac{1}{V}dV + nRT\int_{P_1}^{P_2}\frac{1}{P}dP \qquad \text{(closed, ideal gas, cst. T)} \qquad 3°$$

and integrating gives:

$$\Delta H = \Delta U + nRT\ \ln\left(\frac{V_2}{V_1}\right) + nRT\ \ln\left(\frac{P_2}{P_1}\right) \qquad \text{(closed, ideal gas, cst. T)} \qquad 4°$$

However, for an ideal gas,

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right) \qquad 5°$$

Substituting Eq. 5° into Eq. 4° gives

$$\Delta H = \Delta U + nRT\ \ln\left(\frac{V_2}{V_1}\right) + nRT\ \ln\left(\frac{V_1}{V_2}\right) = \Delta U + nRT\ \ln\left(\frac{V_2}{V_1}\right) - nRT\ \ln\left(\frac{V_2}{V_1}\right) \qquad 6°$$

The last two terms cancel giving:

$$\Delta H = \Delta U \qquad \text{(closed, ideal gas, cst. T)} \qquad 7°$$

Once again we find that ΔH is independent of the path and integrating dH = dU + d(PV) or dH = dU + P dV + V dP is equivalent. The choice of the form of the differential to use is just dependent on convenience.

12. Given that: $\left(\frac{\partial H}{\partial P}\right)_T = 0$, show that $\left(\frac{\partial H}{\partial V}\right)_T = 0$.

Answer: Since the enthalpy is usually considered a function of the independent variables P and T, the "misplaced" variable is the derivative with respect to V. Using the chain rule:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T\left(\frac{\partial P}{\partial V}\right)_T$$

Using the given partial derivative $(\partial H/\partial P)_T = 0$:

$$\left(\frac{\partial H}{\partial V}\right)_T = 0$$

13. We will prove in a later chapter that the internal pressure for a Van der Waals gas is given by:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$$

Find $C_p - C_v$ for a Van der Waals gas.

Answer: From Eq. 9.4.7:

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad 1$$

For a Van der Waals gas: $P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$, which upon substitution into Eq. 1 gives:

$$C_p - C_v = \left[\frac{an^2}{V^2} + \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}\right]\left(\frac{\partial V}{\partial T}\right)_P = \frac{nRT}{(V - nb)}\left(\frac{\partial V}{\partial T}\right)_P \qquad 2$$

The remaining partial derivative is difficult to find directly. Notice however that the inverse is easier. Solving the Van der Waals equation for T:

$$T = \frac{1}{nR}\left(P + \frac{an^2}{V^2}\right)(V - nb) \qquad 3$$

Using the product rule:

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{nR}\left[\left(P + \frac{an^2}{V^2}\right) + (V - nb)\left(\frac{-2an^2}{V^3}\right)\right] \qquad 4$$

We will do a bit of algebra below, but it is sufficient for our purposes to simply divide Eq. 2 by Eq. 4 to get the final result:

$$C_p - C_v = nR\,\frac{\frac{nRT}{(V - nb)}}{\left[\left(P + \frac{an^2}{V^2}\right) + (V - nb)\left(\frac{-2an^2}{V^3}\right)\right]} \qquad 5$$

In the denominator we can substitute for the first term:

$$\left(P + \frac{an^2}{V^2}\right) = \frac{nRT}{(V - nb)} \qquad 6$$

to give:

$$C_p - C_v = nR\,\frac{\frac{nRT}{(V - nb)}}{\left[\left(\frac{nRT}{(V - nb)}\right) + (V - nb)\left(\frac{-2an^2}{V^3}\right)\right]} = nR\,\frac{1}{\left[1 + \frac{(V - nb)^2}{nRT}\left(\frac{-2an^2}{V^3}\right)\right]} \qquad 7$$

Notice that when $a = 0$, that this last equation reduces to $C_p - C_v = nR$, which is the correct result for an ideal gas.

14. For CO_2, $\mu_{JT} = 1.11\ K\ bar^{-1}$ and $C_{p,m}$ for CO_2 is $37.11\ J\ K^{-1}mol^{-1}$. Calculate the change in enthalpy per mole of CO_2 for an isothermal process for a change in pressure of 1.00 bar. Assume that both μ_{JT} and C_p are constant over the pressure range.

Answer: The process corresponds to the partial derivative $(\partial H/\partial P)_T$. The value of this partial derivative is given by the Joule-Thompson coefficient:

$$\mu_{JT} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T \qquad \text{or equivalently} \qquad \left(\frac{\partial H}{\partial P}\right)_T = -\,\mu_{JT}\, C_p$$

Integration assuming a constant μ_{JT} and C_p gives:

$$\Delta H = -\,\mu_{JT}\, C_p\, \Delta P$$

Substitution of the values for this problem gives:

$$\Delta H = -\,1.11 \text{ K bar}^{-1}(37.11 \text{ J K}^{-1}\text{mol}^{-1})\ (1.00 \text{ bar}) = -41.2 \text{ J mol}^{-1}$$

For an ideal gas, the change would be zero since the process is isothermal.

15. Determine the "misplaced" variable for $(\partial H/\partial V)_T$ and express the result in terms of C_v, C_p, α, κ_T, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$.

Answer: The partial derivative that is required is $(\partial H/\partial V)_T$. Substituting the definition of enthalpy, $H \equiv U + PV$, gives using the product rule:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial(U+PV)}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P\left(\frac{\partial V}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T \tag{1}$$

Given that $(\partial V/\partial V)_T = 1$ and from Eq. 7.6.14:

$$\left(\frac{\partial V}{\partial P}\right)_T = -\,V\,\kappa_T \qquad \text{or the inverse:} \quad \left(\frac{\partial P}{\partial V}\right)_T = \frac{-1}{V\,\kappa_T} \tag{2}$$

Substituting Eq. 2 into Eq. 1 gives:

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P - \frac{1}{\kappa_T}$$

Everything on the right-hand side is in the form of a fundamental partial derivative or can be obtained from the equation of state of the substance. Compare this problem to Problem 5.

16. Show that for an ideal gas C_v is not a function of the volume of the system and that C_p is not a function of the pressure of a system. In other words show that, for a closed system:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = 0 \qquad\qquad \left(\frac{\partial C_p}{\partial P}\right)_T = 0$$

Answer: (a). The definition of the constant volume heat capacity is:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Substitution into the partial derivative with respect to V, above, gives:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$$

The order of differentiation can be reversed because U is a state function. The fact that mixed partials are equal is the basis of the Euler criterion for exactness for state functions. For an ideal gas, $(\partial U/\partial V)_T = 0$, giving:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = 0$$

In other words C_v is not a function of volume for an ideal gas.
(b). The definition of the constant pressure heat capacity is:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

Substitution into the partial derivative with respect to V, above, gives:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P$$

The order of differentiation can be reversed because H is a state function. For an ideal gas, $(\partial H/\partial P)_T = 0$, giving:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = 0$$

In other words C_p is not a function of pressure for an ideal gas.

17. Show that $\left(\frac{\partial H}{\partial T}\right)_V = C_P + \left(\frac{\partial H}{\partial P}\right)_T\left(\frac{\alpha}{\kappa_T}\right)$.

Answer: We can get a hint of how to proceed by substituting in the definition of C_p and also that $\alpha/\kappa_T = (\partial P/\partial T)_V$. Correspondingly we need to show that:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$$

Since we normally consider H(P,T) and not H(V,T), we can consider the "misplaced" variable the constant V specification. Notice that given H(P,T) the total differential of H is:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Notice that the partials in this total differential also occur in the relationship we are trying to derive. Simply "dividing" this last equation by dT and specifying constant V for any new partial derivative gives:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial P}\right)_V + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

Using the definition of the constant pressure heat capacity, $C_p = (\partial H/\partial T)_P$, and the result from Eq. 7.6.21, that is $\alpha/\kappa_T = (\partial P/\partial T)_V$, gives:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\alpha}{\kappa_T}\right)$$

Notice that it is often helpful to "work backwards" from the original statement of the problem. Working "backwards" can help give you hints on how to proceed. Just remember to present the full derivation in the "forward" direction as we did here.

18. The Joule-Thomson coefficient is $\mu_{JT} = (\partial T/\partial P)_H$. Show that the corresponding coefficient for constant internal energy processes is given by:

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_v}\left(\frac{\partial U}{\partial V}\right)_T$$

Answer: Starting with $(\partial T/\partial V)_U$, the "misplaced" variable is the constant internal energy. Since U is held constant, we can set the total differential ofU equal to zero. As normal we consider U(V,T), in other words the independent variables for U are V and T:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = 0$$

Subtracting the volume dependent term from both side sof the equality:

$$\left(\frac{\partial U}{\partial T}\right)_V dT = -\left(\frac{\partial U}{\partial V}\right)_T dV$$

"Dividing" both sides of the equation by dV and applying constant U:

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V}$$

Using the definition of the constant volume heat capacity: $C_v = \left(\frac{\partial U}{\partial T}\right)_V$

gives the final result:

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_v}\left(\frac{\partial U}{\partial V}\right)_T$$

This result is an example of the Euler chain relationship.

19. Rewrite Figure 9.7.1 for the partial derivatives:

$$\left(\frac{\partial \mathbf{U}}{\partial T}\right)_P \qquad \left(\frac{\partial \mathbf{T}}{\partial U}\right)_V \qquad \left(\frac{\partial U}{\partial \mathbf{P}}\right)_T \qquad \left(\frac{\partial U}{\partial T}\right)_{\mathbf{P}} \qquad \left(\frac{\partial T}{\partial V}\right)_{\mathbf{U}}$$

Answer: The partial derivative conversions are shown below:

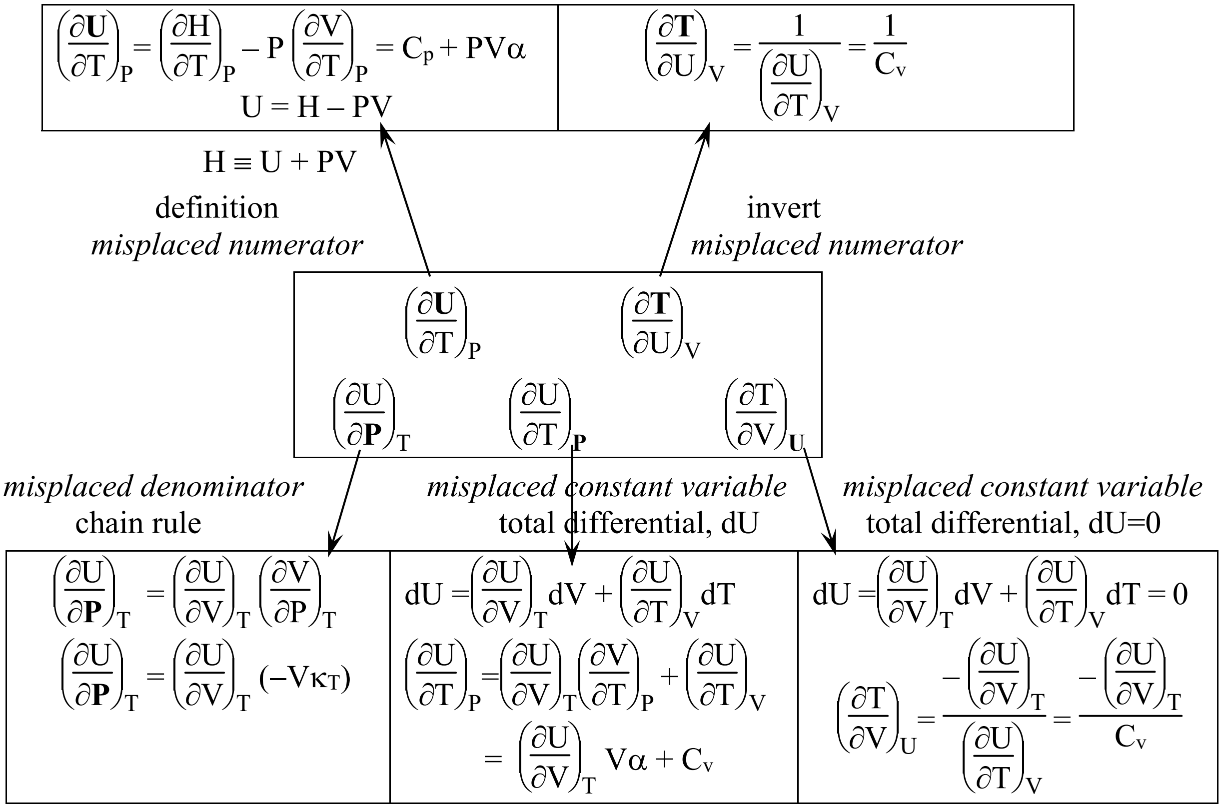


Figure P.1: Partial Derivative Conversion. Partial derivative manipulations to convert unknown partial derivatives to those involving C_v, C_p, α, κ_T, $(\partial U/\partial V)_T$, and $(\partial H/\partial P)_T$.

20. One mole of an ideal diatomic gas at 200. K is compressed in a reversible adiabatic process until its temperature reaches 300. K. Given that $C_{v,m} = {}^5\!/_2 R$, calculate q, w, ΔU, and ΔH.

Answer: For a reversible adiabatic expansion of an ideal gas q = 0, which gives ΔU = w. In addition, $\Delta U = C_v\,\Delta T$ and $\Delta H = C_p\,\Delta T$ for any process in an ideal gas:

$$\Delta U = C_v\,\Delta T = {}^5\!/_2\, nR\Delta T = {}^5\!/_2\,(1\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(300. - 200.\text{ K}) = 2078.\text{ J}$$
$$\Delta U = 2.08\text{ kJ} = w$$

With $C_p–C_v = nR$, $C_p = {}^7/_2\, nR$:

$$\Delta H = C_p\, \Delta T = {}^7/_2\, nR\Delta T\ = {}^7/_2\,(1\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(300. – 200.\text{ K}) = 2910.\text{ J}$$
$$\Delta H = 2.91\text{ kJ}$$

21. Calculate q, w, ΔU, and ΔH for a reversible isothermal expansion of 10.0 mol of an ideal diatomic gas. The initial pressure is 5.00 bar, and the temperature is 298.2 K. The final pressure is 1.00 bar. Assume $C_v = {}^5/_2$ nR (equipartition neglecting vibration).

Answer: The plan is to use ΔT=0, q = –w, ΔU = ΔH = 0 for an isothermal expansion of an ideal gas. For a reversible isothermal expansion in an ideal gas, $w = – nRT \ln(V_2/V_1)$.

Using $P_2V_2= P_1V_1$ to relate the work to the pressure change gives Eq. 9.8.25°:

$$w = – nRT \ln(V_2/V_1) = – nRT \ln(P_1/P_2) = nRT \ln(P_2/P_1)$$
$$w = 10.0\text{ mol}(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(1\text{ kJ}/1000\text{ J})(298.15\text{ K}) \ln(1.00/5.00) = -39.9\text{ kJ}$$
$$q = – w = 39.9\text{ kJ}$$

22. Calculate q, w, ΔU, and ΔH for an isothermal expansion of 10.0 mol of an ideal diatomic gas against a constant external pressure of 1.00 bar. The final pressure of the gas is equal to the external pressure, $P_2 = P_{ext}$. The initial pressure is 5.00 bar, and the temperature is 298.2 K. Assume $C_v = {}^5/_2$ nR (equipartition neglecting vibration).

Answer: The plan is to use ΔT=0, q = –w, ΔU = ΔH = 0 for an isothermal expansion of an ideal gas. For an irreversible expansion, $w = – P_{ext}\Delta V$.

The initial and final volumes are calculated from the ideal gas equation of state:

$$V_1 = (10.0\text{ mol})(0.083145\text{ L bar K}^{-1}\text{ mol}^{-1})(298.15\text{ K})/(5.0\text{ bar}) = 49.58\text{ L}$$
$$V_2 = (10.0\text{ mol})(0.083145\text{ L bar K}^{-1}\text{ mol}^{-1})(298.15\text{ K})/(1.00\text{ bar}) = 247.9\text{ L}$$

The work done is: $w = – P_{ext}\Delta V$:

$$w = –(1.00\text{ bar})(1\text{x}10^5\text{Pa}/1\text{ bar})(247.9 – 49.58\text{ L})(1\text{ m}^3/1000\text{ L}) = -19.8\text{ kJ}$$
$$q = – w = 19.8\text{ kJ}$$

Notice that the magnitude of the work done is significantly less than the reversible case in the last problem, because the gas is expanding against a constant external pressure.

23. The volume of 1.00 mol of an ideal diatomic gas exactly doubles in a reversible adiabatic expansion. The initial pressure is 5.00 bar and the initial temperature is 298.2 K. Calculate q, w, ΔU, and ΔH. Use the constant volume heat capacity for water vapor, $C_v = 25.3\text{ J K}^{-1}\text{ mol}^{-1}$.

Answer: The plan is to use Eq. 9.8.13° to find the final temperature, and then for an adiabatic expansion of an ideal gas, q = 0, ΔU = w, $\Delta U = C_v\, \Delta T$, $\Delta H = C_p\, \Delta T$.

Using the heat capacity for water $C_v/nR = 25.3\ \text{J K}^{-1}\ \text{mol}^{-1}/8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 3.04$. From Eq. 9.8.13°:

$$\left(\frac{T_2}{T_1}\right)^{C_v/nR} = \left(\frac{V_1}{V_2}\right) \qquad \text{giving} \qquad T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{1/3.04}$$

$$T_2 = 298.15\ \text{K}\ (½)^{0.3286} = 298.15\ \text{K}(0.7963) = 237.4\ \text{K}$$

$$w = \Delta U = C_v\ \Delta T = (1.00\ \text{mol})(25.3\ \text{J K}^{-1}\ \text{mol}^{-1})(237.4 - 298.15\ \text{K}) = -1537.\ \text{J}$$

$$w = \Delta U = -1.54\ \text{kJ}$$

Assuming ideal gas behavior $C_p = C_v + nR = 25.3 + 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 33.6\ \text{J K}^{-1}\ \text{mol}^{-1}$:

$$\Delta H = C_p\ \Delta T = (1.000\ \text{mol})(33.6\ \text{J K}^{-1}\ \text{mol}^{-1})\ (237.4 - 298.15\ \text{K}) = -2041.\ \text{J}$$
$$= -2.04\ \text{kJ}$$

The temperature difference is -60.8 K, so you might expect only 2 significant figures in the result. But a quick propagation of errors treatment allows 3 significant figures for ΔU, with $\Delta T = -60.79 \pm 0.18$ K based on 3 significant figures in the heat capacity. On a test, however, when you don't have time to do an error analysis, it would be safest to report only 2 significant figures in the final ΔU and ΔH. The heat capacity limits the number of significant figures to no more than three.

24. Calculate q, w, ΔU, and ΔH for a reversible adiabatic expansion of an ideal diatomic gas. The initial volume is 50.0 L, the initial pressure is 5.00 bar, and the initial temperature is 298.2 K. The final volume is 157.8 L. Assume $C_v = {}^5/_2\, nR$ (equipartition neglecting vibration).

Answer: The plan is to use Eq. 9.8.13° to find the final temperature, and then for an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v\ \Delta T$, $\Delta H = C_p\ \Delta T$.

The number of moles of gas is calculated from the ideal gas equation of state:

$$n = PV/RT = 5.00\ \text{bar}\ 50.0\ \text{L}/0.083145\ \text{J K}^{-1}\ \text{mol}^{-1}/298.15\ \text{K} = 10.08\ \text{mol}$$

Using the equipartition predicted heat capacity, neglecting vibrations, $C_v = {}^5/_2\, nR$, gives $C_v/nR = {}^5/_2$. From Eq. 9.8.13°:

$$\left(\frac{T_2}{T_1}\right)^{C_v/nR} = \left(\frac{V_1}{V_2}\right) \qquad \text{giving} \qquad T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{2/5}$$

$$T_2 = 298.15\ \text{K} \left(\frac{50.0}{157.8}\right)^{2/5} = 298.15\ \text{K}(0.6315) = 188.3\ \text{K}$$

$$w = \Delta U = C_v\ \Delta T = {}^5/_2\ (10.08\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(188.3 - 298.15\ \text{K})$$
$$= -23.0\ \text{kJ}$$

Assuming ideal gas behavior $C_p = C_v + nR = {}^7/_2\ nR$:

$$\Delta H = C_p\ \Delta T = {}^7/_2\ (10.08\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(188.3 - 298.15\ \text{K}) = -32.2\ \text{kJ}$$

25. Calculate the initial and final volume, q, w, ΔU, and ΔH for a reversible adiabatic expansion of 2.000 mol of an ideal monatomic gas. The initial pressure is 10.00 bar and the initial temperature is 298.2 K. The final pressure is 1.000 bar. Use the heat capacities predicted by equipartition. Verify that Eqs. 9.8.19° and 9.8.21°, $P_2 V_2^{\gamma} = P_1V_1^{\gamma}$, give the same result.

Answer: For an adiabatic expansion of an ideal gas, q = 0, ΔU = w, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$. For a monatomic gas $C_v = {}^3/_2\, nR$ and $C_p = C_v + nR = {}^5/_2\, nR$. Using Eq. 9.8.19° to determine the final temperature:

$$\left(\frac{T_2}{T_1}\right)^{C_p/nR} = \left(\frac{P_2}{P_1}\right) \qquad \text{and} \qquad T_2 = T_1\,(P_2/P_1)^{2/5} = 298.15\text{ K}(1.000/10.00)^{2/5}$$

$T_2 = 118.70$ K

$\Delta U = C_v\,(T_2 - T_1) = {}^3/_2\,(1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(118.70 - 298.15 \text{ K})$
$\Delta U = -2238.$ J

$\Delta H = C_p\,(T_2 - T_1) = {}^5/_2\,(1.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(118.70 - 298.15 \text{ K})$
$\Delta H = -3730.$ J

The initial and final volumes are determined from the ideal gas equation of state:

$V_1 = (1.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(10.00 \text{ bar}) = 2.4790$ L
$V_2 = (1.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(118.70 \text{ K})/(1.000 \text{ bar}) = 9.8689$ L

Alternatively, for the final volume, $\gamma = C_p/C_v = 5/3$ and using $P_2V_2^{\gamma} = P_1V_1^{\gamma}$:

$V_2 = V_1(P_1/P_2)^{1/\gamma} = 2.4790 \text{ L}(10.00/1.000)^{3/5} = 9.8689$ L

26. Calculate the initial and final volume, q, w, ΔU, and ΔH for a reversible adiabatic expansion of an ideal diatomic gas. The initial pressure is 5.000 bar and the initial temperature is 298.2 K for 10.00 moles. The final pressure is 1.000 bar. Assume $C_v = {}^5/_2\, nR$ (equipartition neglecting vibration).

Answer: The plan is to use Eq. 9.8.19° to calculate the change in temperature for the reversible adiabatic expansion. Then, for an adiabatic expansion of an ideal gas, q = 0, ΔU = w, $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$.

Assuming ideal gas behavior $C_p = C_v + nR = {}^7/_2\, nR$. For a reversible expansion, the change in temperature is given by Eq. 9.8.19°:

$$\left(\frac{T_2}{T_1}\right)^{C_p/nR} = \left(\frac{P_2}{P_1}\right) \qquad \text{and} \qquad T_2 = T_1\,(P_2/P_1)^{2/7} = 298.15\text{ K}(1.000/5.000)^{2/7}$$

$T_2 = 188.25$ K

$\Delta U = C_v\,(T_2 - T_1) = {}^5/_2\,(10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(188.25 - 298.15 \text{ K})$
$w = \Delta U = -22.844$ kJ

$\Delta H = C_p\,(T_2 - T_1) = {}^7/_2\,(10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(188.25 - 298.15 \text{ K})$

$\Delta H = -31.982$ kJ

The initial and final volumes are determined from the ideal gas equation of state:

$V_1 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(5.000 \text{ bar}) = 49.579 \text{ L}$
$V_2 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(154.43 \text{ K})/(1.000 \text{ bar}) = 128.40 \text{ L}$

Alternatively, for the final volume, using $P_2V_2^{\gamma} = P_1V_1^{\gamma}$:

$V_2 = V_1(P_1/P_2)^{1/\gamma} = 49.579 \text{ L}(5.000/1.000)^{5/7} = 156.52 \text{ L}$

Notice that the magnitude of the work done is significantly less than the corresponding isothermal expansion in Problem 21, since the temperature drops, causing the pressure to decrease, decreasing the pressure against which the gas expands.

27. Calculate the final pressure, initial and final volume, q, ΔU, and ΔH for a reversible adiabatic expansion of an ideal diatomic gas that does -10.00 kJ of work in the process. The initial pressure is 10.00 bar and the initial temperature is 298.2 K for 10.00 moles. Assume $C_v = {}^5/_2\, nR$ (equipartition neglecting vibration).

Answer: The plan is to calculate the final temperature from $w = \Delta U = C_v\, \Delta T$, and from the final temperature the final pressure is calculated from Eq. 9.8.19°.

For an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v\, \Delta T$, $\Delta H = C_p\, \Delta T$. Solving for the change in temperature from the work specified:

$w = \Delta U = C_v\, \Delta T = -10000.$ J
giving:
$-10000. \text{ J} = {}^5/_2\,(10.00 \text{ mol})(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(T_2 - 298.15 \text{ K})$
$T_2 = 250.04$ K
$\Delta H = C_p\,(T_2 - T_1) = {}^7/_2\,(10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(250.04 - 298.15 \text{ K})$
$\Delta H = -14.00$ kJ

Assuming ideal gas behavior $C_p = C_v + nR = {}^7/_2\, nR$. For a reversible expansion, the change in temperature and pressure are related by Eq. 9.8.19°:

$$\left(\frac{T_2}{T_1}\right)^{C_p/nR} = \left(\frac{P_2}{P_1}\right) \qquad \text{and} \qquad P_2 = P_1\,(T_2/T_1)^{7/2} = 10.0 \text{ bar}(250.04 \text{ K}/298.15 \text{ K})^{7/2}$$

$P_2 = 5.4015$ bar

The initial and final volumes are determined from the ideal gas equation of state:

$V_1 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(10.00 \text{ bar}) = 24.790 \text{ L}$
$V_2 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(250.04 \text{ K})/(5.4015 \text{ bar}) = 38.488 \text{ L}$

Alternatively, for the final volume, using $P_2V_2^{\gamma} = P_1V_1^{\gamma}$:

$V_2 = V_1(P_1/P_2)^{1/\gamma} = 24.790 \text{ L}(10.00/5.4015)^{5/7} = 38.488 \text{ L}$

The temperature drops less in this problem as compared to Example 9.8.1c, the magnitude of the work done per mole is less, and $w = \Delta U = C_v\,\Delta T$. The work comes at the expense of the internal energy, since less work is done the internal energy change is less.

28. Calculate the initial and final volume, q, w, ΔU, and ΔH for an adiabatic expansion of an ideal diatomic gas against a constant external pressure, with the final pressure of the gas equal to the external pressure, $P_2 = P_{ext}$. The initial pressure is 5.000 bar and the initial temperature is 298.2 K for 10.00 moles. The external pressure is 1.000 bar. Use the heat capacities predicted by equipartition, neglecting vibration.

Answer: For an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v\,\Delta T$, $\Delta H = C_p\,\Delta T$. For an adiabatic irreversible expansion against a constant external pressure of P_{ext}:

$$\Delta U = C_v\,(T_2 - T_1) \qquad \Delta U = w = -\,P_{ext}\,(V_2 - V_1) \qquad 1$$

Solve these two expressions simultaneously for T_2 gives:

$$C_v\,(T_2 - T_1) = -\,P_{ext}\,(V_2 - V_1) \qquad 2$$

For the final state to be in equilibrium with the surroundings, $P_2 = P_{ext}$. Then for an ideal gas $V_2 = nRT_2/P_2 = nRT_2/P_{ext}$:

$$C_v\,(T_2 - T_1) = -\,P_{ext}\left(\frac{nRT_2}{P_{ext}} - \frac{nRT_1}{P_1}\right) \qquad 3$$

Divide both sides of the equation by nR:

$$\frac{C_v}{nR}\,(T_2 - T_1) = -\,P_{ext}\left(\frac{T_2}{P_{ext}} - \frac{T_1}{P_1}\right) = -\,T_2 + \frac{P_{ext}}{P_1}\,T_1 \qquad 4$$

Collecting terms in T_2 and T_1:

$$\left(\frac{C_v}{nR} + 1\right) T_2 = \frac{C_v}{nR}\,T_1 + \frac{P_{ext}}{P_1}\,T_1 \qquad 5$$

Solving for T_2:

$$T_2 = \frac{\left(\dfrac{C_v}{nR} + \dfrac{P_{ext}}{P_1}\right)}{\left(\dfrac{C_v}{nR} + 1\right)}\,T_1 \qquad 6$$

For a diatomic gas, neglecting vibrations, $C_v/nR = {}^5\!/_2$:

$$T_2 = \frac{\left({}^5\!/_2 + \dfrac{1.000\text{ bar}}{5.000\text{ bar}}\right)}{\left({}^5\!/_2 + 1\right)}\,298.2\text{ K} \qquad 7$$

$T_2 = 230.00\text{ K}$
$\Delta U = C_v\,(T_2 - T_1) = {}^5\!/_2\,(10.000\text{ mol})(8.314\text{ J K}^{-1}\text{ mol}^{-1})(230.00 - 298.15\text{ K})$

$= -14.17 \text{ kJ}$

Using $C_p = C_v + nR = {}^5/_2\, nR + nR = {}^7/_2\, nR$:

$$\Delta H = C_p\,(T_2 - T_1) = {}^7/_2\,(10.000 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(230.00 - 298.15 \text{ K})$$
$$= -19.83 \text{ kJ}$$

The initial and final volumes are determined from the ideal gas equation of state:

$$V_1 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/(5.000 \text{ bar}) = 49.579 \text{ L}$$
$$V_2 = (10.000 \text{ mol})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(230.00 \text{ K})/(1.000 \text{ bar}) = 191.23 \text{ L}$$

The work is given by $w = \Delta U = -14.17$ kJ, or checking for consistency:

$$w = -P_{ext}\Delta V = -(1.000 \text{ bar})(1\text{x}10^5 \text{ Pa}/1 \text{ bar})(191.23 - 49.579 \text{ L})(1 \text{ m}^3/1000 \text{ L}) =$$
$$= -14.17 \text{ kJ}$$

The magnitude of the work is less than the reversible expansion, Problem 26, as expected, since the gas is expanding against a constant external pressure. The magnitude of the work is much less than Problem 21, because in addition to being irreversible, the temperature also decreases.

29. Consider an adiabatic expansion against a constant external pressure, P_{ext}, with the final pressure of the gas equal to the external pressure. The initial pressure is 10.00 bar and the initial temperature is 298.2 K for 10.00 moles of an ideal diatomic gas. Calculate the external pressure that is required for -10.00 kJ of work to be done by the gas. Calculate the final temperature, volume, q, ΔU, and ΔH. Use the heat capacities predicted by equipartition, neglecting vibration.

Answer: For an adiabatic expansion of an ideal gas, $q = 0$, $\Delta U = w$, $\Delta U = C_v\,\Delta T$, $\Delta H = C_p\,\Delta T$. For an adiabatic irreversible expansion against a constant external pressure of P_{ext}:

$$\Delta U = C_v\,(T_2 - T_1) \qquad \Delta U = w = -P_{ext}\,(V_2 - V_1) \qquad 1$$

Solve these two expressions simultaneously for P_{ext} to give:

$$C_v\,(T_2 - T_1) = -P_{ext}\,(V_2 - V_1) \qquad 2$$

For the final state to be in equilibrium with the surroundings, $P_2 = P_{ext}$. Then for an ideal gas $V_2 = nRT_2/P_2 = nRT_2/P_{ext}$:

$$C_v\,(T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_{ext}} - \frac{nRT_1}{P_1}\right) \qquad 3$$

Divide both sides of the equation by nR:

$$\frac{C_v}{nR}\,(T_2 - T_1) = -P_{ext}\left(\frac{T_2}{P_{ext}} - \frac{T_1}{P_1}\right) = -T_2 + \frac{P_{ext}}{P_1}\,T_1 \qquad 4$$

Collecting terms in T_2 and T_1:

$$\left(\frac{C_v}{nR} + 1\right) T_2 = \frac{C_v}{nR}\,T_1 + \frac{P_{ext}}{P_1}\,T_1 \qquad 5$$

Solving Eq. 5 for $P_{ext} = P_2$:

$$\left(\frac{C_v}{nR} + 1\right)\frac{T_2}{T_1} - \frac{C_v}{nR} = \frac{P_{ext}}{P_1} \qquad 6$$

$$P_{ext} = P_1\left[\left(\frac{C_v}{nR} + 1\right)\frac{T_2}{T_1} - \frac{C_v}{nR}\right] \qquad 7$$

For a diatomic gas, neglecting vibrations, $C_v/nR = {}^5/_2$. Solving for the final temperature from the work gives:

$w = \Delta U = C_v\,(T_2 - T_1)$
$-10000.\ \text{J} = {}^5/_2\,(10.00\ \text{mol})(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(T_2 - 298.15\ \text{K})$
$T_2 = 250.04\ \text{K}$

The constant pressure for the expansion from Eq. 7 is:

$$P_{ext} = P_1\left[({}^5/_2 + 1)\frac{250.04\ \text{K}}{298.15\ \text{K}} - {}^5/_2\right]$$

$P_{ext} = 4.3525\ \text{bar}$

The initial and final volumes are determined from the ideal gas equation of state:

$V_1 = (10.000\ \text{mol})(0.083145\ \text{L bar K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})/(10.00\ \text{bar}) = 24.790\ \text{L}$
$V_2 = (10.000\ \text{mol})(0.083145\ \text{L bar K}^{-1}\ \text{mol}^{-1})(250.04\ \text{K})/(4.3525\ \text{bar}) = 47.765\ \text{L}$

Using $C_p = C_v + nR = {}^5/_2\,nR + nR = {}^7/_2\,nR$:

$\Delta U = w = -10000.\ \text{J} = -10.00\ \text{kJ}$
$\Delta H = C_p\,(T_2 - T_1) = {}^7/_2\,(10.000\ \text{mol})\,(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(250.04 - 298.15\ \text{K})$
$= -14.00\ \text{kJ}$

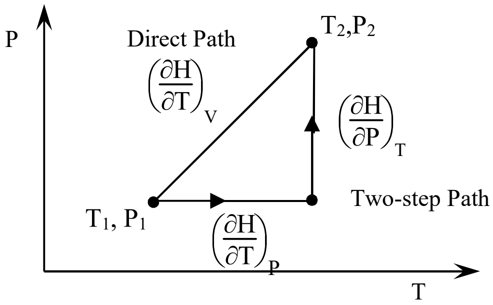
Notice that the change in temperature for this problem is the same as in Problem 27, since $w = \Delta U = C_v\Delta T$ for an adiabatic process, reversible or irreversible.

30. The relationships of the variables that are being held constant for the partial derivative transformation in Eq. 9.4.5 are sketched Figure 9.10.1. (a). Sketch the corresponding relationships for the transformation:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P$$

(b). Rewrite this expression in terms of the fundamental properties, C_v, C_p, α, κ_T, and μ_{JT}, and integrate the resulting expression assuming that the temperature range is sufficiently narrow that the system properties are constant.

Answer: The change in state for the constant volume path may simply be accomplished using a constant temperature path followed by a constant pressure path.



The direct path is shown as a straight line because, assuming an ideal gas with P = nRT/V:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \qquad \text{gives a linear relationship at cst. V:} \quad dP = \frac{nR}{V}\, dT$$

(b).The two-step path is a more convenient way of accomplishing the same change in state, since the values of the partial derivatives are available from experiment; which are tabulated in the form of Joule-Thomson coefficients and constant pressure heat capacities. Using Eq. 9.6.10, Eq. 7.6.16, and the constant pressure heat capacity, Eq. 7.8.24:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P = -\,C_p\ \mu_{JT} \left(\frac{\alpha}{\kappa_T}\right) + C_p$$

If these system properties are all constant then the infinitesimals may be replaced by finite differences (Sec. 9.3):

$$\frac{\Delta H}{\Delta T} = -\,C_p\ \mu_{JT} \left(\frac{\alpha}{\kappa_T}\right) + C_p$$

Chapter 10 Problems: Entropy, Temperature, and Heat Transfer

1. What is the change in entropy for the system for an adiabatic reversible expansion?

Answer: For any adiabatic process $đq = 0$. For an adiabatic reversible process $đq = đq_{rev}$ and the entropy change is $dS = đq_{rev}/T = 0$. Adiabatic reversible processes are constant entropy processes.

2. Calculate the change in entropy for the isothermal reversible expansion of one mole of an ideal gas from an initial volume of 1.00 m^3 to a final volume of 10.0 m^3.

Answer: Integrating the definition of the entropy change for an isothermal process from Eq. 10.2.18:

$$\int_{S_1}^{S_2} dS = \frac{1}{T} \int đq_{rev} \qquad \text{(isothermal reversible)}$$

Entropy is a state function so that integration gives:

$$\Delta S = \frac{q_{rev}}{T} \qquad \text{(isothermal reversible)}$$

This equation is specific to an isothermal reversible process. For an isothermal expansion of an ideal gas, $dH = dU = 0$ and $đq = -đw$. For a reversible isothermal ideal gas expansion remember that $P = P_{ext}$, $đw_{rev} = -PdV$, and $w_{rev} = -nRT \ln(V_2/V_1)$ giving:

$$q_{rev} = nRT \ln \frac{V_2}{V_1} \qquad \text{(isothermal reversible, closed, ideal gas)}$$

Dividing by T to determine the corresponding entropy change gives:

$$\Delta S = \frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1} \qquad \text{(isothermal, ideal gas)}$$

From the values given in the problem:

$$\Delta S = nR \ln \frac{V_2}{V_1} = 1.00 \text{ mol } (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln(10.0 \text{ m}^3/1.00 \text{ m}^3) = 19.1 \text{ J K}^{-1}$$

Notice that you can use any volume units, since the units cancel in the ratio. Notice also that the same change in entropy per mole results from any expansion by a factor of 10: 1 mL→10 mL, or 100 L→1000 L.

3. Evapotranspiration is the process of conversion of liquid water into vapor by the earth's surface. Evapotranspiration is the sum of evaporation and transpiration. Evaporation is the direct vaporization of water from water bodies, plant surfaces, and the soil. Transpiration is the conversion of liquid water into water vapor by movement of water within plants and the subsequent loss of water vapor through stomata in the leaves. Approximately 60% of the energy

available from the solar flux in a forest is consumed by evapotranspiration. The solar flux at the equator at midday is about 1000 W m^{-2}. The evaporation of water results in a large increase in entropy in vegetated areas. Evapotranspiration also moderates the surface temperature and maintains the local humidity. To provide a very rough model, consider a flat surface that is heated to the boiling point of water by the sun. Assume that 60% of the solar flux is available for the vaporization of water on this surface. Calculate the rate of the production of entropy from the vaporization of water per second per m^2 at midday at the equator for a forest. The enthalpy of vaporization of water at the normal boiling point is $\Delta_{vap}H = 40.7$ kJ mol^{-1}.

Answer: Using Eq. 10.2.19 and the normal boiling point of water, $T_b = 373.15$ K at 1 atm, the molar entropy of vaporization is:

$$\Delta_{tr}S_m = \frac{\Delta_{tr}H}{T_{tr}} = \frac{40.7\ \text{kJ mol}^{-1}\ (1000\ \text{J/1 kJ})}{373.15\ \text{K}} = 108.\ \text{J K}^{-1}\ \text{mol}^{-1}$$

With 60% of the solar flux utilized for evapotranspiration, the energy flux is given by:

$$J_{ET} = 1000\ \text{W m}^{-2}\ (1\ \text{J s}^{-1}/1\ \text{W})(0.60) = 600.\ \text{J s}^{-1}\ \text{m}^{-2}$$

and the evapotranspiration rate in moles of water per unit area is then

$$R_{ET} = J_{ET}/\Delta_{vap}H = \frac{600.\ \text{J s}^{-1}\ \text{m}^{-2}}{40.7\ \text{kJ mol}^{-1}(1000\ \text{J/1 kJ})} = 0.0147\ \text{mol s}^{-1}\ \text{m}^{-2}$$

and the entropy production is the product of the evapotranspiration rate and the molar entropy of vaporization. A common symbol for the entropy production is σ:

$$\sigma = R_{ET}\ \Delta_{tr}S_m = 0.0147\ \text{mol s}^{-1}\ \text{m}^{-2}(108\ \text{J K}^{-1}\ \text{mol}^{-1}) = 1.59\ \text{J K}^{-1}\ \text{s}^{-1}\ \text{m}^{-2}$$

Much of the sun's energy is used for entropy production by evapotranspiration over vegetated areas. The deforestation of rainforests has the potential to greatly alter the energy balance in tropical regions, which may result in higher temperatures and the loss of productivity because of water scarcity. The humidity above rainforests is recycled as rain.

We used the flat surface at 100°C because at this point, we haven't discussed how to calculate entropy change for irreversible processes. Please see Chapters 11 and 13.

4. The following is a common student question concerning temperature as a measure of the "quality" of the energy in a system. Answer the student's question.

> "The higher the temperature of a substance (for example a gas) the higher the quality of the energy in the system to do useful work. But at the same high temperature, the system has high entropy as well, which accounts for energy dispersal and hence less availability of the energy. How is the concept of temperature as a measure of quality and the concept of entropy consistent?"

Answer: The first bit of confusion is that the change of the entropy for a system is a measure of the energy dispersal, not the value of the entropy itself. Energy dispersal is the result of a process. A second bit of confusion relates to the fact that temperature is an intensive variable and entropy is an extensive variable. The temperature is an intrinsic property of the system, independent of size. The entropy scales with size or total energy transferred into the system. So if you double the size of a system, you double the entropy and you double the internal energy.

However, the spontaneity of the transfer of energy from this system to another system is dependent on the temperature gradient and not the size of the system or the total amount of energy. The entropy of a system does increase with temperature. But this thermal energy is not available unless the system comes into contact with another object that is at a lower temperature. If the system comes into contact with a colder object, energy will be transferred from the hotter to the colder. This transfer causes some of the available energy to spread, or disperse, from the hotter object into the colder object. The transfer of energy stops when the hotter object cools and the colder object heats to the same temperature.

5. A hot cup of coffee has a temperature of 60-70°C and a mass of 250 g. Calculate the change in entropy for 250. g of water when the temperature is increased from 25.0°C to 60.0°C at constant pressure. Assume a constant heat capacity of 4.18 J K^{-1} g^{-1}. [Hint: Remember that at constant pressure dH = C_p dT and then you need to integrate the definition of entropy.]

Answer: At constant pressure from the definition of the constant pressure heat capacity,

$$đq_p = dH = C_p\, dT$$

Since H is a state function, the heat transfer in this particular case is independent of the path, and $đq_p$ is equivalent to a reversible heat transfer, $đq_{rev}$. Substitution into the definition of entropy gives:

$$dS \equiv \frac{đq_{rev}}{T} = \frac{dH}{T} = C_p \frac{dT}{T} \qquad \text{(cst. P, closed)}$$

Integration gives:

$$\Delta S = \int_{T_1}^{T_2} C_p \frac{dT}{T} \qquad \text{(cst. P, closed)}$$

Assuming a constant heat capacity:

$$\Delta S = C_p \ln \frac{T_2}{T_1} \qquad \text{(cst. P, closed)}$$

For the temperatures given in the problem, converting into kelvins, 298.12 K and 333.15 K:

$$\Delta S = C_p \ln \frac{T_2}{T_1} = 250.\text{ g } (4.18\text{ J K}^{-1}\text{ g}^{-1}) \ln \frac{333.15}{298.15} = 116.\text{ J K}^{-1}$$

6. Calculate the change in entropy for the isothermal reversible expansion of an ideal gas from an initial volume of V_1 to a final volume of V_2. This is the same problem as Problem 2. However, this time, approach the derivation using the combined First and Second Laws of thermodynamics, Eq. 10.4.1. Solve for the change in entropy using Eq. 10.4.1 and then make substitutions appropriate for an isothermal reversible expansion of an ideal gas.

Answer: The combined First and Second Laws is dU = TdS – PdV. Solving for the change in entropy gives:

$$dS = \frac{dU}{T} + \frac{P}{T}dV \qquad \text{(closed, PV work)}$$

For an isothermal process in an ideal gas dU = 0, so the first term drops out. For an ideal gas P/T = nR/V. Substitution gives:

$$dS = nR\,\frac{dV}{V} \qquad \text{(isothermal, closed, PV work)}$$

Integration gives:

$$\Delta S = nR \int_{V_1}^{V_2} \frac{dV}{V} = nR \ln \frac{V_2}{V_1} \qquad \text{(isothermal, closed, PV work)}$$

as we derived before in Problem 2.

7. Use the concept of energy dispersal to discuss the specific changes in entropy for the combustion of one mole of glucose:

$$C_6H_{12}O_6\ (s) + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (g)$$

where the water is produced as a gas at high temperature. Do you expect this reaction to be spontaneous?

Answer: There are three sources of energy dispersal in this example. First, there is an increase in the number of moles of gas, $\Delta n_g = [6 + 6] - [6] = 6$ moles, since the problem specifies that the water is released as a gas. Gases are more dispersed, per mole, than liquids and solids. The energy dispersal in the net conversion of a solid into a gas is that the kinetic energy of translation and rotation and the kinetic and potential energy of vibration of the gas molecules is dispersed.

Second, this reaction is very exothermic. The energy stored in the bonds in the glucose and oxygen molecules is much higher than the energy stored in the bonds in the product CO_2 and H_2O. The energy in the chemical bonds is stored in the potential and kinetic energy of the electrons and the potential energy of repulsion of the nuclei. This stored energy is greater in the reactants than the products. The exothermicity provides thermal energy to the product gases that increases the translation, rotation, and vibrational kinetic energy and vibrational potential energy of the products, hence dispersing this extra energy to more molecules in a larger volume.

Third, there is a net increase of non-linear gas molecules. The reactant gas, O_2, is diatomic and therefore linear. While CO_2 is linear, water is bent. Non-linear molecules have one more rotational degree of freedom than linear. In linear molecules the rotation around the internuclear axis has no moment of inertia.

8. Show that $\left(\frac{\partial S}{\partial V}\right)_U = \left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V = \frac{P}{T}$

Answer: The “misplaced” variable, in the sense of Section 9.7, is that the internal energy is held constant in $\left(\frac{\partial S}{\partial V}\right)_U$. Working through the total different of U(S,V) and setting dU = 0:

$$0 = dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{1}$$

and dividing by dV at constant U:

$$0 = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_U + \left(\frac{\partial U}{\partial V}\right)_S \cancelto{1}{\left(\frac{\partial V}{\partial V}\right)_U} \tag{2}$$

and solving for $(\partial S/\partial V)_U$:

$$\left(\frac{\partial S}{\partial V}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V \tag{3}$$

This result is an example of the Euler chain relationship. From Eq. 10.2.10:

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \tag{4}$$

and inverting Eq. 10.2.16: $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$ (5)

Substitution of Eqs. 4 and 5 into Eq. 3 gives the final result: $\left(\frac{\partial S}{\partial V}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V = \frac{P}{T}$

9. Considering that S(U,V), find the total differential of S. From the total differential and the relationship in Problem 8, show that:

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

Answer: Given that S(U,V) the total differential is:

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \tag*{1}$$

Note that from the definition of temperature, Eq. 10.2.16:

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{\left(\frac{\partial U}{\partial S}\right)_V} = \frac{1}{T} \tag*{2}$$

and in Problem 8 we proved $\left(\frac{\partial S}{\partial V}\right)_U = -\left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial S}{\partial U}\right)_V = \frac{P}{T}$ 3

Substitution of Eqs. 2 and 3 into the total differential gives:

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV = \frac{1}{T} dU + \frac{P}{T} dV \qquad 4$$

We could also have derived the same result by solving the combined First and Second Laws, Eq. 10.4.1, for dS. Eq. 4 will be very useful when we show the general properties of entropy. Eq. 4 shows explicitly the differences between the entropy and the internal energy.

10. We will find that $dH = T\,dS + V\,dP$. (see Problem 12) Find the total differential of H assuming that H(S,P). Then determine the values for:

$$\left(\frac{\partial H}{\partial S}\right)_P \text{ and } \left(\frac{\partial H}{\partial P}\right)_S$$

Answer: Given the independent variables for H(S,P), the total differential is:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Comparing term by term with $dH = T\,dS + V\,dP$ gives:

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

11. Prove that $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$

Answer: The definition of temperature is $\left(\frac{\partial U}{\partial S}\right)_V = T$ or inverting gives $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$. This definition suggests that the "misplaced" variable in the partial derivative is T. Therefore, it might be better to have U in the denominator, rather than T. Then expanding $(\partial S/\partial T)_V$ using the chain rule:

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V$$

The definition of the constant volume heat capacity is

$$\left(\frac{\partial U}{\partial T}\right)_V = C_v$$

Substitution gives:

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{T}\, C_v$$

12. Using the combined First and Second Laws, $dU = T\,dS - P\,dV$, and the definition of enthalpy, $H \equiv U + PV$, show that $dH = T\,dS + V\,dP$

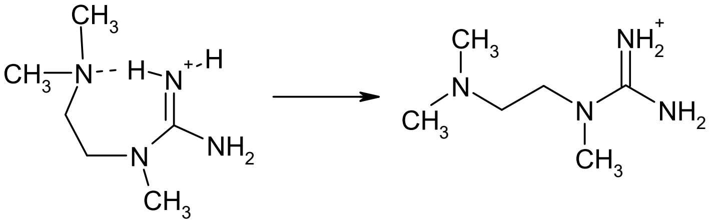
Answer: From $H \equiv U + PV$, the total differential is $dH = dU + PdV + VdP$. Substituting $dU = T\,dS - P\,dV$ into the total differential of H gives:

$$dH = dU + PdV + VdP = T\,dS - P\,dV + P\,dV + V\,dP$$

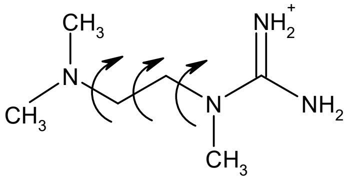
Cancelling terms gives the final result:

$$dH = dU + PdV + VdP = T\,dS + V\,dP$$

13 The N-[2-(dimethylamino)ethyl]-N-methylguanidium ion has a strong intramolecular hydrogen bond. Describe the change in entropy when this ion is heated sufficiently to break the hydrogen bond.



Answer: The torsional vibrations for the C-C bonds to the methylene groups are hindered by the formation of the hydrogen bond. This steric hindrance is released when the hydrogen bond melts producing three free low frequency torsions that more easily accept energy. These torsions are illustrated below. The conformational entropy increases through energy dispersal into the low frequency torsions upon breaking the hydrogen bond



14. Describe the potential of using the oceans of the world as a source of thermal energy. Explicitly consider changes in the internal energy and entropy of the oceans and extraction of energy from the oceans to do useful work.

Answer: The internal energy of the oceans is immense. Since internal energy and entropy are extensive, the internal energy and entropy of the oceans increase from transfers of water to the oceans and the transfer of energy from solar radiation to the oceans. The internal energy and entropy of the oceans is increasing because of sea level rise and global climate change. However, under normal circumstances, this energy is pretty much useless because of the low effective temperature of the oceans. A temperature gradient is necessary to extract useful energy. The vast thermal energy of the oceans is only available if the temperature of the engine or other system that you want to run is lower than the available ocean water temperature (see Chapter 11 for a more careful description of thermal energy conversion).

However, one process is under development that extracts energy from the oceans based on naturally occurring temperature gradients. Ocean thermal energy conversion, OTEC, uses the temperature gradient between deep water and surface water in the ocean to drive specially designed turbines that are linked to electrical generators. To be economical OTEC plants must be located where a difference of about 22°C occurs year round. This requirement restricts the location of OTEC to tropical regions with access to deep water. Maintenance costs and materials durability are current problems for large-scale application of this otherwise straightforward technology. A second possibility for cold regions is the use of the ocean as the high temperature thermal reservoir when the ambient air temperature is significantly lower than the ocean temperature. A Stirling engine or a turbine would be able to convert ocean thermal energy into electricity on cold winter days. However, the low heat capacity and thermal conductivity of air limits the power available from such a system.

Chapter 11 Problems: The Thermodynamic Definition of Entropy

1. Calculate the Carnot efficiency of a solar concentrator–Stirling engine system that operates at 700°C and 37°C.

Answer: The temperatures are 973 K and 310 K in kelvins. The efficiency is then

$\xi = (973\text{-}310)/973 = 68.1\%$

However, most companies stopped development research on solar concentrator–Stirling engine systems in the late 1990's, because the systems were not economically viable. The increase in petroleum and natural gas prices in 2007 caused a resurgence in interest.

2. Is it more efficient to fly in the summer or winter?

Answer: Given Eq. 11.2.14, $\xi_{max} = \left(\frac{T_H - T_L}{T_H}\right)$, T_L is lower in winter so ξ_{max} is greater in winter. [Also, air turbulence decreases in the winter, which probably has a bigger effect.]

3. On a really hot day, is it possible to cool the kitchen by opening the refrigerator door?

Answer: The temperature near the refrigerator will briefly drop, but the room temperature will subsequently steadily rise. The refrigerator acts as a heat pump, using electrical work to transfer heat from a low temperature reservoir to a high temperature reservoir. The best that can happen is that the room stays at constant temperature. This is because the low temperature reservoir is the area in front of the open refrigerator, and the high temperature reservoir is the area in back of the refrigerator, which is heated by the cooling coils on the back of the refrigerator. The temperature in fact must increase. You can argue this question using the First Law or the Second Law. Using the First Law: electrical energy enters the room to run the refrigerator, so $\Delta U_{room} > 0$, so $\Delta T > 0$. Using the Second Law: assume that the refrigerator runs on a battery, even then the temperature would increase. The reason is that no engine or heat pump can be 100% efficient, so some energy will be wasted and the temperature will increase.

4. One mole of an ideal monatomic gas is used as the working substance for a reversible Carnot cycle. The initial temperature is 500. K and the initial volume is 4.00 L. For step I, the gas expands to twice its initial volume. In step II the temperature is lowered to 300. K. What is the volume V_3 after step II, and V_4after step III,? Step IV returns the system to the initial temperature and volume.

Answer: For step II, since the step is adiabatic and reversible: $V_3T_3^c = V_2\, T_2^c$ with $c = C_v/nR$. For a monatomic gas $C_v = 3/2\ nR$, giving $c= 3/2$:

$$V_3 = V_2 \left(\frac{T_2}{T_3}\right)^c = 8.00\ \text{L} \left(\frac{500.}{300.}\right)^{3/2} = 17.21\ \text{L}$$

For step III, we need to calculate V_4 from V_1 using step IV. Step IV is an adiabatic reversible step so that we can calculate V_4 from V_1 by $V_4\, T_4^c = V_1\, T_1^c$:

$$V_4 = V_1\left(\frac{T_1}{T_4}\right)^c = 4.00\text{ L}\left(\frac{500.}{300.}\right)^{3/2} = 8.606\text{ L}$$

5. One mole of an ideal monatomic gas is used as the working substance for a reversible Carnot cycle. The initial temperature is 500. K and the initial volume is 4.00 L. For step I, the gas expands to twice its initial volume. In step II the temperature is lowered to 300. K. Notice that for a reversible cycle, the work done in steps II and IV is equal, but opposite in sign. (a) Calculate the work done in step I and step III. (b) Calculate the energy transferred from the high temperature reservoir, q_H. (c) Calculate the efficiency for the cycle.

Answer: (a) For step I, n = 1.00 mol, T_H=500. K, V_1 = 4.00 L and V_2 = 8.00 L as given in the problem. Since the expansion is isothermal and reversible: $w_I = -nRT_H \ln(V_2/V_1)$ giving:

$$w_I = -(1.00\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})(500.\text{ K})\ln(8.00/4.00) = -2881.\text{ J}$$

(b) Please see Problem 4 for the calculation of V_3 = 17.21 L and V_4 = 8.606 L. Since step III is isothermal reversible at T_L = 300. K:

$$w_{III} = -(1.00\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})(300.\text{ K})\ln(8.606/17.21) = 1729.\text{ J}$$

(c) The total work is $w = w_I + w_{III}$ for a reversible cycle:

$$w = -2881.\text{ J} + 1729.\text{ J} = -1152.\text{ J}$$

For isothermal step I, ΔU = 0, so that $q_H = -w_I$ = 2881. J giving the efficiency, using Eq. 11.1.5:

$$\xi = \frac{-w}{q_H} = \frac{-(-1152.)}{2881.} = 0.400$$

We can check our calculation using Eq. 11.2.14 giving:

$$\xi_{max} = \left(\frac{T_H - T_L}{T_H}\right) = \left(\frac{500. - 300.}{500.}\right) = 0.400$$

So our calculations are correct. Notice that the comparison of the results from Eq. 11.1.5 and Eq. 11.2.14 shows that the maximum efficiency for a process operating in a cycle is an exclusive function of the operating temperatures. We chose a process where the volume doubles in step I. However, this choice does not, in the end, have an effect on the efficiency.

6. A 0.200-mol sample of a monatomic ideal gas is used as the working substance in a reversible Carnot cycle that operates between 700 K and 300 K. The starting volume is 0.500 L. The heat transferred into the gas from the high temperature reservoir is 1000. J. (a) Calculate q, w, ΔU, and ΔS for each of the steps in the Carnot cycle. (b) Calculate q, w, ΔU, and ΔS for the complete cycle.

Answer: (a) For step I, n = 0.200 mol, q_H = 1000. J, T_H=700. K, T_L= 300. K, and V_1 = 0.500 L as given in the problem. For this isothermal step, ΔU = 0, so that $w_I = -q_H = -1000.$ J and

$$\Delta S = q_{rev}/T_H = 1000.\text{ J}/700.\text{ K} = 1.429\text{ J K}^{-1}$$

For the subsequent step we will need to know V_2. Since the expansion is isothermal and reversible: $w = -nRT\ln(V_2/V_1)$ giving:

$$w_I = -1000\text{ J} = -(0.200\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})(700.\text{ K})\ln(V_2/V_1)$$

or $\ln(V_2/V_1) = 0.8591$ and finally:

$$V_2 = 0.500\text{ L } e^{0.8591} = 1.181\text{ L}$$

For step II, since the step is adiabatic and reversible, $q = q_{rev} = 0$, $\Delta S = 0$, and for a monatomic gas $C_v = 3/2\ nR$:

$$w_{II} = \Delta U = C_v\,\Delta T = \frac{3}{2}\,nR(T_L - T_H) = \frac{3}{2}\ (0.200\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})(300. - 700.\text{ K})$$

$$w_{II} = \Delta U = -997.7\text{ J}$$

For the subsequent step we will need to know V_3. Since the expansion is adiabatic and reversible: $V_3T_3^c = V_2\,T_2^c$ with $c = C_v/nR$. For a monatomic gas $C_v = 3/2\ nR$, giving $c= 3/2$:

$$V_3 = V_2\left(\frac{T_2}{T_3}\right)^c = 1.181\text{ L}\left(\frac{700.}{300.}\right)^{3/2} = 4.208\text{ L}$$

For step III, which is again isothermal, $\Delta U = 0$ so that $w_{III} = -\,q_L$ and $w = -\,nRT_L\ln(V_4/V_3)$. We need to calculate V_4. Step IV is an adiabatic reversible step so that we can calculate V_4 from V_1 by $V_4\,T_4^c = V_1\,T_1^c$:

$$V_4 = V_1\left(\frac{T_1}{T_4}\right)^c = 0.500\text{ L}\left(\frac{700.}{300.}\right)^{3/2} = 1.782\text{ L}$$

So the work in step III is:

$$w_{III} = -\,nRT\ln(V_4/V_3) = -\,(0.200\text{ mol})(\,8.314\text{ J mol}^{-1}\text{ K}^{-1})(300.\text{ K})\ln(1.782/4.208)$$
$$= 428.6\text{ J}$$

with $q_L = q_{rev} = -w_{III} = -428.6$ J and $\Delta S = q_{rev}/T_L = -\,428.6\text{ J}/300.\text{ K} = -1.429\text{ J K}^{-1}$
which is the same absolute value as for step I.

For step IV, since the step is adiabatic and reversible, $q = q_{rev} = 0$, $\Delta S = 0$, and for a monatomic gas $C_v = 3/2\ nR$:

$$w_{IV} = \Delta U = C_v\,\Delta T = \frac{3}{2}\,nR(T_H - T_L) = \frac{3}{2}\ (0.200\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})(700. - 300.\text{ K})$$

giving $w_{IV} = \Delta U = 997.7$ J which is just the negative of step II, as expected.

(b) The results and totals are summarized in the following table.

Step	q (J)	w (J)	ΔU (J)	ΔS (J K^{-1})
I: isothermal, T_H	1000.	– 1000.	0	1.429
II. adiabatic	0	–997.7	–997.7	0
III. isothermal, T_L	– 428.6	428.6	0	– 1.429
IV. adiabatic	0	997.7	997.7	0
totals	571.4	-571.4	0	0

We can check our results by calculating the overall efficiency using the numbers from the table and comparing with Eq. 11.2.14. Using w and q_H, explicitly from the table, and using Eq. 11.1.5 gives:

$$\xi = \frac{-w}{q_H} = \frac{-(-\,571.4\text{ J})}{1000.\text{ J}} = 0.5714$$

Now using Eq. 11.2.14 gives:

$$\xi_{max} = \left(\frac{T_H - T_L}{T_H}\right) = \left(\frac{700. - 300.}{700.}\right) = 0.5714$$

So our calculations are correct. Note that the overall change in ΔS for this cyclic process is zero, since the cycle is reversible.

7. The peak sun solar flux that reaches a surface pointed directly at the sun is about 1.00 kW m^{-2}. Using a solar collector of area 10.0 m^2, calculate the collector temperature that would be necessary to produce 4.00 kW of power using a steam turbine coupled to an electric generator at peak sun flux. Assume the discharge temperature of the turbine is 35°C and that the combined steam turbine and electrical generator operate at 60.0% of the maximum theoretical efficiency (due to frictional losses, etc.). Neglect radiative losses from the solar collector absorber surface.

Answer: The final output power, P, is:

$$P = J_{solar}\, A\, \xi_{max}\,(0.600)$$

using the fact that the combined steam turbine and electrical generator operate at 60% of the maximum theoretical efficiency. The required power is 4 kW:

$$P = 4 \text{ kW} = (1.00 \text{ kW m}^{-2})(10.0 \text{ m}^2)\, \xi_{max}\,(0.600)$$

solving for ξ_{max} gives $\xi_{max} = 0.667$

Using ξ_{max} and solving for T_H from Eq. 11.2.14 using $T_L = 35 + 273.\text{ K} = 308.\text{ K}$:

$$\xi_{max} = 0.667 = \left(\frac{T_H - T_L}{T_H}\right) = \left(\frac{T_H - 308.\text{ K}}{T_H}\right)$$

or $0.667\, T_H = T_H - 308 \text{ K}$

gives $T_H = 925.\text{ K}$

8. In problem 7, we neglected radiative losses from the solar collector absorber surface. Assuming the same conditions and operating temperatures as in problem 7, calculate the output power when radiative losses from the solar collector absorber surface are taken into account. Assume that the absorber surface is 0.1 m^2 (this concentration ratio is $A/a = 100$).

Answer: From Eq. 11.2.20, and using $T_H = 925.\text{ K}$ and $T_L = 308.\text{ K}$ from problem 7:

$$\xi_{max} = \left(\frac{T_H - T_L}{T_H}\right)\left(\frac{J_{solar} A - a\,\sigma\, T_H^4}{J_{solar} A}\right)$$

$$= (0.667)\left(\frac{1000 \text{ W m}^{-2}\,(10.0 \text{ m}^2) - 0.1 \text{ m}^2\,(5.6704\times10^{-8} \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-4})(925.)^4}{1000 \text{ W m}^{-2}(10.0 \text{ m}^2)}\right)$$

$$= (0.667)\left(\frac{1.00\text{x}10^4 - 4151.3 \text{ W}}{1.00\text{x}10^4 \text{ W}}\right) = (0.667)(0.585) = 0.390$$

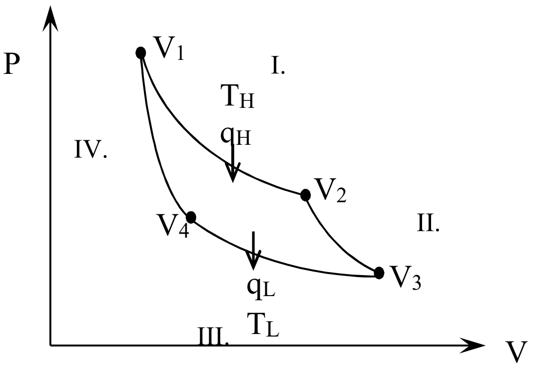
The radiative loss from the absorber area is significant. Then the final output power is decreased almost by a factor of two:

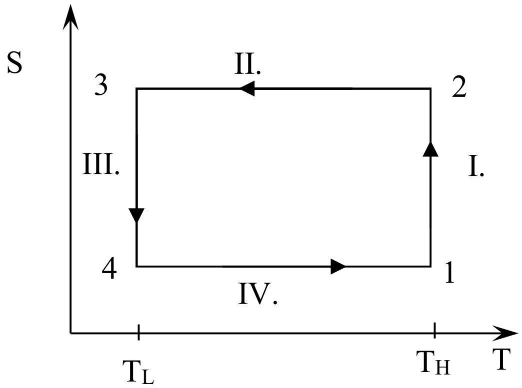
$$P = J_{solar}\, A\, \xi_{max}\,(0.600) = (1.00 \text{ kW m}^{-2})(10.0 \text{ m}^2)(0.390)(0.600) = 2.34 \text{ kW}$$

The implication for chemists from this example is that many diverse energy sources must be found to decrease our dependence on fossil fuels. Solar power alone will not solve the problem; the materials requirements are too large.

9. Give a rough sketch of the progress for a reversible Carnot cycle on a plot of entropy versus temperature. Label the steps I-IV so that you can compare with Figure 11.2.1. Also indicate the starting point.

Answer: Please review problem 4, for explicit example numbers. The starting point in Figure 11.2.1 is chosen at T_H. Step I is isothermal with an increase in entropy, since $\Delta S = q_{rev}/T_H$ with $q_{rev}>0$. Step II is adiabatic reversible, so ΔS is zero and then S is constant. The temperature drops from T_H to T_L. Step III is isothermal, again, but with a decrease in entropy since $q_L < 0$. Step IV is adiabatic again, but the temperature increases from $T_L$to T_H.





10. The solar concentration ratio of a solar collector is defined as the total collector area divided by the absorber area, c = *A*/*a*. The solar collection area for a very large "power tower" is on the order of 200. m^2. For a small solar absorber area of 0.1 m^2 (~1 ft^2), the corresponding concentration ratio is 2000. Plot the solar thermal efficiency for this concentration ratio as a function of absorber temperature, T_H, including the Carnot efficiency and radiative losses. Assume that the low temperature reservoir for the solar thermal process is at 300. K and the solar flux is 1000. W m^{-2}.

Answer: Using Eq. 11.2.20:

$$\xi_{max} = \left(\frac{T_H - T_L}{T_H}\right)\left(\frac{J_{solar}A - a\,\sigma\,T_H^4}{J_{solar}A}\right)$$

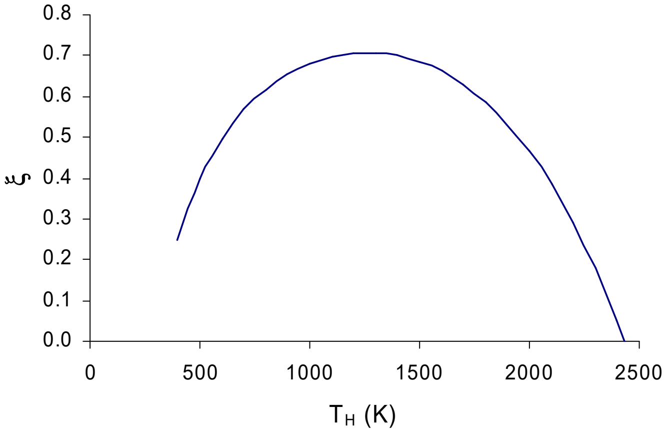
where the first term in brackets is the Carnot efficiency. With the given values:

$$\xi_{max} = \left(\frac{T_H - 300.\ \mathrm{K}}{T_H}\right)\left(\frac{1000\ \mathrm{W\,m^{-2}}\,(200.\ \mathrm{m^2}) - 0.1\ \mathrm{m^2}\,(5.6704\times10^{-8}\ \mathrm{W{\cdot}m^{-2}{\cdot}K^{-4}})\,T_H^4}{1000\ \mathrm{W\,m^{-2}}\,(200.\ \mathrm{m^2})}\right)$$

The following table lists the calculated values. The efficiency peaks at 1300 K. The chemical importance of this problem is that, even for very large collection areas, the maximum temperature available to drive chemical fuel cycles is limited. Additionally, finding materials that are robust at these temperatures is an important research area in materials chemistry.

T_H	Carnot	SB*	efficiency
400	0.250	0.999	0.250
500	0.400	0.998	0.399
600	0.500	0.996	0.498
700	0.571	0.993	0.568
800	0.625	0.988	0.618
900	0.667	0.981	0.654
1000	0.700	0.972	0.680
1100	0.727	0.958	0.697
1200	0.750	0.941	0.706
1300	0.769	0.919	0.707
1400	0.786	0.891	0.700
1500	0.800	0.856	0.685
1600	0.813	0.814	0.662
1700	0.824	0.763	0.629
1800	0.833	0.702	0.585
1900	0.842	0.631	0.531
2000	0.850	0.546	0.464

* SB = Stefan-Boltzmann factor



11. The electrolysis of water is a potential source of hydrogen for use as a transportation fuel. However, H_2 production is very costly. From your General Chemistry course, you might remember that the direct electrolysis of water is based on the two standard reduction half-cells:

$2\,H^+\,(aq) + 2\,e^- \rightarrow H_2\,(g)$ $\quad E° \equiv 0$ V
$O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \rightarrow 2\,H_2O\,(l)$ $\quad E° = 1.23$ V

with the standard cell potential:

$H_2O\,(l) \rightarrow H_2\,(g) + \frac{1}{2}\,O_2(g)$ $\quad E°_{cell} = E°_{cathode} - E°_{anode} = -1.23$ V.

This cell potential is large and unfavorable. The Westinghouse-S cycle was developed in the 1970s to use solar thermal energy to lower the cost of the production of hydrogen.[17] The Westinghouse-S cycle consists of two reactions, the net result of which is the production of H_2:

$$\begin{array}{ll} H_2SO_4\,(aq) \rightarrow SO_2\,(g) + H_2O\,(g) + \frac{1}{2}\,O_2\,(g) & \text{at 1140 K} \\ SO_2\,(g) + 2\,H_2O\,(l) \rightarrow H_2SO_4\,(aq) + H_2(g) & \text{at 320-350 K} \\ \hline H_2O\,(l) \rightarrow H_2\,(g) + \frac{1}{2}\,O_2(g) & \end{array}$$

The first step, the dehydration of sulfuric acid, is run in a concentrating solar collector. The second step is run in an electrolytic cell with the standard reduction half reactions:

$2\,H^+\,(aq) + 2\,e^- \rightarrow H_2\,(g)$ $\quad E° \equiv 0$ V
$SO_4^{2-}\,(aq) + 4\,H^+\,(aq) + 2\,e^- \rightarrow 2\,H_2O\,(l) + SO_2\,(g)$ $\quad E° = +0.17$ V

giving the standard cell potential $E°_{cell} = E°_{cathode} - E°_{anode} = -0.17$ V. Even though this cell potential is still negative, the energy requirement is greatly diminished from the direct hydrolysis. Of course, electrical energy is required to run the second step, which must be obtained from conventional sources. The solar thermal efficiency for this process covers only the production of SO_2 (g). (a) Calculate the change in enthalpy for both steps in the Westinghouse-S cycle. (b) Calculate the maximum solar thermal efficiency for the production of SO_2 (g) for the thermal part of the process operating between 1140 K and 350 K. Neglect radiative losses. (c) Calculate the electrical work necessary to produce one mole of H_2 for $E°_{cell}$ at -1.23 V and -0.17 V. [Hint: for electrochemical cells z_i is given by the number of electrons transferred in the balanced cell reaction.]

Answer: (a)Using the thermochemical tables in the appendix, the standard enthalpies of formation are listed below:

	H_2SO_4 (aq) →	SO_2 (g)	+	H_2O (g)	+ ½ O_2 (g)		
$\Delta_fH°$	-909.27	-296.83		-241.82	0	$kJ\ mol^{-1}$	$\Delta_rH° = 370.62\ kJ\ mol^{-1}$

	SO_2 (g)	+	2 H_2O (l)	→	H_2SO_4 (aq) + H_2(g)		
$\Delta_fH°$	-296.83		-285.83		-909.27	0 $kJ\ mol^{-1}$	$\Delta_rH° = -40.78\ kJ\ mol^{-1}$

The reaction enthalpy change is $\Delta_rH° = [\text{products}] - [\text{reactants}] = \sum \nu_i \Delta_fH°_i$

The first reaction is highly endothermic, requiring a significant input of thermal energy.

(b) The Carnot efficiency for the production of SO_2 is:

$$\xi_{max} = \left(\frac{T_H - T_L}{T_H}\right) = \left(\frac{1140 - 350}{1140}\right) = 0.693$$

The question is if the value of the H_2 as a replacement for fossil fuels is sufficient to outweigh the production costs.

(c). The electrical work is given by $w = -z_i F \Delta\phi$. For this electrochemical cell to produce one mole of H_2, $z_i = 2$ mol of electrons. The difference in electric potential $\Delta\phi$ is the cell voltage, $\Delta\phi = E_{cell}$. For the direct production of hydrogen by electrolysis,

$$w = -(2\ mol)(96{,}485\ C\ mol^{-1})(-1.23\ V)(1\ J/1\ C\ V)(1\ kJ/1000\ J) = 237.\ kJ\ mol^{-1}$$

For the Westinghouse-S cycle, the electrolysis requires:

$$w = -(2\ mol)(96{,}485\ C\ mol^{-1})(-0.17\ V)(1\ J/1\ C\ V)(1\ kJ/1000\ J) = 32.8\ kJ\ mol^{-1}$$

Even though the process still requires electrical energy, the electrical energy required is greatly decreased by providing the difference from the sun.

12. In Eq. 11.2.20:

$$\xi_{max} = \left(\frac{T_H - T_L}{T_H}\right)\left(\frac{J_{solar} A - a\,\sigma\,T_H^4}{J_{solar} A}\right)$$

The second term in brackets is the correction for the efficiency caused by radiative loss from the absorber surface. This correction results from the Stefan-Boltzmann equation, Eq. 11.2.16. Derive this radiative loss correction from Eq. 11.2.16.

Answer: The flux is the power gain or loss per unit area. Given the solar collector area, A, the incident power from the sun is $J_{solar}\,A$. From Eq. 11.2.16, $J_{blackbody} = \sigma\,T^4$: $J_{blackbody}$ is the flux emitted by the absorber surface. Given the absorber surface area, a, the emitted power from the surface at temperature T_H is

$$\text{emitted power} = J_{blackbody}\,a = a\,\sigma\,T_H^4$$

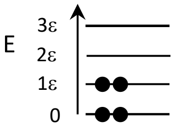
The net power absorbed is the difference: $J_{solar}\,A - a\,\sigma\,T_H^4$. The efficiency of the net absorption is the ratio of the net power absorbed to the incident power:

$$\xi_{absorb} = \left(\frac{J_{solar}\,A - a\,\sigma\,T_H^4}{J_{solar}\,A}\right)$$

The overall efficiency is $\xi_{max} = \xi_{Carnot}\,\xi_{absorb}$

Chapter 12 Problems: The Statistical Definition of Entropy

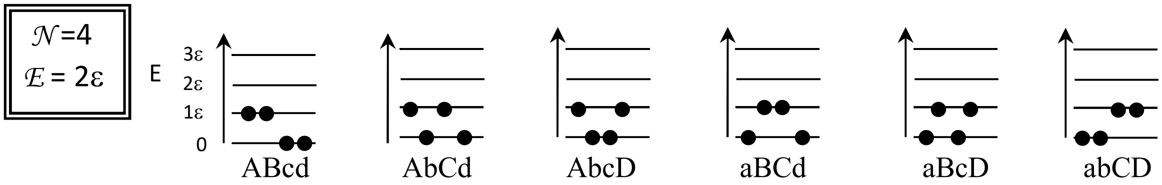
1. Calculate the number of ways of arranging the energy states and find all the microstates consistent with the distribution numbers (2,2,0,0). Find the average energy for the distribution. (Assume distinguishable systems.)



Answer: There are four total systems, $\mathcal{N} = 4$, and two packets of energy, $\mathcal{E} = 2\varepsilon$. Using Eq. 12.2.8, the number of ways of arranging the energy states is given as:

$$\mathcal{W}(2,2,0,0) = \frac{\mathcal{N}!}{n_o!\ n_1!\ n_2!\ldots} = \frac{4!}{2!\ 2!\ 0!\ 0!} = \frac{4\cdot3\cdot2\cdot1}{(2\cdot1)(2\cdot1)} = 6$$

So we should find six microstates:



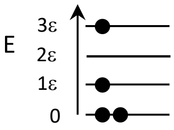
The average energy using Eq. 12.2.4 is:

$$\langle E\rangle = \frac{1}{\mathcal{N}}\sum_i n_iE_i = \frac{2\,(0) + 2\,(1) + 0\,(2) + 0\,(3)}{4} = ½\ \varepsilon$$

Alternately, we could just use the ensemble values and Eq. 12.1.1:

$$\langle E\rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{2\varepsilon}{4} = ½\ \varepsilon$$

2. Calculate the number of ways of arranging the energy states and find all the microstates consistent with the distribution numbers (2,1,0,1). Find the average energy for the distribution. (Assume distinguishable systems.)

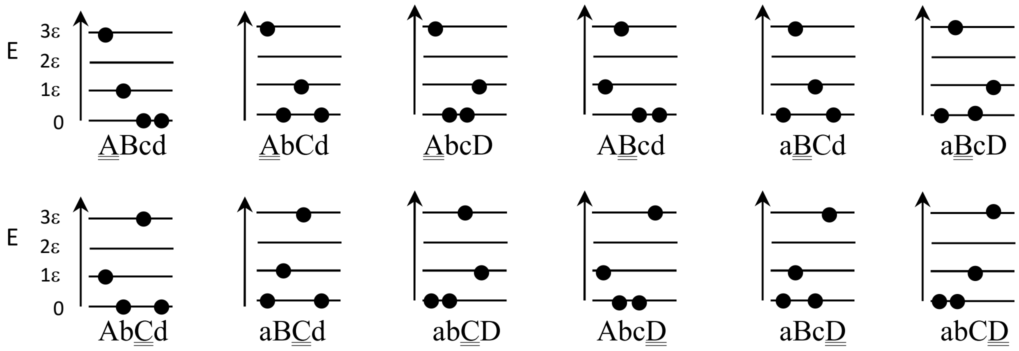


Answer: There are four total systems, $\mathcal{N} = 4$, and four packets of energy, $\mathcal{E} = 4\varepsilon$. Using Eq. 12.2.8, the number of ways of arranging the energy states is given as:

$$\mathcal{W}(2,1,0,1) = \frac{\mathcal{N}!}{n_o!\; n_1!\; n_2!\ldots} = \frac{4!}{2!\; 1!\; 0!\; 1!} = \frac{4\cdot3\cdot2\cdot1}{(2\cdot1)(1)(1)(1)} = 12$$

So we should find 12 microstates:

$$\boxed{\begin{matrix}\mathcal{N}=4\\ \mathcal{E}=4\varepsilon\end{matrix}}$$



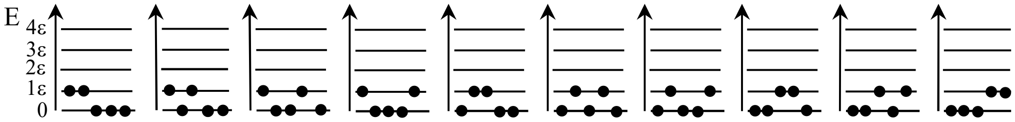
The average energy using Eq. 12.2.4 is:

$$\langle E\rangle = \frac{1}{\mathcal{N}}\sum_i n_iE_i = \frac{2\,(0) + 1\,(1) + 0\,(2) + 1\,(3)}{4} = \varepsilon$$

Alternately, we could just use the ensemble values and Eq. 12.1.1:

$$\langle E\rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{4\varepsilon}{4} = \varepsilon$$

3. Given the following microstates:



(a). Find the set of distribution numbers.
(b). Specify the macrostate.
(c). Find the number of ways of arranging the energy states for the system for the set of distribution numbers. Is the given set of microstates complete?
(d). Find the statistical weight for the macrostate.
(e). Find the degeneracy for the macrostate.
(f). Find $\langle E\rangle$ and U – U(0).
(g). Find the probability of occurrence of the first microstate, within the given macrostate.
(h). Find another macrostate with the same number of systems and the same energy. Which is more probable, the given macrostate or the new macrostate?
(i). What is the most probable distribution and $\mathcal{W}_{\max}$ subject to $\mathcal{N} = 5$ and $\mathcal{E} = 2\varepsilon$?
(j). What is the equilibrium distribution?

Answers: (a). The distribution numbers are (3,2,0,0). (b) The macrostate is specified by the set of distribution numbers, (3,2,0,0). (c). Using Eq. 12.2.8, the number of ways of arranging the energy states is given as:

$$\mathcal{W}(3,2,0,0) = \frac{\mathcal{N}!}{n_o!\, n_1!\, n_2! \ldots} = \frac{5!}{3!\; 2!\; 0!\; 0!} = \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(3 \cdot 2 \cdot 1)(2 \cdot 1)} = 10$$

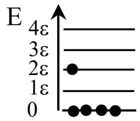
The given ten microstates are complete, since $\mathcal{W} = 10$. (d). The statistical weight is $\mathcal{W}$. (e). The degeneracy is also $\mathcal{W}$. (f). The average energy and internal energy using Eq. 12.2.4 are:

$$U - U(0) = \langle E \rangle = \frac{1}{\mathcal{N}} \sum_i n_i E_i = \frac{3\,(0) + 2\,(1) + 0\,(2) + 0\,(3)}{5} = {}^2/_5\; \varepsilon$$

Alternately, we could just use the ensemble values and Eq. 12.1.1:

$$U - U(0) = \langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{2\varepsilon}{5} = {}^2/_5\; \varepsilon$$

(g). Each microstate has an equal *a priori* probability. The probability of each individual microstate within the given macrostate is $^1/_{10}$. Each microstate appears one-tenth of the time. (h). The only other macrostate with the same number of systems and energy is (4,0,1,0):



The new statistical weight is:

$$\mathcal{W}(4,0,1,0) = \frac{\mathcal{N}!}{n_o!\, n_1!\, n_2! \ldots} = \frac{5!}{4!\; 0!\; 1!\; 0!} = \frac{5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(4 \cdot 3 \cdot 2 \cdot 1)(1)(1)(1)} = 5$$

which is less probable than the original macrostate. (i). The most probable distribution is (3,2,0,0) with $\mathcal{W}_{max} = 10$, subject to the constraints. (h). The equilibrium distribution is the most probable distribution, (3,2,0,0), subject to the given constraints.

4. Assume a system has equally spaced energy states with spacing ε. (a). Find $\mathcal{N}$, $\mathcal{E}$, $\langle E \rangle$, and $U - U(0)$ for the distributions (26,14,9,5,3,2,1) and (25,16,8,5,3,2,1). (b). Which distribution is the more probable macrostate? (c). Find the difference between the two macrostates in the number of ways of arranging the energy states for the system. (d). One of the two is the most probable distribution. Which macrostate corresponds to the equilibrium state?

Answer: (a). Both sets of distribution numbers correspond to $\mathcal{N} = 60$ and $\mathcal{E} = 75$ for

$$U - U(0) = \langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = \frac{75\;\varepsilon}{60} = 1.25\;\varepsilon$$

(b). Using Eq. 12.2.8, the number of ways of arranging the energy states is given using a calculator or Excel as:

$$\mathcal{W}(26,14,9,5,3,2,1) = \frac{\mathcal{N}!}{n_o!\ n_1!\ n_2!\ldots} = \frac{60!}{26!\ 14!\ 9!\ 5!\ 3!\ 2!\ 1!} = 4.5292\text{x}10^{35}$$

and $$\mathcal{W}(25,16,8,5,3,2,1) = \frac{\mathcal{N}!}{n_o!\ n_1!\ n_2!\ldots} = \frac{60!}{25!\ 16!\ 8!\ 5!\ 3!\ 2!\ 1!} = 4.4160\text{x}10^{35}$$

The first distribution is the more probable.
(c). The difference is $1.13\text{x}10^{34}$. The first distribution is more probable by a very large number of microstates. (d). The first macrostate, (26,14,9,5,3,2,1), is the most probable state and correspondingly is the equilibrium state.

5. Calculate the residual entropy for a crystalline solid like N=N=O assuming the energy difference for the two crystalline alignments is 0.300 kJ mol^{-1}. Assume that the distribution of alignments is "frozen in" at the melting point. Assume the melting point is -90.8°C. Compare the result to Eq. 12.4.10. Why is there a difference?

Answer: The plan is to use $S = -R\ \Sigma\ p_i \ln p_i$, Eq. 12.4.14, with a Boltzmann distribution over two states at energies $\varepsilon_o = 0$ and $\varepsilon_1 = 0.300\text{ kJ mol}^{-1}$. At the melting point:

$$RT = 8.314\text{ J K}^{-1}\text{mol}^{-1}(273.2 - 90.8\text{ K}) = 1516.\text{ J K}^{-1}\text{ mol}^{-1}$$

The lower energy state has a Boltzmann weighting factor of $e^{-\varepsilon_o/RT} = e^0 = 1$. The higher energy alignment has a Boltzmann weighting factor of:

$$e^{-\varepsilon_1/RT} = e^{-300.\text{ J mol}^{-1}/1516.\text{ J K}^{-1}\text{ mol}^{-1}} = 0.8205$$

The partition function, which is the probability normalization factor, is the sum of the weighting factors:

$$q = e^{-\varepsilon_o/RT} + e^{-\varepsilon_1/RT} = 1 + 0.8205 = 1.8205$$

The corresponding probabilities are:

$$p_1 = e^{-\varepsilon_1/RT}/q = 0.8205/1.8205 = 0.4507$$
$$p_o = e^{-\varepsilon_o/RT}/q = 1/1.8205 = 0.5493$$

Finally the entropy, based on Eq. 12.4.14, is:

$$S = -R\ \Sigma\ p_i \ln p_i = -\ 8.314\text{ J K}^{-1}\text{ mol}^{-1}\ (0.5493 \ln 0.5493 + 0.4507 \ln 0.4507)$$
$$= -\ 8.314\text{ J K}^{-1}\text{ mol}^{-1}\ (-0.6882) = 5.722\text{ J K}^{-1}\text{ mol}^{-1}$$

The result using Eq. 12.4.10 is $S = -R \ln 2 = 5.763\text{ J K}^{-1}\text{ mol}^{-1}$, with $w = 2$. The difference is that Eq. 12.4.10 with $w = 2$ assumes that the two orientations are equally probable, which is true if the difference in alignment energies is less than RT, $\varepsilon_1 - \varepsilon_o = \Delta\varepsilon << RT$. In this problem, $\Delta\varepsilon/RT = 0.2$, which is small enough to give the equal populations result, to within expected experimental error.

6. The goal of this problem is to help you become more comfortable with partition functions. Consider the residual entropy of N=N=O. Define the lowest energy alignment as having energy

ε_o and the higher energy alignment at ε_1. A reasonable way to assess the degree of alignment is to calculate the fraction of molecules in the low energy state, f_o, and the fraction of the molecules in the high energy state, f_1:

$$f_o = \frac{n_o}{n_o + n_1} \qquad f_1 = \frac{n_1}{n_o + n_1}$$

where n_o is the number of molecules in the low energy alignment and n_1 is the number of molecules in the high energy alignment.[1] Of course, $f_o + f_1 = 1$. (a). The number of molecules in a specific energy state is proportional to the Boltzmann weighting factor, $n_i \propto e^{-\varepsilon i/kT}$. Use this proportionality to find the fractions f_o and f_1. (b). Alternatively, the probability of finding a molecule in a specific energy state, ε_i, is given by Eqs. 12.4.13 (Eq. 8.9.5). Show that your answers to part (a) are consistent with Eqs. 12.4.13.

Answer: (a). Given the proportionality $n_i \propto e^{-\varepsilon i/kT}$, the fractions are:

$$f_o = \frac{n_o}{n_o + n_1} = \frac{e^{-\varepsilon o/kT}}{e^{-\varepsilon o/kT} + e^{-\varepsilon 1/kT}} \qquad f_1 = \frac{n_1}{n_o + n_1} = \frac{e^{-\varepsilon 1/kT}}{e^{-\varepsilon o/kT} + e^{-\varepsilon 1/kT}}$$

(b). The partition function for the two-state system is:

$$q = \sum_i e^{-\varepsilon i/kT} = e^{-\varepsilon o/kT} + e^{-\varepsilon 1/kT}$$

Notice that the partition function is the same as the denominators for the fractions in part (a). The Boltzmann probabilities using Eqs. 12.4.13 (Eq. 8.9.5) are then:

$$p_o = f_o = \frac{e^{-\varepsilon o/kT}}{q} = \frac{e^{-\varepsilon o/kT}}{e^{-\varepsilon o/kT} + e^{-\varepsilon 1/kT}}$$

$$p_1 = f_1 = \frac{e^{-\varepsilon 1/kT}}{q} = \frac{e^{-\varepsilon 1/kT}}{e^{-\varepsilon o/kT} + e^{-\varepsilon 1/kT}}$$

as we derived in part (a). The partition function, q, and the denominator of the fractions, $n_o + n_1$, play the same role; they normalize the probability to give either $\Sigma\, p_i = 1$ or $\Sigma\, f_i = 1$.

7. Calculate the number of ways of arranging 10 distinguishable balls in three boxes with 3 in the first box, 5 in the second box, and 2 in the third box.

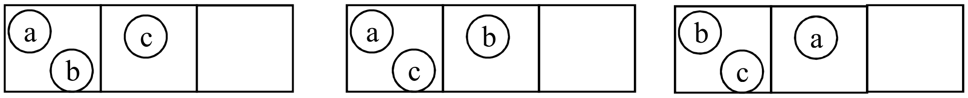
Answer: The statistical weight is given by Eq. 12.2.8 with the distribution numbers (3,5,2):

$$\mathcal{W} = \frac{\mathcal{N}!}{n_o!\, n_1!\, n_2! \ldots} = \frac{10!}{3!\, 5!\, 2!} = 2520$$

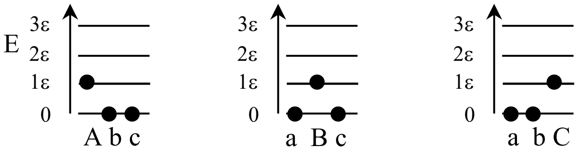
8. (a). Calculate the number of ways of arranging 3 distinguishable balls among 3 boxes with 2 balls in the first box, 1 ball in the second box, and 0 balls in the third box. (b). Calculate the number of ways of arranging the energy states of the system with 3 molecules given that 2 molecules are in the first energy level, 1 molecule is in the second energy level, and 0 molecules are in the third energy level. Draw the arrangements.

Answer: (a) The number of ways of arranging 3 distinguishable balls among 3 boxes with 2 balls in the first box, 1 ball in the second box, and 0 balls in the third box is given by Eq. 12.2.8 with the distribution numbers (2,1,0):

$$\mathcal{W} = \frac{\mathcal{N}!}{n_o!\; n_1!\; n_2! \ldots} = \frac{3!}{2!\; 1!\; 0!} = 3$$



(b). The statistical weight is the same as in part (a):



$$\mathcal{W} = 3$$

9. Find the set of distribution numbers that maximizes the number of arrangements for 3 balls in 3 boxes.

Answer: The statistical weight is given by Eq. 12.2.8 with n_1 balls in box 1, n_2 balls in box 2, and n_3 balls in box 3:

$$W = \frac{3!}{n_1!\; n_2!\; n_3!}$$

Notice that permuting the same set of distribution numbers among the boxes gives the same statistical weight. That is W(3,0,0) = W(0,3,0) = W(0,0,3), so we only need to look for unique sets of (n_1,n_2,n_3). The possibilities are:

$$W(3,0,0) = \frac{3!}{3!\; 0!\; 0!} = 1 \qquad W(2,1,0) = \frac{3!}{2!\; 1!\; 0!} = 3 \qquad W(1,1,1) = \frac{3!}{1!\; 1!\; 1!} = 6$$

W_{max} results for (1,1,1). The distribution with equal occupancies is called the uniform distribution. The distribution with the maximum number of ways of arrangement is always the uniform distribution in the absence of any constraints. The Boltzmann distribution arises because of the constraint on the total energy of the ensemble.

10. (a). Starting with $N! \approx (N/e)^N$ show that $\ln N! \approx N \ln N - N$. (b). Starting with $N! \approx \sqrt{2\pi N}\,(N/e)^N$ show that $\ln N! = N \ln N - N + \frac{1}{2} \ln 2\pi N$. (c) Compare the exact value of $\ln N!$ and the two approximations for the largest number your calculator can use.

Answer: (a). Taking the log of $N! \approx (N/e)^N$:

$$\ln N! \approx \ln((N/e)^N) = N \ln(N/e) = N \ln N + N \ln(1/e) = N \ln N - N \ln e$$

since $\ln(1/x) = -\ln(x)$. For the last term, $\ln(x)$ and e^x are inverse functions and $\ln(e^1) = 1$.

$$\ln N! \approx N \ln N - N \qquad \text{(Eq. 12.4.2)}$$

(b). Taking the log of $N! = \sqrt{2\pi N}\,(N/e)^N$:

$$\ln N! \approx \ln((N/e)^N) + \ln\sqrt{2\pi N}$$

Using the result for $\ln((N/e)^N)$ from part (a) simplifies the first term and noting that $\sqrt{x} = x^{½}$:

$$\ln N! \approx N \ln N - N + \ln (2\pi N)^{½}$$
$$\ln N! \approx N \ln N - N + ½ \ln 2\pi N \qquad \text{(Eq. 12.9.12)}$$

(c). The following values were calculated for $N = 69$:

$69! = 1.71122\text{x}10^{98}$ with the exact $\ln N! = 226.1905$

The approximations give:

$\ln N! \approx N \ln N - N + ½ \ln 2\pi N = 226.1893$ for a negligible error

and $\ln N! \approx N \ln N - N = 223.1533$ for a 1.34% error from the exact value.

11. Show that the percent error using Sterling's approximation for $\ln(N!)$ decreases with increasing N. (Excel has a larger range for valid N than most calculators.)

Answer: Excel maintains 15 significant figures for N! up to N = 170. The following spreadsheet was set-up using Eqs. 12.4.2 and 12.9.12 as approximations for ln N!. The percent error is the error using $\ln N! \approx N \ln N - N$ compared to the exact value to 15 significant figures.

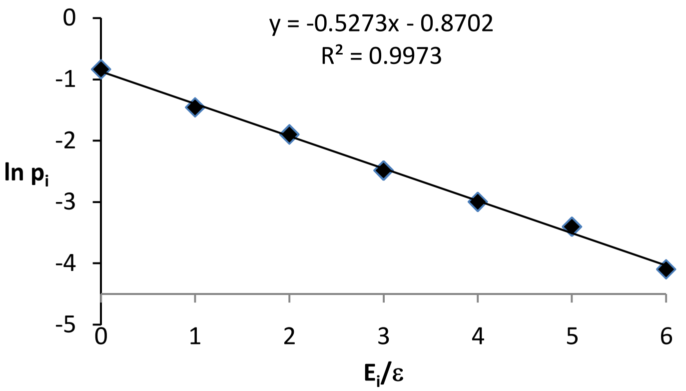
N	N!	ln N! exact	N ln N - N + (ln 2πN)/2	N ln N - N	% error
30	2.65253E+32	74.6582	74.6555	72.0359	3.51
69	1.71122E+98	226.1905	226.1893	223.1533	1.34
80	7.15695E+118	273.6731	273.6721	270.5621	1.14
90	1.48572E+138	318.1526	318.1517	314.9829	1.00
100	9.33262E+157	363.7394	363.7385	360.5170	0.89
150	5.71338E+262	605.0201	605.0196	601.5953	0.57
170	7.25742E+306	706.5731	706.5726	703.0857	0.49

The thermodynamic limit is for very large numbers of systems, where $N \approx 10^{23}$. Sterling's approximation introduces negligible error for such large numbers.

12. In Problem 4 the most probable distribution was determined, choosing from (26,14,9,5,3,2,1) and (25,16,8,5,3,2,1). Verify that the most probable distribution is a Boltzmann distribution.

Answer: The first distribution is the most probable distribution, (26,14,9,5,3,2,1). You can verify that the first macrostate corresponds to a Boltzmann distribution, as closely as possible given the small number of systems, by plotting ln p_i versus E_i as in Example 12.4.2:

E_i/ε	n_i	p_i	ln p_i
0	26	0.4333	-0.8363
1	14	0.2333	-1.4553
2	9	0.15	-1.8971
3	5	0.0833	-2.4849
4	3	0.05	-2.9957
5	2	0.0333	-3.401
6	1	0.0167	-4.0943



13. The fundamental vibration frequency for I_2 is 214.50 cm^{-1}. Assume the vibrational states are equally spaced with spacing 214.50 cm^{-1}. Iodine vapor is held in an oven at elevated temperature. The relative occupations of the vibrational states were found to be 1.000 : 0.467 : 0.222 : 0.100. Calculate the temperature.

Answer: Following Example 12.4.2, the spacing between the energy states is given by:

$$\varepsilon = \Delta E = \frac{hc}{\lambda} = h\, c\, \tilde{\nu}_o\, N_A \qquad 1$$

$$= 6.626\text{x}10^{-34}\ \text{J s}(2.998\text{x}10^{8}\text{m s}^{-1})(214.5\ \text{cm}^{-1})(100\ \text{cm}/1\ \text{m})(6.022\text{x}10^{23}\ \text{mol}^{-1})$$

$$= 2.566\ \text{kJ mol}^{-1}$$

The relative populations of the states, r_i, is determined by dividing the probability by the population of the i = 0 state; so the probability of the ith state is determined by:

$$r_i = \frac{p_i}{p_o} \qquad \text{giving } p_i = r_i\, p_o \qquad 2$$

The sum of the p_i is given by normalization: $\Sigma\, p_i = 1$. The sum of the r_i values is:

$$\Sigma\, r_i = \frac{\Sigma\, p_i}{p_o} = \frac{1}{p_o} \qquad \text{giving } p_o = \frac{1}{\Sigma r_i} \qquad 3$$

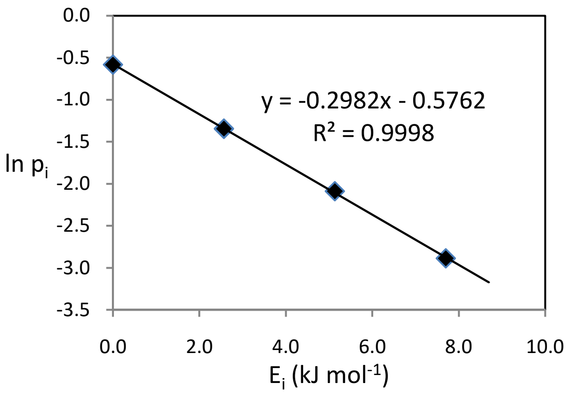
Substitution of this last value for p_o into Eq. 2 gives:

$$p_i = \frac{r_i}{\Sigma r_i} \qquad 4$$

Using Eq. 4 the probabilities are calculated and the data are plotted as in Example 12.4.2:

i	Ei (kJ mol^{-1})	Rel. pop.	pi	ln pi
0	0.000	1	0.559	-0.582
1	2.566	0.467	0.261	-1.343
2	5.132	0.222	0.124	-2.087
3	7.698	0.1	0.056	-2.884

slope	-0.2982	-0.5762	intercept
±	0.0030	0.0143	±
r^2	0.9998	0.0171	s(y)
F	10059.0807	2.0000	df
$SS_{regression}$	2.9272	0.0006	$SS_{residual}$

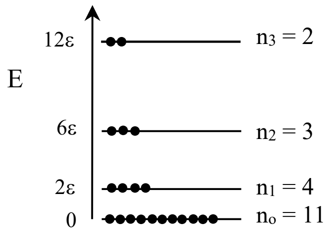


$$\text{slope} = -1/RT = -0.2982 \text{ kJ}^{-1} \text{ mol}$$
$$RT = 3.353 \text{ kJ mol}^{-1}$$

$$T = \frac{3.353 \text{ kJ mol}^{-1}}{8.314\text{x}10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} = 403.\ \text{K} \pm 4.\ \text{K}$$

The relative populations for vibrational states can be easily determined by the intensity of vibrational transitions that start from states higher than $\upsilon = 0$. These bands are called **hot bands**.

14. Is the following system at thermal equilibrium? Give the approximate temperature, assuming the unit of energy, ε, is 10.0 cm^{-1}.

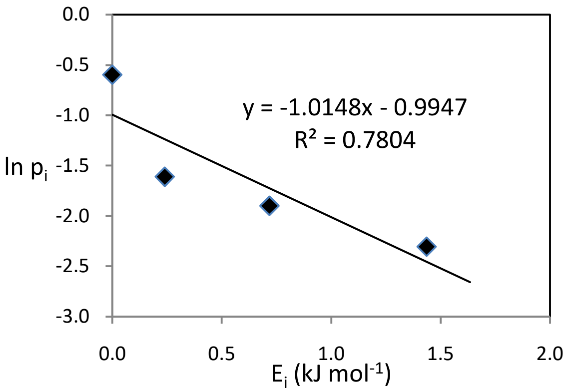


Answer: The plan is to make a plot using Eq. 12.4.29 to check for linearity, similar to Example 12.4.2. There are 20 systems for this problem. The value for ε in kJ mol^{-1} is given by:

$$\varepsilon = \Delta E = \frac{hc}{\lambda} = h\ c\ \tilde{\nu}_o\ N_A \qquad 1$$
$$= 6.626\text{x}10^{-34} \text{ J s}(2.998\text{x}10^{8}\text{m s}^{-1})(10.0 \text{ cm}^{-1})(100 \text{ cm}/1 \text{ m})(6.022\text{x}10^{23} \text{ mol}^{-1})$$
$$= 0.1196 \text{ kJ mol}^{-1}$$

The plot using Eq. 12.4.29 with units in kJ mol^{-1} is:

state i	E_i (kJ mol^{-1})	n_i	p_i	ln p_i
0	0.000	11	0.550	-0.598
1	0.239	4	0.200	-1.609
2	0.718	3	0.150	-1.897
3	1.436	2	0.100	-2.303



$$\text{slope} = -1/RT = -1.015 \text{ kJ}^{-1} \text{ mol}$$

$$RT \approx 0.985 \text{ kJ mol}^{-1}$$

$$T \approx \frac{0.985 \text{ kJ mol}^{-1}}{8.314\text{x}10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}} \approx 120 \text{ K}$$

The plot is not linear so the system is not at equilibrium. Since the system is not at equilibrium, an effective temperature cannot be determined. However, using the slope of the fit curve, a rough measure of the temperature for the equivalent Boltzmann distribution is 120 K with a large error.

The energy states in this problem are further apart as the energy increases. The energy states are said to "diverge" instead of being equally spaced. Translational and rotational energy states diverge. However, rotational energy states have a degeneracy of (2J+1), where J is the index for the energy state. The energy states in this problem then energetically equivalent to rotational levels but are non-degenerate.

15. The conformational entropy for butane was determined in Example 12.4.3 using the *gauche-anti*-energy difference from molecular mechanics. Use a molecular orbital calculation to estimate the energy difference and determine the corresponding conformational entropy. How sensitive is the conformational entropy to the value of the energy difference? Your instructor will assign a molecular orbital method from the following list depending on the resources available: AM1, PM3, HF 3-21G(*), HF 6-31G*, B3LYP/6-31G*, MP2/6-311G*//HF 6-31G* (single point energy at MP2/6-311G* for the geometry calculation at 6-31G*).

Answer: The energies are given below in the energy units normally associated with the calculation method:

State	units	E_{gauche}	E_{anti}	ΔE
MMFF	kcal mol^{-1}	-4.2554	-5.0348	0.7794
AM1	kcal mol^{-1}	-30.4195	-31.1262	0.7067
PM3	kcal mol^{-1}	-28.5375	-29.0632	0.5257
HF 3-21G(*)	Hartrees	-156.431	-156.432	0.001223
HF 6-31G*	Hartrees	-157.297	-157.298	0.001514
B3LYP 6-31G*	Hartrees	-158.457	-158.458	0.001388
MP2 6-311G*	Hartrees	-157.885	-157.886	0.000999

The difference in energy was converted to kJ mol^{-1} and the entropy calculated following Example 12.4.3:

State	ΔE (kJ mol^{-1})	gauche $e^{-E/RT}$	q	p_{gauche}	p_{anti}	S (J K^{-1} mol^{-1})
MMFF	3.26101	0.26839	1.53677	0.174643	0.65072	7.39
AM1	2.956833	0.30342	1.60684	0.18883	0.6223	7.69
PM3	2.199529	0.41182	1.82363	0.225822	0.54836	8.33
HF 3-21G(*)	3.210987	0.27386	1.54771	0.176943	0.64612	7.44
HF 6-31G*	3.974744	0.20125	1.40250	0.143493	0.71301	6.64
B3LYP 6-31G*	3.643406	0.23003	1.46005	0.157546	0.68491	7.00
MP2 6-311G*	2.622087	0.34728	1.69456	0.204939	0.59012	7.99

The MP2/6-311G* calculation was a single point energy based on the HF 6-31G* optimized geometry. It is interesting to note that, at least for this simple compound, molecular mechanics represents the torsional interaction as well as lower level quantum mechanical calculations. The torsional entropy is moderately sensitive to the level of the calculation. The experimental value is 0.67 kcal mol^{-1} or 2.8 kJ mol^{-1}.[2]

16. Determine the conformational entropy for 1,2-dichlorobutane. Your instructor will assign a molecular mechanics or molecular orbital method from the following list depending on the resources available: MMFF, PM3, HF 3-21G(*), HF 6-31G*, B3LYP/6-31G*, MP2/6-311G*//HF 6-31G* (single point energy at MP2/6-311G* for the geometry calculation at 6-31G*)

Answer: The energies are given below in the energy units normally associated with the calculation method:

State	units	E_{gauche}	E_{anti}	ΔE
MMFF	kcal mol^{-1}	6.2564	5.0273	1.2291
PM3	kcal mol^{-1}	-24.0718	-24.6829	0.6111
HF 3-21G(*)	Hartrees	-992.435	-992.438	0.002923
HF 6-31G*	Hartrees	-997.028	-997.031	0.003047
B3LYP 6-31G*	Hartrees	-999.016	-999.019	0.002713
MP2 6-311G*	Hartrees	-997.646	-997.648	0.002430

The difference in energy was converted to kJ mol^{-1} and the entropy calculated following Example 12.4.3 and Eq. 12.4.11:

State	ΔE (kJ mol^{-1})	gauche $e^{-E/RT}$	q	p_{gauche}	p_{anti}	S (J K^{-1}mol^{-1})
MMFF	5.142554	0.12565	1.25130	0.10042	0.79917	5.33
PM3	2.556842	0.35654	1.71308	0.20813	0.58374	8.04
HF 3-21G(*)	7.674337	0.04526	1.09051	0.04150	0.91700	2.86
HF 6-31G*	7.999899	0.03969	1.07937	0.03677	0.92646	2.61
B3LYP 6-31G*	7.121931	0.05655	1.11310	0.05080	0.89839	3.32
MP2 6-311G*	6.379177	0.07630	1.15261	0.06620	0.86760	4.01

The results are surprisingly dependent on the method. The experimental ΔE is 1.08 kcal mol^{-1} or 4.52 kJ mol^{-1}.[2%%WJH]

17. The process of folding a protein to produce the active conformation restricts torsions along the polypeptide backbone and side chain torsions for amino acids that are buried in the interior of the protein. Calculate the conformational entropy of the side chain of the amino acid valine at 298.2 K. Use molecular mechanics with the MMFF force field in the gas phase for the zwitter-ionic form to determine the low energy side chain conformations and the corresponding energies.

Answer: The calculation of the entropy parallels Example 12.4.3. The low energy conformations for zwitter-ionic valine in the gas phase using the MMFF94x force field are -3.0881, -5.3433, -4.4024 kcal $\mathrm{mol^{-1}}$ at -51.8°, 57.6°, -168.7° respectively. The dihedral angle was measured from the carbonyl carbon to the side chain methine-hydrogen, O=C–$\mathrm{C_\alpha}$–C–H. Using the lowest energy conformer as the reference, the energies in kJ $\mathrm{mol^{-1}}$ in increasing order are then: 0, 3.937, 9.436 kJ $\mathrm{mol^{-1}}$.

The Boltzmann weighting factor for the lowest energy conformer is 1, since $e^0 = 1$. The Boltzmann weighting factors for the higher energy conformers are:

$$e^{-\varepsilon_2/RT} = e^{-9.436\mathrm{x}10^3\,\mathrm{J}/(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\ 298.2\ \mathrm{K})} = 0.0222$$
$$e^{-\varepsilon_1/RT} = e^{-3.937\mathrm{x}10^3\,\mathrm{J}/(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\ 298.2\ \mathrm{K})} = 0.2043$$

The partition function, Eq. 12.4.13 (Eq. 8.9.7), is the normalization for the probability distribution:

$$q = \sum_i e^{-\varepsilon_i/kT} = 1 + 0.2043 + 0.0222 = 1.2265$$

The probabilities for each state are then:

$$p_2 = e^{-\varepsilon_2/RT}/q = 0.0222/1.2265 = 0.0181$$
$$p_1 = e^{-\varepsilon_1/RT}/q = 0.2043/1.2265 = 0.1666$$
$$p_0 = e^{-\varepsilon_o/RT}/q = 1/q = 1/1.2265 = 0.8153$$

The molar conformational entropy as given by Eq. 12.4.14:

$$S = -R \sum_i p_i \ln p_i \qquad \text{(molecular probabilities)}$$

$$\begin{aligned} S &= -8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\ [0.8153 \ln(0.8153) + 0.1666 \ln(0.1666) + 0.0181 \ln(0.0181)] \\ &= -8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\ [-0.1665 + (-0.2986) + (-0.0726)] \\ &= 4.47\ \mathrm{J\ K^{-1}\ mol^{-1}} \end{aligned}$$

When the side chain is bound in a restricted environment, most of this entropy is lost. Notice that the highest energy conformer plays a minor role in the overall entropy, because the state is not easily accessible at 298.2 K. In other words, at room temperature RT = 2.48 kJ $\mathrm{mol^{-1}}$ and the highest energy conformer is at 9.44 kJ $\mathrm{mol^{-1}}$. If the energy differences were very small the conformational entropy would have been $S = R \ln 3 = 9.13\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Torsional conformational isomers are often called rotomeric states. The side chain of valine has three rotomeric states.

18. Assume that the *gauche*-energy states for a 1,2-disubstituted ethane, $X–CH_2–CH_2–Y$, are at energy ε above the *anti*-state. The *anti*-state is set at the reference state. Show that the conformational entropy for the C–C bond in disubstituted ethane compounds is given by:

$$S = -\frac{R}{(1 + 2\,e^{-\varepsilon/RT})}\left[\ln\left(\frac{1}{1 + 2\,e^{-\varepsilon/RT}}\right) + 2\,e^{-\varepsilon/RT}\ln\left(\frac{e^{-\varepsilon/RT}}{1 + 2\,e^{-\varepsilon/RT}}\right)\right]$$

Answer: The Boltzmann weighting factor for the *anti*-conformer is 1, since we chose a reference energy of zero for the *anti*-conformer and $e^0 = 1$. The Boltzmann weighting factor for the *gauche*-conformer with the given energy of ε is:

$$e^{-E_{gauche}/RT} = e^{-\varepsilon/RT}$$

The partition function is the normalization for the probability distribution:

$$q = \sum_i e^{-E_i/kT} = 1 + 2\,e^{-\varepsilon/RT}$$

The probabilities for each *gauche* and *anti*-energy state are then:

$$p(\text{gauche}) = \frac{e^{-E_{gauche}/RT}}{q} = e^{-\varepsilon/RT}/(1 + 2\,e^{-\varepsilon/RT})$$

$$p(\text{anti}) = \frac{e^{-E_{anti}/RT}}{q} = 1/q = 1/(1 + 2\,e^{-\varepsilon/RT})$$

The conformational entropy as given by Eq. 12.4.9 is for a sum over all the energies for a system. The entropy is given using Eq. 12.4.11:

$$S = -R\sum_i p_i \ln p_i = -R\,[p_{anti}\ln p_{anti} + p_{gauche}\ln p_{gauche} + p_{gauche}\ln p_{gauche}]$$

$$S = -\frac{R}{(1 + 2\,e^{-\varepsilon/RT})}\left[\ln\left(\frac{1}{1 + 2\,e^{-\varepsilon/RT}}\right) + 2\,e^{-\varepsilon/RT}\ln\left(\frac{e^{-\varepsilon/RT}}{1 + 2\,e^{-\varepsilon/RT}}\right)\right]$$

19. Show that the maximum conformational entropy for freely rotating sp_3 hybridized bonds is given by S = R ln 3. In other words, assume that the energy differences between the three conformational states is much less than RT. You also need to assume that the three conformations are distinguishable, as in the central butane dihedral or the side chain of valine but not $–CH_3$ torsions.

Answer: Assign the lowest energy conformer as the reference state with $\varepsilon_o = 0$. Then the remaining conformers have energies ε_1 and ε_2. Assume that $\varepsilon_1 \ll RT$ and $\varepsilon_2 \ll RT$. The Boltzmann weighting factor for each level is then essentially equivalent, $e^{-\varepsilon i/RT} \approx 1$. The partition function is then $\Sigma\, e^{-\varepsilon i/RT} = 3$. Then the probability for finding each conformational state is equal,

$p_o = p_1 = p_2 = {}^1/_3$. There is no conformational biasing, because the energy differences are small compared to the available thermal kinetic energy. The conformational entropy, using Eq. 12.4.14, is:

$$S = -R \sum_i p_i \ln p_i = -R\left[{}^1/_3 \ln {}^1/_3 + {}^1/_3 \ln {}^1/_3 + {}^1/_3 \ln {}^1/_3\right] = -R \ln {}^1/_3 = R \ln 3$$

In general, the maximum conformational entropy is given by S = R ln w, where w is the number of distinguishable conformational states. (See the previous problem for more information about distinguishability.)

20. Calculate the conformational entropy for the $C(sp_3)$–$C(sp_2)$ bond torsion leading to the phenyl ring in the side chain of the amino acid phenylalanine. Use molecular mechanics with the MMFF force field for gas phase energies. To obtain values that are appropriate for protein folding studies, build a protein in the alpha-helical form with 11 residues: five alanines followed by phenylalanine followed by five alanines. Acetylate the N-terminus and amidate the C-terminus to help stabilize the alpha-helix. Once the lowest energy structure is found, fix (or freeze) all of the atoms except those in the phenyl side chain. Then determine the low energy conformers as you rotate around the C_α–$C_\beta(sp_3)$–$C_{ring}(sp_2)$–C_{ring} dihedral. You will find four low energy conformers. However, the conformers are in two equivalent pairs. The conformers in each pair differ by rotation of the phenyl ring by 180°. The phenyl ring is symmetrical with respect to rotation by 180°, so the conformational states that differ by 180° are indistinguishable. The counting of states for calculation of the entropy is over distinguishable states. To correct for symmetry, then, calculate the entropy by summing over only the two unique, distinguishable states. The structure and the required dihedral is illustrated below, Figure P12.1.

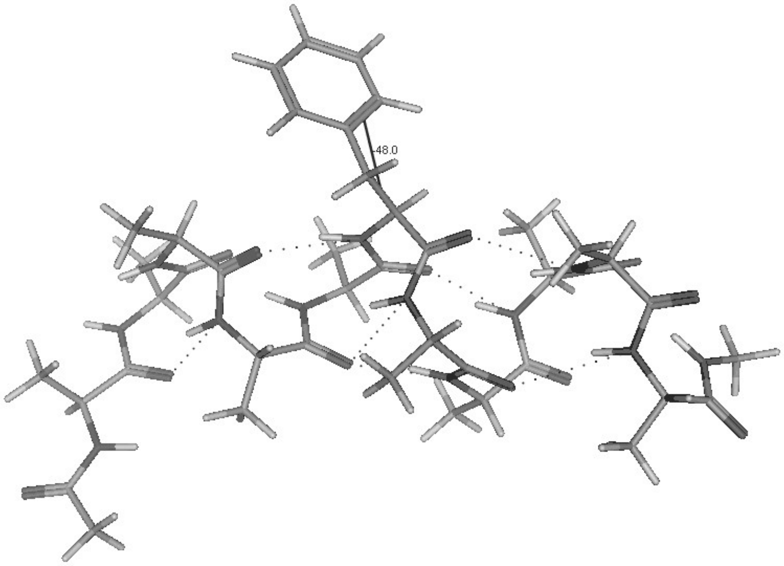


Figure P12.1: An alpha-helical 11-mer with phenylalanine in the center. The required dihedral is depicted with the angle of -48.0°, giving the lowest energy conformer. The dotted lines show the hydrogen-bonding pattern. The distortions in the hydrogen-bonding pattern are caused by the shortness of the peptide. Your model may differ in the conformations of the terminal residues.

Answer: The calculation of the entropy parallels Example 12.4.3. The low energy conformations in the gas phase using the MMFF94x force field are 3.3441 and 6.2248 kcal mol^{-1} at -48.0° and 7.2° respectively. The dihedral angle was measured from the *alpha*-carbon to the side chain *beta*-carbon to the ring sp^2-C, and finishing with another ring-carbon: C_α–C_β(sp^3)–C_{ring}(sp^2)–C_{ring}. The dihedral for the methylene, β-carbon and the alpha-carbon for this structure was 163°. Using the lowest energy conformer as the reference, the relative energy of the higher energy conformer is 12.05 kJ mol^{-1}.

The Boltzmann weighting factor for the lowest energy conformer is 1, since $e^0 = 1$. The Boltzmann weighting factor for the higher energy conformer is:

$$e^{-\varepsilon_1/RT} = e^{-12.05\text{x}10^3 \text{J}/(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\ 298.2 \text{ K})} = 0.00774$$

The partition function, Eq. 12.4.13 (Eq. 8.9.7), is the normalization for the probability distribution:

$$q = \sum_i e^{-\varepsilon_i/kT} = 1 + 0.00774 = 1.0077$$

The probabilities for each state are then:

$$p_1 = e^{-\varepsilon_1/RT}/q = 0.00774/1.0077 = 7.68\text{x}10^{-3}$$

$$p_0 = e^{-\varepsilon_o/RT}/q = 1/q = 1/1.0077 = 0.9924$$

The molar conformational entropy as given by Eq. 12.4.14:

$$S = -R \sum_i p_i \ln p_i \qquad \text{(molecular probabilities)}$$

$$\begin{aligned} S &= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} [0.9924 \ln(0.9924) + 7.68\text{x}10^{-3} \ln(7.68\text{x}10^{-3})] \\ &= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} [(-7.57\text{x}10^{-3}) + (-0.037)] \\ &= 0.37 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The conformational entropy is quite small. Burying phenylalanine side chains in the interior of proteins has favorable energetic and solvation entropic effects with little conformational entropy penalty. Notice that the higher energy conformer plays a minor role in the overall entropy, because the state is not easily accessible at 298.2 K. In other words, at room temperature RT = 2.48 kJ mol^{-1} and the higher energy conformer is at 12.05 kJ mol^{-1}. If the energy differences were very small the conformational entropy would have been S = R ln 2 = 5.76 J K^{-1} mol^{-1}. Torsional conformational isomers are often called rotomeric states. The side chain of phenylalanine has four rotomeric states, but only two distinguishable states.

Your results may have been rather different for this problem. Reliable estimates of the conformational entropy of amino acid side chains is a difficult computational problem and very sensitive to the details of the computation and the computational method.

21. The Boltzmann distribution is often derived directly by maximizing $\mathcal{W}$ instead of maximizing the entropy using Eq. 12.4.9. In this problem, we derive the Boltzmann distribution

in several steps directly from the statistical weights. (a) Starting with Eq. 12.4.1, show that without constraints:

$$d(\ln \mathcal{W}) = \sum \left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) dn_i$$

(b). Add in the constraints to give:

$$0 = \sum \left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) dn_i + \alpha \sum dn_i - \beta \sum E_i \, dn_i$$

(c). Show that the constrained maximization results in

$$\left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) + \alpha - \beta E_i = 0$$

(d). Note that the summation variable in Eq. 12.4.5 is an arbitrary index. We can also write:

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \sum_j n_j \ln n_j$$

Show that the derivative of ln $\mathcal{W}$ with respect to n_i while holding all the other distribution numbers constant gives just one term, which is:

$$\left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) = -(\ln n_i + 1) \approx -\ln n_i$$

(e). Substitute this last result into the result from part (c) and solve for n_i to find:

$$n_i = e^{\alpha - \beta E_i} = e^{\alpha} \, e^{-\beta E_i}$$

(f). Use normalization to find the Boltzmann distribution:

$$\frac{n_i}{\mathcal{N}} = \frac{e^{-\beta E_i}}{Q}$$

Answer: (a). Maximizing the entropy is equivalent to maximizing ln $\mathcal{W}$. The statistical weights are:

$$\mathcal{W} = \frac{\mathcal{N}!}{n_o! \, n_1! \, n_2! \ldots} \qquad 1$$

The total number of systems in the ensemble and the total ensemble energy is:

$$\mathcal{N} = \sum_i n_i \qquad \mathcal{E} = \sum_i n_i E_i \qquad 2$$

where the sum is over all energy states, i. The logarithm of the statistical weights is, Eq. 12.4.1:

$$\ln \mathcal{W} = \ln \mathcal{N}! - \sum \ln n_i! \qquad 3$$

The number of systems in each state is changed by dn_i to find the maximum in ln $\mathcal{W}$. The total differential of ln $\mathcal{W}$ is:

$$d(\ln \mathcal{W}) = \sum \left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) dn_i \qquad 4$$

(b). However, since the ensemble is isolated, we can't change the number of systems in the ensemble nor the total energy. The constraints are:

$$\text{Constraints: } d\mathcal{N} = dn_o + dn_1 + dn_2 + dn_3 + \ldots = \sum dn_i = 0 \qquad 5$$

$$d\mathcal{E} = E_o\, dn_o + E_1\, dn_1 + E_2\, dn_2 + E_3\, dn_3 + \ldots = \sum E_i\, dn_i = 0 \qquad 6$$

Any constant multiple of these constraints will also give zero:

$$\alpha \sum dn_i = 0 \quad \text{and} \quad \beta \sum E_i\, dn_i = 0 \qquad 7$$

where α and β are undetermined multipliers. Adding in the constraints and setting the result equal to zero to find the maximum gives:

$$0 = \sum \left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) dn_i + \alpha \sum dn_i - \beta \sum E_i\, dn_i \qquad 8$$

(c). Now the n_i's can be treated as independent! Combining sums and distributing out the factor of dn_i gives:

$$0 = \sum \left(\left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) + \alpha - \beta E_i\right) dn_i \qquad 9$$

The only way for this sum to always give zero for any changes in the dn_i is for each term in the sum to give zero:

$$\left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) + \alpha - \beta E_i = 0 \qquad 10$$

(d). We can now substitute in Eq. 3 into this last equation. Using Sterling's formula, ln x! = x ln x – x, for the factorials gives:

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \mathcal{N} - \sum_j (n_j \ln n_j - n_j) \qquad 11$$

Notice that the last term in the sum gives the total number of systems in the ensemble, $\Sigma\, n_j = \mathcal{N}$ giving Eq. 12.4.5:

$$\ln \mathcal{W} = \mathcal{N} \ln \mathcal{N} - \sum_j n_j \ln n_j \qquad 12$$

The derivative of this last equation with respect to n_i while holding all the other occupation numbers constant only results in the single term:

$$\left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) = -\left(n_i \frac{\partial \ln n_i}{\partial n_i} + \ln n_i\right) \qquad 13$$

since all the other derivatives are zero. Taking the derivative of $\ln n_i$ gives:

$$\left(\frac{\partial \ln \mathcal{W}}{\partial n_i}\right) = -\left(n_i \frac{1}{n_i} + \ln n_i\right) \qquad 14$$

$$\left(\frac{\partial \ln W}{\partial n_i}\right) = -(\ln n_i + 1) \approx -\ln n_i \qquad 15$$

The final approximation is valid since we work in the thermodynamic limit were all the occupation numbers are very large.

(e). The derivation from this point parallels Eqs. 12.4.7-12.4.14. Substituting this last equation for the derivative into Eq. 10 gives:

$$-\ln n_i + \alpha - \beta E_i = 0 \qquad 16$$

Solving for the $\ln n_i$:

$$\ln n_i = \alpha - \beta E_i \qquad 17$$

and exponentiating both sides of the last equation results in the occupation number for the i^th^ state for the most probable distribution:

$$n_i = e^{\alpha - \beta E_i} = e^{\alpha} e^{-\beta E_i} \qquad 18$$

(f). We can solve for the normalization by substituting Eq. 18 into Eq. 2 to give:

$$\mathcal{N} = \sum_i n_i = \sum_i e^{\alpha} e^{-\beta E_i} = e^{\alpha} \sum_i e^{-\beta E_i} \qquad 19$$

Solving for the normalization constant gives:

$$e^{\alpha} = \frac{\mathcal{N}}{\sum_i e^{-\beta E_i}} \qquad 20$$

The sum in the denominator is defined as the partition function, Q:

$$Q = \sum_i e^{-\beta E_i} \qquad 21$$

which upon substitution into Eq. 20 gives the final result for the occupation numbers in the most probable distribution:

$$n_i = \frac{\mathcal{N}}{Q} e^{-\beta E_i} \qquad 22$$

where n_i is the number of systems in energy state E_i. The probability of occurrence of a system in energy state E_i is then obtained by dividing by the number of systems in the ensemble, to give the ensemble average:

$$\frac{n_i}{\mathcal{N}} = \frac{e^{-\beta E_i}}{Q} \qquad 23$$

which is probability of finding a system in energy state E_i.

22. Consider the bowl shaped function, $f(x,y) = 1 - x^2 - y^2$. Maximize the function subject to the constraint $y = 0.5$ using the Lagrange method of undetermined multipliers.

Answer: The function and the constraint are shown in Figure P.1:

$$f(x,y) = 1 - x^2 - y^2 \tag{1}$$

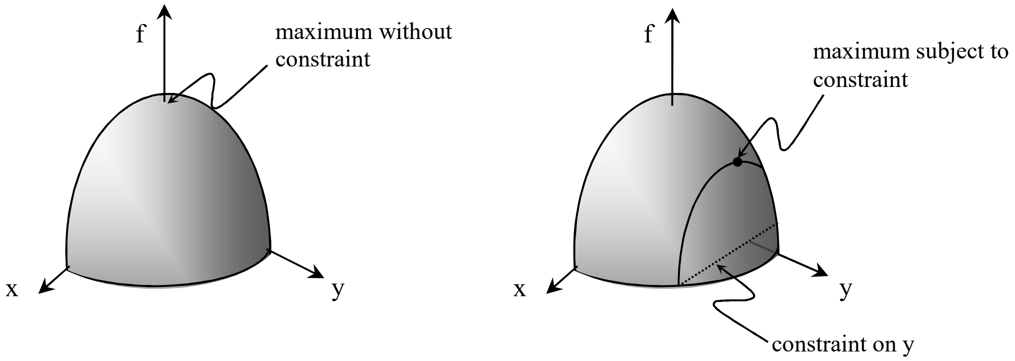


Figure P.1: Constrained maximization of $f(x,y) = 1 - x^2 - y^2$.

The total differential is:

$$df = -2\,x\,dx - 2\,y\,dy = 0 \qquad \text{(maximum)} \tag{2}$$

The unconstrained maximum for this function is calculated by setting df equal to 0, giving $x = 0$ and $y = 0$ for the maximum, $f_{max} = 1$. The constraint is given as:

$$y = 0.5 \qquad \text{or} \quad c = y - 0.5 = 0 \qquad \text{(constraint)} \tag{3}$$

as shown in Figure P.1. As x and y are changed to find the maximum, the differential of the constraint gives:

$$dc = dy = 0 \qquad \text{(constraint)} \tag{4}$$

This equation can be multiplied by a constant, λ, and still give zero; the constant is the Lagrange multiplier:

$$\lambda(\,dy) = 0 \qquad \text{(constraint)} \tag{5}$$

Adding Eqs. 1 and 4 still gives zero:

$$-2\,x\,dx - 2\,y\,dy + \lambda(\,dy) = 0 \qquad \text{(constrained)} \tag{6}$$

or collecting terms in dx and dy:

$$-2\,x\,dx + (-2\,y + \lambda)\,dy = 0 \qquad \text{(constrained)} \tag{7}$$

We can now treat dx and dy as independent of each other. The only way for Eq. 6 to always equal zero is if the coefficients of dx and dy are both always equal to zero:

$$(-2\,x) = 0$$
$$(-2\,y + \lambda) = 0 \qquad \text{(constrained)} \quad 8$$

The first equation gives x = 0. The constraint requires y = 0.5. The maximum in our function occurs when x = 0 and y = 0.5. The value of f at the constrained maximum is then obtained from Eq. 1:

$$f(0,\tfrac{1}{2}) = 1 - (0)^2 - (0.5)^2 = 0.75 \qquad \text{(constrained)} \quad 9$$

as shown in the figure. This problem is really just a one dimensional problem since y is constrained to a constant value. We didn't need to use Lagrange multipliers. However, the problem gives us a simple opportunity to explore the meaning of the Lagrange multiplier. The Lagrange multiplier, λ, is used for the constraint on the value of y. Solving Eq. 8 gives $\lambda = 2y$, which is just $-(\partial f/\partial y)_x$. Looking back to the derivation of the Boltzmann distribution, β is the Lagrange multiplier used to constrain the total energy of the ensemble, which also constrains the average energy of a system in the ensemble. Similarly to this problem, $\beta = (1/k)(\partial S/\partial U)_V = (1/k)(\partial S/\partial\langle E\rangle)_V$, using Eq. 12.5.20. The Lagrange multiplier is proportional to the slope of the function that is being maximized with respect to changes in the corresponding constraint.

23. A scientific instrument company produces two different widgets. Let the number of widgets produced by the factory per day of the two different widgets be n_1 and n_2, respectively. The profit obtained by selling type-one widgets, P_1, and type-two widgets, P_2, is given as:

$$P_1 = 40\,n_1 - n_1^2 \qquad\qquad P_2 = 20\,n_2 - 0.5\,n_2^2$$

The negative terms in the profit equations result because as the production increases, the cost of labor increases (extra people need to be hired) and the marketing costs increase. The factory can make at most 25 widgets per day. Find the optimal level of production for the two widgets to maximize the overall profit. Compare the constrained result to the unconstrained result assuming the factory can produce any number of widgets per day.

Answer: This problem follows the Lagrange Multipliers example in Addendum 12.7. The total profit is given by $P = P_1 + P_2$. The total differential of the profit, as the production rates are varied, is:

$$dP = \left(\frac{\partial P}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial P}{\partial n_2}\right)_{n_1} dn_2$$

$$dP = (40 - 2\,n_1)\,dn_1 + (20 - n_2)\,dn_2 \qquad 1$$

Setting dP = 0 gives the optimum result with no production constraint. If dn_1 and dn_2 can vary freely, then the only way we can guarantee that dP = 0 is if both coefficients are equal to zero:

$$(40 - 2\,n_1) = 0 \qquad \text{and} \qquad (20 - n_2) = 0 \qquad \text{(unconstrained)} \quad 2$$

Solving for the production gives $n_1 = 20$ and $n_2 = 20$, which exceeds the maximum production possible by the factory. The production constraint is given by $n_1 + n_2 = 25$, or subtracting the constant from both sides of the equation to give the constraint equation equal to zero:

$$c = n_1 + n_2 - 25 = 0 \qquad \text{(constraint)} \qquad 3$$

The total differential of the constraint as n_1 and n_2 are varied is:

$$dc = dn_1 + dn_2 = 0 \qquad \text{(constraint)} \qquad 4$$

In other words, the total number of widgets produced is constant. So if more type-one widgets are produced, then an equal number fewer type-two widgets can be produced. Eq. 4 can be multiplied by a constant and still satisfy the constraints:

$$\lambda\,(dn_1 + dn_2) = 0 \qquad \text{(constraint)} \qquad 5$$

Adding Eqs. 1 and 5 still gives zero for the maximum profit:

$$(40 - 2\,n_1)\,dn_1 + (20 - n_2)\,dn_2 + \lambda\,(dn_1 + dn_2) = 0 \qquad \text{(constrained)} \qquad 6$$

Collecting terms in $dn_1$and dn_2:

$$(40 - 2\,n_1 + \lambda)\,dn_1 + (20 - n_2 + \lambda)\,dn_2 = 0 \qquad \text{(constrained)} \qquad 7$$

Since dn_1 and dn_2 can now be treated as independent variables, the only way we can guarantee $dP = 0$ is if both coefficients are separately equal to zero:

$$40 - 2\,n_1 + \lambda = 0$$
$$20 - n_2 + \lambda = 0$$

Subtracting the second equation from the first gives:

$$20 - 2\,n_1 + n_2 = 0 \quad \text{and then} \quad n_2 = 2\,n_1 - 20 \qquad \text{(constrained max.)} \qquad 8$$

Since $n_1 + n_2 = 25$ from the constraint, we can solve for n_1 and substitute $n_1 = 25 - n_2$ into the last equation to give:

$$n_2 = 50 - 2\,n_2 - 20 \quad \text{giving } n_2 = 10 \qquad \text{(constrained max.)} \qquad 9$$

and then from the original constraint, $n_1 = 25 - n_2 = 15$,. The maximum profit is then:

$$P = P_1 + P_2 = (40\,n_1 - n_1^2) + (20\,n_2 - 0.5\,n_2^2) = 525 + 150 = 675$$

24. Thermodynamic state functions can be written directly in terms of the partition function, Q, which adds to the importance of this central concept. Using Eqs. 12.4.9, 12.4.12, 12.2.6, and 12.1.2, show that the entropy can be written as:

$$S = k \ln Q + \frac{U - U(0)}{T}$$

Answer: Starting from Eq. 12.4.9, we need to find the ln p_i. Taking the logarithm of p_i from Eq. 12.4.12 gives Eq. 12.5.29:

$$\ln p_i = \frac{-E_i}{kT} - \ln Q$$

Substituting this last equation into Eq. 12.4.9 gives:

$$S = -k \sum_i p_i\left(\frac{-E_i}{kT} - \ln Q\right)$$

$$= \frac{k}{kT}\sum_i p_i E_i + k\sum_i p_i \ln Q$$

The first summation is just the average energy from Eq. 12.2.6. In the second summation, ln Q is a constant, which factors out in front of the summation:

$$S = \frac{\langle E\rangle}{T} + k \ln Q \sum_i p_i$$

The ensemble average energy is U – U(0), Eq. 12.1.2. The sum of the p_i is equal to one, because the probabilities are normalized, $\Sigma\, p_i = 1$, giving:

$$S = k \ln Q + \frac{U - U(0)}{T}$$

The partition function gives the number of accessible states; therefore the more accessible states the greater the energy dispersal. In addition energy transfer into the system, as given by U – U(0), increases the number of accessible states, because more energy is available to the system. The entropy given as a function of Q will play an important role in Chapt. 32.

25. What is the probability of selecting an Ace in 10 total cards? To avoid statistical complications, assume that after each selection the card is returned to the deck, so that each selection is made from a full deck of 52 cards.

Answer: The probability of being dealt an Ace on a single selection is 4/52. The probability of being dealt an Ace in 10 selections is 10(4/52) = 40/52. It doesn't matter which selection of the 10 results in an Ace, so being dealt a single Ace is an "OR" series of events.

26. The next five problems concern the relationship between statistical weights and the probability of occurrence of a particular set of events. The number of ways of selecting n objects from N, which we called C[N choose n], is also called the binomial coefficient and given the symbol $\binom{N}{n}$. Using Eq. 12.9.1 show that the binomial coefficient can be expressed as:

$$\binom{N}{n} = C[N\text{ choose }n] = \frac{N!}{n!(N-n)!}$$

Answer: Starting with Eq. 12.9.1, multiply the numerator and denominator by (N–n)!:

$$\binom{N}{n} = C[N\text{ choose }n] = \frac{N(N-1)\ldots(N-n+1)(N-n)!}{n!(N-n)!}$$

However, the numerator is just the complete series of products from N down to 1, which is equivalent to N!:

$$\binom{N}{n} = C[N \text{ choose } n] = \frac{N!}{n!(N-n)!}$$

27. In the last problem we showed that the binomial coefficient $\binom{N}{n}$ can be defined as:

$$\binom{N}{n} = C[N \text{ choose } n] = \frac{N!}{n!(N-n)!}$$

The binomial coefficient $\binom{N}{n}$ is the numerical coefficient for the nth term in the Nth-order polynomial $(1 + x)^N$. For example:

$$\begin{aligned}(1 + x)^3 &= (1 + 2x + x^2)(1 + x)\\ &= 1 \quad + 3x \quad + \quad 3x^2 \quad + \quad x^3\\ &= \binom{3}{0} 1 + \binom{3}{1} x + \binom{3}{2} x^2 + \binom{3}{3} x^3\end{aligned}$$

Verify the corresponding result for $(1 + x)^4$.

Answer: Start with the explicit polynomial:

$$(1 + x)^4 = (1 + 3x + 3x^2 + x^3)(1+x) = 1 + 4\,x + 6\,x^2 + 4\,x^3 + x^4$$

In terms of the binomial coefficients, following the pattern from the cubic polynomial, we should find:

$$(1 + x)^4 = \binom{4}{0} 1 + \binom{4}{1} x + \binom{4}{2} x^2 + \binom{4}{3} x^3 + \binom{4}{4} x^4$$

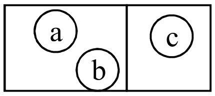
Do the evaluations of the binomial coefficients match up with the expected coefficients: 1 : 4 : 6 : 4 : 1?

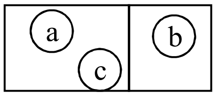
$$\binom{4}{0} = \binom{4}{4} = \frac{4!}{0!(4-0)!} = 1 \qquad \binom{4}{1} = \binom{4}{3} = \frac{4!}{1!(4-1)!} = 4 \qquad \binom{4}{2} = \frac{4!}{2!(4-2)!} = 6$$

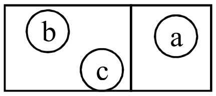
28. Assume that 3 distinguishable balls are selected at random for placement into two boxes. The volume of box 1 is V_1 and the volume of box 2 is V_2. The probability of a single ball landing in box 1 is proportional to its volume, $p_1 = V_1/(V_1 + V_2)$. The probability of a single ball landing in box 2 is proportional to its volume, $p_2 = V_2/(V_1 + V_2)$. What is the probability that all 3 balls land in the first box? There is only one way for all 3 balls to land in box 1 giving the probability as $p(3,0) = p_1^3$. There is only one way for all 3 balls to land in box 2 giving $p(0,3) = p_2^3$. Find the probability of 2 balls landing in box 1 and the remaining ball landing in box 2. Relate the results to the statistical weight W(2,1).

Answer: The probability of a single ball landing in box 1 is p_1. The probability of two specific balls landing in box 1 is p_1^2 and then the probability of the remaining ball landing in box 2 is p_2.

The overall probability for a set of <u>specific</u> balls is given as ($p_1^2p_2$). However, there is more than one way of achieving this distribution:







$$W(2,1) = \frac{3!}{2!\ 1!} = 3$$

The final probability is then $p(2,1) = W(2,1)\ (p_1^2p_2) = 3\ (p_1^2p_2)$. This example shows the relationship between W and the probability of occurrence of a particular set of distribution numbers. Notice that this result can also be expressed using the binomial coefficient, which is the subject of the next problem.

29. Show that for a two-category problem with N distinguishable objects the binomial coefficient and statistical weight are related by:

$$W(n_1,n_2) = \binom{N}{n_1}$$

An example is the previous two-box problem. The result also holds for any molecular system that has only two energy levels. Use the result of the last problem as a specific example.

Answer: In general for a two category selection problem, because there are only two categories the distribution numbers are related by $n_2 = N - n_1$ and:

$$W(n_1,n_2) = \frac{N!}{n_1!\ n_2!} = \frac{N!}{n_1!\ (N-n_1)!} = \binom{N}{n_1}$$

Using the last problem as an example, for 3 balls, the probability for finding two balls in the first box and one ball in the second box depends on the statistical weight for the distribution (2,1):

$$W(2,1) = \frac{3!}{2!\ 1!} = \frac{3!}{2!\ (3-2)!} = \binom{3}{2}$$

giving the final probability:

$$p(2,1) = W(2,1)\ (p_1^2p_2) = \binom{3}{2}\ (p_1^2p_2)$$

The binomial coefficients are the statistical weight for two-category problems. The next problem puts this result in a broader context.

30. Assume that 3 distinguishable balls are selected at random for placement into two boxes. The volume of box 1 is V_1 and the volume of box 2 is V_2. The probability of a single ball landing in box 1 is proportional to its volume, $p_1 = V_1/(V_1 + V_2)$. The probability of a single ball landing in box 2 is proportional to its volume, $p_2 = V_2/(V_1 + V_2)$. There is only one way for all 3 balls to

land in box 1 giving the probability as $p(3,0) = p_1^3$. There is only one way for all 3 balls to land in box 2 giving $p(0,3) = p_2^3$. The probability of 2 balls landing in box 1 and the remaining ball landing in box 2 is $p(2,1) = 3(p_1^2p_2)$, because there are 3 ways of arranging the set of distribution numbers. Likewise $p(1,2) = 3(p_1p_2^2)$. Show the relationship of the probabilities p(3,0), p(2,1), p(1,2), and p(0,3) to the terms in the expansion of the polynomial $(p_1+ p_2)^3$.

Answer: Expanding the polynomial gives:

$$(p_1+p_2)^3 = \underset{\substack{\downarrow\\ p(3,0)}}{p_1^3} \;+\; \underset{\substack{\downarrow\\ p(2,1)}}{3\,p_1^2p_2} \;+\; \underset{\substack{\downarrow\\ p(1,2)}}{3\,p_1\,p_2^2} \;+\; \underset{\substack{\downarrow\\ p(0,3)}}{p_2^3}$$

The first term is the probability of all three balls occurring in the first box. The second term is the probability of finding two balls in the first box and 1 ball in the second box, and so on. The probabilities are related through the statistical weights given by the binomial coefficients. The polynomial can be more generally written using the binomial coefficients as:

$$(p_1+p_2)^3 = \binom{3}{0} p_1^3 + \binom{3}{1} p_1^2p_2 + \binom{3}{2} p_1\,p_2^2 + \binom{3}{3} p_2^3$$

The probability of occurrence of the different sets of distribution numbers is proportional to the statistical weights. This result is the theoretical foundation for the title of Sec. 12.4.

Literature Cited:

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2. W. J. Hehre, A Guide to Molecular Mechanics and Quantum Chemical Calculations, Wavefunction, Inc., Irvine, CA, 2003. p. 276.

Chapter 13 Problems: Entropy and Applications

1. Eqs. 13.2.10° and 13.2.15° apply for all processes for an ideal gas. Show that the two expressions are equivalent.

Answer: Starting with Eq. 13.2.15°: $\Delta S = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$

Using the ideal gas equation of state to find the pressure ratio:

$$\frac{P_2}{P_1} = \frac{nRT_2/V_2}{nRT_1/V_1} = \frac{T_2V_1}{T_1V_2}$$

Substituting this ratio into the original equation gives:

$$\Delta S = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1} = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{T_2V_1}{T_1V_2}$$
$$= C_p \ln \frac{T_2}{T_1} - nR \ln \frac{T_2}{T_1} - nR \ln \frac{V_1}{V_2}$$

However, $C_p = C_v + nR$ for an ideal gas:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{T_2}{T_1} - nR \ln \frac{T_2}{T_1} - nR \ln \frac{V_1}{V_2}$$

The middle two terms cancel. Flipping the volume ratio, $\ln(V_1/V_2) = -\ln(V_2/V_1)$, gives:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

2. Eq. 13.2.10° applies for all processes for an ideal gas, assuming a constant heat capacity. However, for an adiabatic reversible process, ΔS = 0. Does Eq. 13.2.10° give ΔS = 0 for an adiabatic reversible process?

Answer: For an adiabatic reversible process, $V_2T_2^c = V_1T_1^c$ where $c = C_v/nR$, for solving for the volume ratio:

$$\frac{V_2}{V_1} = \left(\frac{T_1}{T_2}\right)^c = \left(\frac{T_1}{T_2}\right)^{C_v/nR}$$

Substitution into Eq. 13.2.10° gives:

$$\Delta S = C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_v \ln \frac{T_2}{T_1} + nR \ln \left(\frac{T_1}{T_2}\right)^{C_v/nR}$$
$$= C_v \ln \frac{T_2}{T_1} + nR \frac{C_v}{nR} \ln \left(\frac{T_1}{T_2}\right) = C_v \ln \frac{T_2}{T_1} - C_v \ln \left(\frac{T_2}{T_1}\right) = 0$$

3. Calculate the change in entropy for 1.00 mole of ideal gas that is expanded against a constant external pressure of 1.00 atm from an initial pressure of 10.0 atm to a final pressure of 1.00 atm. During this process the temperature also drops from 25.00 ºC to 0.00 ºC. The heat capacity is $C_p = 7/2\ nR$.

Answer: Even though the expansion is irreversible, knowing the initial and final states allows us to construct an equivalent reversible process. Using Eq. 13.2.15° gives:

$$\Delta S = C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

You can think of this equation as the result of a reversible constant pressure process followed by a reversible isothermal process.

$$\Delta S = 7/2(1.00\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1}) \ln \frac{273.2\text{ K}}{298.2\text{ K}} - (1.00\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1}) \ln \frac{1.00\text{ atm}}{10.0\text{ atm}}$$
$$= -2.548\text{ J K}^{-1} + 19.14\text{ J K}^{-1} = 16.6\text{ J K}^{-1}$$

Notice that we can use any pressure units for the ratio, since the units cancel out.

4. For a closed system we know that $\Delta U = q + w$, $\Delta U = q_{rev} + w_{max}$, and that a reversible process does maximum work on expansion and minimum work on contraction. Use these statements to derive the Clausius inequality.

Answer: Since internal energy is a state function and independent of the path for a process:

$$\Delta U = q + w = q_{rev} + w_{max} \qquad 1$$

Rearranging this expression to group the work terms and the heat transfer terms gives:

$$q - q_{rev} = w_{max} - w \qquad 2$$

Consider the expansion first. In doing comparisons, we like to arrange equations so that we are comparing positive quantities. In an expansion, the internal energy of the system drops and w_{max} and w are negative. Multiplying the last equation by -1 allows us to compare positive values for the work terms:

$$q_{rev} - q = (-w_{max}) - (-w) > 0 \qquad 3$$

The inequality holds because a reversible process does maximum work on expansion. Adding q to both sides of the inequality gives:

$$q_{rev} > q \qquad 4$$

Dividing both sides of this equation by T and using the definition of the entropy, $\Delta S = q_{rev}/T$ gives the Clausius inequality:

$$\Delta S > \frac{q}{T} \qquad 5$$

Now consider contraction. The work terms for a contraction are positive and a reversible process does minimum work on contraction. Eq. 2 then becomes:

$$q - q_{rev} = w_{max} - w < 0 \qquad \text{or} \quad q - q_{rev} < 0 \qquad\qquad 6$$

Adding q_{rev} to both sides of this inequality gives Eq. 4 again. So the derivation works for both expansions and contractions.

You may wonder why we didn't use this derivation in this chapter. First, this derivation requires a rigorous proof of the statement that "a reversible process does maximum work on expansion and minimum work on contraction." Secondly, the form of Eq. 13.1.8 and the concept of "lost work" plays an important role in the development of irreversible thermodynamics.

5. In the section on "*Temperature as an Integrating Factor*" we derived Eq. 13.2.28° using Eq. 13.2.10°. Repeat the derivation of the entropy change for path 2, Eq. 13.2.28°. However, this time start from the heat transfers directly, Eqs. 13.2.16° and 13.2.18°, find dS_1 and dS_2. Then do the integrals. Note when path specific information is eliminated.

Answer: For path 2, we need to calculate the entropy change for each step and then add. For the constant pressure first step from Eq. 13.2.16°:

$$dS_1 = \frac{\text{đ}q_{rev,1}}{T} = \frac{C_v}{T}\,dT + \frac{P_1}{T}\,dV \qquad \text{(cst P, reversible, closed, ideal gas)} \quad 1$$

Notice that both T and V change along this path. We can use the ideal gas equation of state for the second term, $P_1/T = nR/V$:

$$\Delta S_1 = \int_T^{T_i} \frac{C_v}{T}\,dT + \int_{V_1}^{V_2} \frac{nR}{V}\,dV \qquad \text{(cst. P, closed, ideal gas)} \quad 2$$

Eq. 1 is path specific, but after substitution of $P_1/T = nR/V$, the second term only depends on the initial and final states! Integrating the last equation results in:

$$\Delta S_1 = C_v \ln\frac{T_i}{T} + nR\ln\frac{V_2}{V_1} \qquad \text{(cst. P \& } C_v\text{, closed, ideal gas)} \quad 3$$

For the second step, at constant volume, dividing Eq. 13.2.18° by T gives:

$$dS_2 = \frac{dq_{rev,2}}{T} = \frac{C_v}{T}\,dT \qquad \text{(cst V, reversible, closed)} \quad 4$$

Integrating from T_i to back to the original temperature, T, gives:

$$\Delta S_2 = C_v \ln\frac{T}{T_i} \qquad \text{(cst. V \& } C_v\text{, reversible, closed)} \quad 5$$

The total change in entropy is the sum of 3 and 5:

$$\Delta S = C_v \ln\frac{T_i}{T} + nR\ln\frac{V_2}{V_1} + C_v\ln\frac{T}{T_i} \qquad \text{(cst. } C_v\text{, closed, ideal gas)} \quad 6$$

However, the temperature dependent terms cancel to give:

$$\Delta S = nR \ln \frac{V_2}{V_1} \qquad \text{(closed, ideal gas)} \qquad 7$$

The intermediate temperature no longer appears in the equation, so the final result is path independent and only depends on the initial and final states.

6. Given the total differential for the function z(x,y):

$$dz = \frac{y}{x}\,dx - dy$$

Show that dz is not an exact differential. The integrating factor for dz is (1/x). Define a new differential as df = dz/x. Show that df is exact. In other words, df is a state function.

Answer: Comparing the total differential dz to:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad 1$$

Gives: $\left(\frac{\partial z}{\partial x}\right)_y = \frac{y}{x}$ and $\left(\frac{\partial z}{\partial y}\right)_x = -1$ 2

The mixed partials are not equal:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right)_x = \left(\frac{\partial\, y/x}{\partial y}\right)_x = \frac{1}{x} \quad \text{and} \quad \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y = \left(\frac{\partial\,(-1)}{\partial x}\right)_y = 0 \qquad 3$$

So, dz is not an exact differential. However, multiplying both sides of Eq. 1 by the integrating factor (1/x) gives:

$$df = (1/x)\,dz = \frac{y}{x^2}\,dx - \frac{1}{x}\,dy \qquad 4$$

with $\left(\frac{\partial f}{\partial x}\right)_y = \frac{y}{x^2}$ and $\left(\frac{\partial f}{\partial y}\right)_x = -\frac{1}{x}$ 5

Now the mixed partials give:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial\, y/x^2}{\partial y}\right)_x = \frac{1}{x^2} \quad \text{and} \quad \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial\,(-1/x)}{\partial x}\right)_y = \frac{1}{x^2} \qquad 6$$

Therefore df is an exact differential and f is a state function.

7. The lowest temperature heat capacity measurement for benzene is 3.79 K, where $C_p = 0.051463$ J K^{-1} mol^{-1}. The heat capacity data for crystalline and liquid benzene in Figure 13.4.1 can be fit to power series expansions. Because of the complex shape of the curve, this fitting is best done over three temperature ranges. The breaks between the ranges are arbitrary and are simply chosen to get a good fit to the overall curve. There are no solid-state phase transitions. The enthalpy of fusion for benzene is 10.59 kJ mol^{-1} at the normal melting point of 278.6 K. Calculate the absolute entropy of benzene at 298.2 K.

Table Problem 6: Approximate Heat Capacity for Solid and Liquid Benzene

solid	C_p (J K^{-1} mol^{-1})
3.79 – 20 K	$C_p = 0.10321\ T + 0.02431\ T^2$
20 – 84 K	$C_p = -\ 16.5375 + 1.3854\ T - 0.00770\ T^2$
84 -278.6 K	$C_p = 38.2869 + 0.01075\ T + 1.097 \times 10^{-3}\ T^2$
liquid	
278.6 – 300 K	$C_p = 81.228 + 0.1794\ T$

Answer: For the cubic polynomial C_p curve fits, the integrals are given by:

$$\int_{T_1}^{T_2} \frac{C_p^{solid}}{T}\, dT = \int_{T_1}^{T_2} \frac{a + b\ T + c\ T^2}{T}\, dT = \int_{T_1}^{T_2} (a/T + b + c\ T)\, dT =$$

$$= a\ (\ln T\Big|_{T_1}^{T_2} + b\ (T\Big|_{T_1}^{T_2} + \frac{c}{2}\,(T^2\Big|_{T_1}^{T_2} =$$

$$= a \ln \frac{T_2}{T_1} + b\ (T_2 - T_1) + \frac{c}{2}\,(T_2^2 - T_1^2)$$

The low temperature Debye extrapolation is covered in the text. The results of the integrals are given in the following table:

T_1 (K)	T_2 (K)	a $\ln(T_2/T_1)$ J K^{-1} mol^{-1}	b $(T_2\text{-}T_1)$ J K^{-1} mol^{-1}	$\frac{c}{2}(T_2^2\text{-}T_1^2)$ J K^{-1} mol^{-1}	$\frac{A}{3}(T_2^3\text{-}T_1^3)$ J K^{-1} mol^{-1}	total J K^{-1} mol^{-1}
0	3.79				0.0172	0.017
3.79	20	0	-1.673	4.687		3.01
20	84	-23.733	88.666	-25.626		39.31
84	278.6	45.904	2.092	38.703		86.70
278.6	298.2	5.501	3.502			9.00

The entropy of fusion is: $\Delta_{fus}S = \frac{\Delta_{fus}H}{T_{melt}} = \frac{10.59 \times 10^3 J\ mol^{-1}}{278.6\ K} = 38.01\ J\ K^{-1}\ mol^{-1}$

The total then is $S°_{298\ K} = 176.04\ J\ K^{-1}\ mol^{-1}$
The literature value is 173.3 J K^{-1} mol^{-1}, which is close considering the approximations in the curve fitting. The coefficients from the curve fits don't have a particular interpretation. The curve fits are presented only as a way to make the integrals easier to do.

8. Calculate the absolute entropy of methylammonium chloride at 298.15 K. There are three crystalline forms. For the low temperature β-form, the heat capacity is 0.4209 J K^{-1} mol^{-1} at 12.04 K. The enthalpy of the equilibrium solid-state phase transition from the β to γ-form is 1.7790 kJ mol^{-1} at 220.4 K. The enthalpy of the equilibrium solid-state phase transition from the γ to α-form is 2.8183 kJ mol^{-1} at 264.5 K. All values are at standard state. The integrals of C_p/T for the three phases are:[1]

$$\int_{12.04\text{ K}}^{220.4\text{ K}} \frac{C_p^{\beta}}{T}\,dT = 93.412 \qquad \int_{220.4\text{ K}}^{264.5\text{ K}} \frac{C_p^{\gamma}}{T} = 15.439 \qquad \int_{264.5\text{ K}}^{298.15\text{ K}} \frac{C_p^{\alpha}}{T} = 10.690\text{ J K}^{-1}\text{ mol}^{-1}$$

Answer: The plan is to add the C_p/T integrals and the entropy changes for the phase transitions. The integral from 0 K to 12.04 K is done using the Debye relationship for the heat capacity.

The transition entropies for the solid-state phase transitions are:

$$\beta \rightarrow \gamma:\quad \Delta_{tr}S° = \Delta_{tr}H°/T_{tr} = 1.7790\text{ kJ mol}^{-1}(1000\text{ J}/1\text{ kJ})/220.4\text{ K} = 8.0717\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\gamma \rightarrow \alpha:\quad \Delta_{tr}S° = \Delta_{tr}H°/T_{tr} = 2.8183\text{ kJ mol}^{-1}(1000\text{ J}/1\text{ kJ})/264.5\text{ K} = 10.6552\text{ J K}^{-1}\text{ mol}^{-1}$$

The Debye form for the heat capacity is Eq. 13.4.3 giving $C_p = AT_{low}^3 = 0.4209\text{ J K}^{-1}\text{ mol}^{-1}$ at the lowest experimental temperature, T_{low}. The integral from 0 K is, Eq. 13.4.6:

$$\int_{0\text{ K}}^{T_{low}} \frac{C_p^{\beta}}{T}\,dT = \int_{0\text{ K}}^{T_{low}} AT^2\,dT = \frac{AT_{low}^3}{3} = \frac{0.4209\text{ J K}^{-1}\text{ mol}^{-1}}{3} = 0.1403\text{ J K}^{-1}\text{ mol}^{-1}$$

The absolute entropy, which is also called the Third Law entropy, is the sum:

$$\begin{aligned} &\scriptstyle (0\,\rightarrow\,12.04\text{ K})\;+\;(12.04\,\rightarrow\,220.4\text{ K})\;+\;\Delta_{tr}S°(\beta\rightarrow\gamma)\;+\;(220.4\,\rightarrow\,264.5\text{ K})\;+\;\Delta_{tr}S°(\gamma\rightarrow\alpha)\;+\;(264.5\,\rightarrow\,298.15\text{ K}) \\ S^{\circ}_{298.15\text{ K}} &= 0.1403 + 93.412 + 8.0717 + 15.439 + 10.6552 + 10.690\text{ J K}^{-1}\text{ mol}^{-1} \\ &= 138.41\text{ J K}^{-1}\text{ mol}^{-1} \end{aligned}$$

9. One mole of an ideal gas undergoes an isothermal reversible compression from an initial pressure of 1.00 bar to a final pressure of 10.00 bar. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: For an isothermal expansion of an ideal gas, $P_2V_2 = P_1V_1$ or $(V_2/V_1) = (P_1/P_2)$. For an isothermal expansion of an ideal gas $T = T_{surr}$ and Eq. 13.2.4° gives:

$$\Delta S = nR\ln(V_2/V_1) = nR\ln(P_1/P_2) = 1\text{ mol }(8.314\text{ J K}^{-1}\text{ mol}^{-1})\ln(1.00/10.0) = -19.1\text{ J K}^{-1}$$

$$\Delta S_{surr} = -\Delta S = 19.1\text{ J K}^{-1}$$

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$$

10. One mole of an ideal gas undergoes an isothermal expansion against a constant external pressure of 1.00 bar. In this process the system does 900.0 J or work from an initial volume of 1.00 L, that is w = -900.0 J. The temperature is 298.2 K. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: The work for an isothermal expansion against a constant external pressure of P_{ext} is:

$$w = -P_{ext}\,\Delta V = -P_{ext}\,(V_2 - V_1)$$

Solving for the final volume gives:

$$w = -900.0\text{ J} = -1.00\text{x}10^5\text{ Pa }(V_2 - 1.00\text{ L})(1\text{ m}^3/1000\text{ L})$$

or $V_2 = 10.0$ L. The entropy change for the system is the same as a reversible expansion, since entropy is a state function and Eq. 13.2.4° again applies:

$$\Delta S = nR\ln(V_2/V_1) = 1\text{ mol }(8.314\text{ J K}^{-1}\text{ mol}^{-1})\ln(10.0\text{ L}/1.00\text{ L}) = 19.1\text{ J K}^{-1}$$

For the surroundings we use Eq. 13.5.2:

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q}{T}$$

Since $\Delta U = 0$ for an isothermal process in an ideal gas, $q = -w = 900.$ J

$$\Delta S_{surr} = \frac{-q}{T} = \frac{-900.\text{ J}}{298.2\text{ K}} = -3.02\text{ J K}^{-1}$$

The entropy change of the surroundings is negative, because the surroundings transfer heat into the system to "pay" for the work done. Finally the total entropy is given by:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 19.1\text{ J K}^{-1} - 3.02\text{ J K}^{-1} = 16.1\text{ J K}^{-1}$$

The expansion is spontaneous.

11. The volume of one mole of an ideal gas changes from 1.00 L to 2.00 L in an adiabatic reversible expansion. The initial temperature is 298.2 K. The gas is diatomic. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: Since this is an adiabatic reversible expansion, $q = q_{rev} = 0$:

$$\Delta S = \frac{q_{rev}}{T} = 0 \quad\text{and}\quad \Delta S_{surr} = \frac{-q}{T} = 0$$

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 0$$

We assume an isolated composite system consisting of the system and the surroundings. A reversible process is not spontaneous, so ΔS for the composite, isolated system is zero. If the system and surroundings are taken to be the universe, and if we assume that the universe is isolated, then $\Delta S_{tot} = \Delta S_{univ} = 0$.

12. The pressure of one mole of an ideal gas drops from 10.0 bar to 1.00 bar in an adiabatic expansion against a constant external pressure of 1.00 bar. The initial temperature is 298.2 K. Assume the gas is diatomic. Calculate the change in entropy of the system, the surroundings, and the total entropy change.

Answer: The temperature and pressure change for an adiabatic expansion so Eq. 13.2.15° must be used. However, the change in temperature must be calculated from $\Delta U = w$, Eq. x.x.x:

$$C_v(T_2 - T_1) = -P_{ext}(V_2 - V_1)$$

For a diatomic gas $C_v = 5/2\ nR$. The volumes can be calculated using the ideal gas law:

$$5/2\ nR\ (T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

The nR is a common factor and cancels out. Substituting in the initial conditions and the final pressure gives:

$$5/2\ (T_2 - 298.2\ K) = -1.00\ bar\left(\frac{T_2}{1.00\ bar} - \frac{298.2\ K}{10.0\ bar}\right)$$

Simplifying:

$$5/2\ T_2 - 745.5\ K = -T_2 + 29.82\ K$$

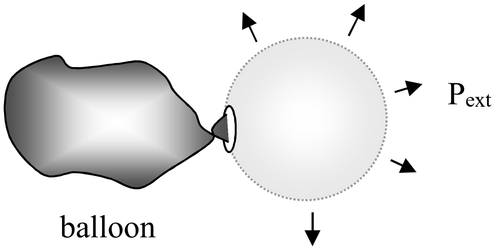
Solving for T_2 gives 221.5 K. Using $C_p = C_v + nR = 7/2\ nR$, the entropy change is then:

$$\Delta S = C_p \ln\frac{T_2}{T_1} - nR \ln\frac{P_2}{P_1}$$
$$= (1\ mol)(8.314\ J\ mol^{-1}\ K^{-1})[7/2 \ln(221.5\ K/298.2\ K) - \ln(1.00\ bar/10.0\ bar)]$$
$$= 10.5\ J\ K^{-1}$$

Since q = 0, then $\Delta S_{surr} = 0$ and $\Delta S_{tot} = \Delta S$. As expected, this expansion is spontaneous. Note that $\Delta U = w = C_v\ \Delta T = -1.59$ kJ and $\Delta H = C_p\ \Delta T = -2.23$ kJ for this example.

13. The pressure inside an inflated balloon filled with 1.00 mol of helium is 112.0 kPa. Assume the gas expands from the opening in the balloon in an adiabatic expansion. In other words, assume the gas expands quickly and we measure the final temperature of the gas before any thermal energy can be transferred from the surroundings. The initial temperature is 298.2 K. The atmospheric pressure is 101.3 kPa. Calculate the entropy change of the system and the surroundings and the entropy change of the universe.

Answer: To help visualize this expansion, as the helium leaves the balloon, think of the gas expanding inside a soap bubble. The surface of the soap bubble pushes back the atmosphere and work is done against the constant external ambient pressure.



The temperature and pressure change for an adiabatic expansion so Eq. 13.2.15° must be used. However, the change in temperature must be calculated from $\Delta U = w$, Eqs. 9.8.23-9.8.24:

$$C_v\ (T_2 - T_1) = -P_{ext}\ (V_2 - V_1)$$

For a monatomic gas $C_v = 3/2\ nR$. The volumes can be calculated using the ideal gas law:

$$3/2\ nR\ (T_2 - T_1) = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

The nR is a common factor and cancels out. The gas expands until the pressure of the helium is equal to the ambient pressure $P_2 = P_{ext}$. Substituting in the initial conditions and the final pressure gives:

$$3/2\,(T_2 - 298.2\text{ K}) = -101.3\text{ kPa}\left(\frac{T_2}{101.3\text{ kPa}} - \frac{298.2\text{ K}}{112.0\text{ kPa}}\right)$$

Simplifying:

$$3/2\,T_2 - 447.3\text{ K} = -T_2 + 269.7\text{ K}$$
$$5/2\,T_2 = 717.0\text{ K}$$

Solving for T_2 gives 286.8 K. Using $C_p = C_v + nR = 5/2\,nR$, the entropy change is then:

$$\begin{aligned}\Delta S &= C_p \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}\\ &= (1\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})[5/2\ln(286.8\text{ K}/298.2\text{ K}) - \ln(101.3\text{ kPa}/112.0\text{ kPa})]\\ &= (1\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})[-0.09745 + 0.1004]\\ &= (1\text{ mol})(8.314\text{ J mol}^{-1}\text{ K}^{-1})[0.00295]\\ &= 0.0245\text{ J K}^{-1}\end{aligned}$$

The ln(101.3/112.0) term has only three significant figures; then normal significant figure rules give only one significant figure in the final result. Since $q = 0$, then $\Delta S_{surr} = 0$ and $\Delta S_{tot} = \Delta S$. As expected, this expansion is spontaneous. Note that $\Delta U = w = C_v\,\Delta T = -142.$ J and $\Delta H = C_p\,\Delta T = -237.$ J for this example.

14. One mole of an ideal gas at 298.2 K triples its volume in an isothermal irreversible expansion against $P_{ext} = 0$. Calculate the changes in entropy of the system, the surroundings, and the total entropy change.

Answer: The entropy change for the system is the same as a reversible expansion, since entropy is a state function and Eq. 13.2.4° again applies:

$$\Delta S = nR\ln(V_2/V_1) = 1\text{ mol }(8.314\text{ J K}^{-1}\text{ mol}^{-1})\ln(3.00) = 9.13\text{ J K}^{-1}$$

For the surroundings we use Eq. 13.5.2:

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q}{T}$$

The work for an isothermal expansion against an external pressure of zero, $P_{ext} = 0$, is:

$$w = -P_{ext}\,\Delta V = 0$$

Since $\Delta U = 0$ for an isothermal process in an ideal gas, $q = -w = 0$

$$\Delta S_{surr} = 0$$

Finally the total entropy is given by:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 9.13\text{ J K}^{-1}$$

The expansion is spontaneous.

15. Calculate the molar entropy change for the phase transition of water to water vapor at room temperature, 298.15K, and one atmosphere pressure. The difference in heat capacity on vaporization is -41.9 J K^{-1} mol^{-1}. The standard enthalpy of vaporization of water at 373.15 K is 40.7 kJ mol^{-1}.

Answer: When the pressure is at 1 atm, we can only use Eq. 13.3.2 at the normal boiling point, because only at that temperature is the system in equilibrium:

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b} = \frac{40.7\text{x}10^3\text{J mol}^{-1}}{373.15\text{ K}} = 109.1\text{ J K}^{-1}\text{ mol}^{-1}$$

To find the entropy change at room temperature, use Eq. 13.3.7:

$$\begin{aligned}\Delta_{tr}S_{T2} &= \Delta_{tr}S_{T1} + \Delta_{tr}C_p \ln\frac{T_2}{T_1} \\ &= 109.1\text{ J K}^{-1}\text{ mol}^{-1} + (-41.9\text{ J K}^{-1}\text{ mol}^{-1})\ln\frac{298.15\text{ K}}{373.15\text{ K}} \\ &= 109.1 + 9.36\text{ J K}^{-1}\text{ mol}^{-1} = 118.5\text{ J K}^{-1}\text{ mol}^{-1}\end{aligned}$$

16. Consider the reaction:

pyruvic acid → acetaldehyde + CO_2 (g)

(which is catalyzed by the enzyme pyruvate decarboxylase.) Calculate $\Delta_rS°$ for this reaction for the system and the surroundings at 298.2 K. The values in the table below are at 298.2 K.

Table for Problem 2:

substance	$\Delta_fH°$ (kJ mol^{-1})	S°(J K^{-1} mol^{-1})
acetaldehyde	-192.30	160.2
CO_2	-393.51	213.74
pyruvic acid	-584.5	179.5

Answer: The data are:

	pyruvic acid →	acetaldehyde +	CO_2 (g)	
$\Delta_fH°$	-584.5	-192.30	-393.51	kJ mol^{-1}
S°	179.5	160.2	213.74	J K^{-1} mol^{-1}

$$\begin{aligned}\Delta_rH° &= [\text{products}] - [\text{reactants}] \\ &= [1\text{mol}(-192.30\text{ kJ mol}^{-1}) + 1\text{ mol}(-393.51\text{ kJ mol}^{-1})] - [1\text{ mol}(-584.5\text{ kJ mol}^{-1})] \\ &= -1.3\text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta_rS° &= [\text{products}] - [\text{reactants}] \\ &= [1\text{mol}(160.2\text{ J K}^{-1}\text{ mol}^{-1}) + 1\text{ mol}(213.74\text{ J K}^{-1}\text{ mol}^{-1})] - [1\text{ mol}(179.5\text{ J K}^{-1}\text{ mol}^{-1})] \\ &= 194.4\text{ J K}^{-1}\end{aligned}$$

which is dominated by the increase in number of moles of gas. The change in entropy for the surroundings is:

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-\Delta_r H}{T} = \frac{1.3 \text{ kJ } (1000 \text{ J}/1\text{kJ})}{298.2} = 4.36 \text{ J K}^{-1}$$

which is spontaneous.

17. The chemical reaction that corresponds to the enthalpy of formation of urea, $(NH_2)_2CO$, is:

$$\text{C (graph)} + 2\,\text{H}_2\text{ (g, 1 bar)} + \text{N}_2\text{ (g, 1bar)} \rightarrow (\text{NH}_2)_2\text{CO (s)} \qquad \Delta_f H° = -333.1 \text{ kJ mol}^{-1}$$

Calculate the reaction entropy for the formation reaction, at standard state and at 298.15 K.

Answer: The formation reaction is the production of one mole of substance from the constituent elements in their standard states:

	C (graph) +	2 H_2 (g, 1 bar) +	N_2 (g, 1bar) →	$(NH_2)_2CO$ (s)	$\Delta_f H° = -333.1$ kJ mol^{-1}
S°	5.740	130.574	191.50	104.6	J K^{-1} mol^{-1}

Remember that the enthalpy is an extensive function, so the stoichiometric coefficients are important. The reaction enthalpy change is given by Eq. 13.6.1 at standard state:

$$\Delta_r S° = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \textstyle\sum \nu_i\, S°$$
$$\Delta_r S° = [104.6] - [5.740 + 2(130.574) + 191.50] \text{ J K}^{-1}\text{ mol}^{-1} = -353.7_9 \text{ J K}^{-1}\text{ mol}^{-1}$$

18. (a). The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide:

$$(\text{NH}_2)_2\text{CO (s)} + \text{H}_2\text{O (l)} \rightarrow 2\,\text{NH}_3\text{ (g, 1 bar)} + \text{CO}_2\text{ (g, 1bar)}$$

Using the data in the appendix, calculate the reaction enthalpy, at standard state and at 298.15 K.
(b). Consider the reaction as an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. Calculate the change in entropy for the surroundings and the total entropy change at 298.15 K. (See Chapter 8 Problem 2b).

Answer: The plan is to note that the entropy change of the surroundings is determined from the reaction enthalpy, since at constant pressure, $q_{reaction} = q_p = \Delta_r H$.
The enthalpies of formation and absolute entropies, from Tables 8.4.1 and 8.4.2, are:

	$(NH_2)_2CO$ (s) +	H_2O (l) →	2 NH_3 (g, 1 bar) +	CO_2 (g, 1bar)	units
$\Delta_f H°$	-333.1	-285.830	-46.11	-393.509	kJ mol^{-1}
S°	104.6	69.92	192.34	213.74	J K^{-1} mol^{-1}

Remember that enthalpy and entropy are extensive functions, so the stoichiometric coefficients are important. The reaction enthalpy and entropy changes are given by Eqs. 8.4.9 and 13.6.1 at standard state:

$$\Delta_r H° = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \textstyle\sum \nu_i\, \Delta_f H°$$

$$\Delta_r S° = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \textstyle\sum \nu_i\, S°$$

(a). The reaction entropy is:

$$\Delta_r S° = [2(192.34) + 213.74] - [104.6 + 69.92] \text{ J K}^{-1}\text{ mol}^{-1} = 423.9 \text{ J K}^{-1}\text{ mol}^{-1}$$

The reaction entropy is strongly favorable because three moles of gas are produced.
(b). The reaction enthalpy is (see Chapter 8 Problem 2b):

$$\Delta_r H° = [2(-46.11) + (-393.509)] - [(-333.1) + (-285.83)] \text{ kJ mol}^{-1} = 133.2 \text{ kJ mol}^{-1}$$

The entropy change of the surroundings is given by Eq. 13.5.4:

$$\Delta_r S_{surr} = -\Delta_r H°/T = -(133.2 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})/298.15 \text{ K} = -446.7_5 \text{ J K}^{-1}\text{ mol}^{-1}$$

The total entropy change is:

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} = 423.9 \text{ J K}^{-1}\text{ mol}^{-1} + (-446.7_5 \text{ J K}^{-1}\text{ mol}^{-1}) = -22.9 \text{ J K}^{-1}\text{ mol}^{-1}$$

The reaction is not spontaneous at 298.15 K. Of course, enzyme catalysis won't change the spontaneity.

19. The aging of marine aerosols produces $NaHSO_4$ cloud condensation nuclei, CCN. The distribution of CCN determines the formation and reflectivity of clouds, which play an important role in determining the albedo of the atmosphere (see Chapter 8 Problem 3). (a). Using the data in the appendix, calculate the entropy change for the system and for the surroundings for the following reactions separately and in sum, under standard conditions and at 298.15 K.

H_2S (g, 1bar) + 2 O_2 (g, 1bar) → SO_3 (g, 1bar) + H_2O (g, 1bar)
SO_3 (g, 1 bar) + H_2O (l) → H_2SO_4 (l)
NaCl (s) + H_2SO_4 (l) → HCl (g, 1bar) + Na^+ (ao) + HSO_4^- (ao)

(b). Combine the three reactions to show the overall process. Use the combined reaction to calculate the overall reaction enthalpy. Compare with the result in part (a).

Answer: The plan is to use Hess's Law for each reaction and then the three reactions in sequence. Note that both gaseous and liquid water are involved in the reactions. Use the absolute entropy for pure liquid H_2SO_4. The reaction enthalpies are given in Chapter 8 Problem 3.

(a). The absolute entropies, from Table 8.4.1, combine to give the reaction entropies:

	H_2S (g, 1bar) +	2 O_2 (g, 1bar) →	SO_3 (g, 1bar) +	H_2O (g, 1bar)	units	1
S°:	205.8	205.029	256.76	188.715	$\text{J K}^{-1}\text{mol}^{-1}$	

	SO_3 (g, 1 bar) +	H_2O (l) →	H_2SO_4 (l)	2
S°:	256.76	69.92	156.904	$\text{J K}^{-1}\text{mol}^{-1}$

	NaCl (s) +	H_2SO_4 (l) →	HCl (g, 1bar) +	Na^+ (ao) +	HSO_4^- (ao)	3
S°:	72.4	156.904	186.799	59.0	131.8	$\text{J K}^{-1}\text{ mol}^{-1}$

Each reaction enthalpy change is given by Eq. 8.4.9:

$$\Delta_r S° = [\Sigma\text{products}] - [\Sigma\text{reactants}] = \sum \nu_i S°$$

For reaction 1:

$$\Delta_r S° = [188.715 + 256.76] - [205.8 + 2(205.029)] \text{ J K}^{-1}\text{mol}^{-1} = -170.38 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta_r S_{surr} = -\Delta_r H°/T = -(-616.91 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})/298.15 \text{ K} = 2069.13 \text{ J K}^{-1} \text{ mol}^{-1}$$

For reaction 2:

$$\Delta_r S° = [156.904] - [256.76 + 69.92] \text{ J K}^{-1} \text{ mol}^{-1} = -169.776 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta_r S_{surr} = -\Delta_r H°/T = -(-132.44 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})/298.15 \text{ K} = 444.131 \text{ J K}^{-1} \text{ mol}^{-1}$$

For reaction 3:

$$\Delta_r S° = [131.8 + 59.0 + 186.799] - [72.4 + 156.904] \text{ J K}^{-1} \text{ mol}^{-1} = 148.30 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta_r S_{surr} = -\Delta_r H°/T = -(5.23 \text{ J K}^{-1} \text{ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})/298.15 \text{ K} = -17.54 \text{ J K}^{-1} \text{ mol}^{-1}$$

The overall sequence gives:

$$\Delta_r S° = (-170.38) + (-169.776) + 148.30 \text{ J K}^{-1}\text{mol}^{-1} = -191.86 \text{ J K}^{-1}\text{mol}^{-1}$$
$$\Delta_r S_{surr} = 2069.13 + 444.131 + (-17.54) \text{ J K}^{-1} \text{ mol}^{-1} = 2495.72 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b). We can check the results by working directly with the overall reaction. The sum of the three steps gives:

$$H_2S\ (g) + 2O_2\ (g) + NaCl\ (s) + H_2O\ (l) \rightarrow HCl\ (g) + Na^+(ao) + HSO_4^-\ (ao) + H_2O\ (g)$$

S°: 205.8 205.029 72.4 69.92 186.799 59.0 131.8 188.715 J K^{-1} mol^{-1}

$$\Delta_r S° = [186.799 + 59.0 + 131.8 + 188.715] - [205.8 + 2(205.029) + 72.4 + 69.92] \text{ J K}^{-1} \text{ mol}^{-1}$$
$$= -191.86 \text{ J K}^{-1} \text{ mol}^{-1}$$

The combined reaction enthalpy is $\Delta_r H° = -744.12$ kJ mol^{-1} , giving the entropy change of the surroundings:

$$\Delta_r S_{surr} = -\Delta_r H°/T = -(-744.12 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})/298.15 \text{ K} = 2495.79 \text{ J K}^{-1} \text{ mol}^{-1}$$

The step-wise and combined reactions give the same result, to within round-off error. The combined reaction entropy is unfavorable. The overall reaction is enthalpy driven, since the entropy change of the surroundings is the dominant factor.

20. Use normal mode analysis to decide whether propane or 2-methylpropane has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.

Answer: The results of a normal mode analysis using Spartan at the AM1 level is given in the table below. You didn't need to get the thermodynamic analysis, but it is included for comparison.

Table: Normal Mode Analysis for Several Hydrocarbons

Compound	translation	rotation	vibration	total	literature	$\tilde{\nu}$ < 500 cm-1
methane	143.3	42.8	0.4	186.6	186.26	
acetylene	149.4	45.4	2.7	197.5	200.94	
ethylene	150.3	66.4	2.4	219.1	219.56	
ethane	151.2	68.1	10.9	230.3	229.60	204
cyclopropane	155.4	75.8	4.8	236.0	237.55	
propane	156.0	89.0	32.8	277.7	269.91	79, 190, 414(b)
2-methylpropane	159.4	93.5	44.4	297.3	294.64	149, 191x2, *398*x2, *478*
butane	159.4	96.7	45.4	301.4	310.23	103, 196, 206, *302*, *473*
cyclohexane	164.0	95.2	36.8	296.0	298.19	214x2, 331, *467*x2
benzene	163.1	86.7	19.1	268.9	269.31	*371*x2

Notice that 2-methylpropane has six low frequency normal modes, while propane has three. The lower the frequency of the normal mode the bigger the contribution to the entropy and heat capacity. From the table above, propane has the smallest frequency normal mode. However, the overall result for 2-methylpropane is a larger vibrational contribution to the entropy.

The normal modes for propane, using MOPAC are a little different:

```
142.40391   187.97537   412.50857
```

The normal modes for 2-methylpropane, using MOPAC are:

```
144.44885   182.36068   199.92640   395.61601   398.93565   477.33557
```

The thermodynamic analysis is at the bottom of the output for Spartan, GAMESS, Gaussian, and MOPAC. The thermodynamic analysis for propane from MOPAC, with the THERMO keyword, at 300 K is:

```
                CALCULATED THERMODYNAMIC PROPERTIES
                                        *
TEMP. (K)   PARTITION FUNCTION   H.O.F.    ENTHALPY   HEAT CAPACITY   ENTROPY
                                 KCAL/MOL   CAL/MOLE     CAL/K/MOL   CAL/K/MOL

 300  VIB.          4.226                  1173.47287    8.68840    6.77570
      ROT.      .200E+05                    894.267       2.981     22.664
      INT.      .846E+05                   2067.740     11.669      29.439
      TRA.      .286E+27                   1490.445       4.968     37.291
      TOT.                       -24.224   3558.1849    16.6374     66.7306
```

The thermodynamic analysis for 2-methylpropane from MOPAC at 300 K is:

```
   CALCULATED THERMODYNAMIC PROPERTIES
                                        *
TEMP. (K)   PARTITION FUNCTION   H.O.F.    ENTHALPY   HEAT CAPACITY   ENTROPY
                                 KCAL/MOL   CAL/MOLE     CAL/K/MOL   CAL/K/MOL

 300  VIB.          9.160                  1911.82988   13.87179   10.77417
      ROT.      .517E+05                    894.267       2.981     24.547
      INT.      .473E+06                   2806.097     16.853      35.321
      TRA.      .433E+27                   1490.445       4.968     38.114
      TOT.                       -29.325   4296.5419    21.8208     73.4355
```

The vibrational frequencies for torsional modes are very sensitive to the level of the calculation. You will see large differences, especially for the lowest frequency normal modes, from program to program. However, the number of low frequency normal modes will be reproducible. There is another problem with this approach. The normal mode analysis assumes that the vibrations are purely harmonic oscillators. We will see in the vibrational spectroscopy chapter that torsions are strongly anharmonic. Normal mode analysis does a poor job, quantitatively, in predicting the frequencies of these vibrations. For now, just counting low frequency normal modes will help you to visualize the vibrational contribution to the entropy. We will argue later about how to get good quantitative predictions.

21. Use normal mode analysis to decide whether cyclohexane or benzene has a higher absolute entropy. You can use any convenient normal mode analysis program based on molecular mechanics or molecular orbital theory.

Answer: Since cyclohexane has more atoms, we would predict that cyclohexane would have the higher absolute entropy. The larger number of atoms predicts a greater moment of inertia for the molecule and thus a greater rotational contribution to the entropy. Also, remember that the number of normal modes for a non-linear molecule is 3N-6. So the number of vibrational normal modes for cyclohexane is greater, which would also predict a higher entropy.

Please consult the table for the last problem for the results of the normal modes analysis. Cyclohexane has five vibrations with low wavenumbers, while benzene has only two. Therefore, cyclohexane will have a higher contribution from vibrations than benzene. The three lowest frequency vibrations for cyclohexane are hindered ring torsions. The low frequency vibrations for benzene are out-of-plane C-H bending vibrations.

22. Give an example for each of the following types of processes. Choose your examples from ideal gas expansions or compressions or phase transitions of pure substances. Specify the difference in the variable, P or T, that is responsible for the spontaneous or non-spontaneous direction of the process:

(a). a spontaneous adiabatic and isothermal process,
(b). a spontaneous isothermal process with a decrease in entropy for the system,
(c). a non-spontaneous isothermal process with an increase in entropy for the system,
(d). a spontaneous adiabatic process that decreases the temperature of the system.

Answers: (a). a spontaneous adiabatic and isothermal process: an irreversible expansion of an ideal gas against a vacuum. (Ideal mixing of gases is an additional example that will be covered in the next chapter.) The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow 0$ with $P_{ext} = 0$.

(b). a spontaneous isothermal process with a decrease in entropy for the system: an irreversible compression of an ideal gas with an external pressure greater than the system pressure. The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow P_{high}$ with $P_o < P_{ext}$. Another example is the liquefaction of 1 mol of a gas or freezing of 1 mol of a liquid at a temperature below the equilibrium phase transition temperature, at the chosen ambient pressure. A specific example is the freezing of water at -5°C at 1 bar ambient pressure. The independent variable is the number of moles of gas or liquid, respectively: $dn_g = -1$ mol or $dn_{liq} = -1$ mol. The variable controlling the spontaneous direction is the temperature, $T < T_b^*$ or T_f^* with $T = T_{surr}$.

(c). a non-spontaneous isothermal process with an increase in entropy for the system: the isothermal expansion of an ideal gas against an external pressure greater than the system pressure. The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow P_{low}$ with $P_o < P_{ext}$ giving a non-spontaneous process. Another example is the melting of 1 mol of a solid at a temperature below the equilibrium phase transition temperature, at the chosen ambient pressure. The variable controlling the spontaneous direction is the temperature, $T < T_f^*$ with $T = T_{surr}$.

(d). a spontaneous adiabatic process that decreases the temperature of the system: an irreversible adiabatic expansion of an ideal gas against an external pressure less than the system pressure. The variable controlling the spontaneous direction is the pressure: $P_o \rightarrow P_{low}$ with $P_o > P_{ext}$. For an adiabatic process for a phase transition, consider a phase transition in a thermos bottle. Melting decreases the temperature of the system for an adiabatic process. Then for a spontaneous adiabatic process that decreases the temperature of the system, the melting of 1 mol of a solid at a temperature above the equilibrium phase transition temperature is a good example. The variable controlling the spontaneous direction is the temperature, $T_o \rightarrow T_{low}$ with $T_o > T_f^*$.

23. The Clausius inequality relates the entropy changes of the system and surroundings. Consider an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. Use the Clausius inequality, Eq. 13.1.9, to show that $dS > -dS_{surr}$ for a spontaneous process.

Answer: Consider the system and surroundings as an isolated composite. The Clausius inequality, Eq. 13.1.9, gives $dS > đq/T$. For a spontaneous isothermal process, $T = T_{surr}$ giving $dS_{surr} = -\, đq/T$. Substitution of this result for the surroundings into the right-side of the Clausius inequality gives, for a spontaneous isothermal process: $dS > -dS_{surr}$.

24. Determine if the following statements are true of false. If the statement is false, describe the changes that are required to make the statement true, if possible. Assume that the system and surroundings are an isolated composite. (Hint: three of the following statements are true.)

(a). The heat transfer for the system is equal in magnitude and opposite in sign to the heat transfer for the surroundings ($đq = -\, đq_{surr}$).

(b). The entropy change of the system is equal in magnitude and opposite in sign to the entropy change of the surroundings ($dS = -\, dS_{surr}$).

(c). For a spontaneous process, the magnitude of the entropy change of the system is never greater than the magnitude of the entropy change of the surroundings.

(d). Heat transfer to a system at low temperature gives a larger change in the entropy of the system than the transfer of the same amount of heat at high temperature.

(e). Spontaneous processes always result in dispersal of energy to the surroundings.

(f). The entropy of every system is zero at absolute zero.

(g). For a given heat transfer, the entropy change of the surroundings is independent of the details of the process for the system.

(h). One mole of xenon gas at 1 bar and 298.2 K is mixed with another mole of xenon gas at 1 bar and 298.2 K. The total entropy change of the combined systems is positive for the process.

Answers: (a). True: heat and work are transfers of energy and so necessarily for the transfer, $đq = -đq_{surr}$ and $đw = -đw_{surr}$.

(b). False: The entropy change for a spontaneous process is always positive for an isolated composite of the system and surroundings, by the Second Law, $dS + dS_{surr} > 0$. Only for a reversible process is $dS = -dS_{surr}$, since then $đq = đq_{rev}$.

(c). False: For a spontaneous endothermic process in a closed system, the entropy change of the system is positive and the entropy change of the surroundings is negative. By the Second Law for an isolated composite of the system and the surroundings, $dS + dS_{surr} > 0$. To give an increase in total entropy for an endothermic process, the magnitude of the entropy change of the system must be greater than the magnitude of the entropy change of the surroundings.

However, to be more precise, we should use the Clausius inequality. Consider an isothermal process in a closed system in thermal contact with the surroundings acting as a constant temperature reservoir. The Clausius inequality, Eq. 13.1.9, is $dS > đq/T$. For a spontaneous isothermal process, $T = T_{surr}$ giving $dS_{surr} = -đq/T$. Substitution of the last result into the Clausius inequality gives for a spontaneous isothermal process: $dS > -dS_{surr}$. For an endothermic process, dS_{surr} is negative. The magnitude of dS_{surr} is then $|dS_{surr}| = -dS_{surr}$. To satisfy the Second Law, if the entropy change of the surroundings is negative then the entropy change of the system must be positive, and then $|dS| = dS$. The Clausius inequality then gives for a spontaneous endothermic process $|dS| > |dS_{surr}|$; the magnitude of the entropy change of the system must be greater than the magnitude of the entropy change of the surroundings.

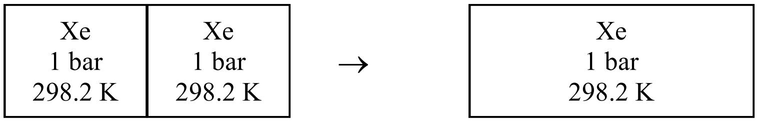
(d). True: refer to Figure 13.1.1.

(e). False: By the Second Law, for an isolated composite of the system and the surroundings, $dS + dS_{surr} > 0$. However, the change in entropy of the surroundings can be negative, as for an endothermic process, or zero, as for an adiabatic process. The total entropy change can be dominated by the entropy change of the system, which allows an unfavorable entropy change of the surroundings. A spontaneous process may or may not give an increase of the entropy of the surroundings. A spontaneous process may or may not result in energy dispersal to the surroundings.

(f). False: the entropy of all pure, perfect crystalline substances is zero at absolute zero. Residual entropy can be locked into a system before cooling to absolute zero. Such a system is metastable, being trapped into a non-zero entropy state by a kinetic barrier.

(g). True: For a given heat transfer, đq, the entropy change of the surroundings is given by $dS_{surr} = -đq/T_{surr}$, irrespective of whether the process is reversible or irreversible.

(h). False: the entropy change is zero, because the xenon atoms in the two systems are indistinguishable. Consider the two systems as an isolated composite. The process is diagrammed as follows:



The instant that the barrier is removed, the combined system is at equilibrium. There are no gradients, so no process occurs.

25. Heat capacities are often approximated by a power series: $C_p = a + b\,T + c\,T^{-2}$, for a, b, and c constants. Find the change in enthalpy and entropy of a substance for a constant pressure process with a temperature change from T_1 to T_2.

Answer: The plan is to integrate the partial derivative relationships $(\partial H/\partial T)_P = C_p$ and $(\partial S/\partial T)_P = C_p/T$. For a constant heat capacity, $\Delta H = C_p(T_2 - T_1)$ and $\Delta S = C_p \ln(T_2/T_1)$.

The enthalpy integral is:

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} C_p\, dT = \int_{T_1}^{T_2} (\, a + b\,T + c\,T^{-2})\, dT \\ &= \int_{T_1}^{T_2} a\, dT + \int_{T_1}^{T_2} bT\, dT + \int_{T_1}^{T_2} cT^{-2}\, dT \\ &= a\,[\,T\,|_{T_1}^{T_2} + \frac{b}{2}\,[\,T^2\,|_{T_1}^{T_2} - c\,[\,T^{-1}\,|_{T_1}^{T_2} \\ &= a\,(T_2 - T_1) + \frac{b}{2}\,(T_2^2 - T_1^2) + c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\end{aligned}$$

Compare this result with Chapter 7 Problem 29, which uses a different heat capacity power series expansion. The leading term, in both cases, agrees with the expression that assumes a constant heat capacity, $\Delta H = C_p(T_2 - T_1)$.

The entropy integral is:

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} C_p/_T\, dT = \int_{T_1}^{T_2} \left(\frac{a}{T} + b + c\,\frac{1}{T^3}\right) dT \\ &= \int_{T_1}^{T_2} \frac{a}{T}\, dT + \int_{T_1}^{T_2} b\, dT + \int_{T_1}^{T_2} cT^{-3}\, dT \\ &= a\,[\,\ln(T)|_{T_1}^{T_2} + b\,[\,T\,|_{T_1}^{T_2} - \frac{c}{2}\,[\,T^{-2}\,|_{T_1}^{T_2} \\ &= a\,\ln\!\left(\frac{T_2}{T_1}\right) + b\,(T_2 - T_1) - \frac{c}{2}\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)\end{aligned}$$

Compare this result with Eq. 13.2.34, which uses a different heat capacity power series expansion. An example from the NIST WebBook online database that uses a term in T^{-2} is carbon dioxide (g) (http://webbook.nist.gov).

26. Calculate the residual entropy at 0 K for NO, assuming random NO and ON orientations.

Answer: Given the two ways of orienting NO is the same as for CO and N_2O, the residual entropy is approximated as S_o= R ln w = (8.314 J K^{-1} mol^{-1}) ln(2) = 5.76 J K^{-1} mol^{-1}.

Chapter 14 Problems: Focusing on Chemical Reactivity

1. Find the number of thermodynamic constituents and components for a solution of hexane and chloroform. Find the expression for dG for changes in the number of components in an open system at constant temperature and pressure.

Answer: The number of constituents and components is the same since there are no chemical reactions or chemical constraints. There are no chemical constraints because there are no special chemical conditions relating the amounts of each constituent. There are two components, which can be expressed as n_h for hexane and n_c for choloroform. At constant temperature and pressure:

$$dG = \mu_h\, dn_h + \mu_c\, dn_c$$

2. Lime is made commercially through the thermal decomposition of limestone, which is composed primarily of calcium carbonate:

$$CaCO_3\ (s) \rightleftarrows CaO\ (s) + CO_2\ (g)$$

Find the number of thermodynamic components starting with only $CaCO_3$. In other words, assume that there are no other sources of CaO or CO_2 other than the decomposition of $CaCO_3$.

Answer: There are three constituents: $CaCO_3$, CaO, and CO_2. So $n_s = 3$. However, there is one chemical reaction and one chemical constraint. The chemical constraint is that the initial reaction is prepared from just $CaCO_3$ with no other sources of the products than the chemical reaction. The number of components is then given by Eq. 14.2.1:

$$\begin{aligned} c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 3 - 1 - 1 = 1 \end{aligned}$$

Once the system attains equilibrium the amounts of products can be obtained from the equilibrium expression: the partial pressure of CO_2 at equilibrium is given by:

$$K_p = P_{CO_2}.$$

3. Solid ammonium chloride decomposes at high temperatures to give ammonia and hydrogen chloride gas:

$$NH_4Cl\ (s) \rightleftarrows NH_3\ (g) + HCl\ (g)$$

Find the number of components for a system prepared from only NH_4Cl (s).

Answer: There are three constituents: NH_4Cl (s), NH_3 (g), and HCl (g). However, there is one chemical reaction and one chemical constraint. The chemical constraint is that the initial reaction is prepared from just NH_4Cl (s) with no other sources of the products than the chemical reaction.

$c = n_s$ – no. of reactions – no. of chemical constraints
$= 3 - 1 - 1 = 1$

At equilibrium the amounts of reactants and products can be obtained from the equilibrium expression:

$$K_p = P_{NH_3}\, P_{HCl}$$

Since the only source of products is the chemical reaction and from the 1:1 stoichiometry, $P_{NH_3} = P_{HCl}$.

4. Gas phase ammonia and hydrogen chloride gas react to form solid ammonium chloride:

$$NH_3\ (g) + HCl\ (g) \rightleftarrows NH_4Cl\ (s)$$

(a). Find the number of components for a system prepared from arbitrary amounts of NH_3 and HCl. (b). Find the number of components for a system prepared from equal-molar amounts of NH_3 and HCl.

Answer: There are three constituents: NH_3 (g), HCl (g), and NH_4Cl (s). There is one chemical reaction. For (a) there are no additional chemical constraints and from Eq. 14.2.1:

$c = n_s$ – no. of reactions – no. of chemical constraints
$= 3 - 1 - 0 = 2$

For (b) the specification of equal-molar amounts of reactants is a chemical constraint and then the number of components is given by:

$c = n_s$ – no. of reactions – no. of chemical constraints
$= 3 - 1 - 1 = 1$

The information from the chemical reactions is algebraically expressed by the equilibrium expressions. At equilibrium the amounts of reactants and products can be obtained from the equilibrium expression:

$$K_p = \frac{1}{P_{NH_3}\, P_{HCl}}.$$

and since the reactants are supplied in equal-molar amounts and the reaction stoichiometry is 1:1, $P_{NH_3} = P_{HCl}$. This problem is just the reverse of Problem 3; but as always we should get the same result since at equilibrium every chemical reaction is reversible. It shouldn't matter what direction the reaction is written, from the point of view of the number of components. K_p in this problem is equal to $1/K_p$ in Problem 3.

5. Consider the dissociation of the weak acid, acetic acid, in aqueous solution:

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq)$$

Find the number of constituents and thermodynamic components starting with only acetic acid and water. In other words, assume that there are no other sources of CH_3COO^- other than the dissociation of CH_3COOH. Also, include the dissociation of water as a source of H^+. Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

Answer: The number of constituents is five: CH_3COOH, H^+, CH_3COO^-, OH^-, and H_2O. The solution is made from acetic acid and water, so the number of components is 2. There are two chemical reactions, the dissociation of acetic acid and water:

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq)$$
$$H_2O \rightleftarrows H^+(aq) + OH^-\ (aq)$$

and then the number of chemical constraints is one, as is given by:

$$\begin{aligned} c &= n_s - \text{no. of reactions} - \text{no. of chemical constraints} \\ &= 5 - 2 - 1 = 2 \end{aligned}$$

Charge balance is the chemical constraint:

$$[H^+] = [CH_3COO^-] + [OH^-]$$

The two components are most easily expressed as the mole amounts of CH_3COOH and H_2O, although the choice is not unique.

The information from the chemical reactions is algebraically expressed by the equilibrium expressions. At equilibrium the amounts of reactants and products can be obtained by solving:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \qquad \text{and} \qquad K_w = [H^+][OH^-].$$

6. Consider the dissociation of the weak acid, acetic acid, in aqueous solution:

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq)$$

Find the number of constituents and thermodynamic components starting with a solution prepared from acetic acid, sodium acetate, and water. Also, include the dissociation of water as a source of H^+. Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

Answer: Since the solution is prepared from acetic acid and sodium acetate there are two sources of CH_3COO^-, the dissociation of CH_3COOH and added sodium acetate. The sources of H^+ are the dissociation of CH_3COOH and H_2O. The number of constituents is six: CH_3COOH, H^+, CH_3COO^-, OH^-, Na^+, and H_2O. The number of components is three, since the solution can be made up from arbitrary amounts of acetic acid, sodium acetate, and water. There are two chemical reactions, the dissociation of acetic acid and water:

$$CH_3COOH\ (aq) \rightleftarrows H^+\ (aq) + CH_3COO^-\ (aq)$$
$$H_2O \rightleftarrows.\ H^+(aq) + OH^-\ (aq)$$

Charge balance is the chemical constraint:

$$[H^+] + [Na^+] = [CH_3COO^-] + [OH^-]$$

The number of thermodynamic chemical components is then:

$$c = n_s - \text{no. of reactions} - \text{no. of chemical constraints}$$
$$= 6 - 2 - 1 = 3$$

The three components are most easily expressed as the mole amounts of acetic acid, sodium acetate, and H_2O, although the choice is not unique.

The information from the chemical reactions is algebraically expressed by the equilibrium expressions. At equilibrium the amounts of reactants and products can be obtained from the equilibrium expressions:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \qquad \text{and} \qquad K_w = [H^+][OH^-].$$

7. Find the number of constituents and thermodynamic components starting with a solution prepared from phosphoric acid, sodium hydroxide, and water. Relate the number of components to the number of independent chemical reactions and the number of chemical constraints.

Answer: There are three chemical components, phosphoric acid, sodium hydroxide, and water. There are eight constituents: Na^+, H^+, OH^-, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and H_2O. The equilibria are:

$$H_3PO_4 \overset{K_{a1}}{\rightleftarrows} H_2PO_4^- + H^+$$

$$H_2PO_4^- \overset{K_{a2}}{\rightleftarrows} HPO_4^{2-} + H^+$$

$$HPO_4^{2-} \overset{K_{a3}}{\rightleftarrows} PO_4^{3-} + H^+$$

$$H_2O \overset{K_w}{\rightleftarrows} H^+ + OH^-$$

giving four chemical reactions. With three components and four reactions, there must be only one chemical constraint: $c = 8 - 4 - 1 = 3$. The charge balance is the chemical constraint:

$$[Na^+] + [H^+] = [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}] + [OH^-]$$

8. Hydrogen peroxide, which is used as a topical disinfectant, decomposes to give O_2 gas in a highly exothermic reaction. This reaction is often used as a rather spectacular chemical demonstration:

$$2\ H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$$

Hydrogen peroxide is also important in redox reactions in the environment and in biological processes. During this reaction many things can change: V, P, S, T, U, H, and the mole amounts of the reactants and products. Keeping track of all these variables can be daunting. How can we simplify the definition of our system so that we can focus on the chemical changes?

Answer: One possibility to study this reaction is as follows.
Step 1: The reaction is set up in a closed piston initially containing only the H_2O_2 solution so that the only source of $O_2(g)$ is from the decomposition of the hydrogen peroxide. Therefore, there is only one chemical component and this quantity is fixed by the closed system. There are three dependent chemical constituents, H_2O_2, H_2O, and O_2:

$$dU = TdS - PdV + 2\,\mu_{H2O}\,d\xi + \mu_{O2}\,d\xi - 2\,\mu_{H2O2}\,d\xi \qquad 1.$$

However, there is only one composition variable, ξ, because there is one chemical reaction. Starting with reactants only, if the reaction were to go to completion, ξ ranges from 0 to 1 mol. In the final equilibrium state, the extent of the reaction will also be constrained to the equilibrium value with $\xi < 1$.

Step 2: Consider the closed chemical reaction as a system which is held at constant temperature and pressure by contact with the surroundings. The surroundings are large in extent so that the surroundings act as a constant temperature and pressure reservoir. Therefore the temperature and pressure in Eq. 1 are constrained: $T = T_{surr}$, $P = P_{ext}$. In other words, the T and P in Eq. 1 are not independent variables.

Step 3: The composite of the system and surroundings is assumed to be isolated. Therefore,
$đq = -đq_{surr}$, $dw = -dw_{surr}$
$dV_{tot} = dV + dV_{surr} = 0$, giving $dV = -\,dV_{surr}$,
$dU_{tot} = dU + dU_{surr} = 0$, giving $dU = -\,dU_{surr}$

9. For the reaction in the last problem, evaluate the change in entropy of the system, the surroundings, and the total change in entropy. Don't use any specific numbers; just consider the appropriate equations and inequalities. Compare the results for the entropy with the results from the last problem for the change in internal energy.

Answer: The entropy change for the system is dS. The entropy change in the surroundings is always straightforward; from Eq. 12.5.2:

$$dS_{surr} = \frac{đq_{surr}}{T_{surr}} = \frac{-đq}{T} \qquad 1$$

and since the system is at constant pressure, Eq. 12.5.4, $đq = đq_p$:

$$dS_{surr} = \frac{đq_{surr}}{T_{surr}} = \frac{-dH}{T} \qquad 2$$

However, entropy is not conserved for a spontaneous process:

$$dS_{tot} = dS + dS_{surr} > 0 \qquad 3$$

The inequality is from the Second Law. For the internal energy, $dU_{tot} = dU + dU_{surr} = 0$ because the internal energy is conserved. Equations 1-3 are the basis for the next chapter.

10. The decomposition of hydrogen peroxide is a spontaneous process:

$$2\ H_2O_2\ (aq) \rightleftarrows 2\ H_2O\ (l) + O_2\ (g)$$

How can we use thermodynamics, which only applies to systems at equilibrium, to study this process?

Answer: To calculate the change in internal energy, enthalpy, entropy, and as we shall see Gibbs energy for the reaction, we consider a temporary internal constraint that prevents the reaction from occurring. Then the changes ΔU, ΔH, ΔS, and ΔG can be calculated from the state of the system before and after the internal constraint is removed.

Since there is only one reactant for this reaction you might be wondering how we might establish such an internal constraint. One way is to measure the properties of the hydrogen peroxide in a long enough time interval after it has been placed in the closed piston that the initial equilibrium state can be established, but before the reaction has had a chance to proceed to an appreciable extent. For such a short time interval, the system can be considered as at equilibrium with respect to temperature and pressure gradients, but not at equilibrium with respect to the overall course of the chemical reaction. However, this reaction is slow in the absence of a catalyst. Hydrogen peroxide can be purchased in drug stores for this reason. The kinetic stability of this metastable system acts as a *de facto* internal constraint. So the properties of the hydrogen peroxide solution would be measured and then a catalyst would be added to accelerate the attainment of equilibrium. If you have ever seen this reaction as a lecture demonstration, the catalyst that is used is solid MnO.

11. Consider the following chemical reaction at room temperature and in the absence of a catalyst:

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (l)$$

This reaction is spontaneous and therefore the process is irreversible. This reaction is in fact the primary source of propulsion for the space shuttle. Describe how we can apply thermodynamics to calculating the change in internal energy and entropy for this process when the reaction goes to equilibrium by an irreversible reaction.

Answer: The reaction of H_2 and O_2 at room temperature and in the absence of a catalyst is very slow. A mixture of H_2 and O_2 is metastable at room temperature. The kinetic stability of this metastable system acts as a temporary internal constraint. It is very easy to measure the properties of a mixture of H_2 and O_2, giving U_1 and S_1. After addition of a catalyst (a piece of Pt metal) the reaction quickly proceeds to equilibrium and then the final U_2 and S_2 can be measured. Then $\Delta U = U_2 - U_1$ and $\Delta S = S_2 - S_1$.

12. Devise an internal constraint for an electrochemical reaction that you wish to maintain at the initial conditions. For example consider the reaction:

$$AgCl\,(s) + \tfrac{1}{2}\,H_2\,(g,\,1\,bar) \rightarrow Ag\,(s) + Cl^-\,(1\,m) + H^+\,(1\,m)$$

Answer: The application of an external voltage to the electrochemical cell that is equal to the initial emf maintains the initial conditions in the cell. The electrochemical reaction can be broken into two half-cells: $AgCl\,(s) + 1\,e^- \rightarrow Ag\,(s) + Cl^-$

$$\tfrac{1}{2}\,H_2\,(g) \rightarrow H^+ + 1\,e^-$$

The electrochemical cell: $Pt|\,H_2\,(g)\,|\,H^+\,(1\,m),\,Cl^-\,(1\,m)\,|\,AgCl\,(s)|Ag(s)$ has a cell potential (the standard state cell potential) of E = 1.223 V. If a battery with a voltage of 1.223 V were attached to this electrochemical cell, the cell would be at equilibrium and no AgCl (s) would react. After removing the battery and connecting the cell electrodes with a wire, the reaction will reach equilibrium with increased $H^+$and Cl^- concentrations with a final cell emf of 0 V. $\Delta_rG = -nFE$ for this reaction, even though the course of the reaction is very irreversible.

An even easier way to arrange for a temporary internal constraint is to simply leave the electrodes unconnected. However, we wouldn't be able to experimentally measure the initial voltage of the system. Stated in other terms, an unused battery maintains its initial voltage.

13. Determine the change in internal energy for a reaction in terms of the change in extent of the reaction, $d\xi$, for the reaction in a closed system:

$$\tfrac{1}{2}\,N_2\,(g) + {}^{3}/_{2}\,H_2\,(g) \rightarrow NH_3\,(g)$$

Answer:

$$dU = TdS - PdV + \mu_{NH_3}\,d\xi - \tfrac{1}{2}\,\mu_{N_2}\,d\xi - {}^{3}/_{2}\,\mu_{H_2}\,d\xi$$

14. Determine the change in internal energy for a reaction in terms of the change in extent of the reaction, $d\xi$, for the reaction in a closed system:

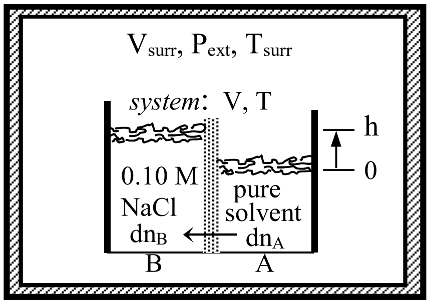
$$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l)$$

Answer:

$$dU = TdS - PdV + 6\,\mu_{H_2O}\,d\xi + 6\,\mu_{CO_2}\,d\xi - \mu_{C_6H_{12}O_6}\,d\xi - 6\,\mu_{O_2}\,d\xi$$

15. A 0.10 M NaCl aqueous solution is separated from pure water by a semi-permiable membrane. The height difference between the solution and the pure solvent is h and the corresponding equilibrium osmotic pressure is π. The system and the surroundings are in equilibrium. Assume the molar volume of the solvent in the solution is essentially the pure molar volume. Construct a isolated composite system with this membrane system and the surroundings. Consider the transfer of dn_A moles of solvent from the pure solvent through the membrane into the solution. Consider h = 0 as the reference height. Relate P_{ext} and T_{surr} with P_A, P_B, and T, where P_A is the pressure at h = 0 for the pure solvent and P_B is the pressure at h = 0 for the NaCl

solution. Relate dU, đq, đw, and dV for the total composite, the surroundings, the system (A and B), and for the pure solvent (A) and the NaCl solution (B).



Answer: The system is closed with no exchange of matter between the system and the surroundings (no evaporation of the solvent). The exchange of energy between the system and surroundings is restricted to transfers of heat and PV-work. Let the pure solvent compartment be side A and the NaCl solution be side B with:

$$\text{đ}q = \text{đ}q_A + \text{đ}q_B \qquad \text{đ}w = \text{đ}w_A + \text{đ}w_B \qquad \text{and} \qquad dU = dU_A + dU_B$$

The surroundings act as a constant temperature and pressure reservoir with $T_{surr} = T = 298.2$ K. The compartment pressures are $P_A = P_{ext} = 1.00$ bar and $P_B = P_{ext} + \pi$. The composite is isolated giving:

$$\begin{aligned} dU_{tot} &= 0 & dU &= dU_A + dU_B = -\,dU_{surr} \\ \text{đ}q_{tot} &= 0 & \text{đ}q &= \text{đ}q_A + \text{đ}q_B = -\,\text{đ}q_{surr} \\ \text{đ}w_{tot} &= 0 & \text{đ}w &= \text{đ}w_A + \text{đ}w_B = -\,\text{đ}w_{surr} \\ dV_{tot} &= 0 & dV &= dV_A + dV_B = -\,dV_{surr} \end{aligned}$$

In other words, the total internal energy is conserved. The membrane acts as a temporary constraint. Assuming the molar volume of the solvent is the same on both sides of the membrane gives $dV_B = -\,dV_A$. There is no net change in volume of the system or surroundings:

$$dV = dV_A + dV_B = 0 \qquad \text{and} \qquad dV_{surr} = 0$$

16. (*Challenge Problem*) For the previous problem, find the PV-work, đw, for the the transfer of dn_A moles of solvent from the pure solvent through the membrane into the NaCl solution.

Answer: The plan is to evaluate the PV-work in each compartment separately and then add the results to find the net work for the system.

In the transfer of dn_A moles of solvent from the A compartment into the B compartment, the surroundings does work on the A compartment, in compression at P_{ext}, and the system does work on the surroundings in the B compartment, in expansion against $P_{ext} + \pi$:[1]

$$\text{đ}w_A = -\,P_{ext}\,dV_A \qquad \text{đ}w_B = -\,(P_{ext} + \pi)\,dV_B = (P_{ext} + \pi)\,dV_A$$

The net work for the system is $\text{đ}w = \pi\,dV_A$. The change in volume is given by:

$$dV_A = -\,(\mathfrak{M}_A/d_A)(1\text{x}10^6\ \text{mL}/1\ \text{m}^3)\,dn_A$$

where $\mathfrak{M}_A$ is the molar mass of the solvent and d_A is the density of the solvent. We will find in the ideal solutions chapter that the energy requirement for the process is supplied by the dilution of the NaCl solution. The reverse of the process described in this problem is called reverse osmosis. Reverse osmosis is commonly used for water purification. The energy requirement for reverse osmosis systems is large and is given by $đw = \pi \, dV_A$.

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Chapter 15: Spontaneity

1. The water gas shift reaction is an important process in the gasification of coal or biomass to produce transportation fuels:

$$CO\ (g) + H_2O\ (g) \rightleftarrows CO_2\ (g) + H_2\ (g)$$

What is the relationship among the chemical potentials for the reaction at equilibrium?

Answer: At equilibrium: $\mu_{CO} + \mu_{H2O} = \mu_{CO2} + \mu_{H2}$

2. Some authors use "=" instead of "⇄" for chemical equations at equilibrium. For example:

$$ATP^{4-} + H_2O = ADP^{3-} + HPO_4^{2-} + H^+$$

Why is the use of the equals sign a good idea?

Answer: The equals sign is appropriate because the chemical potentials of the reactants and products are equal at equilibrium: $\mu_{ATP4-} + \mu_{H2O} = \mu_{ADP3-} + \mu_{HPO42-} + \mu_{H+}$

3. Calculate $\Delta_{fus}H°$, $\Delta_{fus}S°$, and $\Delta_{fus}G°$ for freezing one mole of supercooled water at –10.0 °C and 1.00 bar pressure:

$$H_2O\ (l) \rightarrow H_2O\ (s)$$

At 273.15 K, $\Delta_{fus}H° = 6.008$ kJ mol^{-1}. Assume the heat capacities are constant over the temperature range with $C_{p,m}(s) = 37.66$ J K^{-1} mol^{-1} and $C_{p,m}(l) = 75.29$ J K^{-1} mol^{-1}.

Answer: Lets first work with the phase transition in the normal direction from low entropy phase to high entropy phase:

$$H_2O\ (s) \rightarrow H_2O\ (l)$$

Then at the end we will reverse the direction to give the required results. We can use $\Delta_{fus}S° = \Delta_{fus}H°/T_m^*$, but only at the normal melting point, which is at 0°C:

$$\Delta_{fus}S° = \Delta_{fus}H°/T_m^* = 6.008\text{x}10^3 \text{ J mol}^{-1}/273.15 \text{ K} = 22.00 \text{ J K}^{-1} \text{ mol}^{-1}$$

The change in heat capacity for the phase transition is:

$$\Delta_{fus}C_p = C_p(l) - C_p(s) = (75.29 - 37.66\ ) \text{ J K}^{-1} \text{ mol}^{-1} = 37.63 \text{ J K}^{-1} \text{ mol}^{-1}$$

At –10°C: $\Delta_{fus}S^\circ_{T_2} = \Delta_{fus}S^\circ_{T_1} + \Delta_{fus}C_p \ln(T_2/T_1)$

$$= 22.00 \text{ J K}^{-1} \text{ mol}^{-1} + (37.63 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(263.15/273.15) = 20.59 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_{fus}H^\circ_{T_2} = \Delta_{fus}H^\circ_{T_1} + \Delta_{fus}C_p\ (T_2 - T_1)$$

$$= 6.008 \text{ kJ mol}^{-1} + 37.63 \text{ J K}^{-1} \text{ mol}^{-1}\ (-10.0 \text{ K})(1 \text{ kJ}/1000\text{J}) = 5.632 \text{ kJ mol}^{-1}$$

The Gibbs energy change at -10°C is then:

$$\Delta_{fus}G^{\circ}_{T_2} = \Delta_{fus}H^{\circ}_{T_2} - T_2\,\Delta_{fus}S^{\circ}_{T_2} \qquad \text{for}\quad H_2O\,(s) \rightarrow H_2O\,(l)$$
$$= 5.632\text{ kJ mol}^{-1} - 263.15\text{ K }(20.59\text{ J K}^{-1}\text{ mol}^{-1})(1\text{kJ}/1000\text{ J})$$
$$= 5.632\text{ kJ mol}^{-1} - 5.419\text{ kJ mol}^{-1} = 0.213\text{ kJ mol}^{-1}$$

The direction for the transition in the original problem is the reverse of this process giving:

$$\Delta_{tr}G^{\circ}_{T_2} = -0.213\text{ kJ mol}^{-1} \qquad \text{for}\quad H_2O\,(l) \rightarrow H_2O\,(s)$$

It is not surprising that the result is small, since at 273.15 K, $\Delta_{tr}G^{\circ} = 0$. However at –10°C, the result is negative as it should be, since the freezing of water is spontaneous at $T < 0$°C.

4. Determine the energy necessary to form a peptide bond by determining Δ_rG° for the following reaction at 298.2 K:

2 glycine → glycylglycine + H_2O (l)

Use the data table below.

Substance	$\Delta_fH^{\circ}_m$ (kJ mol^{-1})	S°_m (J K^{-1} mol^{-1})
glycine	-528.5	103.5
glycylglycine	-747.7	190.0
H_2O (l)	-285.830	69.92

Answer: The trick is to remember that the thermodynamic potentials are extensive, so we need to take into account the stoichiometric coefficients.

	2 glycine →	glycylglycine +	H_2O (l)	units
$\Delta_fH^{\circ}_m$	-537.2	-745.3	-285.8	kJ mol^{-1}
S°_m	103.5	190.0	69.9	J K^{-1} mol^{-1}
$\Delta_fH^{\circ}_m$	-528.5	-747.7	-285.83	kJ mol^{-1}
S°_m	103.5	190.0	69.92	J K^{-1} mol^{-1}

Then the reaction changes are given by:

$$\Delta_rH^{\circ} = \sum_{i=1}^{n_s} \nu_i\Delta_fH^{\circ} = [\Sigma\text{products}] - [\Sigma\text{reactants}]$$
$$= [1\,(-285.83\text{ kJ mol}^{-1}) + 1(-747.7\text{ kJ mol}^{-1})] - [2(-528.5\text{ kJ mol}^{-1})]$$
$$= 23.4_7\text{ kJ mol}^{-1}$$

$$\Delta_rS^{\circ} = \sum_{i=1}^{n_s} \nu_i\,S^{\circ} = [\Sigma\text{products}] - [\Sigma\text{reactants}]$$
$$= [1(69.92\text{ J K}^{-1}\text{ mol}^{-1}) + 1(190.0\text{ J K}^{-1}\text{ mol}^{-1})] - [2(103.5\text{ J K}^{-1}\text{ mol}^{-1})]$$
$$= 52.9_2\text{ J K}^{-1}\text{ mol}^{-1}$$

and from the definition of the Gibbs energy change for the reaction:

$$\Delta_r G^\circ = \Delta_r H^\circ - T\,\Delta_r S^\circ = 23.47\text{ kJ} - 298.15\text{ K}(52.92\text{ J K}^{-1})(1\text{ kJ}/1000\text{J})$$
$$= 7.7\text{ kJ mol}^{-1}$$

This final result is per mole of peptide bonds formed: $\Delta_r G^\circ_m = 7.7$ kJ mol^{-1} under standard state conditions. In living cells, the energy to drive this reaction is provided by the hydrolysis of ATP.

5. The enzyme pyruvate decarboxylase catalyzes the following reaction:

pyruvic acid → acetaldehyde + CO_2 (g)

Calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$, and $\Delta_r G^\circ$ for this reaction at 298.2K given the following data. Is this process enthalpy or entropy driven?

substance	$\Delta_f H^\circ_m$ (kJ mol^{-1})	$\Delta_f G^\circ_m$ (kJ mol^{-1})
acetaldehyde	-166.19	-128.86
CO_2 (g)	-393.509	-394.359
pyruvic acid	-584.5	-463.4

Answer: $\Delta_r H^\circ = \sum_{i=1}^{n_s} \nu_i \Delta_f H^\circ = [\Sigma\text{products}] - [\Sigma\text{reactants}]$

$$= [1(-166.19\text{ kJ mol}^{-1}) + 1(-393.509\text{ kJ mol}^{-1})] - [1(-584.5\text{ kJ mol}^{-1})]$$
$$= 24.80\text{ kJ mol}^{-1}$$

$$\Delta_r G^\circ = \sum_{i=1}^{n_s} \nu_i \Delta_f G^\circ = [\Sigma\text{products}] - [\Sigma\text{reactants}]$$
$$= [1(-128.86\text{ kJ mol}^{-1}) + 1(-394.359\text{ kJ mol}^{-1})] - [1(-463.4\text{ kJ mol}^{-1})]$$
$$= -59.82\text{ kJ mol}^{-1}$$

Using the definition of the Gibbs energy allows the calculation of the entropy change for the reaction:

$$\Delta_r G^\circ = \Delta_r H^\circ - T\,\Delta_r S^\circ \qquad \text{or} \quad \Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{[24.80\text{ kJ} - (-59.82\text{ kJ})](1000\text{ J}/1\text{ kJ})}{298.2\text{ K}}$$

giving $\Delta_r S^\circ = 284.$ J K^{-1}. This process is entropy driven. The fact that CO_2 is a gas, which is a high entropy state, and also chemically quite stable helps make this reaction favorable under standard state conditions.

6. Before glucose can be used as an energy source in your body, it must first be phosphorylated:

glucose + HPO_4^{-2} → glucose-6-phosphate $\qquad \Delta_r G^\circ_m = 16.7$ kJ mol^{-1} $\Delta_r H^\circ_m = 35.1$ kJ mol^{-1}

the energy for this process is supplied by the hydrolysis of ATP:

$ATP^{4-} + H_2O \rightarrow ADP^{3-} + HPO_4^{2-} + H^+$ $\qquad \Delta_r G^\circ_m = -31.0$ kJ mol^{-1} $\Delta_r H^\circ_m = -24.3$ kJ mol^{-1}

at pH 7. The overall reaction is then:

$$\text{glucose} + \text{ATP}^{4-} + H_2O \rightarrow \text{glucose-6-phosphate} + \text{ADP}^{3-}$$

Calculate the entropy change for the overall reaction at 298.2 K from the given values of $\Delta_rG°$ and $\Delta_rH°$. Is the phosphorylation of glucose enthalpy or entropy driven?

Answer: According to Hess's law when chemical reactions are added, the enthalpies and Gibbs energies also add. In other words, enthalpy and Gibbs energy are state functions:

$$\text{glucose} + HPO_4^{-2} \rightarrow \text{glucose-6-phosphate} \qquad \Delta_rG° = 16.7 \text{ kJ mol}^{-1} \quad \Delta_rH° = 35.1 \text{ kJ mol}^{-1}$$

$$\text{ATP}^{4-} + H_2O \rightarrow \text{ADP}^{3-} + HPO_4^{2-} + H^+ \qquad \Delta_rG° = -31.0 \text{ kJ mol}^{-1} \quad \Delta_rH° = -24.3 \text{ kJ mol}^{-1}$$

$$\text{glucose} + \text{ATP}^{4-} + H_2O \rightarrow \text{glucose-6-phosphate} + \text{ADP}^{3-}$$

Overall: $\Delta_rG° = 16.7 \text{ kJ mol}^{-1} + (-31.0 \text{ kJ mol}^{-1}) = -14.3 \text{ kJ mol}^{-1}$
$\Delta_rH° = 35.1 \text{ kJ mol}^{-1} + (-24.3 \text{ kJ mol}^{-1}) = 10.8 \text{ kJ mol}^{-1}$

Using the definition of the Gibbs energy allows the calculation of the entropy change for the reaction:

$$\Delta_rG° = \Delta_rH° - T\,\Delta_rS° \qquad \text{or} \quad \Delta_rS° = \frac{\Delta_rH° - \Delta_rG°}{T} = \frac{10.8 \text{ kJ mol}^{-1} - (-14.3 \text{ kJ mol}^{-1})}{298.2 \text{ K}}$$

giving $\Delta_rS° = 84.2 \text{ J K}^{-1} \text{ mol}^{-1}$ at pH 7. This process is entropy driven.

7. Ethanol is used as an additive in gasoline to increase the octane rating and to help decrease air pollution. Calculate $\Delta_rH°$, $\Delta_rS°$, and $\Delta_rG°$ for the combustion of ethanol at 298.2 K using standard data tabulations:

$$CH_3CH_2OH\ (l) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$$

Answer: The relevant data from the data tables in the appendix are given in below.

Substance at 298.15 K	$\Delta_fG°$ (kJ mol^{-1})	$\Delta_fH°$ (J K^{-1} mol^{-1})	S° (J K^{-1} mol^{-1})
CH_3CH_2OH (l)	-174.2	-277.0	161.0
O_2 (g)	0	0	205.029
CO_2 (g)	-394.359	-393.509	213.74
H_2O (l)	-237.178	-285.830	69.92

$$\Delta_rG° = \sum_{i=1}^{n_s} \nu_i \Delta_fH° = [\Sigma\text{products}] - [\Sigma\text{reactants}]$$
$$= [2(-394.359 \text{ kJ mol}^{-1}) + 3(-237.178 \text{ kJ mol}^{-1})] - [1(-174.2 \text{ kJ mol}^{-1}) + 3(0)]$$
$$= -1326.0_5 \text{ kJ mol}^{-1}$$

$$\Delta_rS° = \sum_{i=1}^{n_s} \nu_i\, S° = [\Sigma\text{products}] - [\Sigma\text{reactants}]$$

$$= [2(213.74\ \mathrm{J\ K^{-1}\ mol^{-1}}) + 3(69.92\ \mathrm{J\ K^{-1}\ mol^{-1}})] - [1(161.0\ \mathrm{J\ K^{-1}\ mol^{-1}}) + 3(205.029)]$$
$$= -138.8_5\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\Delta_r H° = \sum_{i=1}^{n_s} \nu_i \Delta_f H° = [\Sigma\text{products}] - [\Sigma\text{reactants}]$$
$$= [2(-393.509\ \mathrm{kJ\ mol^{-1}}) + 3(-285.830\ \mathrm{kJ\ mol^{-1}})] - [1(-277.0\ \mathrm{kJ\ mol^{-1}}) + 3(0)]$$
$$= -1367.5_1\ \mathrm{kJ\ mol^{-1}}$$

As a check, we should also find $\Delta_r G°$ using:

$$\Delta_r G° = \Delta_r H° - T\,\Delta_r S°$$
$$= -1367.5_1\ \mathrm{kJ\ mol^{-1}} - 298.15\ \mathrm{K}(-138.8_5\ \mathrm{J\ K^{-1}\ mol^{-1}})(1\ \mathrm{kJ}/1000\ \mathrm{J})$$
$$= -1326.1_1\ \mathrm{kJ\ mol^{-1}}$$

which certainly agrees to within the experimental error.

8. Why can we choose the Gibbs energy of formation of an element, in its most stable state at 1 bar pressure, as equal to zero?

Answer: In practical circumstances, we always determine the difference in internal energy, enthalpy, entropy, Helmholtz energy, and Gibbs energy for a process: ΔU, ΔH, ΔS, ΔA, and ΔG. Therefore, the reference point is arbitrary. Figure 8.4.1 applies equally to Gibbs energy differences.

9. The enthalpy change for a reaction can be endothermic or exothermic. The entropy change for a chemical reaction can be positive or negative. Consider the temperature dependence of the spontaneity of a chemical reaction at constant pressure. Assume that the sign of the reaction enthalpy and entropy don't change with temperature. Under what cases, for the signs of the enthalpy and the entropy, is a reaction always spontaneous? Under what cases is a reaction never spontaneous?

Answer: Since $\Delta_r G = \Delta_r H - T\,\Delta_r S$ for a constant temperature process, the relative weighting of the enthalpy and entropy terms depends on temperature. Assuming that the sign of the reaction enthalpy and entropy don't change with temperature, if the enthalpy change is exothermic and the entropy change is positive, the reaction is spontaneous at all temperatures. If the enthalpy change is endothermic and the entropy change is negative, the reaction is non-spontaneous at all temperatures. If the enthalpy is exothermic and the entropy change is negative, or conversely if the enthalpy change is endothermic and the entropy change is positive, the sign of ΔG changes with temperature.

$\Delta_r H$	$\Delta_r S$	$\Delta_r G$	
–	+	–	always spontaneous
–	–		spontaneous at low T
+	+		spontaneous at high T
+	–	+	non-spontaneous

10. The water gas shift reaction is an important process in the gasification of coal or biomass to produce transportation fuels:

$$CO\,(g) + H_2O\,(g) \rightleftarrows CO_2\,(g) + H_2\,(g)$$

What is the relationship between the Gibbs and Helmholtz reaction energy changes at constant pressure? Why?

Answer: Since the change in the number of moles of gases is zero, $\Delta_r n_g = 0$, the Helmholtz and Gibbs energy changes for the reaction are the same: $\Delta_r G = \Delta_r A$. The reason is that no PV work is done since the volume is constant, for all practical purposes.

11. The internal energy of combustion of iso-propyl alcohol is -2003.2 kJ mol^{-1} at 298.2 K and 1.000 bar. The absolute entropy of iso-propyl alcohol is 180.58 J K^{-1} mol^{-1} at 298.2 K and 1.000 bar. Calculate the enthalpy, Helmholtz energy, and Gibbs energy of combustion of iso-propyl alcohol. Treat all gases as ideal.

Answer: The plan is to use the "thermodynamic cube," Figure 15.4.1, and the balanced combustion reaction. In addition, from Eqs. 8.3.1° and 8.3.2°, $\Delta_r(PV) = \Delta_r n_{gas}\,RT$.

The balanced reaction is $C_3H_8O\,(s) + {}^9/_2\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$, giving $\Delta_r n_{gas} = 3 - {}^9/_2 = -{}^3/_2$. The change in entropy is given from standard tabulations as:

	$C_3H_8O\,(s)$ +	${}^9/_2\,O_2\,(g) \rightarrow$	$3\,CO_2\,(g)$ +	$4\,H_2O\,(l)$	units:
S°	181.1	205.029	213.74	69.92	J K^{-1} mol^{-1}

giving: $\Delta_r S = \Delta_c S = [\Sigma\text{products}] - [\Sigma\text{reactants}]$

$$\Delta_c S = [3(213.74) + 4(69.92)] - [1(181.1) + {}^9/_2(205.029)]\ \text{J K}^{-1}\ \text{mol}^{-1} = -182.83\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The entropy change is negative because the number of moles of gases decreases for the reaction. The definitions of the state functions and Figure 15.4.1 gives:

$$\begin{aligned}\Delta_c H &= \Delta_c U + \Delta_r n_{gas}\,RT \\ &= -2003.2\ \text{kJ mol}^{-1} + (-{}^3/_2)(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})(1\ \text{kJ}/1000\ \text{J}) \\ &= -2003.2\ \text{kJ mol}^{-1} - 3.718\ \text{kJ mol}^{-1} = -2006.9\ \text{kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_c A &= \Delta_c U - T\Delta_c S \\ &= -2003.2\ \text{kJ mol}^{-1} - 298.15\ \text{K}(-182.83\ \text{J K}^{-1}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J}) = -1948.69\ \text{kJ mol}^{-1}\end{aligned}$$

$$\Delta_c G = \Delta_c H - T\Delta_c S$$
$$= -2006.9 \text{ kJ mol}^{-1} - 298.15 \text{ K}(-182.83 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -1952.39 \text{ kJ mol}^{-1}$$

As a check, we can use:

$$\Delta_c G = \Delta_c A + \Delta_r n_{gas} RT = -1948.69 \text{ kJ mol}^{-1} - 3.718 \text{ kJ mol}^{-1} = -1952.41 \text{ kJ mol}^{-1}$$

The magnitude of the total maximum work available is less than $|\Delta_c U|$ because of the unfavorable change in entropy. However, more non-PV work is available than total work, $|\Delta_c G| > |\Delta_c A|$, because the surroundings do work on the system, since the number of moles of gas and the corresponding volume of the system decreases.

12. Calculate the change in Gibbs energy when one mole of an ideal gas expands isothermally from an initial volume of 1.00 L to a final volume of 10.0 L at 298.15 K.

Answer: For an isothermal expansion of an ideal gas, Eq. 15.4.6°:

$$\Delta G = -\, nRT \ln(V_2/V_1) = -\,(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(10.0/1.00)$$
$$= -5.708\text{x}10^3 \text{J} = -5.71 \text{ kJ}$$

13. Calculate the changes in Gibbs energy and Helmholtz energy when one mole of an ideal gas expands isothermally from an initial pressure of 2.00 bar to a final pressure of 1.00 bar at 298.15 K.

Answer: For an isothermal expansion, using Eq. 15.4.4°:

$$\Delta G = nRT \ln(P_2/P_1) = (1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(1.00 \text{ bar}/2.00 \text{ bar})$$
$$= -1.718\text{x}10^3 \text{J} = -1.72 \text{ kJ}$$

For the change in Helmholtz energy, we can use Eq. 15.4.2°, $\Delta A = -\, nRT \ln(V_2/V_1)$. From the ideal gas law:

$$V_1 = nRT/P_1 = 1.00 \text{ mol}(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/2.00 \text{ bar} = 12.39 \text{ L}$$
$$V_2 = nRT/P_2 = 1.00 \text{ mol}(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})/1.00 \text{ bar} = 24.79 \text{ L}$$

$$\Delta A = -\, nRT \ln(V_2/V_1) = -\,(1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(24.79/12.39)$$
$$= -1.719\text{x}10^3 \text{J} = -1.72 \text{ kJ}$$

Alternatively, for an isothermal process in an ideal gas, substituting $V_2/V_1 = P_1/P_2$ into Eq. 15.4.2° gives $\Delta A = -\, nRT \ln(V_2/V_1) = -\, nRT \ln(P_1/P_2) = nRT \ln(P_2/P_1) = \Delta G$. So $\Delta A = \Delta G$ for an isothermal process in an ideal gas, as shown in Chap. 15.4, but this time for the expressions written in terms of pressures.

14. General Chemistry texts often use a standard state pressure of 1 atm instead of 1 bar. Does the change in standard state make a significant difference in the tabulated values? Calculate the standard state Gibbs energy of formation for CO_2 at P° = 1 atm, given that the 1 bar standard state is $\Delta_f G°(CO_2) = -394.36 \text{ kJ mol}^{-1}$ at 298.15 K.

Answer: The 1 bar standard state is just slightly less than the 1 atm standard state, 1 atm = 1.01325 bar. To a good approximation, we only need consider the gaseous reactants and products in a chemical reaction. The change in Gibbs energy for each reactant and product gas is given by Eq. 15.4.4°, assuming the gases are ideal. The formation reaction:

$$\text{C (graph)} + \text{O}_2\ \text{(gas, P°)} \rightarrow \text{CO}_2\ \text{(g, P°)}$$

however, has an equal number of moles of reactant and product gases, so the change with pressure is zero, assuming ideal gas behavior. The 1 bar and 1 atm standard state reaction Gibbs energies are identical, for moderate changes in pressure.

15. General Chemistry texts often use a standard state pressure of 1 atm instead of 1 bar. Does the change in standard state make a significant difference in the tabulated values for Gibbs energies of formation? Calculate the standard state Gibbs energy of formation for SO_3 at P° = 1 atm assuming ideal gas behavior, given that the 1 bar standard state is $\Delta_f G°(SO_3, P° = 1\text{ bar}) = -371.06\text{ kJ mol}^{-1}$ at 298.15 K.

Answer: The 1 bar standard state is just slightly less than the 1 atm standard state, 1 atm = 1.01325 bar. To a good approximation, we only need consider the gaseous reactants and products in a chemical reaction. The change in Gibbs energy for each reactant and product gas is given by Eq. 15.4.4°, assuming the gases are ideal. For reactant or product i:

$$G_i(P_i) - G_i(P°) = n_i\, RT \ln P_i/P°$$

where P_i is the new pressure for reactant or product i and P° is the old standard state value. The n_i are given by the stoichiometric coefficients for a chemical reaction, $n_i = \nu_i$. The total change in Gibbs energy with the new pressures is then given by the difference of the products minus the reactants:

$$\Delta_r G = \Delta_r G° + \Sigma\, \nu_i\, RT \ln P_i/P° \qquad (\nu_i \text{ for gases only})$$

If the P_i are identical for all the reactants and products, then the last equation reduces to:

$$\Delta_r G = \Delta_r G° + \Delta_r n_g\, RT \ln P_i/P° \qquad (P_i \text{ equal for all species})$$

where $\Delta_r n_g = \Sigma\, \nu_i$ with the sum over all the gas phase species. The formation reaction:

$${}^1/_8\, \text{S}_8\ \text{(rhombic)} + {}^3/_2\, \text{O}_2\ \text{(gas, P°)} \rightarrow \text{SO}_3\ \text{(g, P°)}$$

gives $\Delta_r n_g = -½$. The change in reaction Gibbs energy with pressure is then:

$$\Delta_r n_g\, RT \ln P_i/P° = -½\,(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K}) \ln (1.01325\text{ bar}/1.0000\text{ bar}) = -16.32\text{ J mol}^{-1}$$

$$\Delta_f G°(SO_3, P° = 1\text{ atm}) = -371.06\text{ kJ mol}^{-1} - 0.01632\text{ kJ mol}^{-1} = -371.08\text{ kJ mol}^{-1}$$

Even though this difference seems to be insignificant, the change in value translates into a ~1% difference in an equilibrium constant involving a reaction of one mole of SO_3 at 298 K (using $\Delta_r G° = -RT \ln K_{eq}$).

16. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the Gibbs energy of formation for CO_2 at 50.0 bar and 298.15 K, relative to the constituent elements in their standard states:

$$C(graph) + O_2\ (g, 1\ bar) \rightarrow CO_2\ (g, P = 50.0\ bar)$$

Assume ideal gas behavior and $\Delta_f G°(CO_2) = -394.36\ kJ\ mol^{-1}$ at 298.15 K.

Answer: The change in Gibbs energy is given by Eq. 15.4.4°, assuming the CO_2 is ideal.

$$\begin{aligned}\Delta G_i &= n_i RT \ln {}^{P_2}/_{P_1} = 8.3145\ J\ K^{-1} mol^{-1}\ (1\ kJ/1000\ J)\ 298.15\ K \ln {}^{50.0\ bar}/_{1\ bar} \\ &= 9.70\ kJ\ mol^{-1}\end{aligned}$$

Which gives the enthalpy of formation as:

$$\begin{aligned}\Delta_f G &= \Delta_f G° + 9.70\ kJ\ mol^{-1} \\ &= -394.36\ kJ\ mol^{-1} + 9.70\ kJ\ mol^{-1} = -384.66\ kJ\ mol^{-1}\end{aligned}$$

17. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the reaction Gibbs energy at 50.0 bar and 298.2 K for:

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g, P = 50.0\ bar)$$

One crystalline form of $CaCO_3$ is the mineral calcite. Neglect the effect of the pressure on the solids and assume ideal gas behavior.

Answer: Under standard state conditions:

	$CaCO_3$ (s)	→	CaO (s)	+	CO_2 (g, P° = 1 bar)
$\Delta_f G°$	-1129.1		-603.3		$-394.359\ kJ\ mol^{-1}$

$$\begin{aligned}\Delta_r G° &= \sum_{i=1}^{n_s} \nu_i \Delta_f G° = [\Sigma products] - [\Sigma reactants] \\ &= [(-394.359) + (-603.3)] - [-1129.1]\ kJ\ mol^{-1} = 131.4_4\ kJ\ mol^{-1}\end{aligned}$$

The Gibbs energy of each <u>gaseous</u> reactant and product is then adjusted for the new pressure:

$$\Delta_r G = \Delta_r G° + \Sigma\ \nu_i\ RT \ln {}^{P_i}/_{P°} \qquad (\nu_i \text{ for gases only})$$

as derived in the previous problems. The ν_i are the stoichiometric coefficients for each gaseous reactant and product, with ν_i negative for reactants. (See Chapter 20 for more information on non-standard state reaction Gibbs energies). For this reaction $\nu_{CO_2} = 1$ is the only gas:

$\Delta_r G = \Delta_r G° + RT \ln {}^{P_2}/_{P°}$

$\Delta_r G = \Delta_r G° + RT \ln {}^{50.0\text{ bar}}/_{1\text{ bar}}$

$= 131.44\text{ kJ mol}^{-1} + 8.3145\text{ J K}^{-1}\text{ mol}^{-1}(1\text{ kJ}/1000\text{ J})(298.15\text{ K}) \ln 50.0$

$= 131.44\text{ kJ mol}^{-1} + 9.70\text{ kJ mol}^{-1} = 141.4\text{ kJ mol}^{-1}$

18. Derive Eq. 15.4.8, $\Delta G = V_o (P - P_o) - ½ V_o \kappa_T (P - P_o)^2$, from $dG = V\,dP$ for an isothermal process, from an initial pressure P_o and a final pressure P.

Answer: The approximation $\Delta G = V_o (P - P_o)$ is at the "good" level, which assumes the volume is essentially unchanged for a small change in pressure. At the "better" level for moderate changes in pressure, we use Eq. 7.6.28, $V = V_o - V_o \kappa_T (P - P_o)$, with P_o the initial pressure and P the final pressure. The change in Gibbs energy with pressure for an isothermal process is given by the thermodynamic force, $(\partial G/\partial P)_T = V$ or $dG = V\,dP$. Integration using Eq. 7.6.28 gives:

$$\int_{G_o}^{G} dG = \int_{P_o}^{P} V_o - V_o \kappa_T (P - P_o)\, dP = V_o \int_{P_o}^{P} dP - V_o \kappa_T \int_{P_o}^{P} (P - P_o)\, dP$$

$$\Delta G = V_o (P - P_o) - ½ V_o \kappa_T (P - P_o)^2 \Big|_{P_o}^{P}$$

Applying the integral limits for the second term gives:

$$\Delta G = V_o (P - P_o) - ½ V_o \kappa_T (P - P_o)^2 + ½ V_o \kappa_T (P_o - P_o)^2$$
$$\Delta G = V_o (P - P_o) - ½ V_o \kappa_T (P - P_o)^2$$

19. Calculate the change in Gibbs energy for one mole of liquid benzene at 298.2 K for a change in pressure from 1.00 bar to 600.0 bar. The isothermal compressibility of benzene is $90.9\text{x}10^{-6}$ bar^{-1} and the density is 0.8765 g/cm^3. Compare the results using Eqs. 15.4.7 and 15.4.8

Answer: The molar volume is:

$$V_o = 1\text{ mol}(78.11\text{ g mol}^{-1})(1\text{ m}^3/1\text{x}10^6\text{ cm}^3)/0.8765\text{ g cm}^{-3} = 8.912\text{x}10^{-5}\text{ m}^3$$

Using the more approximate formula gives:

$$\Delta G = V_o (P - P_o) = 8.912\text{x}10^{-5}\text{ m}^3(599.0\text{ bar})(1\text{x}10^5\text{ Pa/1 bar}) = 5338.\text{ J}$$

Converting the isothermal compressibility to Pa^{-1} is most convenient for this problem:

$$\kappa_T = 90.9\text{x}10^{-6}\text{ bar}^{-1}(1\text{ bar}/1\text{x}10^5\text{Pa}) = 90.9\text{x}10^{-11}\text{ Pa}^{-1}$$

Using the first-order correction for the volume change gives:

$$\Delta G = V_o (P - P_o) - ½ V_o \kappa_T (P - P_o)^2$$
$$= 5338.\text{ J} - ½ (8.912\text{x}10^{-5}\text{ m}^3)(90.9\text{x}10^{-11}\text{ Pa}^{-1})(599.0\text{x}10^5\text{ Pa})^2$$
$$= 5338.\text{ J} - 145.0\text{ J} = 5193.\text{ J} = 5.193\text{ kJ}$$

The volume change correction term is chemically significant at this high pressure. Ultra-high pressure high performance liquids chromatographs, UHPLC, routinely operate at 600 bar using standard organic solvents for the mobile phase. Microwave assisted organic synthesis is routinely operated at 120 bar. The pressure at the bottom of the Mariana Trench is ~1,100 bar, so high pressures are accessible both in and outside the laboratory. However, for pressures near sea level ambient pressure, the more approximate formula, $\Delta G = V_o (P - P_o)$, is adequate for liquids and solids.

20. Calculate the Gibbs energy difference for one mole of water at the bottom of the Mariana Trench compared to 1 bar pressure, given $\kappa_T = 4.587 \times 10^{-10}\ \text{Pa}^{-1}$ at 20°C. The maximum depth of the trench is 10911 m (35798 ft) and the pressure is 1,086. bar (15,750 psi). Use the density of pure water, 0.9982 g mL^{-1} at 1 bar, for this problem, instead of the density of sea water.

Answer: The plan is to compare Eqs. Eq. 15.4.7 and 15.4.8. The molar volume of water at 1 bar is:

$$V_o = 1\ \text{mol}(18.015\ \text{g mol}^{-1})(1\ \text{m}^3/1\text{x}10^6\ \text{cm}^3)/\ 0.9982\ \text{g cm}^{-3} = 1.804_8\text{x}10^{-5}\ \text{m}^3$$

Using the more approximate formula gives:

$$\Delta G = V_o (P - P_o) = 1.804_8\text{x}10^{-5}\ \text{m}^3(1085.0\ \text{bar})(1\text{x}10^5\ \text{Pa}/1\ \text{bar}) = 1958.\ \text{J}$$

Using the first-order correction for the volume change gives:

$$\begin{aligned}\Delta G &= V_o (P - P_o) - \tfrac{1}{2} V_o\, \kappa_T (P - P_o)^2 \\ &= 1958.\ \text{J} - \tfrac{1}{2} (1.804_8\text{x}10^{-5}\ \text{m}^3)(4.587\text{x}10^{-10}\ \text{Pa}^{-1})(1085.0\text{x}10^5\ \text{Pa})^2 \\ &= 1958.\ \text{J} - 97.5\ \text{J} = 1861.\ \text{J} = 1.861\ \text{kJ}\end{aligned}$$

Note the final comments for the previous problem. The relatively small change in Gibbs energy with pressure is the reason that we don't normally need to correct for changes in pressure in thermochemical problems for liquids and solids.

21. Starting from $\Delta A = -\,nRT \ln V_2/V_1$ and the definition of G, in the form $G \equiv A + PV$, show that $\Delta G = nRT \ln P_2/P_1$, for an ideal gas in an isothermal process.

Answer: Using $G = A + PV$ and $PV = nRT$ for an ideal gas gives:

$$\Delta G = \Delta A + \Delta(PV) = \Delta A + nR\Delta T.$$

For an isothermal process $\Delta T = 0$ and then $\Delta G = \Delta A = -\,nRT \ln V_2/V_1$, using Eq. 15.4.2°. For an ideal gas $V_2/V_1 = P_1/P_2$, so then as we showed in Eqs. 15.4.5°-15.4.6°:

$$\Delta G = \Delta A = -\,nRT \ln V_2/V_1 = -\,nRT \ln P_1/P_2 = nRT \ln P_2/P_1$$

22. Reverse osmosis is the most cost effective method for seawater desalinization. However, reverse osmosis is energy intensive. In reverse osmosis, seawater is pressurized to 60-70 bar to

force water to flow through a semi-permeable membrane. The work in reverse osmosis can be estimated using $w = -P\Delta V$, where P is the constant high pressure of the process and ΔV is the volume of water pushed through the membrane. Calculate the change in Helmholtz energy for purifying 1.00 m^3 of water using reverse osmosis with an applied pressure of 65.0 bar. Give your results in joules and kWh (1 kWh = $3.6\text{x}10^6$ J). Why is the change in Helmholtz energy salient for water desalinization?

Answer: The plan is to note that the change in Helmholtz energy for a process is the total work for the process. Integrating Eq. 15.4.1, $dA = -P\,dV$, at constant pressure gives $\Delta A = -P\,\Delta V$, which is the work required for the process:

$$\Delta A = -P\,\Delta V = -65.0\text{ bar}(1\text{x}10^5\text{ Pa/1 bar})(1.00\text{ m}^3) = -65.0\text{x}10^5\text{ J} = -6.5\text{x}10^3\text{ kJ}$$

The conversion from kWh to joules is 1 kWh = $3.6\text{x}10^6$ J, Problem 2.12. The pressure is generated by electrical pumps requiring:

$$\Delta A = -65.0\text{x}10^5\text{ J}(1\text{ kWh}/3.6\text{x}10^6\text{ J}) = 1.81\text{ kWh m}^{-3}$$

If power is \$ 0.10 $(\text{kWh})^{-1}$, the cost is \$ 0.18 m^{-3}, assuming 100% efficiency. The overall efficiency is more likely to be near 50%, giving a minimum cost of \$ 0.36 m^{-3} for processing alone. Daily indoor per capita water use in a US home is 69.3 gallons or 0.262 $\text{m}^3\text{ day}^{-1}\text{ person}^{-1}$. World total fresh water consumption is over 2,000 billion $\text{m}^3\text{ yr}^{-1}$. The Helmholtz energy change is the total work for the process, which is PV work for reverse osmosis. However, the result is a change in composition for dissolved salts, which is a chemical energy change, which is reflected by a change in Gibbs energy. Reverse osmosis converts mechanical work to chemical work.

23. How big of an effect does an electric field have on the electrochemical potential of an ion? Consider a simple electrochemical cell, $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$. Assume the electric potential is 0.500 V at the cathode. Calculate the electrochemical potential for one mole of Cu^{2+} ions, at standard state concentration, in the cathode (right-hand) compartment. In the absence of a field, $\Delta_f G^\circ_m$ for Cu^{2+} from standard tables is 65.49 kJ mol^{-1}.

Answer: The electrochemical potential is given by Eq. 15.3.9: $\bar{\mu}_i \equiv \mu_i + z_i F \phi_i$. The charge on a mole of Cu^{2+} ions is $z_i = 2$ mol.

$$\bar{\mu}_{Cu^{2+}} = \mu_{Cu^{2+}} + 2\text{ mol F }(0.5\text{ V})$$
$$= 65.49\text{ kJ mol}^{-1} + 2\text{ mol }(96485\text{ C mol}^{-1})(0.500\text{ V})(1\text{ kJ}/1000\text{ J})$$

Remembering that 1 J = 1 C V:

$$= 65.49\text{ kJ mol}^{-1} + 96.49\text{ kJ mol}^{-1} = 161.98\text{ kJ mol}^{-1}$$

The electric field component makes a significant contribution to the Gibbs energy of an ion in solution with an electric field. Another way of saying this is that 0.50 V is a significant voltage.

24. Two solutions containing K^+ ions are separated by a K^+ ion-selective membrane. Electrodes are placed in both solutions and the flow of K^+ ions is monitored as a function of applied potential, $\Delta\phi = \phi_{in} - \phi_{out}$. The K^+ ions cease migration across the membrane for an applied potential of -70.0 mV. Calculate the difference in chemical potential of the K^+ ions in the two solutions.

Answer: The plan is to note that when the ion flow is zero, the system is at equilibrium and $\Delta G = \bar{\mu}_{in} - \bar{\mu}_{out} = 0$.

Using Eq. 15.3.15 at equilibrium gives:

$$\Delta G = \bar{\mu}_{in} - \bar{\mu}_{out} = (\mu_{in} + z_+ F \phi_{in}) - (\mu_{out} + z_+ F \phi_{out}) = 0$$

Solving for the difference in chemical potential gives:

$$\mu_{in} - \mu_{out} = - z_+ F (\phi_{in} - \phi_{out}) = - z_+ F \Delta\phi$$

Hopefully, you remember this relationship from the treatment of electrochemistry in your General Chemistry course, where $\Delta\phi = E_{cell}$. For this specific problem, $z_+ = 1$ at -70.0 mV:

$$\mu_{in} - \mu_{out} = - 1 (96485 \text{ C mol}^{-1})(-70.0\text{x}10^{-3} \text{ V})(1 \text{ kJ}/1000 \text{ J}) = 6.75 \text{ kJ mol}^{-1}$$

Substantial differences in chemical potential are generated by simple concentration differences. This potential difference is a typical resting state potential for a nerve cell.

25. Coastal communities may be able to exploit the Na^+ gradient between seawater and fresh river water to generate electricity. Calculate the electric potential available from a seawater-fresh water cell with a Na^+ ion selectively-permeable membrane. Assume the difference in chemical potential, in the absence of electric fields, between seawater and fresh water is 10.5 kJ mol^{-1} (roughly a factor of 100 difference in concentration with an activity coefficient for 0.5 m NaCl of 0.680).

Answer: The plan is to note that the maximum potential difference is for the system at equilibrium, for which $\Delta G = \bar{\mu}_{in} - \bar{\mu}_{out} = 0$, and $z_+ = 1$ for NaCl.

From the previous problem we determined that at equilibrium:

$$\mu_{in} - \mu_{out} = - z_+ F (\phi_{in} - \phi_{out}) = - z_+ F \Delta\phi$$

$$10.5\text{x}10^3 \text{ J mol}^{-1} = - 1(96485 \text{ C mol}^{-1}) \Delta\phi \qquad \text{giving } \Delta\phi = 0.109 \text{ V}$$

Even though the voltage is small, the volume of the ocean is vast, which could potentially generate huge electrical currents. The limiting factors are the supply of fresh water and the large-scale availability of robust ion-selective membranes. The estimates for global production of energy from the seawater-fresh water interface are in the terawatts range.

26. The standard state Gibbs energy of formation of liquid water at 298.15 K is -237.13 kJ mol^{-1}. Normally, we ignore any changes of $\Delta_f G°$ with pressure for liquids and solids if the specific

reaction is run near 1 bar of pressure. How big of an error does this make? Calculate the change in Gibbs energy for one mole of liquid water for a pressure change from 1.00 bar to 50.0 bar.

Answer: Using Eq. 15.4.7 will be sufficiently accurate for this problem. For one mole, the initial volume is the pure molar volume of water:

$$V_o = \mathfrak{M}_{H2O}/d_{H2O} = 18.02 \text{ g mol}^{-1}/\ 0.99705 \text{ g mL} = 18.07 \text{ mL}$$
$$= 18.07 \text{ mL } (1 \text{ m}^3/1\text{x}10^6 \text{ mL}) = 1.807\text{x}10^{-5} \text{ m}^3$$

From Eq. 15.4.7:

$$\Delta G = V_o\Delta P = 1.807\text{x}10^{-5} \text{ m}^3(50.0 \text{ bar} - 1.0 \text{ bar})(1\text{x}10^5\text{Pa}/1\text{bar}) = 88.54 \text{ J} = 0.0885 \text{ kJ}$$

Even such a large change in pressure gives a very small change in the Gibbs energy of the mole of water.

<u>27</u>. Calculate the change in Helmholtz energy and Gibbs energy for the vaporization of 1.00 mol of liquid water at 372.76 K and 1.00 bar. The enthalpy of vaporization at 372.76 K is 40.7 kJ mol^{-1}. Treat water vapor as an ideal gas. What does the difference between the Helmholtz and Gibbs energies tell you about the process? (The standard boiling point of water is 99.61°C or 372.76 K.)

Answer: The phase transition occurs at the equilibrium phase transition temperature, so $\Delta_{tr}G = 0$. $\Delta_{tr}A$ is given by the work necessary to push back the atmosphere for the formation of one mole of water vapor, Eq. 15.4.18°:

$$\Delta_{tr}A = -\, n_{gas}\, RT_{tr} = -\, 1.00 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K})(1 \text{ kJ}/1000 \text{ J}) = -3.10 \text{ kJ}$$

The Gibbs energy change is the net work at constant temperature and pressure; Gibbs energy does not include PV work. The Helmholtz energy change is the total work available from the process at constant temperature. The vaporization process is at equilibrium, so no net work is available. However, the system expands as one mole of liquid is vaporized and the Helmholtz energy reflects the work done by the expansion. The sign of $\Delta_{tr}A$ is negative because the system does work against the surroundings, decreasing the energy of the system.

<u>28</u>. Calculate the change in Gibbs energy for the vaporization of 2.00 mol of liquid water at 372.76 K and 1.000 bar to give water vapor at 0.500 bar and the same temperature. Assume the vapor is ideal. (The standard boiling point of water is 99.61°C or 372.76 K.)

Answer: We divide the process into two steps: step one, the vaporization of 2.00 mol of water at the standard boiling point and 1.000 bar pressure, and step two, the vapor pressure is lowered to 0.500 bar at constant temperature. For step one, under standard conditions, the transition is at equilibrium and $\Delta_{tr}G = 0$. For step two, the vapor is expanded isothermally to give:

$$\Delta G = nRT \ln {}^{P_2}/_{P_1} = 2.00 \text{ mol}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(372.76 \text{ K}) \ln {}^{0.500}/_{1.000}$$
$$= -4297. \text{ J} = -4.30 \text{ kJ}$$

29. Show that for small changes in temperature the last two terms cancel in Eq. 15.4.15:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o} \approx -S_o (T - T_o)$$

To prove this relationship, expand the logarithmic term in a Taylor series and keep just the first non-zero term. (Note: the Taylor series expansion for $\ln(x_2/x_1) \approx x_2/x_1 - 1$, for $x_2/x_1 \approx 1$.)

Answer: First flip the numerator and denominator in the logarithmic term:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) + C_p T \ln \frac{T_o}{T}$$

The Taylor series expansion for $\ln(x_2/x_1) \approx x_2/x_1 - 1$, for $x_2/x_1 \approx 1$. Substitution gives:

$$\Delta G \approx -S_o (T - T_o) + C_p (T - T_o) + C_p T (T_o/T - 1)$$
$$\approx -S_o (T - T_o) + C_p (T - T_o) + C_p (T_o - T)$$
$$\approx -S_o (T - T_o)$$

So simply integrating $dG = -S\, dT$, with $S \approx S_o$ a constant over the temperature range isn't too bad for very narrow temperature ranges. However, in the next Chapter we will find a much better approximation that is easy to use and takes into account the change in entropy with temperature (Eq. 16.3.14, the Gibbs-Helmholtz equation).

30. Prove Eq. 15.4.15, that is $\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o}$.

Answer: We need to integrate $dG = -S\, dT$. The change in entropy for a constant pressure process, starting with initial entropy of S_o is:

$$S = S_o + C_p \ln \frac{T}{T_o}$$

Substitution into $dG = -S\, dT$ gives:

$$dG = -S\, dT = -(S_o + C_p \ln \frac{T}{T_o})\, dT$$

Integration assuming a constant heat capacity gives:

$$\Delta G = -S_o \int_{T_o}^{T} dT - C_p \int_{T_o}^{T} \ln T\, dT + C_p \ln T_o \int_{T_o}^{T} dT$$

Integrating using $\int \ln x\, dx = x \ln x - x$:

$$\Delta G = -S_o (T - T_o) - C_p \big(T \ln T - T \big|_{T_o}^{T} + C_p \ln T_o (T - T_o)$$

Applying the integral limits and multiplying out terms:

$$\Delta G = -S_o (T - T_o) - C_p (T \ln T - T) + C_p (T_o \ln T_o - T_o) + C_p T \ln T_o - C_p T_o \ln T_o$$

Cancelling terms:

$$\Delta G = -S_o(T - T_o) + C_p(T - T_o) - C_p(T \ln T - T \ln T_o)$$

Combining the ln terms:

$$\Delta G = -S_o(T - T_o) + C_p(T - T_o) - C_p T \ln \frac{T}{T_o}$$

31. Calculate the standard state Gibbs energy of formation for H_2S (g) at 500.0 K. Remember that the Gibbs energy of formation is for a chemical reaction and not just a pure substance. The relevant data are given in the table below.

Substance at 298.15 K	$\Delta_f G°$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})	C_p° (J K^{-1} mol^{-1})
H_2S (g)	-33.56	205.79	34.23
H_2 (g)	0	130.684	28.824
S (s, rhombic)	0	31.80	22.64

Answer: The plan is to note that Eq. 15.4.15 is for a pure substance at standard state pressure with $\Delta G = G_T - G_o$:

$$G_T^\circ - G_o^\circ = -S_o^\circ(T - T_o) + C_p^\circ(T - T_o) - C_p^\circ T \ln \frac{T}{T_o}$$

For a chemical reaction from *General Pattern ℘8 Thermodynamic Relationships for Reactions* the last equation becomes:

$$\Delta_r G_T^\circ - \Delta_r G_o^\circ = -\Delta_r S_o^\circ(T - T_o) + \Delta_r C_p^\circ(T - T_o) - \Delta_r C_p^\circ T \ln \frac{T}{T_o}$$

where $\Delta_r S_o^\circ$ is the standard state reaction entropy at the reference temperature, T_o.

For the given reaction H_2 (g) + S (s, rhombic) → H_2S (g):

$$\Delta_r S_o^\circ = [1(205.79)] - [1(130.684) + 1(31.80)]\text{ J K}^{-1}\text{ mol}^{-1} = 43.30_6\text{ J K}^{-1}\text{ mol}^{-1}$$
$$\Delta_r C_p^\circ = [1(34.23)] - [1(28.824) + 1(22.64)]\text{ J K}^{-1}\text{ mol}^{-1} = -17.23\text{ J K}^{-1}\text{ mol}^{-1}$$

Neglecting the terms for the temperature dependence of the reaction entropy gives:

$$\Delta_r G_T^\circ = \Delta_r G_o^\circ - \Delta_r S_o^\circ(T - T_o)$$
$$\Delta_r G_{500\text{ K}}^\circ = -33.56\text{ kJ mol}^{-1} - 43.30_6\text{ J K}^{-1}\text{ mol}^{-1}(500.0\text{ K} - 298.2\text{ K})(1\text{ kJ}/1000\text{ J})$$
$$= -33.56\text{ kJ mol}^{-1} - 8.739\text{ kJ mol}^{-1} = -42.29_9\text{ kJ mol}^{-1}$$

The more exact expression gives:

$$\Delta_r G_T^\circ = \Delta_r G_o^\circ - \Delta_r S_o^\circ(T - T_o) + \Delta_r C_p^\circ(T - T_o) - \Delta_r C_p^\circ T \ln \frac{T}{T_o}$$
$$= -42.30\text{ kJ mol}^{-1} + (-17.23\text{ J K}^{-1}\text{ mol}^{-1})(500.0\text{ K} - 298.2\text{ K})(1\text{ kJ}/1000\text{ J}) -$$
$$(-17.23\text{ J K}^{-1}\text{ mol}^{-1})(500.0\text{ K})(1\text{ kJ}/1000\text{ J}) \ln {}^{500.0\text{ K}}/_{298.2\text{ K}}$$
$$= -42.29_9\text{ kJ mol}^{-1} - 3.477\text{ kJ mol}^{-1} + 4.453\text{ kJ mol}^{-1} = -41.32\text{ kJ mol}^{-1}$$

H_2S is an important component in exhaust from sewage treatment plants, in volcanic gases, and is also produced in large quantities by bacteria in the oceans. H_2S is also a byproduct of coal combustion, although most sulfur in coal is oxidized to SO_2. The H_2S and dimethylsulfide from aquatic bacteria is processed in clouds to form H_2SO_4 over the oceans. Oceanic H_2SO_4 reacts with NaCl particles to produce Na_2SO_4 aerosols that act as efficient cloud condensation nuclei. The extent of cloud cover is important in determining the extent of global climate change.

<u>32</u>. Calculate the standard state Gibbs energy of formation for SO_2 (g) at 500.0 K.

Answer: The plan is to note that Eq. 15.4.15 is for a pure substance. Remember that the Gibbs energy of formation is for a chemical reaction and not just a pure substance. The relevant data from the data tables in the appendix are given in the table below.

Substance at 298.15 K	$\Delta_f G^\circ$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})	C°_p (J K^{-1} mol^{-1})
SO_2 (g)	-300.194	248.223	39.87
O_2 (g)	0	205.029	29.355
S (s, rhombic)	0	32.054	22.64

In the previous problem we showed that for a chemical reaction Eq. 15.4.15 becomes:

$$\Delta_r G^\circ_T - \Delta_r G^\circ_o = -\,\Delta_r S^\circ_o\,(T - T_o) + \Delta_r C^\circ_p\,(T - T_o) - \Delta_r C^\circ_p\, T \ln \frac{T}{T_o}$$

where $\Delta_r S^\circ_o$ is the standard state reaction entropy at the reference temperature, T_o. For the given reaction O_2 (g) + S (s, rhombic) → SO_2 (g):

$$\Delta_r S^\circ_o = [1(248.223)] - [1(205.029) + 1(32.054)]\ \mathrm{J\,K^{-1}\,mol^{-1}} = 11.140\ \mathrm{J\,K^{-1}\,mol^{-1}}$$
$$\Delta_r C^\circ_p = [1(39.87)] - [1(29.355) + 1(22.64)]\ \mathrm{J\,K^{-1}\,mol^{-1}} = -12.12_5\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Neglecting the terms for the temperature dependence of the reaction entropy gives:

$$\Delta_r G^\circ_T = \Delta_r G^\circ_o - \Delta_r S^\circ_o\,(T - T_o)$$
$$\Delta_r G^\circ_{500\,K} = -300.194\ \mathrm{kJ\,mol^{-1}} - 11.140\ \mathrm{J\,K^{-1}\,mol^{-1}}(500.0\ \mathrm{K} - 298.15\ \mathrm{K})(1\ \mathrm{kJ}/1000\ \mathrm{J})$$
$$= -300.194\ \mathrm{kJ\,mol^{-1}} - 2.248_6\ \mathrm{kJ\,mol^{-1}} = -302.442_6\ \mathrm{kJ\,mol^{-1}}$$

The more exact expression gives:

$$\Delta_r G^\circ_T = \Delta_r G^\circ_o - \Delta_r S^\circ_o\,(T - T_o) + \Delta_r C^\circ_p\,(T - T_o) - \Delta_r C^\circ_p\, T \ln \frac{T}{T_o}$$
$$= -302.443\ \mathrm{kJ\,mol^{-1}} + (-12.12_5\ \mathrm{J\,K^{-1}\,mol^{-1}})(500.0\ \mathrm{K} - 298.15\ \mathrm{K})(1\ \mathrm{kJ}/1000\ \mathrm{J}) -$$
$$(-12.12_5\ \mathrm{J\,K^{-1}\,mol^{-1}})(500.0\ \mathrm{K})(1\ \mathrm{kJ}/1000\ \mathrm{J}) \ln {}^{500.0\ \mathrm{K}}/_{298.15\ \mathrm{K}}$$
$$= -302.443\ \mathrm{kJ\,mol^{-1}} - 2.447\ \mathrm{kJ\,mol^{-1}} + 3.134\ \mathrm{kJ\,mol^{-1}} = -301.756\ \mathrm{kJ\,mol^{-1}}$$

The difference between the more approximate and more exact results is 0.2%. Notice that the two terms that are proportional to the reaction heat capacity difference roughly cancel. SO_2 is a byproduct of coal combustion, which is processed in clouds to form SO_3 and H_2SO_4. Atmospheric H_2SO_4 contributes to acidification of fresh water lakes and rivers through the formation of acid rain.

33. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). When a change in state occurs at constant pressure, the increase in the Gibbs energy of the system must equal the decrease in the Gibbs energy of the surroundings.

(b). The entropy change of the universe is a spontaneity criterion only for isolated systems.

(c). Gibbs energy is minimized for processes at constant temperature and pressure and no electrical work.

(d). For a chemical reaction at constant pressure, the changes in Helmholtz and Gibbs energies are identical if the volume of the products is identical to the volume of the reactants.

(e). For phase transitions, the Gibbs energy change is zero.

Answer: (a). False: Gibbs energy, in general, is not conserved. The Gibbs energy change of the surroundings is not necessarily equal in magnitude and opposite in sign to the Gibbs energy change of the system. The Gibbs energy change of the surroundings, which are at constant temperature and pressure, is just $\Delta G_{surr} = \Delta H_{surr} - T_{surr}\,\Delta S_{surr}$ where:

$$\Delta H_{surr} = q_{surr} = -q \qquad \text{and} \qquad \Delta S_{surr} = q_{surr}/T_{surr} = -q/T_{surr}$$

where q is the heat transfer for the system. If the process for the system is at constant pressure, $q = q_p = \Delta H$ giving:

$$\Delta H_{surr} = -\Delta H \qquad \text{and} \qquad \Delta S_{surr} = -q/T_{surr} = -\Delta H/T_{surr} \qquad \text{(cst. P)}$$

and then $\Delta G_{surr} = 0$. Transfers of energy to the surroundings are always reversible, and the surroundings therefore remain at equilibrium, so that $\Delta G_{surr} = 0$. In other words, the Gibbs energy change of the universe for a process at constant pressure is entirely a property of the system. $\Delta G_{surr} = 0$ at constant pressure explains why the Gibbs energy is such a useful concept for constant pressure processes. A correct statement for the problem is "only for equilibrium processes is $\Delta G = -\Delta G_{surr}$, under which conditions $\Delta G = \Delta G_{surr} = 0$." Another statement is that "for a constant pressure process, the Gibbs energy of the surroundings is constant."

(b). False: the entropy change of the universe is always a good spontaneity criterion. The entropy change of the system is a good spontaneity criterion only for isolated systems. A restatement is "the entropy change of the universe is always positive for a spontaneous process."

(c). Too restrictive: Gibbs energy is minimized at constant temperature and pressure. The change in Gibbs energy can result from chemical, electrical, or any other form of work. Eq. 15.3.11 is explicitly for the case of chemical and electrical work.

(d). True. If the constant pressure restriction was removed, the statement would no longer necessarily be true; at constant volume considering only gas phase reactants and products $\Delta_r G = \Delta_r A + \Delta_r(PV) = \Delta_r A + \Delta_r n_{gas}\,RT$, even though the volume is constant.

(e). False: the Gibbs energy change for a phase transition is positive at temperatures below the equilibrium phase transition temperature (e.g. the standard boiling point or melting point) and negative above the equilibrium phase transition temperature. Were the phase transition Gibbs energy always zero, then phase transitions would never be spontaneous. A restatement is "the Gibbs energy for a phase transition is zero at the equilibrium phase transition temperature."

34. Show that the internal energy change gives the work for an adiabatic process and the enthalpy change gives the maximum non-PV work for an adiabatic constant pressure process.

Answer: In general $\Delta U = q + w$. Consider an adiabatic process, then $q = 0$ and $\Delta U = w$. The work has a PV and non-PV component, w_{net}. For the system in contact with the surroundings as a constant pressure reservoir the PV-work is reversible, $P_{ext} = P$, and then $w_{max} = - P\, dV + w_{net}$. Also at constant pressure, $\Delta H = \Delta U + P\Delta V$. Substituting $\Delta U = q + w$ gives:

$$\Delta H = \Delta U + P\Delta V = q_{rev} - P\, dV + w_{net} + P\Delta V = q_{rev} + w_{net}$$

For an adiabatic process $q = 0$ giving finally $\Delta H = w_{net}$.

Chapter 16: Foundation of Thermodynamics Problems

1. Assume you are a diver. To a good degree of approximation, you are essentially just a 70 kg mass of water. Calculate the change in Gibbs energy for 70.0 kg of water in an isothermal expansion from a pressure of 2.00 bar to a final pressure of 1.00 bar at a constant temperature of 298.2 K. This pressure difference corresponds to surfacing from a depth of 10 m. Start with the required partial derivative.

Answer: The required partial derivative is $(\partial G/\partial P)_T$. This partial derivative is a thermodynamic force, $(\partial G/\partial P)_T = V$, which integrates to give $\Delta G = \int V\,dP$. This expression is given in the last column of the table in Figure 16.4.1. For small changes in pressure, we can consider $V \approx V_o$, where V_o is the initial volume. To calculate ΔG in joules, we must find V_o in m^3 and ΔP in Pa, with 1 bar = $1\text{x}10^5$ Pa:

$$V_o = 70.0\text{x}10^3\text{ g}(1\text{ mL}/0.99705\text{ g})(1\text{ m}^3/1\text{x}10^6\text{ mL}) = 0.07021\text{ m}^3$$

$$\begin{aligned}\Delta G &= V_o\,\Delta P \\ &= 0.07021\text{ m}^3\,(1.00\text{ bar} - 2.00\text{ bar})(1\text{x}10^5\text{ Pa}/1\text{ bar}) \\ &= -7021.\text{ J} = -7.02\text{ kJ}\end{aligned}$$

Given the large amount of water representing the diver, this is a small change in Gibbs energy. The effect of small pressure changes on the Gibbs energy of a condensed phase is often less than the experimental uncertainty in the Gibbs energy. See also Chapter 15 Problem 14.

2. What is the thermodynamic force that corresponds to the change in Gibbs energy with temperature at constant pressure? Explain your reasoning.

Answer: The partial derivative that corresponds to the thermodynamic force for changes in temperature at constant pressure is:

$$\left(\frac{\partial G}{\partial T}\right)_P = ?$$

We can get this force by comparing with the total differentials for the Gibbs energy, Eq. 16.3.4:

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \\ &\qquad\ \downarrow \qquad\qquad\quad \downarrow \\ dG &= -\,SdT \qquad + \qquad VdP \end{aligned}$$

Alternatively, we can use the process outlined in Figure 16.3.1:

change in G when T changes is the thermodynamic force, –S

$$dG = -S\,dT + V\,dP \qquad \text{giving:} \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

at constant P

3. What is the thermodynamic force that corresponds to the change in Helmholtz energy with volume at constant temperature? Explain your reasoning.

Answer: The partial derivative that corresponds to the thermodynamic force for changes in volume at constant temperature is:

$$\left(\frac{\partial A}{\partial V}\right)_T = ?$$

We can get this force by comparing the total differentials for the Helmholtz energy, Eq. 16.3.3:

$$\begin{array}{rcccc} dA = & \left(\frac{\partial A}{\partial T}\right)_V dT & + & \left(\frac{\partial A}{\partial V}\right)_T dV \\ & \downarrow & & \downarrow \\ dA = & -\,SdT & - & PdV \end{array}$$

Alternatively, we can use the process outlined in Figure 16.3.1:

change in A when V changes is the thermodynamic force, –P

$$dA = -\,S\,dT - P\,dV \qquad \text{giving:} \qquad \left(\frac{\partial A}{\partial V}\right)_T = -\,P$$

at constant T

4. Calculate the change in Gibbs energy for one mole of ideal gas for a change in pressure from 1.00 bar to 2.00 bar at a constant temperature of 298.2 K. Determine the partial derivative that relates to this problem, and integrate the result (review Section 9.7).

Answer: The required partial derivative is $(\partial G/\partial P)_T$. This expression is given in the last column of the table in Figure 16.4.1. However, for practice, let's review the process. In $(\partial G/\partial P)_T$, the dependent variable is a thermodynamic potential. The independent variables are the natural variables for the thermodynamic potential, G(T,P). This partial derivative is then a thermodynamic force. The force is given by comparing the total differentials in general form and the form given by the Legendre transformation of the combined First and Second Laws:

$$\begin{array}{rcccc} dG = & \left(\frac{\partial G}{\partial T}\right)_P dT & + & \left(\frac{\partial G}{\partial P}\right)_T dP \\ & \downarrow & & \downarrow \\ dG = & -\,SdT & + & VdP \end{array} \qquad \text{giving:} \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

Integrating gives $\Delta G = \int V\,dP$. For an ideal gas $V = nRT/P$ and:

$$\Delta G = \int nRT/P\,dP = nRT \ln {}^{P_2}/_{P_1}$$
$$= 1.00\text{ mol}(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.2\text{ K})(1\text{ kJ}/1000\text{ J}) \ln(2.00\text{ bar}/1.00\text{ bar}) = 1.72\text{ kJ}$$

5. Develop a problem that is based on the partial derivative $(\partial A/\partial V)_T$, and solve the problem (review Section 9.7). Choose an ideal gas as the system for simplicity.

Answer: For one example, calculate the change in Helmholtz energy for one mole of an ideal gas for an isothermal expansion from 1.00 L to 2.00 L at 298.2 K.

The required partial derivative is a thermodynamic force, $(\partial A/\partial V)_T = -P$, which for an ideal gas integrates to give Eq. 16.3.9° (see also Figure 16.4.1):

$$\Delta A = -nRT \ln {}^{V_2}/_{V_1}$$
$$= -1.00 \text{ mol}(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(298.2 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln(2.00 \text{ L}/1.00 \text{ L}) = -1.72 \text{ kJ}$$

6. For a given increase in volume, will diamond or liquid water give a larger increase in entropy at constant temperature?

Answer: Consulting Figure 16.4.1, note that $\Delta S = \int \alpha/\kappa_T \, dV = \alpha/\kappa_T \, \Delta V$, assuming constant α and κ_T. For diamond and liquid water, respectively, from Table 7.6.1:

diamond: $\alpha/\kappa_T = 0.030\text{x}10^{-4} \text{ K}^{-1}/0.185\text{x}10^{-6} \text{ bar}^{-1} = 16.2 \text{ bar K}^{-1}$
water: $\alpha/\kappa_T = 2.57\text{x}10^{-4} \text{ K}^{-1}/45.3\text{x}10^{-6} \text{ bar}^{-1} = 5.67 \text{ bar K}^{-1}$

Diamond will give a larger increase in entropy than water for equal changes in volume.

7. Calculate the change in chemical potential for an ideal gas for a change in pressure from 1.00 bar to 20.0 bar at a constant temperature of 25°C.

Answer: Using Eq. 16.6.20° with the reference pressure at 1 bar, P° = 1.00 bar:

$$\mu_1 = \mu_1^\circ + RT \ln \frac{P}{P^\circ}$$

gives the change:

$$\mu_1 - \mu_1^\circ = RT \ln \frac{P}{P^\circ} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K}) \ln(20.0/1.00)$$
$$= 7.426 \text{ J K}^{-1} \text{ mol}^{-1} = 7.43 \text{ kJ mol}^{-1}$$

where the subscript for μ_1 indicates component 1. Alternatively and equivalently, for a single component you can integrate Eq. 16.6.16 directly:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_A^* \qquad \text{(pure substance)}$$

with $V_A^* = RT/P$ for an ideal gas:

$$\Delta\mu = \mu_2 - \mu_1 = \int_{\mu_1}^{\mu_2} d\mu = \int_{P_1}^{P_2} \frac{RT}{P}\, dP$$

where μ_1 is the chemical potential of the initial state and μ_2 is the chemical potential of the final state:

$$\Delta\mu = RT \ln\left(\frac{P_2}{P_1}\right)$$

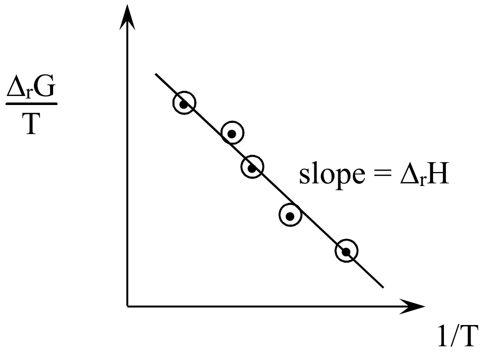
This equation is analogous to Eq. 15.4.4°, $\Delta G = nRT \ln(P_2/P_1)$, for one mole of substance.

8. The temperature dependence of the Gibbs energy of a chemical reaction is expressed as:

$$\frac{\Delta_r G_{T2}}{T_2} - \frac{\Delta_r G_{T1}}{T_1} = \Delta_r H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

What would you plot on the axes of a graph to get a straight line with the slope related to $\Delta_r H$? How is the slope related to $\Delta_r H$?

Answer: This equation is the Gibbs-Helmholtz equation, Eq. 16.3.15. A graph of $\Delta_r G/T$ versus $1/T$ for a chemical reaction gives a straight line with slope = $\Delta_r H$, assuming the reaction enthalpy is constant over the temperature range. An endothermic reaction will give a positive slope and an exothermic reaction a negative slope.



Rearranging the Gibbs-Helmholtz equation into direct straight-line form gives:

$$\frac{\Delta_r G_{T2}}{T_2} = \frac{\Delta_r H}{T_2} + \left(\frac{\Delta_r G_{T1}}{T_1} - \frac{\Delta_r H}{T_1}\right) \qquad \text{with the intercept} = \left(\frac{\Delta_r G_{T1}}{T_1} - \frac{\Delta_r H}{T_1}\right)$$

9. Hydrogen is used as a fuel for internal combustion engines. However, the average combustion temperature is significantly higher than tabulated values. Calculate the standard state Gibbs energy of combustion of H_2 at 700.0 K.

Answer: The plan is to use the Gibbs-Helmholtz equation, Eq. 16.3.15, to find the reaction Gibbs energy at the higher temperature from the tabulated value at 298.2 K. The Gibbs energy of combustion of H_2 is equivalent to the Gibbs energy of formation of H_2O, which at high temperatures is water vapor.

The combustion reaction is the formation reaction, which at 298.15 K gives:

$$H_2\text{ (g, 1bar)} + \tfrac{1}{2}\, O_2\text{ (g, 1bar)} \rightarrow H_2O\text{ (g, 1bar)} \qquad \Delta_f G^\circ = -228.57\text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ = -241.82\text{ kJ mol}^{-1}$$

Using the Gibbs-Helmholtz equation applied to reaction Gibbs energies, Eq. 16.3.15, gives:

$$\frac{\Delta_r G_{T2}}{T_2} - \frac{\Delta_r G_{T1}}{T_1} = \Delta_r H \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{\Delta_r G_{T2}}{700.0\text{ K}} - \frac{-228.57\text{ kJ mol}^{-1}}{298.15\text{ K}} = -241.82\text{ kJ mol}^{-1}\left(\frac{1}{700.0\text{ K}} - \frac{1}{298.15\text{ K}}\right)$$

$$\frac{\Delta_r G_{T2}}{700.0\text{ K}} + 0.766628\text{ kJ mol}^{-1}\text{ K}^{-1} = -241.82\text{ kJ mol}^{-1}\ (-1.9254\text{x}10^{-3}\text{ K}^{-1}) = 0.46561\text{ kJ mol}^{-1}\text{ K}^{-1}$$

$$\frac{\Delta_r G_{T2}}{700.0\text{ K}} = -0.30102\text{ kJ mol}^{-1}\text{ K}^{-1}$$

$$\Delta_r G_{T2} = -210.7\text{ kJ mol}^{-1}$$

The combustion of H_2 at high temperatures provides less energy than at room temperature, as predicted by LeChâtelier's Principle and the exothermic $\Delta_r H^\circ$. For the $(1/T_2 - 1/T_1)$ term, remember to keep at least one extra significant figure to avoid round-off error.

10. The Gibbs-Helmholtz expression, Eq. 16.3.15, gives the temperature dependence of the reaction Gibbs energy. You should remember from General Chemistry that the equilibrium constant for a chemical reaction is related to the reaction Gibbs energy by $\Delta_r G^\circ = -RT \ln K$. Use the Gibbs-Helmholtz equation to find the temperature dependence of the equilibrium constant.

Answer: Solving $\Delta_r G^\circ = -RT \ln K$ for ln K gives:

$$\ln K = -\Delta_r G^\circ / RT$$

Dividing the Gibbs-Helmholtz equation by – R and specifying standard state pressure gives:

$$\frac{\Delta_r G^\circ_{T_2}}{-RT_2} - \frac{\Delta_r G^\circ_{T_1}}{-RT_1} = \frac{\Delta_r H^\circ}{-R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting in $\ln K_{eq} = -\Delta_r G^\circ/RT$ at both temperatures gives:

$$\ln K_{T2} - \ln K_{T1} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_{T2}}{K_{T1}}\right) = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where $\Delta_r H^\circ$ is evaluated at the average temperature. This equation is found in most General Chemistry texts.

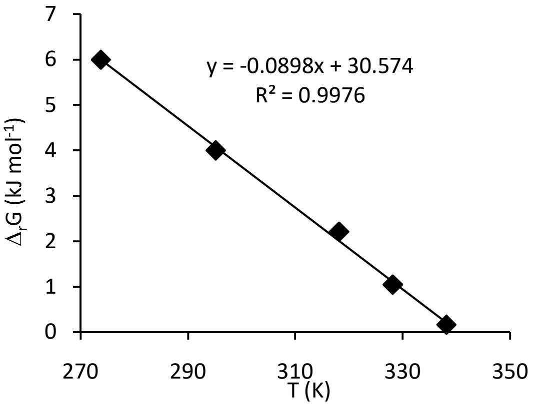
11. Potassium hydrogen phthalate, KHP, is a commonly used primary standard for acid-base titrations. KHP is moderately soluble in water. For the reaction: KHP (s) $\rightleftarrows$ K^+ (aq) + HP^- (aq), the reaction Gibbs energy is given in the table, below, versus temperature at constant pressure.[1] Calculate the reaction enthalpy and entropy, including uncertainties. Assume the reaction enthalpy and entropy are not functions of temperature.

T (°C)	0.6	22.0	45.0	55.0	65.0
Δ_rG (kJ mol^{-1})	5.995	3.999	2.208	1.044	0.1591

Answer: The plan is to use the thermodynamic force $(\partial\Delta_rG/\partial T)_P = -\Delta_rS$ and the Gibbs-Helmholtz expression, Eq. 16.3.15, with suitable linear plots to extract the thermodynamic parameters from the slopes.

A spreadsheet was written to plot Δ_rG versus T and also Δ_rG/T versus 1/T, as required by the Gibbs-Helmholtz expression, Eq. 16.3.15.

T (°C)	T (K)	Δ_rG (kJ mol^{-1})	1/T (K^{-1})	Δ_rG/T (J K^{-1} mol^{-1})
0.6	273.75	5.995	0.003653	218.993
22	295.15	3.999	0.003388	135.496
45	318.15	2.208	0.003143	69.402
55	328.15	1.044	0.003047	31.822
65	338.15	0.1591	0.002957	4.704

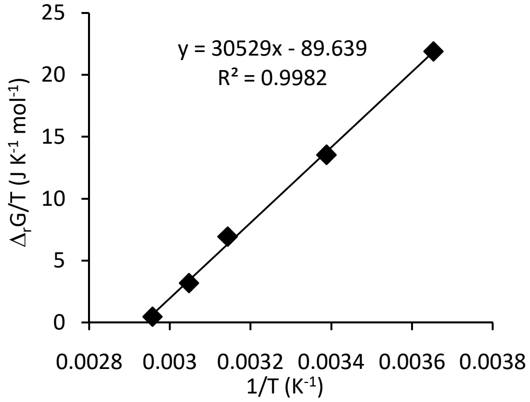


Δ_rG vs. T

slope	-0.089782	30.57353	intercept
±	0.00254	0.791182	±
r^2	0.99761	0.132461	st.dev. y
F	1249.86	3	dof
ss_{reg}	21.930	0.052638	ss_{resid}

Δ_rG/T vs. 1/T

slope	30529.3	-89.63895	intercept
±	7389.73	2.39990	±
r^2	0.99825	0.417286	st.dev. y
F	1706.78	3	dof
ss_{reg}	297.197	0.522383	ss_{resid}



The slope of Δ_rG versus T is $-\Delta_rS$ giving: $\Delta_rS = 89.8 \pm 2.5$ J K^{-1} mol^{-1}

The slope of $\Delta_r G/T$ versus $1/T$ gives: $\Delta_r H = 30.53 \pm 0.74\ \text{kJ mol}^{-1}$

12. Starting with the internal energy as a function of entropy and volume, give the Legendre transformation that defines a new function that will be a good spontaneity criterion at constant temperature and volume.

Answer: Consider the case with PV and chemical work. The natural variables for internal energy are S, V, and the mole amounts:

$$dU = T\,dS - P\,dV + \sum_{i=1}^{c} \mu_i\,dn_i$$

The Legendre transformation must be defined to switch the role of T and S to obtain a good spontaneity criterion at constant temperature:

$$A \equiv U - TS$$

so that dA has natural variables T and V. To show that the natural variables of the new thermodynamic potential are T, V and the mole amounts, the total differential is given by:

$$dA = dU - T\,dS - S\,dT$$

and substituting for dU gives:

$$dA = T\,dS - P\,dV + \sum_{i=1}^{c} \mu_i\,dn_i - T\,dS - S\,dT = -S\,dT - P\,dV + \sum_{i=1}^{c} \mu_i\,dn_i$$

At constant T and V the first two terms vanish giving:

$$dA = \sum_{i=1}^{c} \mu_i\,dn_i$$

which focuses our attention of the chemical work. For a spontaneous process at constant T and V, $dA < 0$, thus minimizing A.

13. Show that C_v is not a function of volume for an ideal gas, in a closed system.

Answer: In other words show that, for a closed system: $\left(\frac{\partial C_v}{\partial V}\right)_T = 0$

The definition of the constant volume heat capacity is:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Substitution into the partial derivative with respect to V, above, gives:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$$

The order of differentiation can be reversed because U is a state function, just as we did for the Maxwell relationships. For an ideal gas, $(\partial U/\partial V)_T = 0$, giving:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = 0$$

In other words C_v is not a function of volume.

14. Calculate the change in Helmholtz energy for V_o liters of a liquid substance with isothermal compressibility κ_T when the pressure is changed from P_1 to P_2 at constant temperature. Start by proving that:

$$\left(\frac{\partial A}{\partial P}\right)_T = PV\kappa_T$$

Then integrate assuming the volume may be considered a constant $V \approx V_o$.

Answer: Start with the desired partial derivative: $\left(\frac{\partial A}{\partial P}\right)_T = ?$

We note that the natural variables for Helmholtz energy are V and T, not the given independent variables P and T. The "misplaced variable," in the sense discussed in Section 9.7, is the derivative with respect to P in the denominator. Using the chain rule then gives:

$$\left(\frac{\partial A}{\partial P}\right)_T = \left(\frac{\partial A}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

The first partial derivative on the right of the equality is the thermodynamic force, Eq. 16.3.7, $(\partial A/\partial V)_T = -P$. The second partial is given from the definition of the isothermal compressibility:

$$\left(\frac{\partial V}{\partial P}\right)_T = -V\kappa_T$$

which upon substitution gives: $\left(\frac{\partial A}{\partial P}\right)_T = \left(\frac{\partial A}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = -P(-V\kappa_T) = PV\kappa_T$

This expression may be integrated after separating variables:

$$dA = PV\kappa_T\, dP$$

Assuming κ_T is constant and the volume change is small for moderate changes in pressure, $V \approx V_o$, gives:

$$\Delta A = \int_{P_1}^{P_2} P\, V_o\, \kappa_T\, dP = \frac{V_o\kappa_T}{2}(P_2^2 - P_1^2)$$

The Helmholtz energy for a substance increases with an increase in pressure.

15. Derive the Maxwell relationship that is based on the Helmholtz energy: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Answer: The independent variables for this relationship are V and T. The thermodynamic potential that has natural variables V and T is the Helmholtz energy, Eq. 16.3.3. In analogy with Figure 16.4.2, the general form of the total differential and the Legendre transformed First and Second Laws are:

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$dA = -S \; dT - P \; dV$$

Thermodynamic force Thermodynamic force

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right)_T = -\left(\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right)_V = \left(\frac{\partial P}{\partial T}\right)_V$$

switch order

16. Starting with the thermodynamic force for the change in internal energy with respect to entropy, prove that:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$$

Answer: The thermodynamic force for the change in internal energy with respect to entropy is:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \text{or inverting:} \qquad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

We can use the chain rule for the desired partial derivative with respect to temperature:

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V$$

Using the thermodynamic force and the definition of C_v, Eq. 7.8.7, gives:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T}$$

No approximations are made in this derivation. The equation holds for real gases, ideal gases, liquids, and solids.

17. Show that if S is regarded as a function of T and V then, for a closed system:

$$T\,dS = C_v\,dT + T\left(\frac{\alpha}{\kappa_T}\right) dV$$

Answer: Consider S(T,V), giving the total differential:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad 1$$

We can use the chain rule for the partial derivative with respect to temperature (Problem 14):

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V \qquad 2$$

Notice that the thermodynamic force is:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \text{or inverting:} \qquad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \qquad 3$$

Using this thermodynamic force and the definition of C_v gives:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \qquad 4$$

Note that the partial derivative in Eq. 1 with respect to V is a Maxwell relationship, Eq. 16.4.10, which using Eq. 7.6.21 gives

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\alpha}{\kappa_T}\right) \qquad 5$$

Substituting Eqs. 4 and 5 into Eq. 1 gives:

$$dS = \frac{C_v}{T} dT + \left(\frac{\alpha}{\kappa_T}\right) dV \qquad 6$$

Finally, multiplying both sides of this last equation by T gives the final result:

$$T\,dS = C_v\,dT + T\left(\frac{\alpha}{\kappa_T}\right) dV \qquad 7$$

18. Show for an isothermal change in pressure for a liquid or a solid, $\Delta S = -\int \alpha V\,dP$.

Answer: The change in entropy for a change in pressure at constant temperature is given by the partial derivative:

$$\left(\frac{\partial S}{\partial P}\right)_T = ?$$

We can recognize this partial derivative as the Maxwell Relationship that is derived from the Gibbs energy, Eq. 16.4.11, since T and P are the independent variables:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

The right-hand side is given by the thermal expansion coefficient, Eq. 7.6.13, in the form $(\partial V/\partial T)_P = V\,\alpha$:

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\,\alpha$$

Separating variables and integrating gives $\Delta S = -\int \alpha V\, dP$

19. Pressure perturbation calorimetry has become a useful tool in studies of protein folding. In interpreting the effects of solvation on protein conformation and folding, the following derivative is centrally important. Show that:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Answer: Substituting from the definition of $C_p = (\partial H/\partial T)_P$ and switching the order of diffentiation:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P$$

We can reverse the order of differentiation, since enthalpy is a state function. Using the thermodynamic equation of state, Eq. 16.5.11, for $(\partial H/\partial P)_T$ gives:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial}{\partial T}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]\right)_P$$

Using the product rule gives the temperature derivatives as:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial T}\right)_P$$

The first and the last terms on the right cancel giving the final result:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

This equation is very useful for understanding solute-solvent interactions, because changes in volume are easy to visualize.

20. Show that: $\left(\frac{\partial V}{\partial S}\right)_P = \frac{\alpha VT}{C_p}$

Answer: Starting with the partial derivative:

$$\left(\frac{\partial V}{\partial S}\right)_P = ? \qquad 1$$

Which variable is the "misplaced" variable in this partial derivative? Consider the definitions of α and κ_T, Eqs. 7.6.13 and 7.6.14, respectively:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad 2$$

These relationships suggest the "misplaced" variable in Eq. 1 is the derivative with respect to S in the denominator. Referring to Figure 9.7.2, the suggestion is to use the chain rule:

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P \qquad 3$$

The first partial derivative on the right is given by the thermal expansion coefficient:

$$(\partial V/\partial T)_P = V\,\alpha \qquad 4$$

The second partial derivative in Eq. 3 can be inverted to find a more familiar form, Eq. 16.3.18:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad \text{or inverting:} \quad \left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_p} \qquad 5$$

Substituting Eqs. 4 and 5 into Eq. 3 gives the final result:

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{\alpha VT}{C_p} \qquad 6$$

This partial derivative is important because it is the result of the Maxwell relationship based on the enthalpy, Eq. 16.4.9. The Maxwell relationship and Eq. 6 allow the derivative involving the entropy to be expressed entirely in terms of a heat capacity and α.

Method 2: Like many derivations in thermodynamics, this relationship can be derived in several ways. An alternative and equivalent derivation is based on the Maxwell Relationships. Returning to Eq. 1, one quick place to look for partial derivatives involving the entropy is a Maxwell Relationship. This partial derivative is given by the Maxwell Relationship that is derived from the enthalpy, which has natural variables S and P, Eq. 16.4.9:

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \qquad 7$$

At first this relationship doesn't look like it helps much, because we don't often work with processes at constant entropy. The "misplaced" variable is the constant entropy. We need to use the Euler chain relationship. Writing the total differential of the entropy in terms of independent variables T and P gives:

$$dS = 0 = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad 8$$

Solving for $(\partial T/\partial P)_S$ gives:

$$\left(\frac{\partial T}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} \qquad 9$$

The partial derivative in the numerator is related through the Maxwell Relationship, Eq. 16.4.11, to the thermal expansion coefficient,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha \qquad 10$$

and the partial derivative in the denominator is given by Eq. 16.3.18:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \qquad 11$$

Substituting Eqs. 9-11 into Eq. 7 gives:

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S = -\frac{(-V\alpha)}{\left(\frac{C_p}{T}\right)} = \frac{\alpha VT}{C_p} \qquad 12$$

This equation allows the change in volume for a constant pressure process to be calculated from the change in entropy or the change in temperature for an adiabatic reversible process from the change in pressure.

21. Show that: $\left(\frac{\partial P}{\partial S}\right)_V = \frac{\alpha T}{\kappa_T C_V}$

Answer: Starting with the partial derivative:

$$\left(\frac{\partial P}{\partial S}\right)_V = ? \qquad 1$$

Which variable is the "misplaced" variable in this partial derivative? Consider the definitions of α and κ_T, Eqs. 7.6.13 and 7.6.14, respectively and Eq. 7.6.16:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{and} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa_T} \qquad 2$$

These relationships suggest the "misplaced" variable in Eq. 1 is the derivative with respect to S in the denominator. Referring to Figure 9.7.2, the suggestion is to use the chain rule:

$$\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V \qquad 3$$

The first partial derivative on the right of the equality is given by Eq. 7.6.16. The second partial derivative in Eq. 3 can be inverted to find a more familiar form (see Problem 14 and Problem 15 Eqs. 2-4):

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \quad \text{or inverting:} \quad \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_v} \qquad 4$$

Substituting α/κ_T and Eq. 4 into Eq. 3 gives the final result:

$$\left(\frac{\partial P}{\partial S}\right)_V = \frac{\alpha T}{\kappa_T C_V} \qquad 5$$

This partial derivative is important because it is the result of the Maxwell relationship based on the internal energy, Eq. 16.4.8. The Maxwell relationship and Eq. 5 allow the derivative involving the entropy to be expressed entirely in terms of a heat capacity, α, and κ_T.

<u>22</u>. Reversible adiabatic processes are constant entropy processes. Derive Eq. 9.8.12° directly from $(\partial T/\partial V)_S$. Do this derivation in two steps. (a). Show that:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{T}{C_v}\right)$$

(b). Integrate this last equation for an ideal gas from the initial state, T_1 and V_1, to the final state, T_2 and V_2.

Answer: The plan is to note that partial derivatives involving entropy can often be simplified using a Maxwell relationship.

The Maxwell relation based on the internal energy, Eq. 16.4.8, relates the required partial derivative to a derivative with respect to the entropy:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Using Eqs. 1-5 in the last problem gives the required partial derivative as:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{T}{C_v}\right)$$

(b). For an ideal gas, $P = nRT/V$ giving $(\partial P/\partial T)_V = nR/V$:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{nR}{V}\right)\left(\frac{T}{C_v}\right)$$

Separating variables gives:

$$C_v \frac{dT}{T} = -nR\frac{dV}{V} \quad \text{and integrating:} \quad C_v \int_{T_1}^{T_2} \frac{dT}{T} = -nR\int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_v \ln \frac{T_2}{T_1} = -\,nR \ln \frac{V_2}{V_1} \qquad (9.8.12°)$$

Eq. 9.8.12° was originally derived using explicit consideration of the heat and work transfers. The derivation in this problem more clearly shows the relationship of the overall changes to the constancy of the entropy for the process. Since entropy is a state function, the overall process can be broken into the sum of a constant volume process and a constant temperature process, with the same initial and final conditions. The first term in Eq. 9.8.12° is the change in entropy for a constant volume process and the second term is the negative of the change in entropy for an isothermal process in an ideal gas. The two changes are equal in magnitude and opposite in sign so that the overall change in entropy is zero.

23. Reversible adiabatic processes are constant entropy processes. Derive Eq. 9.8.18° directly from $(\partial T/\partial P)_S$. Do this derivation in two steps. (a). Show that:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{T}{C_p}\right)$$

(b). Integrate this last equation for an ideal gas from the initial state, T_1 and P_1, to the final state, T_2 and P_2.

Answer: The plan is to note that partial derivatives involving entropy can often be simplified using a Maxwell relationship.

The Maxwell relation based on the enthalpy, Eq. 16.4.9, relates the required partial derivative to a derivative with respect to the entropy:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Using Problem 20, Eqs. 1-5, gives the required partial derivative as:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{T}{C_p}\right)$$

(b). For an ideal gas, $V = nRT/P$ giving $(\partial V/\partial T)_P = nR/P$:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{nR}{P}\right)\left(\frac{T}{C_p}\right)$$

Separating variables gives:

$$C_p \frac{dT}{T} = nR \frac{dP}{P} \qquad \text{and integrating:} \qquad C_p \int_{T_1}^{T_2} \frac{dT}{T} = nR \int_{P_1}^{P_2} \frac{dP}{P}$$

$$C_p \ln \frac{T_2}{T_1} = nR \ln \frac{P_2}{P_1} \qquad (9.8.18°)$$

Eq. 9.8.18° was originally derived using the change in enthalpy for the process. The derivation in this problem more clearly shows the relationship of the overall changes to the constancy of the entropy for the process. Since entropy is a state function, the overall process can be broken into the sum of a constant pressure process and a constant temperature process, with the same initial and final conditions. The first term in Eq. 9.8.18° is the change in entropy for a constant pressure process and the second term is the negative of the change in entropy for an isothermal process in an ideal gas. The two changes are equal in magnitude and opposite in sign so that the overall change in entropy is zero.

24. The heat capacity of a substance can be determined without heat flow measurements by determining the change in temperature of a substance with pressure at constant entropy, $(\partial T/\partial P)_S$. Constant entropy conditions are obtained by changing the pressure rapidly, so that heat flow is minimal. Reversible adiabatic processes are constant entropy processes. Show that:[2]

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{T}{C_P}\right) = \frac{TV\alpha}{C_P}$$

(b). The coefficient of thermal expansion for benzene is $1.24\text{x}10^{-3}$ K^{-1} and the density is 0.8765 g/cm^3 at 298.15 K. The temperature of a sample of benzene increased by 0.0484 K for a sudden increase in pressure of 2.02 bar. Calculate the heat capacity of benzene.[2]

Answer: The plan is to note that partial derivatives involving entropy can often be simplified using a Maxwell relationship.

(a). The Maxwell relation based on the enthalpy, Eq. 16.4.9, relates the required partial derivative to a derivative with respect to the entropy:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Using Problem 20, Eqs. 1-6, gives the required partial derivative as:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{T}{C_P}\right) = \frac{TV\alpha}{C_P}$$

(b). The heat capacity is usually expressed as a molar value; the molar volume of benzene is:

$$V_o = 1 \text{ mol}(78.11 \text{ g mol}^{-1})(1 \text{ m}^3/1\text{x}10^6 \text{ cm}^3)/0.8765 \text{ g cm}^{-3} = 8.912\text{x}10^{-5} \text{ m}^3$$

Substituting the required values and solving for C_P gives:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{0.0484 \text{ K}}{2.02\text{x}10^5\text{Pa}} = \frac{TV\alpha}{C_P} = \frac{298.15 \text{ K}(8.912\text{x}10^{-5} \text{ m}^3)(1.24\text{x}10^{-3} \text{ K}^{-1})}{C_P}$$

$$C_p = 137.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

This expression shows the importance of the Maxwell relationships in their ability to uncover relationships among important system properties. This relationship is also important in modeling the mechanism of impulse welding techniques. In impulse welding, two dissimilar metals are accelerated towards each other by an explosion, an intense magnetic field pulse, or a laser pulse. The impact creates a large pressure, up to $1\text{x}10^9$ Pa, that plastically deforms and heats the materials. For example, explosion welding is necessary to fabricate components of high field magnet dewars for NMR.

25. Consider the change in Gibbs energy for an isothermal change in pressure for a liquid or a solid. Assume the volume changes and that the isothermal compressibility, κ_T, is constant.
(a). Show that for initial volume V_o, initial pressure P_o, and final pressure P, for moderate changes in pressure:

$$\Delta G = V_o (P - P_o) - \tfrac{1}{2} V_o \kappa_T (P - P_o)^2$$

(b). Repeat Problem 1 with this more accurate formula, and compare the results.

Answer: (a). The plan is to integrate Eq. 7.6.9 for small changes in pressure (see Problem 7.11) and then use the volume as a function of pressure in $\Delta G = \int V\,dP$ (see Problem 1, above, in comparision).

Reviewing Problem 7.11, integrating $dV = -V \kappa_T\, dP$ from V_o, P_o to V, P gives:

$$\int_{V_o}^{V} dV = -\int_{P_o}^{P} V \kappa_T\, dP$$

For small changes in pressure, we can approximate the volume in the integrand as $V \approx V_o$:

$$V - V_o = -\int_{P_o}^{P} V_o \kappa_T\, dP = -V_o \kappa_T (P - P_o) \qquad \text{and} \qquad V = V_o - V_o \kappa_T (P - P_o)$$

Using this last expression for the volume as a function of pressure in $\Delta G = \int V\,dP$ gives:

$$\begin{aligned}\Delta G &= \int_{P_o}^{P} [V_o - V_o \kappa_T (P - P_o)]\, dP = \int_{P_o}^{P} V_o\, dP - \int_{P_o}^{P} V_o \kappa_T (P - P_o)\, dP \\ &= V_o (P - P_o) - \tfrac{1}{2} V_o \kappa_T (P - P_o)^2 \Big|_{P_o}^{P} \\ &= V_o (P - P_o) - \tfrac{1}{2} V_o \kappa_T (P - P_o)^2 - \tfrac{1}{2} V_o \kappa_T (P_o - P_o)^2 \\ &= V_o (P - P_o) - \tfrac{1}{2} V_o \kappa_T (P - P_o)^2\end{aligned}$$

(b). The second term in the last expressions is a correction term for the approximate formula that was derived in Problem 1. Using Table 7.6.1, $\kappa_T = 4.53\text{x}10^{-5}\ \text{bar}^{-1} = 4.53\text{x}10^{-10}\ \text{Pa}^{-1}$ for water:

$$\begin{aligned}\Delta G &= 0.07021\ \text{m}^3\,(-1.00\text{x}10^5\ \text{Pa}) - \tfrac{1}{2}(0.07021\ \text{m}^3)(4.53\text{x}10^{-10}\ \text{Pa}^{-1})(-1.00\text{x}10^5\ \text{Pa})^2 \\ &= -7021.\ \text{J} - 0.32\ \text{J} = -7.02\ \text{kJ}\end{aligned}$$

The correction is negligible for small changes in pressure, but important for work under extreme conditions in geochemistry and chemical engineering.

26. (a). Calculate the change in internal energy for one mole of liquid water for an isothermal decrease in volume from 1.0000 L to 0.9900 L at 298.2 K and an initial pressure of 1.00 bar. Assume that α and κ_T are approximately constant over this volume range. Note that to a good approximation:

$$P = P_o - \frac{1}{V_o \kappa_T}(V - V_o)$$

(b). Calculate the final pressure.

Answer: The plan is to follow Example 16.5.1, but using the thermodynamic equation of state for the change in internal energy with respect to volume, Eq. 16.5.8:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\frac{\alpha}{\kappa_T}$$

Substituting for P and integrating Eq 16.5.8 gives:

$$\Delta U = -\int_{V_o}^{V} P\,dV + \int_{V_o}^{V} T\frac{\alpha}{\kappa_T}\,dV = -\int_{V_o}^{V} P_o\,dV + \int_{V_o}^{V} \frac{1}{V_o\,\kappa_T}(V - V_o)\,dV + \int_{V_o}^{V} T\frac{\alpha}{\kappa_T}\,dV$$

Given that α and κ_T are assumed constant over this volume range, for an isothermal process:

$$\Delta U = -P_o\,\Delta V + \frac{1}{2\,V_o\,\kappa_T}(V - V_o)^2 + T\frac{\alpha}{\kappa_T}\Delta V$$

The pure molar volume for water at 25°C is (1.00 mol)(18.02 g mol^{-1})/0.99705 g mL^{-1} = 18.07 mL = 18.07x10^{-6} m^3. From Table 7.6.1 and using 1 bar = 1x10^5 Pa, α = 2.57x10^{-4} K^{-1}, κ_T = 4.53x10^{-5} bar^{-1} = 4.53x10^{-10} Pa^{-1}, ΔV = (1.0000 – 0.9900 L) = -0.0100 L = -1.00x10^{-5} m^3, giving:

$$\Delta U = -\,1.00\text{x}10^{5}\ \text{Pa}(-1.00\text{x}10^{5}\ \text{m}^3) + \frac{1}{2(1.00\text{x}10^{-3}\ \text{m}^3)(4.53\text{x}10^{-10}\ \text{Pa}^{-1})}(-1.00\text{x}10^{-5}\ \text{m}^3)^2 +$$
$$298.2\ \text{K}\,\frac{2.57\text{x}10^{-4}\ \text{K}^{-1}}{4.53\text{x}10^{-10}\ \text{Pa}^{-1}}(-1.0\text{x}10^{-5}\ \text{m}^3)$$

$$\Delta U = 1.00\ \text{J} + 110.4\ \text{J} - 1691\ \text{J} = -1.58\text{x}10^{3}\ \text{J} = -1.58\ \text{kJ}$$

The first two terms are the PV work for the compression, which increases the internal energy. The third term is the change in internal energy caused by the change in entropy with respect to volume. As the volume decreases the entropy decreases, especially with respect to the intermolecular forces, which correspondingly decreases the internal energy by TdS.

(b). The final pressure is:

$$P = P_o - \frac{1}{V_o\,\kappa_T}(V - V_o) = 1.00\text{x}10^{-5}\ \text{Pa} - \frac{1}{1.00\text{x}10^{-3}\ \text{m}^3(4.53\text{x}10^{-10}\ \text{Pa}^{-1})}(-1.00\text{x}10^{5}\ \text{m}^3)$$
$$P = 2.2175\text{x}10^{7}\ \text{Pa} = 222.\ \text{bar}$$

The compression requires a large increase in pressure, comparable to the increase in pressure generated while ice skating.

<u>27</u>. Calculate the change in Gibbs energy of a liquid substance with isothermal compressibility κ_T when the volume is changed from V_1 to V_2 at constant temperature. Start by proving that:

$$\left(\frac{\partial G}{\partial V}\right)_T = -\frac{1}{\kappa_T}$$

Then integrate from V_1 to V_2 assuming κ_T is constant.

Answer: The plan is to note that since the natural variables for G are P and T, the "misplaced" variable is V as the independent variable in the denominator.

Reference to Figure 9.7.1 suggests using the chain rule:

$$\left(\frac{\partial G}{\partial V}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

The partial $(\partial G/\partial P)_T$ is the thermodynamic force, $(\partial G/\partial P)_T = V$. From the definition of the isothermal compressibility, Eq. 7.6.9:

$$\kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{or inverting:} \qquad \left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{1}{-V\kappa_T}\right)$$

Substituting this last result and the thermodynamic force gives:

$$\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{1}{-V\kappa_T}\right) = -\frac{1}{\kappa_T}$$

This expression is listed in the table Figure 16.4.1. Integration for constant κ_T gives: $\Delta G = -(1/\kappa_T)\,\Delta V$.

28. The Gibbs-Helmholtz relationship is useful at constant pressure. Show that for constant volume processes:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

Answer: The plan is to follow Eqs. 16.3.9-16.3.10, but for constant volume processes.

Consider A/T as the product (A)(1/T) and use the product rule:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = A\left(\frac{\partial\left(\frac{1}{T}\right)}{\partial T}\right)_V + \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V = -\frac{A}{T^2} + \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V$$

Using Eq. 16.3.7 for the thermodynamic force, $(\partial A/\partial T)_V = -S$, gives:

$$= -\frac{A}{T^2} - \frac{S}{T}$$

Then taking T^2 as the common denominator gives:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{(A + TS)}{T^2}$$

The definition of the Helmholtz energy is $A \equiv U - TS$. Rearrangement of the definition gives $A + TS = U$, which upon substitution simplifies to:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

29. Rewrite Figure 9.7.1 for the partial derivatives:

$$\left(\frac{\partial \mathbf{G}}{\partial T}\right)_V \qquad \left(\frac{\partial \mathbf{T}}{\partial G}\right)_P \qquad \left(\frac{\partial G}{\partial \mathbf{V}}\right)_T \qquad \left(\frac{\partial G}{\partial T}\right)_{\mathbf{V}} \qquad \left(\frac{\partial P}{\partial T}\right)_{\mathbf{G}}$$

Answer: The plan is to rewrite Figure 9.7.1 using the same five partial derivative conversion techniques, α, κ_T, and the thermodynamic forces, Eqs. 16.3.7 and 16.3.8:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

The conversion for $(\partial G/\partial V)_T$ is given in Problem 24. The partial derivative conversions are shown below:

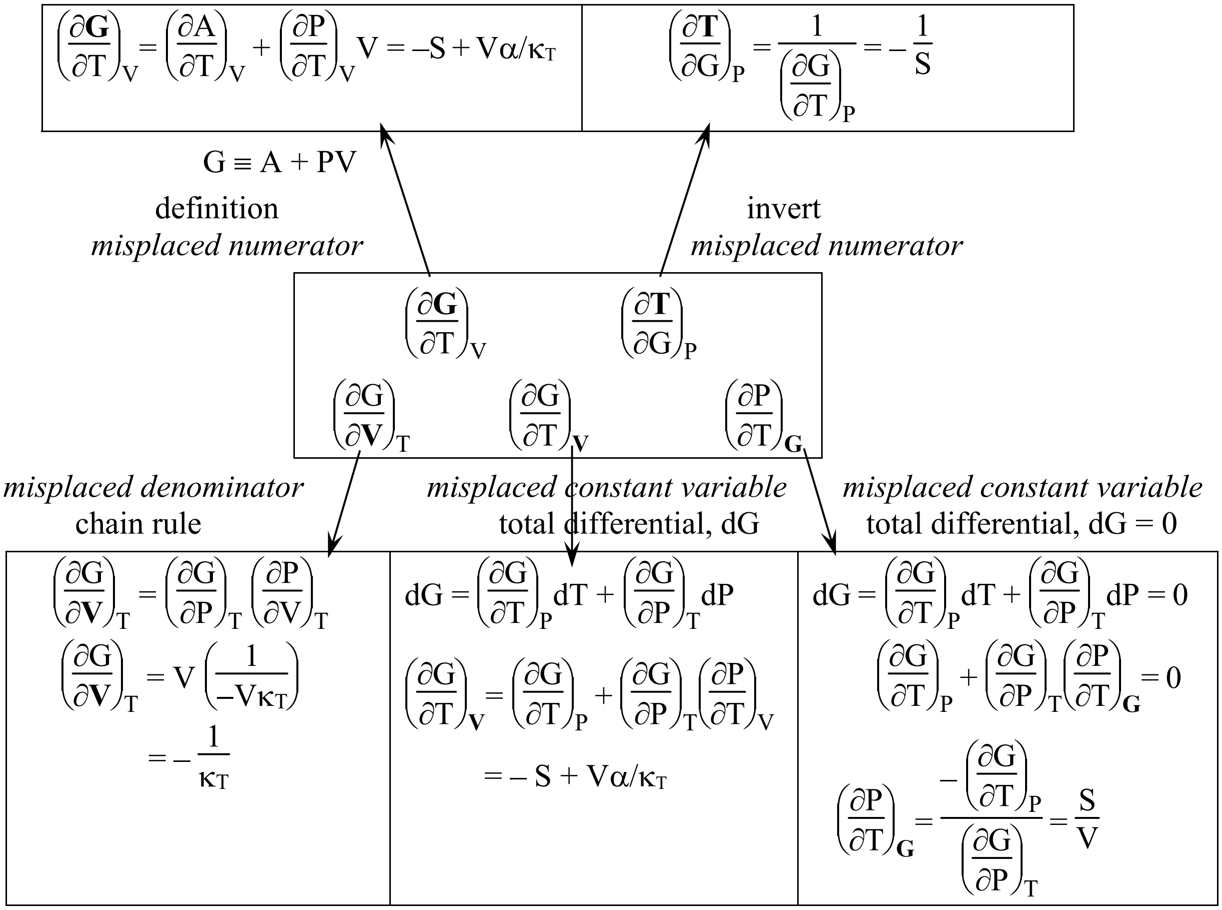


Figure P29.1: Partial Derivative Conversion. Partial derivative manipulations to convert unknown partial derivatives to those involving C_v, C_p, α, and κ_T.

The last example, using the Euler chain relationship, is used with equilibrium phase transitions of pure substances. For a phase transition at equilibrium, $\Delta_{tr}G = 0$ and then the change in pressure necessary for the system to remain at equilibrium for a change in temperature is given using *General Pattern* ℘ ***8***:

$$\left(\frac{\partial P}{\partial T}\right)_{\mathbf{G}} = \frac{\Delta_{tr}S}{\Delta_{tr}V} \tag{17.1.7}$$

where $\Delta_{tr}S$ is the entropy change for the phase transition and $\Delta_{tr}V$ is the change in molar volume. This last result gives Eq. 17.1.7, which is one form of the famous Clapeyron equation.

30. In an isothermal expansion of an ideal gas $\Delta U = 0$. The value is not zero for a real gas. Using the Van der Waals equation of state, find ΔU for an isothermal expansion from V_1 to V_2.

Answer: The plan is to integrate the thermodynamic equation of state, Eq. 16.5.5:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \tag{1}$$

The Van der Waals equation of state, Eq. 7.5.1, rearranges to give:

$$P = \frac{nRT}{(V-nb)} - a\frac{n^2}{V^2} \tag{2}$$

The mechanical derivative is:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{(V-nb)} \tag{3}$$

Using this partial derivative and the Van der Waals equation, Eq. 2, to substitute for P into the thermodynamic equation of state, Eq. 3, gives:

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{nRT}{(V-nb)} + \frac{an^2}{V^2} + T\frac{nR}{(V-nb)} = \frac{an^2}{V^2} \tag{4}$$

We can now separate variables and integrate:

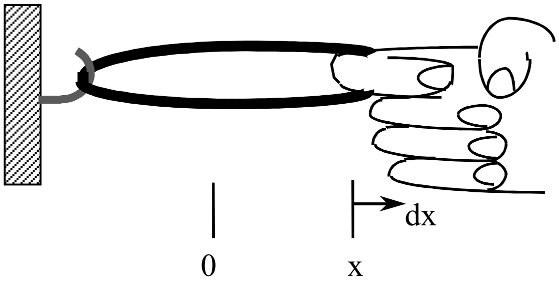
$$dU = \frac{an^2}{V^2}\,dV \qquad \text{giving:} \qquad \int_{U_1}^{U_2} dU = \int_{V_1}^{V_2} \frac{an^2}{V^2}\,dV \tag{5}$$

Using $\int \frac{1}{x^2}\,dx = -\frac{1}{x}$ gives:

$$\Delta U = -a\,n^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \tag{6}$$

31. The work for the system in stretching a rubber band is $w_{net} = -F\,dx$, where F is the restoring force, $F = -kx$. At constant temperature and pressure, $\Delta G = w_{net}$, where w_{net} is the non-PV work. Therefore, the total change in Gibbs energy for a process involving stretching a rubber band is:

$$dG = -S\,dT + V\,dP - F\,dx.$$



k="stretchiness"
x= extension

(a). Under what conditions is ΔG be a good spontaneity criterion (i.e. when what is held constant)? (b). For an initial state with a stretched rubber band, $x > 0$, find the direction for spontaneous change, either $dx > 0$ or $dx < 0$, at constant temperature and pressure. (c). Define a new state function: $R \equiv G + F\,x$. What are the independent variables for R?

Answer: (a). ΔG is a good spontaneity criterion at constant T and P. Setting T and P as constant gives $dG = -F\,dx$, which focuses attention on the work of extension.
(b). For a spontaneous process at constant T and P, $dG = -F\,dx < 0$. Substituting in the force, $F = -kx$, gives:

$$dG = kx\,dx < 0$$

For an initial stretched state with $x > 0$, then $dx < 0$ to make dG negative overall. With $dx < 0$ the rubber band relaxes toward $x = 0$, the equilibrium position, as expected.
(c). This definition is a Legendre transformation. Taking the total differential using the product rule gives:

$$dR = dG + F\,dx + x\,dF$$

Substituting in for dG gives:

$$dR = -S\,dT + V\,dP - F\,dx + F\,dx + x\,dF$$

Canceling terms gives:

$$dR = -S\,dT + V\,dP + x\,dF$$

The independent variables are T, P, and F. This function would be useful for systems that have extension work with a constant force and then some other form of work, in addition. The additional work might be chemical work, for example in a muscle.

32. Given that $dU = TdS - PdV$ and for an ideal gas the change in entropy is given by:

$$dS = \frac{C_v}{T}\,dT + \frac{nR}{V}\,dV$$

show that $dU = C_v\, dT$ for <u>any</u> process in an ideal gas. (At first it doesn't look like $dU = TdS - PdV$ will give just $dU = C_v\, dT$, does it?)

Answer: Substituting for dS into the combined First and Second Laws gives:

$$dU = TdS - PdV = T\left(\frac{C_v}{T}\, dT + \frac{nR}{V}\, dV\right) - PdV$$

$$dU = C_v\, dT + \frac{nRT}{V}\, dV - PdV$$

However, for an ideal gas $P = nRT/V$ and the last two terms cancel:

$$dU = C_v\, dT + \frac{nRT}{V}\, dV - \frac{nRT}{V}\, dV = C_v\, dT$$

The only restriction we have placed on this equation is that the system is an ideal gas.

<u>33</u>. In Eqs. 16.6.14, the chemical potentials expressed in terms of U, H, A, and G were all shown to be equal based on comparing the total differential of each thermodynamic potential with the Legendre transformed combined First and Second Laws of thermodynamics. As an alternative proof, show that the chemical potentials expressed in terms of the Gibbs energy and the enthalpy are equal using partial derivative conversions:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$$

Answer: The plan is to relate dG and dH using the definition of the Gibbs energy, $G \equiv H - TS$. In other words, treat the G in the numerator as "misplaced."

No generality will be lost if we consider only a single component, but the notation will be simplified. Substituting the definition of the Gibbs energy gives:

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial n}\right)_{T,P} - T\left(\frac{\partial S}{\partial n}\right)_{T,P} \qquad 1$$

Considering $(\partial H/\partial n)_{T,P}$, the natural variables for H are S and P, not the given independent variables T and P. We can treat the constant T as the "misplaced" variable. Consulting Figure 9.7.2, we need to work through the total differential of the enthalpy expressed as a function of independent variables, S, P, and n:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P} dn \qquad 2$$

Dividing by dn at constant T and P gives the desired enthalpy derivative. With $dP = 0$ and using the fact that $(\partial H/\partial S)_{P,n}$ is a thermodynamic force, $(\partial H/\partial S)_{P,n} = T$:

$$\left(\frac{\partial H}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial S}\right)_{P,n}\left(\frac{\partial S}{\partial n}\right)_{T,P} + \left(\frac{\partial H}{\partial n}\right)_{S,P} = T\left(\frac{\partial S}{\partial n}\right)_{T,P} + \left(\frac{\partial H}{\partial n}\right)_{S,P} \qquad 3$$

Substitution of Eq. 3 into Eq. 1 gives the desired result after cancellation:

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = T\left(\frac{\partial S}{\partial n}\right)_{T,P} + \left(\frac{\partial H}{\partial n}\right)_{S,P} - T\left(\frac{\partial S}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial n}\right)_{S,P} \qquad 4$$

The other equalities of the chemical potentials, in terms of the corresponding natural variables in Eqs. 16.6.14, can be proved in an analogous fashion.

34. Calculate the entropy and Gibbs energy of mixing of 0.80 moles of $N_2(g)$ and 0.20 moles of $O_2(g)$ at 298.15 K. Assume the initial pure gases are at 1 bar pressure and the final total pressure is also at 1 bar.

Answer: Using Eqs. 18.2.9° and 18.2.10°:

$$\Delta_{mix}S = -\,n_{tot}R \sum_{i=1}^{n_s} y_i \ln y_i = -\,1.00\text{ mol}(8.3145\text{ J K}^{-1}\text{ mol}^{-1})[0.80 \ln 0.80 + 0.20 \ln 0.20]$$
$$= 4.16\text{ J K}^{-1}$$

$$\Delta_{mix}G = -\,T\,\Delta_{mix}S = -\,298.15\text{ K}(4.16\text{ J K}^{-1})(1\text{ kJ}/1000\text{ J}) = -1.24\text{ kJ mol}^{-1}$$

35. Carbon sequestration is a strategy for ameliorating global climate change caused by the build-up of CO_2 in the atmosphere from fossil fuel combustion. However, the separation of CO_2 from exhaust gases requires work that will necessarily decrease the efficiency of the overall process. Assume that the O_2 in air is replaced completely by CO_2 during a combustion process. Calculate the minimum energy per mole of CO_2 at constant temperature and pressure necessary to separate the CO_2 from the remaining N_2 at 298.15 K. Assume air is 20.9 mol% O_2 and 79.1 mol% N_2. Anthracite coal can be modeled as pure graphite. Compare the energy required for the CO_2 separation to the Gibbs energy of combustion of graphite.

Answer: For one total mole of air as a feed gas for a fossil fuel based power plant or automobile, assuming complete conversion of the O_2 to CO_2 gives a final exhaust gas that is 20.9 mol% CO_2 and 79.1 mol% N_2. The negative of the Gibbs energy of mixing is the minimum work necessary to separate the CO_2 from the N_2:

$$\Delta_{mix}G = n_{tot}RT \sum_{i=1}^{n_s} y_i \ln y_i$$
$$= 1.00\text{ mol}(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})[0.209 \ln 0.209 + 0.791 \ln 0.791]$$
$$= -1.27_1\text{ kJ}$$

Per mole of CO_2 produced: $\Delta_{mix}G_m(CO_2) = -1.27_1\text{ kJ}/0.209\text{ mol} = -6.08\text{ kJ mol}^{-1}$ of CO_2.

The energy required to separate the CO_2 and N_2 is then $+6.08\text{ kJ mol}^{-1}$. The separation is likely to be facilitated using a ceramic membrane based on a zeolite-type molecular sieve material. The Gibbs energy of combustion of carbon graphite, by comparison, yields:

$$C(graph) + O_2\ (g, 1\ bar) \rightarrow CO_2\ (g, 1\ bar) \qquad \Delta_f G^\circ_{298\,K} = -394.36\ kJ\ mol^{-1}$$

The Gibbs energy of combustion of graphite is equivalent to the Gibbs energy of formation of CO_2. The separation requires at least 1.5% of the energy produced by the combustion. The energy lost in separating CO_2 from the exhaust stream is minimal under ideal conditions. However, the CO_2 produced is at low pressure, 1 bar, and must be liquefied or otherwise compacted for disposal.

36. Find the fugacity coefficient for a gas that obeys the Virial equation of state, Eq. 7.5.10: $z = 1 + (B(T)/RT)\,P$. For CO_2 at the critical temperature, 304.14 K, the second Virial coefficient is $B(T) = -0.114\ L\ mol^{-1}$. Calculate the fugacity coefficient for CO_2 at 150 bar and 304.14 K, and compare to the result using Figure 16.7.1 (see Example 16.7.1).

Answer: The plan is to use Eq. 16.7.9 with the given Virial polynomial expansion for the compressibility factor.

Substituting the Virial expansion through the second Virial coefficient into Eq. 16.7.9 gives the integral as:

$$\ln f/P = \int_0^P \frac{(z-1)}{P}\, dP = \int_0^P \frac{B(T)}{RT}\, dP = \frac{B(T)}{RT}\, P$$

With $f = \gamma P$, then $f/P = \gamma$. For the given conditions:

$$\ln \gamma = \frac{-0.114\ L\ mol^{-1}}{0.083145\ bar\ L\ K^{-1}\ mol^{-1}\ 304.14\ K}\ 150\ bar = -0.6762$$

$$\gamma = 0.509$$

The reduced temperature is $T_R = T/T_c = 1$ and the reduced pressure is $P_R = P/P_c$. The critical pressure for CO_2 is 73.843 bar, giving $P_R = 150\ bar/73.843\ bar = 2.03$. Reading the fugacity coefficient from Figure 16.7.1 gives $\gamma \cong 0.43$. Our result of $\gamma = 0.509$ is sufficiently close given that only the second Virial coefficient term was retained in this approximation. Notice when only the second Virial coefficient term is retained that $\ln \gamma = z - 1$.

37. A brief outline of carbon sequestration is given in Problem 32. One proposal for carbon sequestration is to pump liquid or super critical CO_2 deep underground into abandoned oil wells that are sealed by salt domes. CO_2 may be liquefied at temperatures less than the critical temperature and pressures greater than the critical pressure. For CO_2 the critical temperature is 304.14 K and the critical pressure is 73.843 bar. The critical pressure is the maximum vapor pressure for liquid CO_2. At equilibrium, the chemical potential of the liquid is equal to the chemical potential of the vapor, $\mu^*_{CO_2}(l) = \mu_{CO_2}(g)$. Find the chemical potential for CO_2 vapor and liquid at the critical point, relative to the standard state, using Figure 16.7.1. Compare your results to the value assuming ideal gas behavior.

Answer: Reading the fugacity coefficient from Figure 16.7.1 gives $\gamma \cong 0.666$ for $T_R = 1.00$ and $P_R = 1.00$. Using Eq. 16.7.1 the chemical potential is given by:

for real CO_2:

$$\mu_A = \mu_A^\circ(g) + RT \ln f/P^\circ = \mu_A^\circ(g) + RT \ln \gamma P/P^\circ$$
$$= \mu_A^\circ(g) + 8.3145 \text{ J K}^{-1}\text{ mol}^{-1}(304.14 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln[0.666(73.843 \text{ bar})/1 \text{ bar}]$$
$$= \mu_A^\circ(g) + 9.85 \text{ kJ mol}^{-1} \qquad \text{(real)}$$

for ideal CO_2:

$$\mu_A = \mu_A^\circ(g) + RT \ln P/P^\circ = \mu_A^\circ(g) + 10.88 \text{ kJ mol}^{-1} \qquad \text{(ideal)}$$

Attractive intermolecular forces decrease the chemical potential of the real vapor and liquid as compared to the ideal vapor. Notice that in this problem we have not calculated the PV work necessary to condense CO_2. However, we can use the fugacity coefficient as a general indication of the importance of intermolecular forces.

<u>38</u>. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the reaction Gibbs energy at 50.0 bar and 298.2 K for:

$$CaCO_3\text{ (s)} \rightarrow CaO\text{ (s)} + CO_2\text{ (g, P = 50.0 bar)}$$

Approximate the fugacity coefficient using:

$$\ln \gamma \cong z - 1 \cong (B(T)/RT)\, P$$

where B(T) is the second Virial coefficient at the given temperature (see Problem 36 for the justification). For CO_2 at 298.2 K, the second Virial coefficient is $B(T) = -0.125 \text{ L mol}^{-1}$. Neglect the effect of the pressure on the solids. Compare the results to the value assuming an ideal gas (Ch. 15, Problem 17).

Answer: Under standard state conditions:

	$CaCO_3$ (s)	→	CaO (s)	+	CO_2 (g, P° = 1 bar)
$\Delta_f G^\circ$	-1128.8		-604.03		-394.36 kJ mol^{-1}

$$\Delta_r G^\circ = \sum_{i=1}^{n_s} \nu_i \Delta_f G^\circ = [\Sigma\text{products}] - [\Sigma\text{reactants}]$$
$$= [(-394.36) + (-604.03)] - [-1128.8] \text{ kJ mol}^{-1} = 130.41 \text{ kJ mol}^{-1}$$

The Gibbs energy of each <u>gaseous</u> reactant and product is then adjusted for the new pressure:

$$\Delta_r G = \Delta_r G^\circ + \Sigma\, \nu_i\, RT \ln f_i/P^\circ \qquad (\nu_i \text{ for gases only})$$

The ν_i are the stoichiometric coefficients for each gaseous reactant and product, with ν_i negative for reactants. (See Chapter 20 for more information on non-standard state reaction Gibbs energies). For this reaction $\nu_{CO_2} = 1$ is the only gas:

$$\Delta_r G = \Delta_r G^\circ + RT \ln f/P^\circ$$

For the given conditions:

$$\ln \gamma = \frac{-0.125 \text{ L mol}^{-1}}{0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1}\ 298.15 \text{ K}}\ 50 \text{ bar} = -0.2521$$

$$\gamma = 0.777$$

$$\Delta_r G = \Delta_r G° + RT \ln {}^{(0.777)(50.0 \text{ bar})}/_{1 \text{ bar}}$$
$$= 130.41 \text{ kJ mol}^{-1} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln 38.86$$
$$= 130.41 \text{ kJ mol}^{-1} + 9.07 \text{ kJ mol}^{-1} = 139.48 \text{ kJ mol}^{-1}$$

The value assuming $\gamma = 1$ is 140.11 kJ mol^{-1}, as given in Ch. 15, Problem 17.

39. *(Challenge Problem)* Consider a one-component open system: $dU = T\,dS - P\,dV + \mu\,dn$, with the chemical potential given in terms of the natural variables for U by:

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V}$$

For practical problems we often treat the internal energy as a function of T and V, since we often work at constant temperature and constant volume (see Chapter 7). (a). Show using partial derivative conversions that:

$$dU = T\,dS - P\,dV + \mu\,dn = C_v\,dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn$$

(b). Determine dU for a constant temperature and volume process for an open system.

Answer: The plan is to find TdS and μdn for an open system in terms of T, V, and n, and then substitute into $dU = T\,dS - P\,dV + \mu\,dn$.

Consider, first, μ dn. The chemical potential is given in terms of the natural variables, U(S,V, n), by:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn \qquad 1$$

Dividing by dn at constant T and V gives the molar internal energy at constant temperature and volume:

$$\left(\frac{\partial U}{\partial n}\right)_{T,V} = \left(\frac{\partial U}{\partial S}\right)_{V,n} \left(\frac{\partial S}{\partial n}\right)_{T,V} + \left(\frac{\partial U}{\partial n}\right)_{S,V} \qquad 2$$

The internal energy derivative with respect to entropy is the thermodynamic force, $(\partial U/\partial S)_{V,n} = T$. The last term, $(\partial U/\partial n)_{S,V}$, is the chemical potential, μ. Solving for the chemical potential gives:

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{T,V} - T\left(\frac{\partial S}{\partial n}\right)_{T,V} \qquad 3$$

We next need to find TdS, starting from the total differential of S in terms of T, V, and n:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V,n} dT + \left(\frac{\partial S}{\partial V}\right)_{T,n} dV + \left(\frac{\partial S}{\partial n}\right)_{T,V} dn \qquad 4$$

Note that the entropy change includes terms from the temperature change, the volume change, and the change in number of moles of substance. Note that $(\partial S/\partial T)_{V,n} = C_v/T$. We can also use the Maxwell relationship, Eq. 16.4.10, $(\partial S/\partial V)_{T,n} = (\partial P/\partial T)_{V,n}$. Then, TdS is given by:

$$T\,dS = C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_{V,n} dV + T\left(\frac{\partial S}{\partial n}\right)_{T,V} dn \qquad 5$$

Substituting Eqs. 3 and 5 into $dU = T\,dS - P\,dV + \mu\,dn$ gives:

$$dU = C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_{V,n} dV + T\left(\frac{\partial S}{\partial n}\right)_{T,V} dn - P\,dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn - T\left(\frac{\partial S}{\partial n}\right)_{T,V} dn \qquad 6$$

$$dU = C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_{V,n} dV - P\,dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad 7$$

Distributing out the common factor of dV gives:

$$dU = C_v dT + \left[-P + T\left(\frac{\partial P}{\partial T}\right)_{V,n}\right] dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad 8$$

The term in brackets is the thermodynamic equation of state for the internal energy, $(\partial U/\partial V)_{T,n}$, Eq. 16.5.5:

$$dU = C_v\,dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad 9$$

This derivation shows that $dU = T\,dS - P\,dV + \mu\,dn$ and Eq. 9 are consistent and can be derived from each other. The derivation of Eqs. 4 and 5 show that both the TdS and the μ dn terms depend on the change in number of moles of the substance.

(b). At constant temperature and volume, Eq. 9 reduces to:

$$dU = \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad \text{(cst. T\&V)} \qquad 10$$

where the partial derivative is the well-known molar internal energy of the substance. For a chemical reaction, the molar internal energy of the products minus the reactants gives the conventional $\Delta_r U$.

40. (*Challenge Problem*) The molar absolute entropies of substances that are listed in reference tables are given by:

$$S_m = \left(\frac{\partial S}{\partial n}\right)_{T,P}$$

since reference tabulations assume constant temperature and pressure. Consider a single component system. The enthalpy change for a general process in terms of the natural variables is:

$$dH = T\,dS + V\,dP + \mu\,dn$$

The TdS term, however, is more complicated than it might first appear. Show that:

$$T\,dS = C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_{P,n} dP + T\,S_m\,dn$$

Answer: The plan is to write the total differential of S as a function of T, P, and n, and then use a Maxwell Relationship for one of the entropy derivatives.

Starting from the total differential of the entropy in terms of T, P, and n:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,n} dT + \left(\frac{\partial S}{\partial P}\right)_{T,n} dP + \left(\frac{\partial S}{\partial n}\right)_{T,P} dn \qquad 1$$

Note that $(\partial S/\partial T)_{P,n} = C_p/T$. We can also use the Maxwell relationship, Eq. 16.4.11, $(\partial S/\partial P)_{T,n} = -(\partial V/\partial T)_{P,n}$ and the definition of the molar entropy, $(\partial S/\partial n)_{T,P} = S_m$. Substituting these values into Eq. 1 gives TdS as:

$$T\,dS = C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_{P,n} dP + T\,S_m\,dn \qquad 2$$

which can also be expressed as:

$$T\,dS = C_p\,dT - TV\alpha\,dP + T\,S_m\,dn \qquad 3$$

Eqs. 2 and 3 show that both the TdS and μ dn terms depend on the change in number of moles of the substance.

41. (*Challenge Problem*) (a). Starting with the result for TdS from the last problem, show that for a general process in an open system with one component:

$$dH = C_p\,dT + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + T\,S_m\,dn + \mu\,dn$$

(b). The molar enthalpies for substances that are listed in reference tables are given by:

$$H_m = \left(\frac{\partial H}{\partial n}\right)_{T,P}$$

Show that $\mu = \left(\frac{\partial H}{\partial n}\right)_{T,P} - T\,S_m$

(c). Combine the expressions in parts (a) and (b) and compare to the general total differential of H(T,P,n).

(d). Find dH for a constant temperature and pressure process in an open system with one component.

Answer: (a). Substituting Eq. 2 from the last problem into $dH = T\,dS + V\,dP + \mu\,dn$ gives:

$$dH = C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_{P,n} dP + T\,S_m\,dn + V\,dP + \mu\,dn$$

Factoring out the common factor of dP gives:

$$dH = C_p\,dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,n}\right] dP + T\,S_m\,dn + \mu\,dn$$

The term in brackets is the thermodynamic equation of state for the enthalpy, $(\partial H/\partial P)_{T,n}$, Eq. 16.5.11:

$$dH = C_p\,dT + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + T\,S_m\,dn + \mu\,dn$$

(b). The chemical potential, based on the enthalpy is given by Eq. 16.6.14 as:

$$\mu = \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

since the natural variables for H are S and P. The conventional molar enthalpy of a substance listed in reference tables, $(\partial H/\partial n)_{T,P}$, is at constant T and P, however. The "misplaced" variable is the constant T. To find the conventional molar enthalpy, we work from the total differential of H with respect to the natural variables:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P} dn$$

Dividing by dn at constant T and P gives the conventional molar enthalpy:

$$\left(\frac{\partial H}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial S}\right)_{P,n}\left(\frac{\partial S}{\partial n}\right)_{T,P} + \left(\frac{\partial H}{\partial n}\right)_{S,P}$$

The first partial on the right of the equality is the thermodynamic force, $(\partial H/\partial S)_{P,n} = T$. The entropy derivative is the conventional molar entropy S_m. The last term is the chemical potential. Solving for the chemical potential gives:

$$\mu = \left(\frac{\partial H}{\partial n}\right)_{T,P} - T\,S_m$$

This last expression can also be written as $\mu = H_m - T\,S_m$, as expected from the definition, $G \equiv H - TS$. This expression was also proved in Problem 33, Eq. 1 or Eq. 3.

(c). Combining this last expression for the chemical potential with dH from part (a) gives:

$$dH = C_p\,dT + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + T\,S_m\,dn + \left(\frac{\partial H}{\partial n}\right)_{T,P} dn - T\,S_m\,dn$$

$$dH = C_p\,dT + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + \left(\frac{\partial H}{\partial n}\right)_{T,P} dn$$

Substituting the definition of $C_p \equiv (\partial H/\partial T)_{P,n}$ back into this last expression gives:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{P,n} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP + \left(\frac{\partial H}{\partial n}\right)_{T,P} dn$$

This result, which was derived from $dH = T\,dS + V\,dP + \mu\,dn$, is the general total differential of the enthalpy with respect to independent variables T, P and n. This equality shows that dH derived from H(S,P,n) and H(T,P,n) are equivalent, as they must be.

(d). At constant T and P, dH reduces to:

$$dH = \left(\frac{\partial H}{\partial n}\right)_{T,P} dn = H_m\,dn$$

where $(\partial H/\partial n)_{T,P} \equiv H_m$ is the conventional molar enthalpy of the substance as found in standard reference tables. While these results are intuitive and expected, the interpretation of the TdS term in $dH = T\,dS + V\,dP + \mu\,dn$ and the relationship to the constant temperature and pressure molar enthalpy is a common source of confusion, even for experienced physical chemists.

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Chapter 17 Problems: Phase Transitions in Pure Substances

1. Prove that the dependence of the freezing point on the pressure for a pure substance for large changes in pressure is given by:

$$T = T_m\, e^{\Delta P\, \Delta_{fus}V_i/\Delta_{fus}H_i}$$

Answer: The plan is to integrate Eq. 17.1.8 without assuming the temperature on the right side of the equation is constant.

Separating variables in Eq. 17.1.8 and specifying the melting or fusion phase transition:

$$\frac{dP}{dT} = \frac{\Delta_{fus}H_i}{T\, \Delta_{fus}V_i} \qquad \text{gives} \quad dP = \frac{\Delta_{fus}H_i}{T\, \Delta_{fus}V_i}\, dT$$

Integration from an initial pressure of P_o and initial melting point of T_m to a final pressure of P gives:

$$\int_{P_o}^{P} dP = \int_{T_m}^{T} \frac{\Delta_{fus}H_i}{T\, \Delta_{fus}V_i}\, dT$$

Assuming that $\Delta_{fus}H_i$ and $\Delta_{fus}V_i$ are constant over the pressure and temperature range gives:

$$\Delta P = \frac{\Delta_{fus}H_i}{\Delta_{fus}V_i} \ln {}^{T}\!/_{T_m} \qquad \text{or} \qquad \ln {}^{T}\!/_{T_m} = \frac{\Delta P\, \Delta_{fus}V_i}{\Delta_{fus}H_i}$$

Solving for the new melting point, T, gives:

$$T = T_m\, e^{\Delta P\, \Delta_{fus}V_i/\Delta_{fus}H_i}$$

The temperature change, $\Delta T = T - T_m$, is given by:

$$\Delta T = T_m\, (e^{\Delta P\, \Delta_{fus}V_i/\Delta_{fus}H_i} - 1)$$

Note that for small pressure changes, the exponential term can be approximated using a Taylor expansion, $e^x \approx 1 + x$, and the last equation reduces to Eq. 17.1.24.

2. Calculate the change in the melting point for water ice for an increase in pressure of 10.00 bar starting from the melting point at 1.00 bar. The densities of water and ice at 0.00ºC are 1.000 g cm^{-3} and 0.917 g cm^{-3}, respectively. The enthalpy of fusion is 6.008 kJ mol^{-1} at 273.15 K.

Answer: The change in molar volume on melting is:

$$\Delta_{fus}V_m = 18.02 \text{ g mol}^{-1}\left(\frac{1}{1.000 \text{ g cm}^{-3}} - \frac{1}{0.917 \text{ g cm}^{-3}}\right) = -1.63 \text{ cm}^3 \text{ mol}^{-1}$$
$$= -1.63\text{x}10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

Note that 10.00 bar = $1.000\text{x}10^6$ Pa. The change in melting point is then:

$$\Delta T = \frac{T_m^* \,\Delta_{fus}V_m}{\Delta_{fus}H_m}\,\Delta P = \frac{273.15\text{ K }(-1.63\text{x}10^{-6}\text{ m}^3\text{ mol}^{-1})}{6.008\text{x}10^3\text{ J mol}^{-1}}(1.000\text{x}10^6\text{ Pa})$$
$$= -0.074\text{ K}$$

3. The vapor pressure of acetone is 0.377 bar at 30.0°C and 0.817 bar at 50.0°C. Calculate (a) the enthalpy of vaporization of acetone and (b) the normal boiling point.

Answer: The plan is to use the Clausius-Clapeyron equation to find the enthalpy of the phase transition and then again to find the temperature at which the vapor pressure is 1.00 atm.
(a). The Clausius-Clapeyron equation is:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \quad\text{or}\quad \ln\left(\frac{0.817}{0.377}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{323.15}-\frac{1}{303.15}\right)$$

Giving: $0.7734 = -\frac{\Delta_{vap}H_m}{R}(-2.042\text{x}10^{-4}\text{ K}^{-1})$

Make sure to keep sufficient significant figures for the temperature dependent term. Solving for the enthalpy change:

$$\Delta_{vap}H_m = -\frac{0.7734}{-2.042\text{x}10^{-4}\text{ K}^{-1}}(8.314\text{ J K}^{-1}\text{ mol}^{-1}) = 3.149\text{x}10^4\text{ J mol}^{-1} = 31.5\text{ kJ mol}^{-1}$$

(b). The normal boiling point is the temperature where the vapor pressure is equal to 1.00 atm = 1.0132 bar. We can use either of the data points given in the problem and the Clausius-Clapeyron equation. Using the given vapor pressure at the warmer temperature, since it is closest to the normal boiling point:

$$\ln\left(\frac{1.0132}{0.817}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_2}-\frac{1}{323.15}\right) = -\frac{3.149\text{x}10^4\text{ J mol}^{-1}}{8.314\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{T_2}-\frac{1}{323.15}\right)$$

which gives:

$$0.2152 = -3.788\text{x}10^3\text{ K}^{-1}\left(\frac{1}{T_2}-3.0945\text{x}10^{-3}\text{ K}^{-1}\right)$$
$$1/T_2 = 3.0378\text{x}10^{-3}\text{ K}^{-1}$$

Solving for the boiling point gives: $T_2 = 329.20\text{ K} = 56.0°\text{C}$

4. The normal boiling point of methanol is 64.05°C. The vapor pressure of methanol at 20.00°C is 0.1530 bar. Calculate the enthalpy of vaporization of methanol.

Answer: The plan is to use the Clausius-Clapeyron equation to find the enthalpy of the phase transition, given that the normal boiling point is the temperature that gives a vapor pressure of 1.000 atm (1.01325 bar).
(a). The Clausius-Clapeyron equation is:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln\left(\frac{1.01325}{0.153}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{337.20} - \frac{1}{293.15}\right)$$

Giving: $$1.8904 = -\frac{\Delta_{vap}H_m}{R}(-4.45624\text{x}10^{-4}\ \text{K}^{-1})$$

Make sure to keep sufficient significant figures for the temperature dependent term. Solving for the enthalpy change:

$$\Delta_{vap}H_m = -\frac{1.8904}{-4.45624\text{x}10^{-4}\ \text{K}^{-1}}(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) = 3.5269\text{x}10^4\ \text{J mol}^{-1} = 35.27\ \text{kJ mol}^{-1}$$

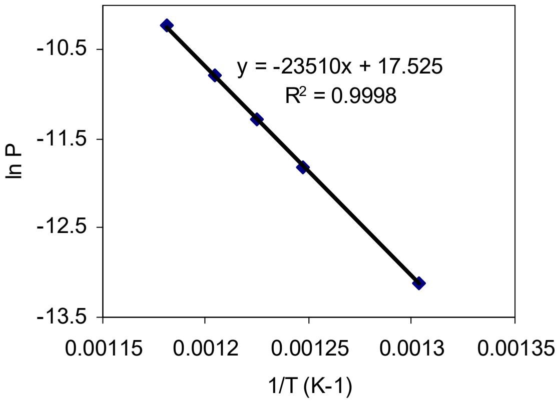
5. The vapor pressure of solid CsI at several temperatures is given in the following table. Calculate the enthalpy of sublimation of CsI.

T (K)	767.2	801.8	816.3	830.3	846.8
$P/10^{-6}$ (bar)	2.03	7.45	12.5	20.5	36.4

Answer: Sublimation follows the Clausius-Clapeyron equation using the molar enthalpy of sublimation. The following spreadsheet and plot were constructed:

T (K)	$P/10^{-6}$ (bar)	1/T (K^{-1})	ln P
767.2	2.03	0.001303	-13.1075
801.8	7.45	0.001247	-11.8073
816.3	12.5	0.001225	-11.2898
830.3	20.5	0.001204	-10.7951
846.8	36.4	0.001181	-10.2209

slope	-23509.9	17.52472	intercept
±	171.5568	0.211513	±
r^2	0.99984	0.016052	st.dev. y
F	18779.64	3	df
ss_{reg}	4.839104	0.000773	ss_{resid}



The slope has three significant figures, and slope = $-\Delta_{sub}H_m/R$, giving:

$$\Delta_{sub}H_m = -(-23509.9\ \text{K})(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) = 1.95\text{x}10^5\ \text{J mol}^{-1} = 195.\ \text{kJ mol}^{-1}$$

This result is very large compared to moderate molar mass organic compounds.

6. The vapor pressure of ethanol as a function of temperature is given in the table below. Determine the enthalpy of vaporization of ethanol. Calculate the standard boiling point of ethanol.

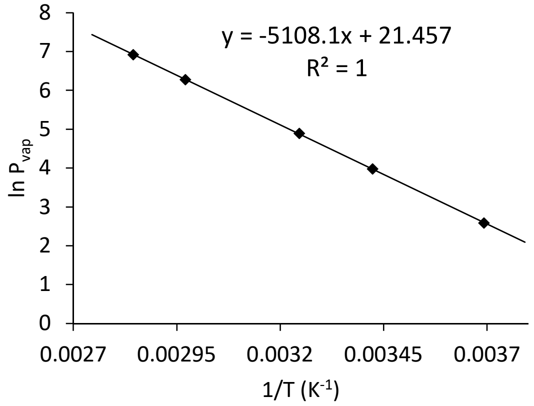
T (°C)	-2.3	19.0	34.9	63.5	78.4
P_{vap} (mbar)	13.3	53.3	133.3	533.3	1013.
P_{vap} (mm Hg)	10.0	40.0	100.0	400.0	760.0

Answer: The plan is to use the Clausius-Clapeyron equation in its linear form to find the enthalpy of vaporization from a plot of ln P vs. 1/T. The enthalpy of vaporization is then used to find the vapor pressure at 1.00 bar to give the standard boiling point.

Any units may be used for the pressure. The following spreadsheet was developed.

T (°C)	T (K)	P_{vap} (mbar)	1/T (K^{-1})	ln P_{vap}
-2.3	270.85	13.3	0.003692	2.5878
19	292.15	53.3	0.003423	3.9759
34.9	308.05	133.3	0.003246	4.8926
63.5	336.65	533.3	0.00297	6.2791
78.4	351.55	1013	0.002845	6.9207

slope	-5108.1	21.45713	intercept
±	18.43946	0.059922	±
r^2	0.999961	0.012598	st.dev. y
F	76740.03	3	df
ss_{reg}	12.18002	0.000476	ss_{resid}



The slope has three significant figures, and slope = – $\Delta_{sub}H_m/R$, giving:

$$\Delta_{vap}H_m = -(-5108.1\text{ K})(8.314\text{ J K}^{-1}\text{ mol}^{-1}) = 4.247\text{x}10^4\text{ J mol}^{-1} = 42.47\text{ kJ mol}^{-1}$$

The Clausius-Clapeyron equation for two data points is:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The normal boiling point, which corresponds to 1.01325 bar, is 351.55 K. Applying the Clausius-Clapeyron equation from 351.55 K and 1.01325 bar to a final pressure of 1.000 bar gives:

$$\ln\left(\frac{1.000}{1.01325}\right) = -\frac{4.247\text{x}10^4\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{T_b^*} - \frac{1}{351.55\text{ K}}\right)$$

$$-0.013163/-5108.1 = \left(\frac{1}{T_b^*} - 2.84455\text{x}10^{-3}\text{ K}\right) \qquad T_b^* = 351.52\text{ K} = 78.4°\text{C}$$

The difference between the normal boiling point and standard boiling point is within experimental error for ethanol.

7. The vapor pressure of benzoic acid is 0.133 bar at 186.2°C and 0.533 bar at 227.0°C. Calculate the standard boiling point.

Answer: The plan is to calculate the enthalpy of vaporization using the Clausius-Clapeyron equation, and then use the same equation to calculate the temperature for which the vapor pressure is 1.000 bar.

The Clausius-Clapeyron equation is:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{or} \quad \ln\left(\frac{0.533}{0.133}\right) = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{500.2\text{ K}} - \frac{1}{459.4\text{ K}}\right)$$

Giving: $$1.388 = -\frac{\Delta_{vap}H_m}{R}\,(-1.7775\text{x}10^{-4}\text{ K}^{-1})$$

Make sure to keep sufficient significant figures for the temperature dependent term. Solving for the enthalpy change:

$$\Delta_{vap}H_m = -\frac{0.7651}{-1.7775\text{x}10^{-4}\text{ K}^{-1}}\,(8.3145\text{ J K}^{-1}\text{ mol}^{-1}) = 6.493\text{x}10^4\text{ J mol}^{-1} = 64.93\text{ kJ mol}^{-1}$$

Applying the Clausius-Clapeyron equation from 227.0°C and 0.533 bar to a final pressure of 1.000 bar gives:

$$\ln\left(\frac{1.000}{0.533}\right) = -\frac{6.493\text{x}10^4\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{T_b^*} - \frac{1}{500.2\text{ K}}\right)$$

$$-0.6292/7809.7 = \left(\frac{1}{T_b^*} - 1.9992\text{x}10^{-3}\text{ K}\right) \qquad T_b^* = 521.1\text{ K} = 247.9°\text{C}$$

8. For methanol, the enthalpy of fusion is 3.215 kJ mol^{-1} and the volume change on melting is 2.75 mL mol^{-1} at the standard melting point of 175.59 K.[1] The enthalpy of vaporization is 35.21 kJ mol^{-1} at the standard boiling point of 337.8 K. Estimate the triple point temperature and pressure for methanol. Assume constant transition enthalpies over the temperature range. [Hint: you may use the Goal Seek option in Excel.]

Answer: The triple point is at the intersection of the melting curve and the vapor pressure curve. The plan is to find the temperature that gives the same equilibrium phase transition pressures for melting and vaporization. The Clausius-Clapeyron equation, Eq. 17.1.14°, is used to find the vapor pressure at the given temperature. Eq. 17.1.24 is used to find the pressure necessary for the melting temperature to equal the given temperature.

Note that P° = 1.00 bar = $1.000\text{x}10^5$ Pa with the corresponding standard melting point, T_m°, and standard boiling point T_b°. The change in melting point is then:

$$\Delta T = \frac{T_m^\circ\,\Delta_{fus}V_i}{\Delta_{fus}H_i}\,\Delta P \qquad \text{or} \qquad P = P^\circ + (T - T_m^\circ)/\mathcal{K} \qquad 1$$

with the constant $\mathcal{K}$ given by:

$$\mathcal{K} = \frac{T_m^\circ\,\Delta_{fus}V_i}{\Delta_{fus}H_i} = \frac{175.59\text{ K }(2.75\text{x}10^{-6}\text{ m}^3\text{ mol}^{-1})}{3.215\text{x}10^3\text{ J mol}^{-1}} = 1.502\text{x}10^{-7}\text{ K Pa}^{-1} \qquad 2$$

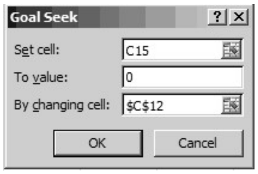
The Clausius-Clapeyron equation, with the reference pressure at P°, is given by Eq. 17.1.14°:

$$P = P^\circ\, e^{-\frac{\Delta_{tr}H_i}{R}\left(\frac{1}{T} - \frac{1}{T_b^\circ}\right)} = 1\text{x}10^5\text{ Pa }\, e^{-\frac{35.31\text{x}10^3\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{T} - \frac{1}{337.8\text{ K}}\right)} \qquad 3$$

A spreadsheet was written to do these two calculations at a variable input temperature (in cell C12). This temperature was changed until the calculated vapor pressure and equilibrium melting pressure were equal.

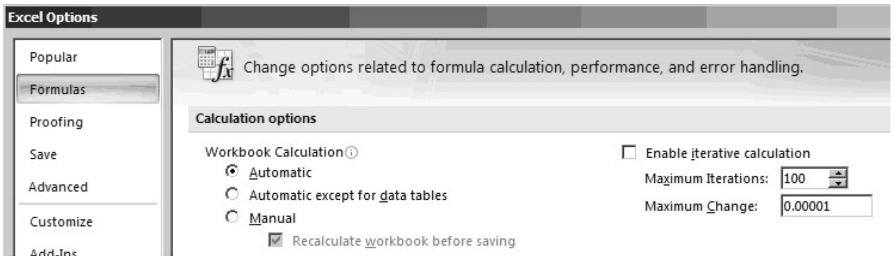
A1	B	C	D	E
2				
3	$\Delta_{fus}H$	3.215	kJ mol^{-1}	
4	$\Delta_{fus}V$	2.75	mL mol^{-1}	
5	$T_{melt}°$	175.59	K	
6	$\mathcal{K}$	1.50194E-07	K Pa^{-1}	
7				
8	$\Delta_{vap}H$	35.21	kJ mol^{-1}	
9	$T_b°$	337.8	K	
10	R	8.3145	J K^{-1} mol^{-1}	
11				
12	T	175.5749808	K	← change this value
13	P_{melt}	0.93221509	Pa	
14	P_{vap}	0.932215156	Pa	
15	ΔP	-6.6131E-08	Pa	← to get a small pressure difference

The equation for the melting constant, $\mathcal{K}$, in cell C6 is "=C5*C4*1E-6/(C3*1000)". In cell C13 is Eq. 1 for the equilibrium melting pressure: "=1E5+(C12-C5)/C6". In cell C14 is Eq. 3 for the vapor pressure: "=1E5*exp(-C8*1000/C10*(1/C12-1/C9))". The search for the triple point can be easily implemented using the Goal Seek option. The Goal Seek option is accessed from the Data tab and "What If Analysis":



Set cell: C15
To value: 0
By changing cell: $C$12

The Goal Seek option uses linear iteration to find the best value. You must be careful, however, to ensure that the calculation has converged. The convergence criteria are given in the Excel options window, which is accessed by clicking on the "Office button". For this calculation, the maximum change was decreased from the default value of 0.001 to a more precise setting of 0.00001, as shown below:



Change options related to formula calculation, performance, and error handling.

Calculation options

Workbook Calculation
● Automatic
○ Automatic except for data tables
○ Manual
☑ Recalculate workbook before saving

☐ Enable iterative calculation
Maximum Iterations: 100
Maximum Change: 0.00001

The final result is at 0.923 Pa and 175.57 K, only slightly less than the standard melting point. The literature value for the triple point is 175.5 K. The triple point is only slightly different than the standard melting point because the P vs. T curve for the melting transition is very steep. That is, the curve has a large slope of $1/\mathcal{K} = 6.7\text{x}10^6$ Pa K^{-1} resulting in small melting point changes even for large changes in pressure.

9. The sublimation pressure versus temperature of ammonia is ln P = 23.03 – 3754./T. The vapor pressure of liquid ammonia is ln P = 19.49 – 3063./T. (a) Find the enthalpy of sublimation and the enthalpy of vaporization. (b). Calculate the triple point for ammonia. (c). Find the enthalpy of fusion at the triple point. [2]

Answer: (a). The Clausius-Clapeyron equation, Eq. 17.1.16°, is:

$$\ln P = -\Delta_{tr}H_i/R\ (1/T) + b.$$

giving for sublimation: $-\Delta_{sub}H_i/R = -3754.$ or $\Delta_{sub}H_i = 31.21\ \text{kJ mol}^{-1}$
and for vaporization: $-\Delta_{vap}H_i/R = -3063.$ or $\Delta_{vap}H_i = 25.47\ \text{kJ mol}^{-1}$

(b). At the triple point solid, liquid, and vapor are in equilibrium. The sublimation pressure and the vapor pressure of the liquid are equal:

$$23.03 - 3754./T_{tp} = 19.49 - 3063./T_{tp}$$
$$3.54 = 691./T_{tp}$$

Solving for the triple point gives: $T_{tp} = 195.$ K.
(c). At the triple point the solid, liquid, and vapor are in equilibrium. The enthalpies of the phase transitions are state functions and independent of the path:

$$NH_3\ (s) \xrightarrow{\Delta_{fus}H_i} NH_3\ (l) \xrightarrow{\Delta_{vap}H_i} NH_3(g) \quad \text{is equivalent to} \quad NH_3\ (s) \xrightarrow{\Delta_{sub}H_i} NH_3\ (g)$$

giving: $\Delta_{sub}H_i = \Delta_{fus}H_i + \Delta_{vap}H_i$

$$31.21\ \text{kJ mol}^{-1} = \Delta_{fus}H_i + 25.47\ \text{kJ mol}^{-1}$$
$$\Delta_{fus}H_i = 31.21\ \text{kJ mol}^{-1} - 25.47\ \text{kJ mol}^{-1} = 5.74\ \text{kJ mol}^{-1} \qquad \text{at } 195.\ \text{K}$$

10. Integrate the differential form of the Clausius-Clapeyron equation:

$$d\ln P = \frac{\Delta_{tr}H_i}{RT^2}\,dT$$

from an initial temperature of T_o to a final temperature of T. In this equation T is the equilibrium phase transition temperature at the given pressure. Assume the phase transition has a molar enthalpy change given by:

$$\Delta_{tr}H_{i,T} = \Delta_{tr}H_{i,T_o} + \Delta_{tr}C_{p,i}\,(T - T_o)$$

where $\Delta_{tr}C_{p,m}$ is the change in heat capacity for the phase transition, which is assumed to be a constant. Show that the result is:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{\Delta_{tr}H_{i,T_o}}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}}{R}\ln\left(\frac{T}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}T_o}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

Answer: Substituting the temperature dependent enthalpy change into the Clausius-Clapeyron equation gives:

$$d\ \ln P = \frac{\Delta_{tr}H_{i,T_o}}{RT^2}\,dT + \frac{\Delta_{tr}C_{p,i}}{RT}\,dT - \frac{\Delta_{tr}C_{p,i}T_o}{RT^2}\,dT$$

Applying the integration limits:

$$\int_{T_o}^{T} d\ \ln P = \int_{T_o}^{T} \frac{\Delta_{tr}H_{i,T_o}}{RT^2}\,dT + \int_{T_o}^{T} \frac{\Delta_{tr}C_{p,i}}{RT}\,dT - \int_{T_o}^{T} \frac{\Delta_{tr}C_{p,i}T_o}{RT^2}\,dT$$

Factoring out the constants gives:

$$\ln\left(\frac{P}{P_o}\right) = \frac{\Delta_{tr}H_{i,T_o}}{R}\int_{T_o}^{T} \frac{1}{T^2}\,dT + \frac{\Delta_{tr}C_{p,i}}{R}\int_{T_o}^{T} \frac{1}{T}\,dT - \frac{\Delta_{tr}C_{p,i}T_o}{R}\int_{T_o}^{T} \frac{1}{T^2}\,dT$$

The integrals are then:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{\Delta_{tr}H_{i,T_o}}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}}{R}\ln\left(\frac{T}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}T_o}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right)$$

Note that the first and last terms may be combined:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{(\Delta_{tr}H_{i,T_o} - T_o\,\Delta_{tr}C_{p,i})}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right) + \frac{\Delta_{tr}C_{p,i}}{R}\ln\left(\frac{T}{T_o}\right)$$

Grouping all the terms in P_o and T_o together into a constant, a, gives:

$$\ln P = a - \frac{b}{T} - c\ln T$$

where $b = (\Delta_{tr}H_{i,To} - T_o\Delta_{tr}C_{p,m})/R$ and $c = -\,\Delta_{tr}C_{p,i}/R$. Reference handbooks sometimes list the vapor pressure of liquids in this form.

11. Reference handbooks sometimes list the vapor pressure of liquids in the form:

$$\ln P = A - \frac{B}{T} - C\ln T + D\,T$$

Show that the result from the last problem can be rewritten in this form. Use *General Pattern ℘4: Exponential Temperature Dependence* as a guide.

Answer: Note that taking a common denominator in the temperature dependent portion of the last term from Problem 6 and approximating $TT_o \approx T_o^2$ gives:

$$\frac{\Delta_{tr}C_{p,m}T_o}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right) = \frac{\Delta_{tr}C_{p,m}T_o}{R}\left(\frac{T_o - T}{TT_o}\right) \approx \frac{\Delta_{tr}C_{p,m}T_o}{R}\left(\frac{T_o - T}{T_o^2}\right) \approx -\frac{\Delta_{tr}C_{p,m}}{RT_o}(T - T_o)$$

The last term from Problem 6 can then be rewritten as:

$$\ln\left(\frac{P}{P_o}\right) = -\frac{\Delta_{tr}H_{m,T_o}}{R}\left(\frac{1}{T}-\frac{1}{T_o}\right) + \frac{\Delta_{tr}C_{p,m}}{R}\ln\left(\frac{T}{T_o}\right) - \frac{\Delta_{tr}C_{p,m}}{RT_o}\,(T - T_o)$$

Grouping all the terms in P_o and T_o together into a constant A gives:

$$\ln P = A - \frac{\Delta_{tr}H_{m,T_o}}{RT} + \frac{\Delta_{tr}C_{p,m}}{R}\ln T - \frac{\Delta_{tr}C_{p,m}}{RT_o}\,T$$

Compariong the reference handbook form with this last equation gives:

$$\ln P = A - \frac{B}{T} - C\ln T + D\,T$$

Comparison shows that $B = \frac{\Delta_{tr}H_{m,T_o}}{R}$, $C = -\frac{\Delta_{tr}C_{p,m}}{R}$, and $D = -\frac{\Delta_{tr}C_{p,m}}{RT_o}$

12. Long's Peak in the Colorado Rocky Mountains is 3962. m high. What is the boiling point of water at this altitude? Assume a constant temperature of 20.0°C (see Problem 1.15) and the pressure at sea level is 1.00 atm. The enthalpy of vaporization of water is 42.00 kJ mol^{-1}.

Answer: Assuming the atmospheric pressure at sea level is 1 atm and the mole fraction averaged molar mass of air is 28.8 g mol^{-1} gives the barometric formula as:

$$\left(\frac{-\mathcal{M}_{gas}\,g\,h}{RT}\right) = \frac{-28.8\text{x}10^{-3}\text{ kg}(9.807\text{ m s}^{-2})(3962.\text{ m})}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}(293.15\text{ K})} = -0.4591$$

$$P = P_o\, e^{\left(\frac{-\mathcal{M}_{gas}\,g\,h}{RT}\right)} = 1.00\text{ atm } e^{-0.4591} = 0.632\text{ atm}$$

The enthalpy of vaporization of water at 100°C is $\Delta_{vap}H° = 42.00$ kJ mol^{-1}. The boiling point is the temperature that gives the vapor pressure equal to the ambient pressure. Applying the Clausius-Clapeyron equation from 100.0°C and 1.00 atm to a final pressure of 0.632 atm:

$$\ln\left(\frac{0.632}{1.00}\right) = -\frac{4.200\text{x}10^{4}\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{T_b^*} - \frac{1}{373.2\text{ K}}\right)$$

$$0.4589/5051.4 = \left(\frac{1}{T_b^*} - 2.6799\text{x}10^{-3}\text{ K}\right) \qquad T_b^* = 360.9\text{ K} = 87.8°C$$

13. For non-ideal gases, from Eq. 7.5.2, PV = z nRT. Find the corresponding integrated form of the Clausius-Clapeyron equation for liquid-vapor or solid-vapor equilibrium. In other words, correct Eq. 17.1.13° for vapor non-ideality. Assume z and $\Delta_{tr}H_m$ are constant over the temperature range for the integration.

Answer: For non-ideal gases, from Eq. 7.5.2, PV = z nRT and Eq. 17.1.9° is corrected to give:

$$\Delta_{tr}V_m \approx V_m(\text{vapor}) = \frac{z\,RT}{P} \qquad \text{(equilibrium)} \qquad 1$$

Substituting this last relationship into the Clapeyron equation gives:

$$\frac{dP}{dT} = \frac{\Delta_{tr}H_m\,P}{zRT^2} \qquad \text{(equilibrium)} \qquad 2$$

Separating variables gives:

$$\frac{dP}{P} = \frac{\Delta_{tr}H_m}{zRT^2}\,dT \qquad \text{(equilibrium)} \qquad 3$$

Integrating Eq. 3 assuming both $\Delta_{tr}H_m$ and z are constant over the temperature range:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{tr}H_m}{zR}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{(equilibrium, cst. z \& }\Delta_{tr}H_m) \qquad 4$$

or alternatively, a plot of ln P versus 1/T gives a straight line with slope $-\Delta_{tr}H_m/(zR)$.

14. Calculate the vapor pressure of methanol at 20.0°C under a total ambient pressure of 10.0 bar of air. The vapor pressure of methanol at 20.00°C is 0.1530 bar, under its own vapor pressure.

Answer: The plan is to use Eq. 17.1.31° to determine the vapor pressure under the ambient conditions.

The molar volume of pure liquid methanol is $V_{MeOH} = \mathcal{M}/d = 32.04\ \text{g mol}^{-1}/0.791\ \text{g mL}^{-1} = 40.51\ \text{mL mol}^{-1} = 4.051\text{x}10^{-5}\ \text{m}^3\ \text{mol}^{-1}$.

$$\ln\frac{P_{\beta,2}}{P_{\beta,1}} = \frac{V_i(\alpha)}{RT}\,(P_2 - P_1)$$

$$\ln\frac{P_{\beta,2}}{0.1530\ \text{bar}} = \frac{4.051\text{x}10^{-5}\ \text{m}^3\ \text{mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}(293.15\ \text{K})}\,(10.0\ \text{bar} - 0.1530\ \text{bar})(1\text{x}10^5\text{Pa}/1\ \text{bar})$$

$$= 0.01637$$

$P_{\beta,2} = 0.1555$ bar

In torr the new pressure is 116.7 torr and the vapor pressure under pure vapor is 114.8 torr, which is roughly a 2% difference.

15. Particulates released from volcanic eruptions can be a significant source of heavy metals in the environment. The magma under a volcano is at high temperature and total pressure. Under these circumstances, normally non-volatile substances can have a significant vapor pressure. NaCl and heavy metal chlorides are found in the vapor phase at high total pressure as volatile molecular species. The concentration of Pb in the minerals formed from the vapor phase in a volcano is much higher than in the original magma. At high pressure, the vapor above a magma is non-ideal and the fugacity must be used. Eq. 17.1.30 assumes the vapor behaves as an ideal gas. Let $P_{\beta,o}$ be the vapor pressure of the pure liquid under its pure vapor pressure. Assume the

pure vapor pressure at the given temperature is sufficiently small that the pure vapor is ideal, giving $f_{\beta,o} = P_{\beta,o}$. Show that the fugacity of the vapor, f_β, in equilibrium with the pure liquid at the elevated total pressure, P, is then:

$$\ln \frac{f_\beta}{P_{\beta,o}} = \frac{V_i(\alpha)}{RT}(P - P_{\beta,o})$$

Answer: The plan is to repeat the derivation of Eqs. 17.1.24-17.1.29°, but with the partial vapor pressure replaced by the fugacity, $\mu_i(g) = \mu_i°(g) + RT \ln f_\beta/P°$.

Consider the partial vapor pressure of a substance, P_β, with a total applied pressure of P. At constant temperature, from Eq. 17.1.26:

$$V_i(\alpha)\, dP = d\mu_i(\beta,P',T') \qquad \text{(equilibrium, cst. T)} \qquad (17.1.26)$$

The chemical potential of the real vapor is dependent on the fugacity of the vapor above the liquid, Eq. 16.6.20°:

$$\mu_i(g) = \mu_i°(g) + RT \ln f_\beta/P° \qquad 1$$

The change in chemical potential is given as:

$$d\mu_i(g) = RT\, d \ln f_\beta \qquad 2$$

Substitution of this last equation into Eq. 17.1.26 gives the dependence of the fugacity on applied pressure:

$$RT\, d \ln f_\beta = V_i(\alpha)\, dP \qquad \text{(equilibrium, cst. T)} \qquad 3$$

Integration of this last equation from the initial vapor fugacity $f_{\beta,1}$ and applied pressure P_1 to the final vapor fugacity $f_{\beta,2}$ and applied pressure P_2, assuming that the molar volume of the liquid is constant, gives:

$$\ln \frac{f_{\beta,2}}{f_{\beta,1}} = \frac{V_i(\alpha)}{RT}(P_2 - P_1) \qquad \text{(equilibrium, cst. T)} \qquad 4$$

Let P_1 be the vapor pressure of the liquid under its pure vapor pressure, $P_1 = P_{\beta,o}$. Assume the pure vapor pressure at the given temperature is sufficiently small that the pure vapor is essentially ideal, then $f_{\beta,o} = P_{\beta,o}$. The fugacity of the vapor, f_β, at the elevated total pressure, P, is then:

$$\ln \frac{f_\beta}{P_{\beta,o}} = \frac{V_i(\alpha)}{RT}(P - P_{\beta,o}) \qquad \text{(equilibrium, } P_{\beta,o} \text{ small, cst. T)} \qquad 5$$

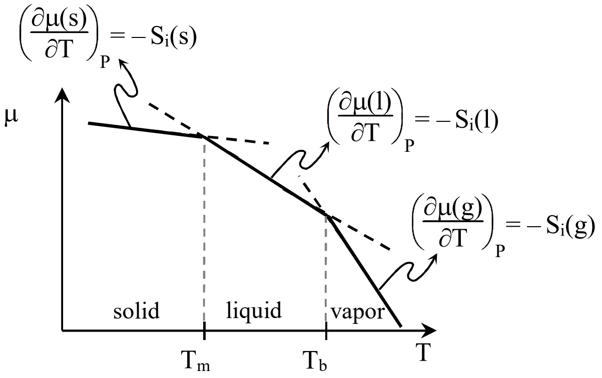
The vapor phase above magmas is composed primarily of water vapor and CO_2. Water at high temperature, and especially above the critical point, is much less polar than at room temperature. The decreased polarity of water decreases the degree of dissociation of electrolytes. The interaction of NaCl and heavy metal molecular chlorides with water vapor is strong, which gives small fugacity coefficients. The fugacity is given by $f_\beta = \gamma_\beta P_\beta$. However, Eq. 5 fixes the value of the fugacity, so that a small fugacity coefficient increases the partial vapor pressure: $P_\beta = f_\beta/\gamma_\beta$. The partial vapor pressure above the liquid is increased by both the increase in total pressure and favorable interactions with the other vapor phase components. Lead is considered a "volatile" element by volcanologists.

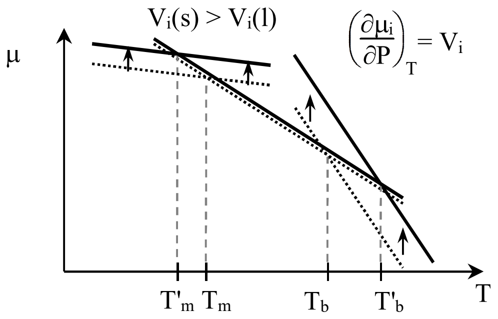
16. Redraw Figure 17.1.1 for water.

Answer: The slope of the chemical potential versus temperature at constant pressure is the negative of the entropy for each individual phase. So Figure 17.1.1a is qualitatively correct for water. An increase in pressure increases the chemical potential of each phase, proportional to the pure molar volume of the phase, through the molar thermodynamic force:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i$$

For water, $V_{H_2O}(s) > V_{H_2O}(l)$, because of the open structure caused by the extensive network of hydrogen bonds in the solid. The increase in chemical potential for solid water is greater than for liquid water. The melting and boiling points are at the intersections of the new chemical potential curves. The result is a decrease in melting point and an increase in boiling point.

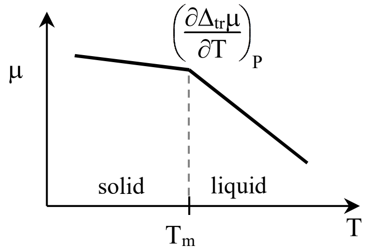




17. Some property needs to be discontinuous to observe a phase transition. What property is discontinuous in a pure Ehrenfest second-order phase transition?

Answer: The heat capacity curve as a function of temperature is discontinuous for a second-order phase transition. For a first-order phase transition, the entropy as a function of temperature is discontinuous.

18. Find the difference in slope across the melting transition for the chemical potential versus temperature curve, $(\partial\Delta_{tr}\mu/\partial T)_P$, at standard pressure.



Answer: The plan is to use Eq. 17.2.3 and reference tabulations.

Rearranging Eq. 17.2.3 to find the difference in slope across the phase transition gives:

$$\left(\frac{\partial \Delta_{tr}\mu}{\partial T}\right)_P = -\Delta_{tr}S_i$$

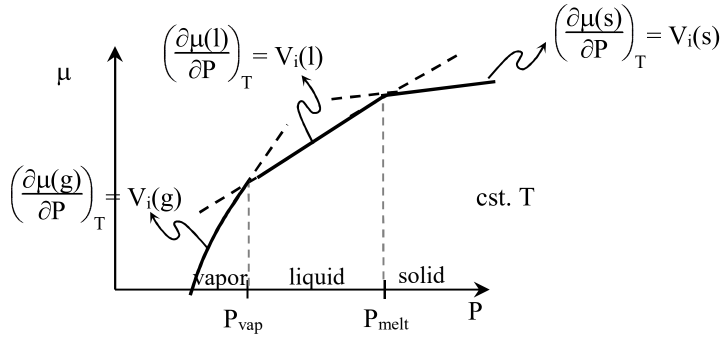
The standard transition temperature is 273.15 K for water, where $\Delta_{tr}S^{o}_{H2O} = S^{o}_{H2O}\,(l) - S^{o}_{H2O}\,(s) = 22.00\ J\ K^{-1}\ mol^{-1}$ and the corresponding difference in slope is $-22.00\ J\ K^{-1}\ mol^{-1}$. Liquid water has higher entropy than solid water and then a more negative slope.

19. Draw the chemical potential versus pressure curves for the solid, liquid, and vapor phases of a pure substance, at constant temperature. Assume that $V_i(s) < V_i(l)$. Describe the process that occurs at the intersection of the chemical potential curves.

Answer: The slope of the chemical potential versus pressure is given by the molar thermodynamic force:

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = V_i$$

The chemical potential of a substance increases with pressure. The assumption that $V_i(s) < V_i(l)$, which corresponds to a "normal" substance, shows that the slope of the liquid curve is greater than the solid. The solid phase is the stable phase at high pressure:

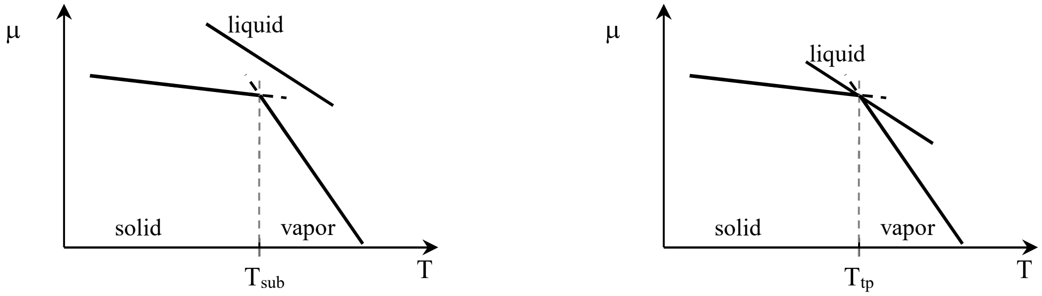


Starting at low pressure, as the pressure is increased, when the pressure exceeds the equilibrium vapor pressure at the chosen temperature, the liquid phase is more stable. The chosen constant temperature is the equilibrium melting point at a specific pressure, P_{melt}. When the pressure exceeds P_{melt}, the solid phase is the stable phase. The intersection of the vapor and liquid curves is the equilibrium boiling point at applied pressure P_{vap}. The intersection of the liquid and solid curves is the equilibrium melting point at applied pressure P_{melt}.

20. (a). Sketch the chemical potential curves versus temperature for the solid, liquid, and vapor phases of substance at a constant pressure below the triple point and (b) for a substance at the triple point pressure.

Answer: The plan is to redraw Figure 17.1.1a for (a) the direct transition from the solid to the vapor phase with no intersection with the liquid line, and (b) for a system where the chemical potential of all three phases is equal at the triple point temperature, T_{tp}.

The slope of the chemical potential versus temperature at constant pressure is the negative of the entropy for each individual phase. So the slopes in Figure 17.1.1a are qualitatively correct. However, for pressures below the triple point pressure, the chemical potential of the liquid phase must be higher than either the solid or the vapor throughout the temperature range, otherwise the liquid phase will form. The equilibrium sublimation temperature, T_{sub}, and triple points are at the intersections of the new chemical potential curves, Figure P17.1.



(a) below triple point pressure (b). at the triple point pressure

Figure P17.1: The chemical potential versus temperature for a substance (a). below the triple point pressure, and (b). at the triple point pressure.

<u>21</u>. If first-order phase transitions are "completely cooperative," how can two-phase systems exist at equilibrium? For example, how can ice and liquid water coexist at equilibrium at the equilibrium phase transition temperature?

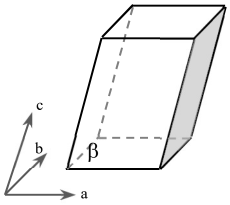
Answer: First-order phase transitions are completely cooperative. The molecules cooperate with each other in gaining new motional freedom; when one molecule gains motional energy then other nearby molecules find it easier to add motional energy. The motions of the molecules are correlated throughout the phase at the phase transition temperature. However, first-order phase transitions have a finite enthalpy for the phase transition (or so-called latent heat). Energy transfer from the surroundings is necessary for the phase transition to occur. Thermal energy is the "limiting reagent" for the phase transition. Once energy is transferred into the two-phase system from the surroundings, additional molecules can make the phase transition, <u>without an increase in temperature</u>. In a first-order phase transition, all the molecules undergo the phase transition together, subject only to the availability of thermal energy.

<u>22</u>. Use the concept of correlation length and domain size to explain why the heat capacity of a substance increases as the temperature increases to the critical point.

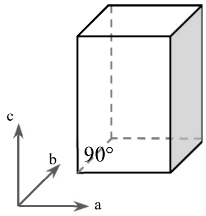
Answer: The plan is to note that thermally activating motional degrees of freedom increases the heat capacity of a substance.

As the temperature increases near the critical point, the correlation length of the intermolecular cooperation increases. As the correlation length increases, the domain size increases, which increases the fraction of the substance in the more mobile, higher entropy phase. The increase in motion corresponds to activating motional degrees of freedom, for example segmental torsions in the fatty acid chains in a phospholipid. The larger fraction of molecules in the more mobile domains increases the heat capacity of the sample.

23. The monoclinic and orthorhombic unit cells are illustrated, below. The unit cell lengths for both unit cells are all different, a ≠ b ≠ c. The orthorhombic unit cell has all 90° angles between the unit cell directions, $\alpha = \beta = \gamma = 90°$. The monoclinic unit cell has one angle not equal to 90°, $\alpha = \gamma = 90°$, β.



Monoclinic



Orthorhombic

Methanol crystallizes into long hydrogen-bonded chains. There are two crystalline forms. Crystal II has a monoclinic unit cell and is the low temperature form. Crystal I has an orthorhombic unit cell and is the high temperature form. The difference is a small displacement of the hydrogen-bonded chains in the direction perpendicular to the direction of the chains. The solid-solid phase transition temperature is 157.4 K at 1 atm. The transition was reported to be second-order. Carlson and Westrum redetermined the heat capacity of very pure methanol samples to determine the thermodynamic parameters for the phase transition, Figure P17.1.[1] Crystal I readily super-cools, so heat capacity data for this phase is available below the equilibrium phase transition temperature. Is the transition first or second order?

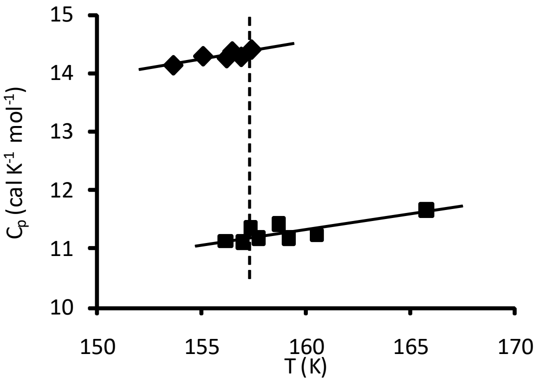
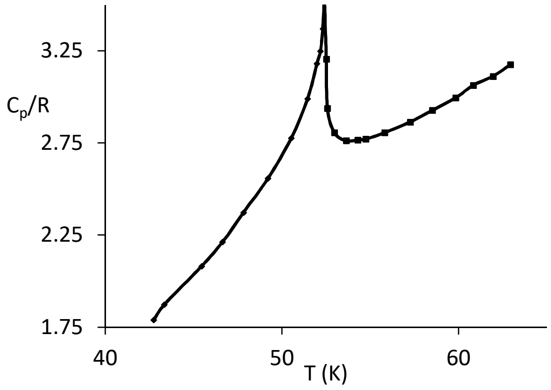


Figure P17.1: Heat capacity data for 99.98 mol% methanol near the solid-solid phase transition at 157.4 K.

Answer: The heat capacity is discontinuous and slowly varying at temperatures less than and greater than the solid-solid phase transition temperature. In other words, there are no pre-transition effects. The transition is first-order.

24. $NiCl_2$ has a solid-state magnetic phase transition at 52 K. The low temperature phase is anti-ferromagnetic, and the high temperature phase is paramagnetic. Antiferromagnetic phases are an ordered lattice of unpaired electrons that alternate spin-up and spin-down. In the absence of an external magnetic field, paramagnetic phases also have an equal, or nearly equal, number of electrons spin-up and spin-down, distributed at random. The paramagnetic phase is at higher entropy at a given finite temperature. A plot of the heat capacity as a function of temperature is shown below.[3] Characterize this solid-state phase transition.



antiferromagnetic: ↑↓↑↓↑↓↑↓↑↓↑↓↑↓
ferromagnetic: ↑↑↑↑↑↓↑↑↑↑↑↑↑↑
paramagnetic: ↑↓↑↑↑↓↓↑↓↓↑↓↑↓

Answer: The transition is lambda-type, second-order. Extensive pre-transition effects are seen approaching the critical temperature from both the high and low temperature side of the transition. Experimental uncertainty prevents the determination of the heat capacity at the critical temperature. Therefore, it is usually impossible to determine if the heat capacity is finite or if the heat capacity diverges to infinity at the critical temperature. Refrigerator magnets are ferromagnetic. The degree of ordering for ferro- and antiferromagnetic substances decreases with increasing temperature. Increasing the temperature provides thermal energy that increases the probability of a spin flip that decreases the order compared to the perfect zero-Kelvin phase.

Literature Cited:

1. H. G. Carlson, E. F. Westrum, Jr., "Methanol: heat capacity, enthalpies of transition and melting, and thermodynamic properties from 5-300K," *J. Chem. Phys.*, **1971**, *54*, 1464-1471.
2. F. C. Andrews, *Thermodynamics: Principles and Applications*, Wiley-Interscience, New York, NY, 1971. Problem 25.13.

3. R. H. Busey, W. F. Giauque, “The Heat Capacity of Anhydrous $NiCl_2$ from 15 to 300 K. The Antiferromagnetic Anomaly near 52 K. Entropy and Free Energy,” *J. Am. Chem. Soc.*, **1953**, *75*, 4443.

Chapter 18 Problems: Ideal Solutions

1. The volume of a solution of methanol in water is less than the corresponding sum of the pure components. The solution temperature rises upon mixing. (a). Does this solution show positive or negative deviations from ideality? (b). Are the forces better described as A-B > A-A, B-B or rather A-B < A-A, B-B? (c). Is the vapor pressure of the solution greater than or less than predicted using Raoult's Law? (d). Is the escaping tendency of methanol from the solution greater than or less than that predicted using Raoult's Law? (e). Is the boiling point of the solution greater than or less than predicted using Raoult's Law? (f). Which is larger, the pure vapor pressure of methanol or the Henry's Law constant of methanol in water?

Answers: (a). Negative deviations; the combined volume is less than the corresponding sum of the pure components. (b). A-B > A-A, B-B; the forces are favorable in solution. (c). The partial vapor pressures of each component and the total vapor pressures are less than predicted by Raoult's Law. (d). The escaping tendency is measured by the vapor pressure; the escaping tendency of methanol from the solution is less than predicted by Raoult's Law. (e). Since the vapor pressures are less, the solution must be heated to a higher temperature to have the total vapor pressure of the solution equal to ambient pressure, as compared to the Raoult's Law prediction. (f). $P^*_B > k_{H,B}$, as is diagrammed in Figure 18.3.3a for negative deviations from ideality.

2. A 2.412 m solution of ethanol in water containing 1000.00 g of solvent has a total volume of 1133.08 mL. The partial molar volume of ethanol in this solution is 53.890 mL mol^{-1}. Calculate the partial molar volume of water in this solution.

Answer: The number of moles of solute in a solution containing 1000.00 g of solvent is:

$$n_B = m_B\ (1\ \text{kg})$$

For a 2.412 m solution containing 1000.00 g of solvent, n_B= 2.412 mol. Using Eq. 18.1.3:

$$V = \overline{V}_A\, n_A + \overline{V}_B\, n_B$$

$$1133.08\ \text{mL} = \overline{V}_A\ 1000.0\ \text{g}/18.0153\ \text{g mol}^{-1} + 53.890\ \text{mL mol}^{-1}(2.412\ \text{mol})$$

$$\overline{V}_A = (1133.08\ \text{mL} - 129.98\ \text{mL})(18.0153\ \text{g mol}^{-1}/1000.0\ \text{g}) = 18.0711\ \text{mL mol}^{-1}$$

3. The density of a solution can be accurately determined by measuring the vibration frequency of a U-shaped tube filled with the solution. The volume of a solution containing 1 kg of solvent can be determined from the density of the solution. (a). Show that:

$$V^{1\text{kg}} = \frac{n_A\mathfrak{M}_A + n_B\mathfrak{M}_B}{d} = \frac{1000\ \text{g} + m_B\ (1\ \text{kg})\mathfrak{M}_B}{d}$$

where $\mathfrak{M}_A$ is the molar mass of the solvent, $\mathfrak{M}_B$ is the molar mass of the solute, m_B is the molality of the solute, and d is the density of the solution.
(b). The density of a 5.4266 m solution of ethanol in water is 0.96808 g mL^{-1} at 25°C. The partial molar volume ethanol in this solution is 54.183 mL mol^{-1}. Calculate the partial molar volume of water in this solution.

Answer: (a). The number of moles of solute in a solution containing 1000.00 g of solvent is: $n_B = m_B$ (1 kg). The total mass of the solution, solute plus solvent, is $n_A\mathfrak{M}_A + n_B\mathfrak{M}_B$. The volume of the solution is the mass divided by the density:

$$V^{1kg} = \frac{\text{mass solution}}{\text{density of solution}} = \frac{n_A\mathfrak{M}_A + n_B\mathfrak{M}_B}{d} = \frac{1000\text{ g} + m_B\text{ (1 kg)}\mathfrak{M}_B}{d}$$

For the particular solution in this problem with $\mathfrak{M}_B = 46.06904$ g mol^{-1} for ethanol:

$$V^{1kg} = \frac{1000.00\text{ g} + 5.4266\text{ m (1 kg)(46.06904 g mol}^{-1})}{0.96808\text{ g mL}^{-1}} = 1291.21_4\text{ mL}$$

Using Eq. 18.1.3 to find the partial molar volume of the solvent:

$$V = \bar{V}_A\, n_A + \bar{V}_B\, n_B$$

$$1291.21_4\text{ mL} = \bar{V}_A\ 1000.0\text{ g}/18.0153\text{ g mol}^{-1} + 54.183\text{ mL mol}^{-1}(5.4266\text{ mol})$$

$$\bar{V}_A = (1291.21_4\text{ mL} - 294.02_9\text{ mL})(18.0153\text{ g mol}^{-1}/1000.0\text{ g}) = 17.964_6\text{ mL mol}^{-1}$$

4. The relationship between density and the volume of solution that contains 1 kg of solvent is (derived in Problem 3):

$$V^{1kg} = \frac{n_A\mathfrak{M}_A + n_B\mathfrak{M}_B}{d} = \frac{1000\text{ g} + m_B\text{ (1 kg)}\mathfrak{M}_B}{d}$$

The density at 25°C as a function of the concentration of *p*-toluenesulfonic acid in water is given below. The molar mass of *p*-toluenesulfonic acid is 172.205 g mol^{-1}. Calculate the partial molar volumes of *p*-toluenesulfonic acid and water at 2.0000 m at 25°C.[1]

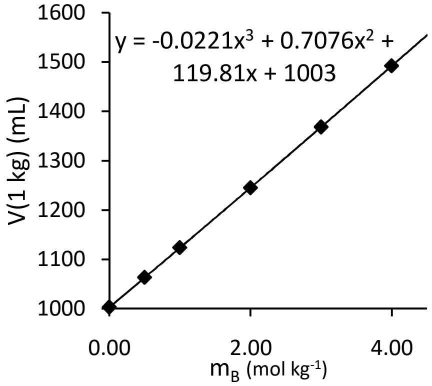
m_B (mol kg^{-1})	0.0000	0.5000	1.0000	2.0000	3.0000	4.0003	4.5005
d (g mL^{-1})	0.99707	1.02159	1.04334	1.07970	1.10846	1.13178	1.14187

Answer: The plan is to calculate V^{1kg} for each solution and fit the results to a cubic polynomial in the molality. Then Eq. 18.1.8 is used to find the partial molar volume of the solute and Eq. 18.1.3 is used to find the partial molar volume of the solvent, as in Example 18.1.1.

A spreadsheet was set up to do the calculations. The V^{1kg} vs. m_B values were fit to a cubic polynomial using the 4-parameter version of the "Non-Linear Least Squares" applet on the textbook Web site or the companion CD. The applet allowed the determination of the uncertainties of the fit parameters. The fit parameters were entered into the spreadsheet and Eq. 18.1.8 was used to calculate the partial molar volumes:

$$\bar{V}_B = \left(\frac{\partial V}{\partial m_B}\right)_{T,P,n_A} \text{kg}^{-1} = 3(-0.0221)\ m^2 + 2(0.708)\ m + 119.81\ \text{mL mol}^{-1}$$

	$\mathcal{M}_A$	18.0153	g mol^{-1}	
	$\mathcal{M}_B$	172.205	g mol^{-1}	
	a	-0.0221	± 0.0152	
	b	0.708	± 0.1	
	c	119.81	± 0.19	
m_B (mol kg^{-1})	d (g mL^{-1})	V^{1kg} (mL)	V_B (mL mol^{-1})	V_A (mL mol^{-1})
0.0000	0.99707	1002.939	119.810	18.068
0.5000	1.02159	1063.149	120.501	18.068
1.0000	1.04334	1123.512	121.160	18.058
2.0000	1.07970	1245.17	122.377	18.023
3.0000	1.10846	1368.218	123.461	17.976
4.0003	1.13178	1492.226	124.413	17.917
4.5005	1.14187	1554.475	124.840	17.883



The partial molar volumes of the solvent are then calculated using Eq. 18.1.3:

$$V^{1kg} = \bar{V}_A \frac{1000\ \text{g}}{\mathcal{M}_A} + \bar{V}_B\, m_B\ (1\ \text{kg})$$

and solving for the partial molar volume of the solvent, for example at 2.000 m:

$$\bar{V}_A = \frac{[V^{1kg} - \bar{V}_B\, m_B\ (1\ \text{kg})]\mathcal{M}_A}{1000\ \text{g}}$$

$$= \frac{[1245.17\ \text{mL} - 122.377\ \text{mL mol}^{-1}(2.000\ \text{mol kg}^{-1})(1\ \text{kg})]18.0153\ \text{g mol}^{-1}}{1000\ \text{g}}$$

$$= 18.023\ \text{mL mol}^{-1}$$

Notice that as the partial molar volume of *p*-toluenesulfonic acid increases that the partial molar volume of water decreases, as required by the Gibbs-Duhem relationship. One caution, however: a cubic curve fit isn't statistically justified with only seven data points. The original literature reference had more data points, but some points were dropped to make the problem more tractable for this homework. Never-the-less, the results here are sufficiently close to the literature values.

5. Prove the relationship for the partial molar volume in Eqs. 18.1.10:

$$\text{Given}\ \ V = n_A V_A^* + n_B\, {}^{\phi}V \qquad \text{show that}\ \ \bar{V}_B = {}^{\phi}V + m_B \left(\frac{\partial\, {}^{\phi}V}{\partial m_B}\right)_{T,P,n_A}$$

Answer: Using the definition of partial molar volume from Eq. 18.1.8 and the volume in terms of the apparent molar volume gives:

$$\bar{V}_B = \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A} = \left(\frac{\partial\, n_A V_A^*}{\partial n_B}\right)_{T,P,n_A} + \left(\frac{\partial\, n_B\, {}^{\phi}V}{\partial n_B}\right)_{T,P,n_A}$$

The first term is zero because n_A and the pure molar volume of the solvent are constants. Using the product rule for the second term gives:

$$\bar{V}_B = {}^{\phi}V + n_B \left(\frac{\partial {}^{\phi}V}{\partial n_B}\right)_{T,P,n_A}$$

We can change the independent variable to molality by using the definition, $m_B = n_B/w_A$, with the mass of solvent, w_A, a constant:

$$\bar{V}_B = {}^{\phi}V + n_B \left(\frac{\partial {}^{\phi}V}{\partial m_B}\right)_{T,P,n_A} \left(\frac{\partial m_B}{\partial n_B}\right)_{T,P,n_A} = {}^{\phi}V + \frac{n_B}{w_A} \left(\frac{\partial {}^{\phi}V}{\partial m_B}\right)_{T,P,n_A} \left(\frac{\partial n_B}{\partial n_B}\right)_{T,P,n_A}$$

$$\bar{V}_B = {}^{\phi}V + m_B \left(\frac{\partial\, {}^{\phi}V}{\partial m_B}\right)_{T,P,n_A}$$

6. The apparent molar volume of sucrose in water is given by the following power series expansion.[2]

$${}^{\phi}V = \bar{V}_B^{\ominus} + RT\,[\,\tfrac{1}{2} A\, m_B + \tfrac{1}{3} B\, m_B^2 + \tfrac{1}{4} C\, m_B^3 + \tfrac{1}{5} D\, m_B^4\,]$$

where $\bar{V}_B^{\ominus}$ is the partial molar volume of the solute at infinite dilution, and A, B, C, and D are constants and R is in units of L atm K^{-1} mol^{-1}. All five coefficients are determined using non-linear least squares curve fitting of experimental data. (a). Find the partial molar volume of the solute as a function of $\bar{V}_B^{\ominus}$, A, B, C, and D. (b). The fit coefficients for sucrose at 25°C are: $\bar{V}_B^{\ominus}$ = 0.21149 L mol^{-1}, A = $1.107\text{x}10^{-4}$ kg mol^{-1} atm^{-1}, B = $-1.64\text{x}10^{-5}$ kg^3 mol^{-3} atm^{-1}, C = $1.15\text{x}10^{-6}$ kg^4 mol^{-4} atm^{-1}, and D = 0. Find the partial molar volume of 0.01000 m sucrose at 25°C.

Answer: (a). Using Eqs. 18.1.10 and the given power series expansion of the apparent molar volume, the derivative gives:

$$\begin{aligned}\bar{V}_B &= {}^{\phi}V + m_B \left(\frac{\partial\, {}^{\phi}V}{\partial m_B}\right)_{T,P,n_A}\\ &= {}^{\phi}V + m_B\, RT\,[\,\tfrac{1}{2} A + \tfrac{2}{3} B\, m_B + \tfrac{3}{4} C\, m_B^2 + \tfrac{4}{5} D\, m_B^3\,]\end{aligned}$$

Substituting in the power series for ${}^{\phi}V$:

$$\bar{V}_B = \bar{V}_B^{\ominus} + RT[\tfrac{1}{2}Am_B + \tfrac{1}{3}Bm_B^2 + \tfrac{1}{4}Cm_B^3 + \tfrac{1}{5}Dm_B^4] + RT[\tfrac{1}{2}A\, m_B + \tfrac{2}{3}Bm_B^2 + \tfrac{3}{4}Cm_B^3 + \tfrac{4}{5}Dm_B^4]$$

$$\bar{V}_B = \bar{V}_B^{\ominus} + RT\,[A\, m_B + B\, m_B^2 + C\, m_B^3 + D\, m_B^4\,]$$

(b). Using the given fit coefficients and m_B = 0.0100 m gives:

$$\begin{aligned}\bar{V}_B = {}& 0.21149 \text{ L mol}^{-1} + 0.082058 \text{ L atm K}^{-1}\text{mol}^{-1}(298.15 \text{ K})\cdot\\ & [\,1.107\text{x}10^{-4}\,(0.01000) + (-1.64\text{x}10^{-5})\,(0.01000)^2 + 1.15\text{x}10^{-6}\,(0.01000)^3\,]\text{atm}^{-1}\end{aligned}$$

$$\bar{V}_B = 0.21152 \text{ L} = 211.52 \text{ mL}$$

This partial molar volume was used in Example 18.4.8. The density of pure sucrose is d_{pure} = 1.588 g mL^{-1}. The partial molar volume of sucrose is not far from the pure molar volume, $V_B^* = \mathfrak{M}_B/d_{B,pure}$ = 342.30 g mol^{-1}/1.588 g mL^{-1} = 215.5 mL. The pure molar volume could have been used for Example 18.4.8 without excessive error, since the concentration dependent term is so large.

7. Calculate the entropy and Gibbs energy of mixing of 0.80 moles of $H_2O(l)$ and 0.20 moles of ethanol at 298.15 K. Assume an ideal solution.

Answer: Using Eqs. 18.2.10° and 18.2.11° or 16.8.16°:

$$\Delta_{mix}S = -\, n_{tot}R \sum_{i=1}^{n_s} x_i \ln x_i = -\,1.00 \text{ mol}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})[0.80 \ln 0.80 + 0.20 \ln 0.20]$$
$$= 4.16 \text{ J K}^{-1}$$

$$\Delta_{mix}G = -\,T\,\Delta_{mix}S = -\,298.15 \text{ K}(4.16 \text{ J K}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -1.24 \text{ kJ mol}^{-1}$$

8. Ethanol from the fermentation of corn or other sources of biomass has been proposed as a large scale replacement for petroleum based transportation fuels. For use in transportation fuels, ethanol must contain less than 0.7% water. Calculate the minimum energy necessary to produce one mole of ethanol, with a concentration of 99.3% ethanol by volume at 25°C, from a fermentation broth containing 15% by volume ethanol. Assume ideal behavior. Compare this minimum separation requirement to the Gibbs energy of combustion of ethanol. The density of ethanol is 0.789 g mL^{-1}.

Answer: The molar mass of ethanol is 46.07 g mol^{-1}. Assuming a total volume of 100 mL, 15% by volume corresponds to mole amounts: n_{EtOH} = 15 mL(0.789 g mL^{-1})/46.07 g mol^{-1} = 0.257 mol and n_{H_2O} = 85 mL(0.9971 g mL^{-1})/18.02 g mol^{-1} = 4.70 mol. The mole fractions are:

$$x_{EtOH} = \frac{0.257 \text{ mol}}{4.70 \text{ mol} + 0.257 \text{ mol}} = 0.0518 \qquad \text{and} \quad x_{H_2O} = 1 - 0.0518 = 0.948$$

After the separation, 100 mL of 99.3% ethanol by volume corresponds to n_{EtOH} = 99.3 mL(0.789 g mL^{-1})/46.07 g mol^{-1} = 1.701 mol and n_{H_2O} = 0.7 mL(0.9971 g mL-1)/18.02 g mol^{-1} = 0.039 mol. The mole fractions are:

$$x_{EtOH} = \frac{1.701 \text{ mol}}{0.039 \text{ mol} + 1.701 \text{ mol}} = 0.978 \qquad \text{and} \quad x_{H_2O} = 1 - 0.978 = 0.022$$

For the 15% solution, one mole of ethanol is contained in n_{tot} = 1 mol/x_{EtOH} = 1/0.0518 = 19.31 mol of total solution. For the 99.3% solution, one mole of ethanol is contained in n_{tot} = 1 mol/x_{EtOH} = 1/0.978 = 1.02 mol of total solution. The Gibbs energy of mixing, using Eqs. 18.2.10* and 18.2.11*, for the 15% ethanol solution is:

$$\Delta_{mix}S = -\, n_{tot}R \sum_{i=1}^{n_s} x_i \ln x_i$$

$$= -\, 19.31\ \text{mol}(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})[\ 0.0518 \ln 0.0518 + 0.948 \ln 0.948]$$

$$= 32.7\ \text{J K}^{-1}$$

$$\Delta_{mix}G = -\, T\, \Delta_{mix}S = -\, 298.15\ \text{K}(32.7\ \text{J K}^{-1})(1\ \text{kJ}/1000\ \text{J}) = -9.76\ \text{kJ} \qquad (15\ \%\ \text{v/v})$$

The Gibbs energy of mixing for the 99.3% ethanol solution is:

$$\Delta_{mix}S = -\, n_{tot}R \sum_{i=1}^{n_s} x_i \ln x_i$$

$$= -\, 1.02\ \text{mol}(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})[\ 0.978 \ln 0.978 + 0.022 \ln 0.022]$$

$$= 0.897\ \text{J K}^{-1}$$

$$\Delta_{mix}G = -\, T\, \Delta_{mix}S = -\, 298.15\ \text{K}(0.897\ \text{J K}^{-1})(1\ \text{kJ}/1000\ \text{J}) = -0.267\ \text{kJ} \qquad (99.3\ \%\ \text{v/v})$$

The Gibbs energy to prepare one mole of ethanol is then the difference:

$$\Delta G = -0.267\ \text{kJ} - (-9.76\ \text{kJ}) = 9.49\ \text{kJ}$$

The molar Gibbs energy of combustion of ethanol is:

	CH_3CH_2OH (l) +	$^7/_2\ O_2$ (g) $\rightarrow$	2 CO_2 (g) +	3 H_2O (l)	units
$\Delta_fG°$	-174.78	0	-394.36	-237.13	kJ mol^{-1}

$$\Delta_{comb}G° = [2(-394.36) + 3(-237.13)] - [-174.78]\ \text{kJ mol}^{-1} = -1325.33\ \text{kJ mol}^{-1}$$

The ideal minimum Gibbs energy for the separation is a small fraction of the Gibbs energy of combustion, suggesting that biomass conversion to ethanol is an excellent candidate for replacing petroleum. However, distillation and zeolite based drying of ethanol are inefficient processes. All energy inputs need to be considered as well as soil depletion and especially water use. Forest and agricultural waste and hemi-celluose, a bi-product of the paper industry, are good candidates for conversion to ethanol.

9. At 50.0°C the vapor pressure of pure hexane and pure heptane are 0.534 bar and 0.188 bar, respectively. The two liquids form nearly an ideal solution. (a) For a solution with a mole fraction of 0.670 heptane, calculate the total vapor pressure and the mole fraction of each component in the vapor phase.[3] (b) The total vapor pressure of a heptane-hexane solution is 0.405 bar. Calculate the mole fraction of heptane in the solution, the partial vapor pressures of each component, and the mole fractions in the vapor phase.

Answer: (a). Use an "X" subscript for hexane and a "P" subscript for heptane: $P_X^* = 0.534$ bar, $P_P^* = 0.188$ bar, $x_P = 0.670$, $x_X = (1 - x_P) = 0.330$. The total pressure, using Raoult's law for both components, Eq. 18.2.7*, is:

$$P_{tot} = x_X\, P_X^* + x_P\, P_P^* = 0.330(0.534\ \text{bar}) + 0.670(0.188\ \text{bar}) = 0.302\ \text{bar}$$

Using Dalton's Law of partial pressures for the vapor phase with, $P_P = y_P\, P_{tot}$, Eq. 18.4.1*:

$$y_P = P_P/P_{tot} = x_P\, P_P^*/P_{tot} = 0.670(0.188\ \text{bar})/0.302\ \text{bar} = 0.417$$

and $y_X = 1 - y_P = 1 - 0.417 = 0.583$

As a check we note that the vapor is richer than the solution in the more volatile component, hexane, as expected. The literature value for the total pressure is 0.293 bar, so the solution shows small negative deviations from ideality.[3]

(b). This part of the problem works in the opposite direction as in part (a). Using Eq. 18.2.8*, $x_X = (1 - x_P)$, and solving for x_P:

$$P_{tot} = x_X P_X^* + x_P P_P^* = (1 - x_P) P_X^* + x_P P_P^* = P_X^* + x_P (P_P^* - P_X^*)$$

$$x_P = \frac{P_{tot} - P_X^*}{P_P^* - P_X^*}$$

and for $P_{tot} = 0.405$ bar:

$$x_P = \frac{0.405 - 0.534}{0.188 - 0.534} = 0.373 \qquad \text{and} \qquad x_X = 1 - x_P = 0.627$$

Using Raoult's Law for both components in solution, the partial vapor pressures are:

$$P_X = x_X P_X^* = 0.627(0.534 \text{ bar}) = 0.335 \qquad P_P = x_P P_P^* = 0.373(0.188 \text{ bar}) = 0.070$$

As a check on the calculations, we should verify the total pressure as the sum of the partial vapor pressures from the last calculation, $P_{tot} = P_X + P_P = 0.335 + 0.070 = 0.405$, as given. Finally, using Dalton's Law for each component in the vapor phase, the vapor phase mole fractions are, Eq. 2.1.10°:

$$y_X = P_X/P_{tot} = 0.335/0.405 = 0.827 \qquad \text{and} \qquad y_P = 1 - y_X = 0.173$$

As a check we note that the vapor is richer than the solution in the more volatile component, hexane, as expected. The literature value for the mole fraction of heptane in this solution is $x_P = 0.358$ for only a 4% error, caused by the assumption of ideal behavior.[3]

10. At 30.0°C the vapor pressure of pure toluene and pure benzene are 36.7 and 118.2 torr, respectively. The two liquids form a nearly ideal solution. (a) For a solution containing 50.0 mole % of toluene, calculate the total vapor pressure and the mole fraction of each component in the vapor phase. (b) What is the composition of a solution of benzene and toluene that will boil at 30.0°C at a pressure of 50.0 torr?

Answer: (a). Use a "T" subscript for toluene and a "B" subscript for benzene: $P_T^* = 36.7$ torr, $P_B^* = 118.2$ torr, $x_T = 0.500$, $x_B = 0.500$. The total pressure, using Raoult's law for both components, is, Eq. 18.2.7*:

$$P_{tot} = x_T P_T^* + x_B P_B^* = 0.500(36.7 \text{ torr}) + 0.500(118.2 \text{ torr}) = 77.5 \text{ torr}$$

We use Dalton's law of partial pressures for the vapor phase with, $P_T = y_T P_{tot}$, Eq. 18.4.1*:

$$y_T = P_T/P_{tot} = x_T P_T^*/P_{tot} = 0.500(36.7 \text{ torr})/77.5 \text{ torr} = 0.237$$

and $y_B = 1 - y_T = 1 - 0.237 = 0.763$

As a check, we note that the vapor is richer in the more volatile component, benzene, than the liquid, as expected.
(b). This part of the problem corresponds to a reduced pressure distillation. If the solution is boiling, the vapor pressure is equal to the ambient pressure, $P_{tot} = 50$ torr:

$$P_{tot} = x_T\, P_T^* + x_B\, P_B^* = 50 \text{ torr}$$

Substituting in the pure vapor pressures and noting that $x_B = 1 - x_T$:

$$P_{tot} = 50 \text{ torr} = x_T(36.7 \text{ torr}) + (1 - x_T)(118.2 \text{ torr})$$

gives $x_T = 0.837$ and $x_B = 1 - x_T = 0.163$

11. 2-Propanol and 2-methylpropanol form an ideal solution. (a). Calculate the composition of the solution and vapor that boils at 90.0°C and an ambient pressure of 1.00 bar. The standard boiling point of pure 2-propanol is 82.2°C and the enthalpy of vaporization at the standard boiling point is 43.61 kJ mol^{-1}. The standard boiling point of pure 2-methyl-propanol is 107.7°C and the enthalpy of vaporization is 46.26 kJ mol^{-1}. (b). What is the highest purity attainable from a single-plate distillation starting with the composition in Part (a)?

Answer: The plan is to use the Clausius-Clapeyron equation to calculate the pure vapor pressures at 90.0°C. Example 18.4.3 then describes the remaining steps to find the corresponding compositions in Figure 18.4.2.

Using Eq. 17.1.14° for 2-propanol, with $T_b^* = 355.4$ K at 1 bar, gives the vapor pressure at 90.0°C, 363.2 K, as:

$$P_2 = P_1\, e^{-\frac{\Delta_{tr}H_m}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} = 1 \text{ bar}\; e^{-\frac{43.61\text{x}10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{363.2 \text{ K}}-\frac{1}{355.4 \text{ K}}\right)} = 1.374 \text{ bar}$$

and for 2-methyl-propanol, with $T_b^* = 380.9$ K:

$$P_2 = 1 \text{ bar}\; e^{-\frac{46.26 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{363.2 \text{ K}}-\frac{1}{380.9 \text{ K}}\right)} = 0.491 \text{ bar}$$

Let A be 2-propanol. Using Eq. 18.2.8* with the total vapor pressure of 1 bar gives the composition of the solution from:

$$P_{tot} = x_A P_A^* + (1 - x_A)P_B^* = x_A(1.374 \text{ bar}) + (1 - x_A)(0.491 \text{ bar}) = 1 \text{ bar}$$

Solving for the solution concentration of A: $x_A = 0.576$.

The vapor phase concentration is calculated using Eq. 18.4.1*:

$$y_A = P_A/P_{tot} = x_A P_A^*/P_{tot} = 0.576(1.374 \text{ bar})/1.00 \text{ bar} = 0.791$$

These points are consistent with Figure 18.4.2. (b). For a distillation, if the initial pot concentration is $x_A = 0.576$, the solution boils at 90.0°C in equilibrium with the vapor at $y_A = 0.791$. In other words, starting with $x_A = 0.576$, the highest purity that may be achieved for 2-propanol in a single-plate distillation is 79.1 mol%, but only for the first drop of distillate. Continued distillation produces distillate with lower purity.

12. The standard state Gibbs energy of formation of methanol in the gas phase at 25°C is -161.96 kJ mol^{-1}. The Henry's Law constant is $k_{pc} = 4.51\times10^{-3}$ bar L mol^{-1}. (a). Calculate the standard state Gibbs energy of formation of aqueous methanol at 25°C. (b). Calculate the concentration of methanol in an aqueous solution given an equilibrium vapor pressure for methanol above the solution of 0.0100 bar (1.00 kPa or 7.50 torr).

Answer: (a). Follow Example 18.3.1. The small Henry's Law constant shows that methanol is very soluble in water. Methanol-water hydrogen bonds contribute to the stability of the solution. The corresponding Gibbs energy of desolvation is given by Eqs. 18.3.3†:

$$\Delta_{desol}G^{\circ}_{pc} = -\,RT \ln k_{pc} = -\,8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln 4.51\times10^{-3}$$
$$= 13.39 \text{ kJ mol}^{-1}$$

Noting that $\Delta_{sol}G^{\circ} = -\,\Delta_{desol}G^{\circ}_{pc}$ gives the standard state Gibbs energy of formation for aqueous methanol as:

$$\Delta_f G^{\circ}(aq) = \Delta_f G^{\circ}(g) + \Delta_{sol}G^{\circ} = -161.96 \text{ kJ mol}^{-1} + (-13.39 \text{ kJ mol}^{-1}) = -175.35 \text{ kJ mol}^{-1}$$

(b). Using Eq. 18.3.3†, $P_B = k_{pc}\, c_B$:

$$c_B = P_B/k_{pc} = 0.0100 \text{ bar}/4.51\times10^{-3} \text{ bar L mol}^{-1} = 2.22 \text{ M}$$

The concentration of methanol in water must be quite large, 2.22 M (~7% by weight), to establish a vapor pressure of 0.0100 bar (7.5 torr). This concentration assumes ideal-dilute behavior, and so is a lower limit, since negative deviations from ideality are expected.

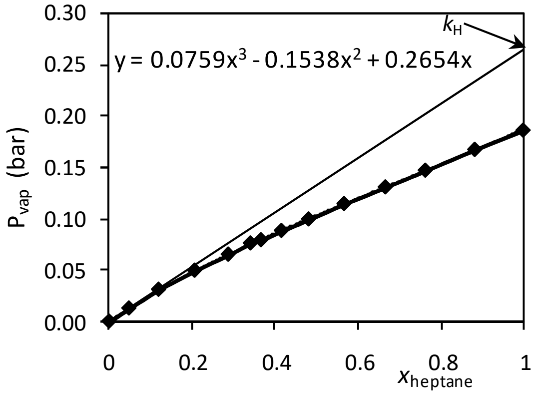
13. The vapor pressure of heptane in solution with 1-bromobutane is given in the table below, at 50°C.[3] Calculate the Henry's Law constants, k_H, k_{cc}, and k_{pc}, for heptane. The data is plotted in Figure 18.3.1. The density of 1-bromobutane at 25°C is 1.276 g mL^{-1} and the molar mass is 137.02 g mol^{-1}. Assume the density is roughly independent of temperature for this small temperature difference.

x(bromobutane)	0	0.1171	0.2362	0.3329	0.4323	0.5182	0.5836	0.6333
P_{vap}(heptane, torr)	140.0	125.8	110.6	98.4	86.1	74.8	66.4	59.6
x(bromobutane)	0.6588	0.7123	0.7935	0.8805	0.9521	1		
P_{vap}(heptane, torr)	57.3	49	37.2	23.3	9.6	0		

Answer: The plan is to fit the vapor pressure data to a cubic polynomial with a constant coefficient of zero, and then follow Example 18.3.2. Alternatively the data could be carefully plotted and then a straight edge used to extrapolate the dilute solution behavior to $x_A = 1$.

The mole fraction of heptane and vapor pressure in bar were calculated using the following spreadsheet and fit to a cubic polynomial using the "Non-linear least Squares Applet," on the textbook Web site or companion CD, $y = a\,x^3 + b\,x^2 + c\,x + d$. The d-parameter was fixed at zero, since the vapor pressure goes to zero at $x_A = 0$. The Henry's Law constant is the value of the dilute solution line extrapolated to $x_A = 1$. The c-fit coefficient is the Henry's Law constant, $k_{H,A} = c = 0.2654 \pm 0.0038$ bar.

$x_{butylbromide}$	P_{vap} (torr)	$x_{heptane}$	P_{vap} (bar)
0	140	1	0.1867
0.1171	125.8	0.8829	0.1677
0.2362	110.6	0.7638	0.1475
0.3329	98.4	0.6671	0.1312
0.4323	86.1	0.5677	0.1148
0.5182	74.8	0.4818	0.0997
0.5836	66.4	0.4164	0.0885
0.6333	59.6	0.3667	0.0795
0.6588	57.3	0.3412	0.0764
0.7123	49	0.2877	0.0653
0.7935	37.2	0.2065	0.0496
0.8805	23.3	0.1195	0.0311
0.9521	9.6	0.0479	0.0128
1	0	0	0



Then substituting Eq. 2.2.16 for the mole fraction into Eq. 18.3.1[†] gives the conversion:

$$P_A = k_{H,A}\, x_A = k_{H,A} \frac{c_A\,(1\text{ L})}{\left(\dfrac{1000\text{ mL } d_{soln}}{\mathfrak{M}_A}\right)} = k_{pc,A}\, c_A \qquad \text{with} \qquad k_{pc,A} = \frac{k_{H,A}\,(1\text{ L})}{\left(\dfrac{1000\text{ mL } d_{soln}}{\mathfrak{M}_A}\right)}$$

Assuming the density of the solution is the density of the solvent, 1-bromobutane, gives:

$$k_{pc,A} = \frac{0.2654\text{ bar }(1\text{ L})}{\left(\dfrac{1000\text{ mL } 1.276\text{ g mL}^{-1}}{137.02\text{ g mol}^{-1}}\right)} = \frac{0.2654\text{ bar L}}{9.313\text{ mol}} = 0.0285\text{ bar L mol}^{-1} = 2.85\text{ Pa m}^3\text{ mol}^{-1}$$

The unitless Henry's Law constant uses concentration in the gas phase as well as the solution phase:

$$k_{cc,A} = \frac{k_H}{9.313\text{ mol L}^{-1}\text{ RT}} = \frac{0.2654\text{ bar}}{9.313\text{ mol L}^{-1}(0.083145\text{ bar L K}^{-1}\text{mol}^{-1})(323.15\text{ K})} = 1.06\text{x}10^{-3}$$

The units for R are chosen to cancel the units for k_H.

Note that a "quick and dirty" approach for calculating the Henry's Law constant is to calculate the slope using the data point with the lowest concentration: $k_H \cong 0.0128$ bar/0.0479 $\cong 0.27$ bar.

14. The Henry's Law constants, k_H, for O_2 and N_2 in water at 25°C are $4.40\text{x}10^4$ bar and $8.68\text{x}10^4$ bar, respectively. Calculate the equilibrium solubility of O_2 and N_2 in water at 25°C in units of molarity and ppm by weight. Find the ratio of O_2 to N_2 in moles. Assume that air is 20.0 mole % O_2 and 80.0 mole % N_2 at a total pressure of 1.00 bar.

Answer: The plan is to convert the gas phase mole fractions to partial pressures, convert k_H to k_{pc}, and then find the equilibrium concentrations. The concentrations are then converted to ppm.

Using Dalton's Law for the gas phase gives, $P_{O_2} = y_{O_2}\,P = 0.20$ bar and $P_{N_2} = y_{N_2}\,P = 0.80$ bar. We next convert k_H to k_{pc} using Eq. 18.3.6†. For O_2:

$$k_{pc,O_2} = \frac{k_H}{55.34 \text{ mol L}^{-1}} = \frac{4.40\text{x}10^4 \text{ bar}}{55.34 \text{ mol L}^{-1}} = 795._1 \text{ bar L mol}^{-1}$$

and $c_{O_2} = P_{O_2}/k_{pc,O_2} = 0.20 \text{ bar}/795._1 \text{ bar L mol}^{-1} = 2.5\text{x}10^{-4}$ M

In ppm, assuming the density of the solution is the density of pure water:

$$c_{O_2} = 2.5\text{x}10^{-4} \text{ mol L}^{-1}(1 \text{ L})(32.0 \text{ g mol}^{-1})(1 \text{ L}/1000 \text{ mL})/0.9971 \text{ g mL}^{-1}\ (1\text{x}10^6 \text{ ppm})$$
$$= 8.0 \text{ ppm}$$

For N_2:

$$k_{pc,N_2} = \frac{k_H}{55.34 \text{ mol L}^{-1}} = \frac{8.68\text{x}10^4 \text{ bar}}{55.34 \text{ mol L}^{-1}} = 156_8. \text{ bar L mol}^{-1}$$

and $c_{N_2} = P_{N_2}/k_{pc,N_2} = 0.80 \text{ bar}/156_8. \text{ bar L mol}^{-1} = 5.1\text{x}10^{-4}$ M

$$c_{N_2} = 5.1\text{x}10^{-4} \text{ mol L}^{-1}(1 \text{ L})(28.02 \text{ g mol}^{-1})(1 \text{ L}/1000 \text{ mL})/0.9971 \text{ g mL}^{-1}\ (1\text{x}10^6 \text{ ppm})$$
$$= 14. \text{ ppm}$$

The mole ratio of oxygen to nitrogen in equilibrium in solution at 25°C is:

$$n_{O_2}/n_{N_2} = 2.5\text{x}10^{-4} \text{ M}/5.1\text{x}10^{-4} \text{ M} = 0.49 \approx ½$$

15. The Henry's Law constant for CO_2 can be expressed using the concentration of dissolved CO_2, only, or the concentration of CO_2 and carbonic acid:

$$k'_{pc,CO_2} = \frac{P_{CO_2}}{c_{CO_2}} \qquad\qquad k_{pc,CO_2} = \frac{P_{CO_2}}{c_{CO_2} + c_{H_2CO_3}}$$

The equilibrium constant for the dehydration of carbonic acid is about 650:[4]

$$H_2CO_3\ (aq) \rightleftarrows CO_2\ (aq) + H_2O\ (l) \qquad\qquad K = 650$$

The Henry's Law constant for CO_2 in sea water at 25°C is $pk_{pc,CO_2} = -1.53$.[4] Show that $k_{pc,CO_2} \cong k'_{pc,CO_2}$, within experimental error.

Answer: Doing the logarithmic conversion for pk_{pc,CO_2} gives $k_{pc,CO_2} = 0.0295 \pm 0.0007$, or 2.4% error. Equivalently, the result should be expressed with two significant figures: $k_{pc,CO_2} = 0.029_5$, which agrees with the normal significant figure rules. The relationship between the two forms of the Henry's Law constant is given by:

$$k'_{pc,CO_2} = k_{pc,CO_2}\left(\frac{c_{CO_2} + c_{H_2CO_3}}{c_{CO_2}}\right)$$

We next need to find $(c_{CO_2} + c_{H_2CO_3})/c_{CO_2}$. The equilibrium expression for the dehydration of carbonic acid is:

$$K = \frac{c_{CO_2}}{c_{H_2CO_3}} \qquad \text{and } c_{H_2CO_3} = c_{CO_2}/K \quad \text{giving} \quad \left(\frac{c_{CO_2} + c_{H_2CO_3}}{c_{CO_2}}\right) = 1 + 1/K$$

Since K is large, K = 650, the predominant form for CO_2 in aqueous solution at equilibrium is as dissolved CO_2, not carbonic acid. The relationship between the two forms of the Henry's Law constant is then:

$$k'_{pc,CO_2} = k_{pc,CO_2}\,(1 + 1/K) = k_{pc,CO_2}\,(1 + 1/650) = k_{pc,CO_2}\,1.0015$$

The two constants differ by 0.15%, which is negligible compared to the experimental uncertainty in $k_{H,PC.}$ Note, however, that the total solubility of all carbonate species, $C_T = c_{CO_2} + c_{H_2CO_3} + c_{HCO_3^-} + c_{CO_3^{2-}}$, increases with pH and is significantly larger than c_{CO_2} alone near neutral pH (see Section 6.1).

16. Show that the temperature dependence of the chemical potential for an ideal constituent is given by: $(\partial\mu_A/\partial T)_{P,n_A,n_B} = -\overline{S}_A = -S^*_A + R\ln x_A$, where S^*_A is the pure molar entropy of the substance A and the concentration in the solution is x_A.

Answer: The plan is to use the same reasoning that we used to derive Eq. 18.2.12*, except finding temperature derivative.

The temperature dependence of the chemical potential for a component in solution is given by the partial molar entropy, Eqs. 18.1.17-18.1.18:

$$\left(\frac{\partial\mu_A}{\partial T}\right)_{P,n_A,n_B} = -\overline{S}_A$$

Using Eq. 18.2.9* for the concentration dependence of the chemical potential for an ideal component, $\mu_A(x_A) = \mu^*_A + RT\ln x_A$, and the product rule gives:

$$-\overline{S}_A = \left(\frac{\partial\mu_A}{\partial T}\right)_{P,n_A,n_B} = \left(\frac{\partial(\mu^*_A + RT\ln x_A)}{\partial T}\right)_{P,n_A,n_B} \qquad \text{(ideal)}$$

$$= \left(\frac{\partial\mu^*_A}{\partial T}\right)_{P,n_A,n_B} + RT\left(\frac{\partial\ln x_A}{\partial T}\right)_{P,n_A,n_B} + R\ln x_A\left(\frac{\partial T}{\partial T}\right)_{P,n_A,n_B} \qquad \text{(ideal)}$$

The derivative of $\ln x_A$ is zero because x_A is constant when n_A and n_B are constant:

$$-\overline{S}_A = \left(\frac{\partial\mu^*_A}{\partial T}\right)_{P,n_A,n_B} + R\ln x_A = -S^*_A + R\ln x_A \qquad \text{(ideal)}$$

The slope of the chemical potential versus temperature curve is $-S^*_A + R\ln x_A$, as shown in Figure 18.4.5. Or finally, the partial molar entropy of an ideal constituent is:

$$\overline{S}_A = S^*_A - R\ln x_A \qquad \text{(ideal)}$$

The entropy of mixing for an ideal solution follows directly from this last equation.

17. The partial molar entropy of a constituent in an ideal solution, at constant temperature and pressure, is $\bar{S}_i = S_i^* - R \ln x_i$, where S_i^* is the pure molar entropy of the substance i and the concentration of i in the solution is x_i. (See the previous problem for a proof of this equation.) Show that the entropy of mixing of an ideal binary solution is $\Delta_{mix}S = -\,n_{tot}R\,(x_A \ln x_A + x_B \ln x_B)$ at constant temperature and pressure.

Answer: The plan is to adapt the derivation for the Gibbs energy of mixing, Eqs. 16.8.6, 16.8.11°-16.8.13°.

Let S_2 be the final entropy for the solution and S_1 be the initial total entropy for the two pure constituents with n_A moles of A with n_B moles of B:

$$\Delta_{mix}S = S_2 - S_1 = (n_A \bar{S}_A + n_B \bar{S}_B) - (n_A S_A^* + n_B S_B^*) = n_A(\bar{S}_A - S_A^*) + n_B(\bar{S}_B - S_B^*)$$

Using $\bar{S}_A = S_A^* - R \ln x_A$ and $\bar{S}_B = S_B^* - R \ln x_B$ for the two ideal constituents gives:

$$\Delta_{mix}S = -\,n_A\,R \ln x_A - n_B\,R \ln x_B$$

The pure molar entropy terms cancel. Let $n_{tot} = n_A + n_B$, with $x_A = n_A/n_{tot}$ and $x_B = n_B/n_{tot}$. Dividing and multiplying each term by n_{tot} and factoring out the common factor of $-\,n_{tot}R$ gives:

$$\Delta_{mix}S = -\,n_{tot}R\left(\frac{n_A}{n_{tot}} \ln x_A + \frac{n_B}{n_{tot}} \ln x_B\right)$$

$$\Delta_{mix}S = -\,n_{tot}R\,(x_A \ln x_A + x_B \ln x_B) \qquad (18.2.10^*)$$

which is the analogous expression to Eq. 16.8.14° for ideal gas mixing.

18. Show that the Raoult's Law and Henry's Law standard states for a solute are related by:

$$\mu_B^\dagger(l) = \mu_B^*(l) + RT \ln k_{H,B}/P_B^*$$

Answer: The definitions of the standard states applied to the solute, B, are:

$$\mu_B^*(l) = \mu_B^\circ(g) + RT \ln P_B^*/P^\circ \qquad \text{(Raoult, pure)} \qquad (18.2.2^\circ)$$

$$\mu_B^\dagger(l) \equiv \mu_B^\circ(g) + RT \ln k_{H,B}/P^\circ \qquad \text{(Henry, solute)} \qquad (18.3.9^\dagger)$$

Subtracting Eq. 18.2.2° from Eq. $18.3.9^\dagger$ gives:

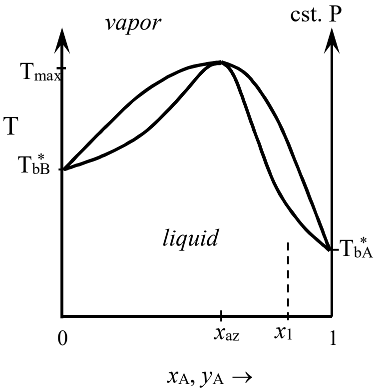
$$\mu_B^\dagger(l) - \mu_B^*(l) = \mu_B^\circ(g) + RT \ln k_{H,B}/P^\circ - \mu_B^\circ(g) - RT \ln P_B^*/P^\circ$$

$$\mu_B^\dagger(l) - \mu_B^*(l) = RT \ln k_{H,B}/P_B^*$$

Adding $\mu_B^*(l)$ to both sides of the last equation gives: $\mu_B^\dagger(l) = \mu_B^*(l) + RT \ln k_{H,B}/P_B^*$.

19. Using the binary liquid-vapor phase diagram shown below, (a). what would be recovered from the distillate and from the pot for an exhaustive fractional distillation, starting with the solution with composition x_1. (b). Does this solution show positive or negative deviations from

ideality. Discuss the forces that act in solution as compared to the forces that act in the pure liquids.



Answer: (a). Starting from a solution with concentration greater than the azeotropic concentration, the more volatile component (lower boiling point) is pure A. Pure A would be recovered from the distillate and azeotrope would be recovered from the pot.

(b). Deviations from ideality are judged from the perspective of the vapor pressure. This system has a maximum boiling azeotrope; the solution temperature must be increased above the pure boiling points of either pure A or B to attain a vapor pressure equal to the ambient pressure. The azeotrope is harder to vaporize than pure A or pure B. The solution shows strong negative deviations from ideality: A-B >> A-A, B-B.

20. When 640. mg of naphthalene is dissolved in 40.0 g of chloroform, the boiling point of the solution is 0.455°C higher than that of pure solvent ($T^*_A = 61.2°C$). Calculate (a) the molal boiling point elevation constant, and (b) the molar enthalpy of vaporization of chloroform.

Answer: The molar mass of naphthalene is $\mathcal{M}_{Naph} = 128.2\ \text{g mol}^{-1}$ and chloroform is $\mathcal{M}_{chloroform} = 119.37\ \text{g mol}^{-1}$. This problem is a colligative properties problem with $\Delta T = K_b\, m_B$. (a). In this equation m_B is the solute molality:

$$m_B = \frac{n_B}{w_{solvent}} = \frac{0.640\ \text{g}\ (1\ \text{mol}/128.2\ \text{g mol}^{-1})}{0.0400\ \text{kg}} = 0.1248\ \text{mol kg}^{-1} = 0.1248\ \text{m}$$

Solving for the molal boiling point elevation constant gives:

$$K_b = \frac{\Delta T}{m_B} = \frac{0.455\ \text{K}}{0.1248\ \text{mol kg}^{-1}} = 3.646\ \text{K kg mol}^{-1}$$

(b). The molal boiling point elevation constant is related to the enthalpy of vaporization of the solvent by Eqs. 18.4.14†:

$$K_b = \frac{R T_A^{*2}\, \mathcal{M}_A\, (1\ \text{kg})}{\Delta_{vap} H^\circ_A\, (1000\ \text{g})}$$

where all the quantities are related to properties of the pure <u>solvent</u>. Solving for the enthalpy change:

$$\Delta_{vap}H^{\circ}_{A} = \frac{RT^{*2}_{A}\,\mathfrak{M}_A\,(1\text{ kg})}{K_b(1000\text{ g})} = \frac{8.314\text{ J K}^{-1}\text{ mol}^{-1}(334.4\text{ K})^2(119.37\text{ g mol-1})(1\text{ kg})}{3.646\text{ K kg mol}^{-1}(1000\text{ g})}$$

$$= 3.044\text{x}10^4\text{ J mol}^{-1} = 30.4\text{ kJ mol}^{-1}$$

21. The freezing point depression of a solution of $1.433\text{x}10^{-3}$ g of butanol in 1.000 g of water is 0.035588 K.[5] Calculate the molar mass of butanol. The enthalpy of fusion of water is 6.008 kJ mol^{-1} at 273.15 K. (b). The freezing point depression of a solution of $2.951\text{x}10^{-3}$ g of butanol in 1.000 g of water is 0.07300 K. Calculate the molar mass of butanol again and compare.

Answer: (a). From Eqs. 18.4.19†, the cryoscopic constant for water is:

$$K_f \equiv \left(\frac{RT^{*2}_{m}\mathfrak{M}_A\,(1\text{ kg})}{1000\text{ g }\Delta_{fus}H_A}\right) = \left(\frac{8.3145\text{ J K}^{-1}\text{mol}^{-1}(273.15\text{ K})^2(18.0153\text{ g mol}^{-1})\,(1\text{ kg})}{1000\text{ g }(6.008\text{x}10^3\text{ J mol}^{-1})}\right)$$

$$= 1.861\text{ mol}^{-1}\text{ kg K}$$

The concentration is given by:

$$\Delta T \cong K_f\, m_B \qquad \text{and} \qquad m_B = \Delta T/K_f = 0.035588\text{ K}/1.861\text{ mol}^{-1}\text{ kg K} = 0.019123\text{ mol kg}^{-1}$$

Then using the given masses, the molality and molar mass of the solute are related by:

$$m_B = \frac{w_B/\mathfrak{M}_B}{w_A} = \frac{1.433\text{x}10^{-3}\text{ g }/\mathfrak{M}_B}{1.000\text{ g }(1\text{ kg}/1000\text{ g})} \qquad \text{giving } \mathfrak{M}_B = 74.94\text{ g mol}^{-1}$$

The literature molar mass of butanol is 74.15 g mol^{-1}.

(b). Repeating the calculations with the more concentrated solution gives:

$$m_B = 0.07300\text{ K}/1.861\text{ mol}^{-1}\text{ kg K} = 0.039226\text{ mol kg}^{-1}$$

$$m_B = \frac{w_B/\mathfrak{M}_B}{w_A} = \frac{2.951\text{x}10^{-3}\text{ g }/\mathfrak{M}_B}{1.000\text{ g }(1\text{ kg}/1000\text{ g})} \qquad \text{giving } \mathfrak{M}_B = 75.23\text{ g mol}^{-1}$$

For an ideal solution, parts (a) and (b) would give the same result. Butanol-water solutions show small but significant deviations from ideal behavior. The more dilute result is potentially more accurate, since the solution is closer to an ideal solution, but the freezing point depression is less precise since it is a smaller value.

22. A sample of benzene has a freezing point of 3.44°C. Calculate the purity of the benzene in mole %. Assume the solution is ideal and the impurities are insoluble in solid benzene. The standard melting point of pure benzene is 5.46°C and the enthalpy of fusion is 10.59 kJ mol^{-1} at the standard melting point.

Answer: The plan is to use Eq. 18.4.16† with benzene as the solvent. The solution freezing point is 276.59 K, the pure freezing point is 278.61 K, and$\Delta T = (278.61 - 276.59 \text{ K}) = 2.02 \text{ K}$

The freezing point depression is most conveniently given in terms of the mole fraction of the solvent using Eq. 18.4.16† with:

$$K' = \left(\frac{\Delta_{fus}H_A}{R\, T_m^{*2}}\right) = \left(\frac{10.59\text{x}10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(278.61 \text{ K})^2}\right) = 0.01640_8 \text{ K}^{-1}$$

$$\ln x_A = K'\,\Delta T = -0.01640_8 \text{ K}^{-1}(2.02 \text{ K}) \qquad \text{giving } x_A = 0.967$$

The purity is 96.7 mol%. See the next problem for the DSC method that is used when the pure substance standard melting point and enthalpy of fusion are not known.

23. A DSC melting curve was determined for a sample of tetracosane, $C_{24}H_{50}$. The sample weight was 2.21 mg. Partial areas were determined and are reported in the table below, in arbitrary units (as shown schematically in Figure 18.4.7). The total area under the melting curve was 7.351, which corresponds to 0.3919 J. Find the pure melting point, molar enthalpy of fusion, and mol % impurity for the sample. The molar mass of tetracosane is 338.66 g mol^{-1}.

T (K)	322.39	322.44	322.51	322.58
Partial area	1.450	1.669	2.122	2.866

Answer: The plan is to determine $\Delta_{fus}H_A$ using the total area under the melting curve, sample mass, and molar mass. The fraction of the sample melted, F, is given by the ratio of the partial area to the total area under the melting curve. The pure melting point and freezing point depression are found from a plot of melting point versus 1/F. Eq. 18.4.16† for the freezing point depression gives the mole fraction of the solvent, with tetracosane as the solvent.

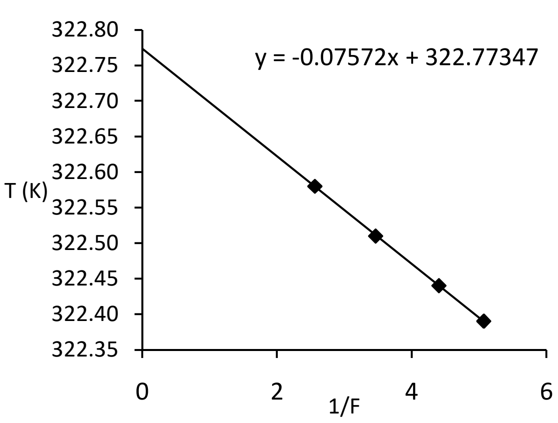
The molar enthalpy of fusion is given by the total area under the melting curve in joules and then converting to the molar quantity:

$$\Delta_{fus}H_A = \Delta H/n_A = \frac{0.3919 \text{ J } (338.66 \text{ g mol}^{-1})}{2.21\text{x}10^{-3} \text{ g}} (1\text{kJ}/1000 \text{ J}) = 60.05 \text{ kJ mol}^{-1}$$

The plot was set-up using the following spreadsheet:

total area	7.351			
	part.area	F	1/F	T (K)
	1.45	0.197252	5.069655	322.39
	1.669	0.227044	4.404434	322.44
	2.122	0.288668	3.464185	322.51
	2.866	0.389879	2.564899	322.58

slope	-0.07572	322.7735	intercept
±	0.000537	0.002141	±
r^2	0.9999	0.001017	s(y)
F	19917.64	2	df
SS_{reg}	0.020598	2.07E-06	SS_{resid}



The intercept is the pure melting point and the slope is the freezing point depression, ΔT, Figure 18.4.7c. The freezing point depression is given directly in terms of the mole fraction of the solvent using Eq. 18.4.16† as:

$$\ln x_A = -\left(\frac{\Delta_{fus}H_A}{R\,T_m^{*2}}\right)\Delta T$$

with $\left(\frac{\Delta_{fus}H_A}{R\,T_m^{*2}}\right) = \left(\frac{60.05\text{x}10^3\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}(322.774\text{ K})^2}\right) = 0.06932_3\text{ K}^{-1}$

$$\ln x_A = -0.06932_3\text{ K}^{-1}(0.0757_2\text{ K}) \qquad \text{giving } x_A = 0.9948$$

The purity is 99.48 mol%, using propagation of errors to determine the final number of significant figures.

24. Prove that the dependence of the freezing point of a solution on the concentration of the solvent is given by (start with the chemical potentials of the pure solvent and the solution):

$$\ln x_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right)$$

Answer: At equilibrium the chemical potential of the pure solid is equal to the chemical potential of the solvent in solution. Assuming an ideal dilute solution gives $P_A = x_A\,P_A^*$:

$$\mu_A^*(s) = \mu_A(x_A) = \mu_A^*(l) + RT\ln x_A \qquad 1$$

Solving for the logarithm of the concentration:

$$\ln x_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT} \qquad 2$$

The Gibbs energy of fusion is given by $\Delta_{fus}G_A = \mu_A^*(l) - \mu_A^*(s)$. For example for aqueous solutions the $\Delta_{fus}G_A$ corresponds to the transition written as $H_2O\,(s) \rightarrow H_2O(l)$, with the liquid phase being the "products" and the solid phase the "reactants." Substitution of $\Delta_{fus}G_A$ into Eq. 2 gives:

$$\ln x_A = -\frac{\Delta_{fus}G_A(T)}{RT} \qquad \text{(solution)} \qquad 3$$

For comparison for a pure solution, $x_A = 1$ and the melting point is the pure solvent melting point, $T = T_m^*$; substitution into Eq. 3 gives for the pure solvent:

$$\ln 1 = -\frac{\Delta_{fus}G_A(T_m^*)}{RT_m^*} \qquad \text{(pure solvent)} \qquad 4$$

Subtracting Eq. 4 from Eq. 3:

$$\ln\frac{x_A}{1} = -\frac{\Delta_{fus}G_A(T)}{RT} + \frac{\Delta_{fus}G_A(T_m^*)}{RT_m^*} \qquad 5$$

Expanding the Gibbs energy in terms of the enthalpy and entropy changes for the phase transition gives:

$$\ln x_A = -\left(\frac{\Delta_{fus}H_A(T)}{RT} - \frac{\Delta_{fus}S_A(T)}{R}\right) + \left(\frac{\Delta_{fus}H_A(T_m^*)}{RT_m^*} - \frac{\Delta_{fus}S_A(T_m^*)}{R}\right) \qquad 6$$

Assuming the temperature change for the phase transition is small, we can assume that $\Delta_{fus}H_A$ and $\Delta_{fus}S_A$ are constant over the temperature range and cancelling the entropy terms gives:

$$\ln x_A = -\frac{\Delta_{fus}H_A(T)}{RT} + \frac{\Delta_{fus}H_A(T_m^*)}{RT_m^*} = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) \qquad 7$$

25. Polyvinyl alcohol is often used in lecture demonstrations to make “slime.” A 4.00% by mass solution of polyvinyl alcohol was placed in an osmometer. The height of the solution above the surface of the pure water at equilibrium was 21.6 cm at 25.0°C. Assume the density of the solution is that of pure water. Calculate the approximate molar mass of the polyvinyl alcohol and the average number of monomers, n, linked in the polymer. [Hint: Polyvinyl alcohol is $CH_3CH(OH)[CH_2CH(OH)]_{n-2}CH_2CH_2OH$, so use $–CH_2CH(OH)-$ for the monomer molar mass.]

Answer: The osmotic pressure is given by Eq. 1.3.2 and h = 21.6 cm = 0.216 m:

$$\pi = dgh = 0.9971\ \text{g mL}^{-1}(1\ \text{kg}/1000\ \text{g})(1\text{x}10^6\text{mL}/1\ \text{m}^3)(9.8067\ \text{m s}^2)(0.216\ \text{m})$$
$$= 2.11_2\text{x}10^3\ \text{Pa} = 0.0211_2\ \text{bar}$$

Using Eq. 18.4.30†, since this is such a dilute solution, gives the concentration as:

$$c_B = \pi/RT = \frac{0.0211_2\ \text{bar}}{0.083145\ \text{bar L mol}^{-1}\ \text{K}^{-1}\ 298.15\ \text{K}} = 8.52\text{x}10^{-4}\ \text{mol L}^{-1}$$

The solution concentration is used to calculate the molar mass from the definition of molarity:

$$c_B = n_B/V_{soln} = w_B/\mathfrak{M}_B/V_{soln} \qquad \text{or solving for } \mathfrak{M}_B: \qquad \mathfrak{M}_B = w_B/c_B/V_{soln}$$

were w_B is the mass of solute in a volume of solution, V_{soln}. Assume 100.0 g of solution. The mass of the solute is w_B= 4.00 g and the volume of the solution is
$V_{soln} = w_{soln}/d_{soln}$ = 100.0 g/0.9971 g mL^{-1} (1 L/1000 mL) = 0.1003 L giving:

$$\mathfrak{M}_B = w_B/c_B/V_{soln} = 4.00\ \text{g}/8.52\text{x}10^{-4}\ \text{mol L}^{-1}/0.1003\ \text{L} = 4.68\text{x}10^4\ \text{g mol}^{-1}$$

The monomer weight, $-CH_2CH(OH)-$, is 44.06 g mol^{-1}, neglecting the difference in mass between the two ends. The average number of monomers per polymer molecule is then:

$$n = 4.68\text{x}10^4\ \text{g mol}^{-1}/44.06\ \text{g mol}^{-1} = 106_2. = 1.06\text{x}10^3$$

The large molecular mass is not at all unusual for commercial polymers. Even though the solution concentration is quite small, 8.52x10^{-4}M, the osmotic pressure is easily measured to high precision.

26. Osmotic pressure is used to determine the molar mass of polymers. However, Eq. 18.4.30† assumes ideal behavior. For real solutions, Eq. 18.4.30† gives an *effective* molar mass. For careful determinations, the *effective* molar mass of a sample is determined at several concentrations and extrapolated to zero concentration, where Eq. 18.4.30† becomes exact. The osmotic pressure of a sample of polystyrene in toluene was determined at several concentrations at 25°C. Find the molar mass of the polystyrene sample.[6]

C_B (g L^{-1})	2.60	5.16	6.54	9.19
π (Pa)	9.80	32.0	51.0	107.

Answer: Eq. 18.4.30† was used to determine the effective molar concentration, $c_B = \pi/RT$, and the effective molar mass was determined using the definition of molarity:

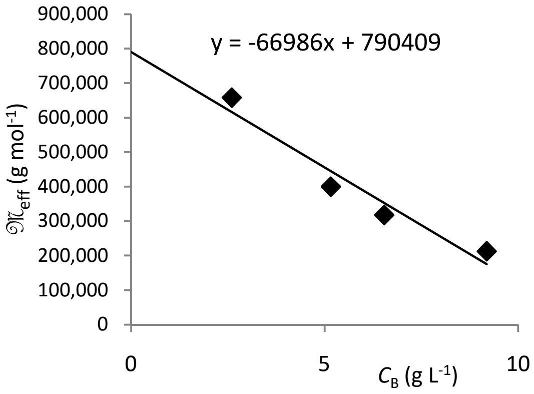
$c_B = n_B/V_{soln} = w_B/\mathfrak{M}_B/V_{soln}$ or solving for $\mathfrak{M}_B$: $\mathfrak{M}_B = w_B/c_B/V_{soln}$

were w_B is the mass of solute in a volume of solution, V_{soln}. The concentrations in the table are given in g mol^{-1}, C_B. Assume 1.000 L of solution. The mass of the solute is $w_B = C_B(1\ L)$:

$\mathfrak{M}_B = C_B(1\ L)/c_B/1\ L = C_B/c_B$

The calculations were implemented in a short spreadsheet:

C_B (g L^{-1})	π (Pa)	c_B (mol L^{-1})	$\mathfrak{M}_{eff}$ (g mol^{-1})
2.6	9.8	3.953E-06	6.576E+05
5.16	32	1.291E-05	3.997E+05
6.54	51	2.057E-05	3.179E+05
9.19	107	4.317E-05	2.129E+05



The linear intercept gives the molar mass, $\mathfrak{M}_B = 8.\text{x}10^5$ g mol^{-1}. If more data points are available, a non-linear curve fit is appropriate and provides better accuracy.[6] The large change in effective molar mass with concentration shows significant deviations from ideality, even at these low concentrations.

27. A 0.1000 m aqueous urea solution and pure water are separated by a membrane that is impermeable to urea and permeable to water, at 25°C and 1 bar. Calculate the chemical potential of urea in the solution, relative to the standard state chemical potential, at equilibrium. The density of the solution is 0.99873 g $mL^{-1}$and the data necessary to obtain partial molar volume is given in Example 18.1.1.

Answer: Using Eq. 2.2.13, the mole fraction of 0.1000 m urea is $x_B = 1.7983\text{x}10^{-3}$. For a dilute solution of a non-electrolyte, the partial molar volume of the solvent is well approximated by the pure molar volume, $V_A^* = \mathcal{M}_A/d_{A,pure} = 18.069$ mL. The osmotic pressure in terms of the mole fraction of solute is given by Eq. 18.4.27†:

$$\pi = x_B\, RT/V_A^* = 1.7983\text{x}10^{-3}(0.083145 \text{ bar L K}^{-1}\text{ mol}^{-1})(298.15 \text{ K})/0.018069 \text{ L}$$
$$= 2.467 \text{ bar}$$

For the partial molar volume of the solute using Eq. 18.1.8 at 0.1000 m gives:

$$\bar{V}_B = \left(\frac{\partial V^{1kg}}{\partial m_B}\right)_{T,P,n_A} \text{kg}^{-1} = 3(-1.9934\text{x}10^{-3})\, m_B^2 + 2(9.03779\text{x}10^{-2})\, m_B + 44.36388$$
$$= 3(-1.9934\text{x}10^{-3})(0.1)^2 + 2(9.03779\text{x}10^{-2})(0.1) + 44.36388 = 44.382 \text{ mL mol}^{-1}$$

For the solute, Eq. 18.4.24†gives the chemical potential at equilibrium with $\Delta P = \pi$:

$$\mu_B(x_B,P+\pi) = \mu_B^\dagger(l,P) + RT \ln x_B + \pi_B\bar{V}_B$$
$$= \mu_B^\dagger(l,P) + 8.3145 \text{ J K}^{-1}\text{ mol}^{-1}(298.15 \text{ K}) \ln 1.7983\text{x}10^{-3}$$
$$+ 2.467 \text{ bar}(44.382 \text{ mL mol}^{-1})(1\text{x}10^5\text{Pa}/1\text{bar})(1 \text{ m}^3/1\text{x}10^6 \text{ mL})$$
$$= \mu_B^\dagger(l,P) + (-15.67 \text{ kJ mol}^{-1}) + 0.011 \text{ kJ mol}^{-1}$$

The concentration dependent term dominates the change in chemical potential for the solute compared to the standard state. On the other hand, for the solvent, which occurs on both sides of the membrane, the concentration dependent term and the osmotic pressure term cancel at equilibrium.

28. Calculate the chemical potential of water in a 0.200 M solution of sucrose at 10.00 bar and 25°C. The partial molar volume of water in this solution is well approximated by the pure molar volume.

Answer: The plan is to use Eq. 18.4.30† to calculate the equilibrium osmotic pressure and then Eq. 18.4.31 to find the chemical potential of the solvent.

The equilibrium osmotic pressure is given by Eq. 18.4.30†:

$$\pi = c_B\, RT = 0.200 \text{ mol L}^{-1}(0.083145 \text{ L bar K}^{-1}\text{ mol}^{-1})(298.15 \text{ K}) = 4.96 \text{ bar}$$

The partial molar volume of water in this dilute solution is not far from the pure molar volume, $V_A^* = \mathcal{M}_A/d_{A,pure} = 18.0153 \text{ g mol}^{-1}/0.997045 \text{ g mL}^{-1} = 18.069 \text{ mL mol}^{-1}$.The chemical potential for water as the solvent is then given by Eq. 18.4.31:

$$\mu_A(x_A,P+\Delta P) = \mu_A^*(l,P) + (\Delta P - \pi)\bar{V}_A$$
$$= \mu_A^*(l,P) + (10.00 - 4.96 \text{ bar})\ 18.069 \text{ mL mol}^{-1}\ (1\text{x}10^5 \text{ Pa}/1 \text{ bar})(1 \text{ m}^3/1\text{x}10^6 \text{ mL})$$
$$= \mu_A^*(l,P) + (9.11 \text{ J mol}^{-1})$$

The chemical potential of pure water is just the Gibbs energy per mole. The standard state Gibbs energy of formation of water is -237.13 kJ mol^{-1}, so the effect of the pressure is small. However, the difference is not negligible since the 10 bar applied pressure corresponds to a hydrostatic head of 102 m and the osmotic pressure corresponds to 51 m. Small differences in chemical potential correspond to large differences in osmotic pressure.

29. Starting with the expression for the chemical potential of the solvent in an ideal-dilute solution, prove Eq. 18.4.15†.

Answer: The freezing point or melting point of a solution is the equilibrium phase transition temperature giving $\mu_A(x_A) = \mu_A^*(s)$. Using Raoult's Law for the solvent, the chemical potential of the solvent in solution is given by Eq. 18.2.9*:

$$\mu_A^*(s) = \mu_A(x_A) = \mu_A^*(l) + RT \ln x_A$$

The molar Gibbs energy of fusion of the pure solvent at temperature T is given by $\Delta_{fus}G_A(T) = \mu_A^*(l) - \mu_A^*(s)$. Solving for the concentration of the solvent that gives the solution freezing point at temperature T gives:

$$\ln x_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT} = -\frac{\Delta_{fus}G_A(T)}{RT}$$

For the pure solvent, $x_A = 1$, and the equilibrium temperature is the melting point of the pure solvent at the ambient pressure, $T = T_m^*$:

$$\ln 1 = -\frac{\Delta_{fus}G_A(T_m^*)}{RT_m^*}$$

We can compare the solution to the pure solvent by subtracting the last two equations:

$$\ln \frac{x_A}{1} = -\frac{\Delta_{fus}G_A(T)}{RT} + \frac{\Delta_{fus}G_A(T_m^*)}{RT_m^*}$$

We can separate enthalpy and entropy effects using $\Delta_{fus}G_A(T) = \Delta_{fus}H_A(T) - T\,\Delta_{fus}S_A(T)$:

$$\ln x_A = -\left(\frac{\Delta_{fus}H_A(T)}{RT} - \frac{\Delta_{fus}S_A(T)}{R}\right) + \left(\frac{\Delta_{fus}H_A(T_m^*)}{RT_m^*} - \frac{\Delta_{fus}S_A(T_m^*)}{R}\right)$$

where $\Delta_{fus}H_A$ is the enthalpy of fusion of the solvent. The change in freezing point is typically only a few degrees. Assuming that $\Delta_{fus}H_A$ and $\Delta_{fus}S_A$ are constant over this small temperature range results in the cancellation of the entropy terms:

$$\ln x_A = -\frac{\Delta_{fus}H_A}{RT} + \frac{\Delta_{fus}H_A}{RT_m^*}$$

Collecting terms gives exactly the same results as for boiling point elevation, except for a change in sign:

$$\ln x_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) \qquad \text{(ideal solvent, cst. P, } \Delta_{fus}H_B^\circ \text{ \& } \Delta_{fus}S_B^\circ\text{)}$$

30. Consider the solubility of a pure solid, B, in a solvent at temperature T. Assume that the solution is ideal-dilute and at constant pressure. (a). Show that: $\mu_B^*(s) = \mu_B^\dagger(l) + RT \ln x_B$.
(b). The standard state Gibbs energy of solution of the pure solid at temperature T is defined as: $\Delta_{sol}G_B^\circ(T) = \mu_B^\dagger(l) - \mu_B^*(s)$. Show that the solubility of the solute is: $\ln x_B = -\Delta_{sol}G_B^\circ(T)/RT$.
(c). At reference temperature T_o the solubility is x_{Bo}. Show that the temperature dependence of the solubility is given by:

$$\ln \frac{x_B}{x_{Bo}} = -\frac{\Delta_{sol}H_B^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad \text{(ideal-dilute, cst. P)} \qquad \text{P18.29.1}^\dagger$$

Answer: The plan is to set the chemical potential of pure solute B equal to its chemical potential in solution. The steps in the derivation parallel Eqs. $18.4.2^\dagger$-$18.4.8^\dagger$, but focus on the solute.
(a). At equilibrium, the chemical potential of a solute is equal to the solute's chemical potential in solution, $\mu_B^*(s) = \mu_B(x_B)$. The chemical potential of the solute is given by Eq. $18.3.10^\dagger$, assuming an ideal-dilute solution:

$$\mu_B^*(s) = \mu_B(x_B) = \mu_B^\dagger(l) + RT \ln x_B$$

where x_B is the solubility, the concentration that is in equilibrium with the pure solid. The difference in standard states is the standard state Gibbs energy of solution, $\Delta_{sol}G_B^\circ = \mu_B^\dagger(l) - \mu_B^*(s)$ at temperature T. Solving for the solubility gives:

$$\ln x_B = [\mu_B^*(s) - \mu_B^\dagger(l)]/RT = -\Delta_{sol}G_B^\circ(T)/RT$$

At reference temperature T_o the solubility is x_{Bo}.

$$\ln x_{Bo} = -\Delta_{sol}G_B^\circ(T_o)/RT_o$$

The difference in solubilities at T and T_o is then:

$$\ln x_B - \ln x_{Bo} = -\Delta_{sol}G_B^\circ(T)/RT + \Delta_{sol}G_B^\circ(T_o)/RT_o$$

The Gibbs energy of solution can be split into enthalpic and entropic terms:

$$\Delta_{sol}G_B^\circ = \Delta_{sol}H_B^\circ - T\Delta_{sol}S_B^\circ$$
$$\ln x_B/x_{Bo} = -\Delta_{sol}H_B^\circ(T)/RT + \Delta_{sol}S_B^\circ(T)/R + \Delta_{sol}H_B^\circ(T_o)/RT_o - \Delta_{sol}S_B^\circ(T_o)/R$$

Assuming that $\Delta_{sol}H_B^\circ$ and $\Delta_{sol}S_B^\circ$ are constant over the temperature range, the entropy terms cancel:

$$\ln \frac{x_B}{x_{Bo}} = -\frac{\Delta_{sol}H_B^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad \text{(ideal-dilute, cst. P, } \Delta_{sol}H_B^\circ \text{ \& } \Delta_{sol}S_B^\circ\text{)}$$

Solubility is another example of *General Pattern ℘4: Exponential Temperature Dependence*, $e^{-E/RT}$, and may be rearranged in the same ways.

31. (a). Show that for small changes in temperature, $\Delta T \equiv T - T_o$, Eq. P18.29.1† reduces to:

$$x_B = x_{Bo} + \left(\frac{\Delta_{sol}H_B^\circ\, x_{Bo}}{RT_o^2}\right)\Delta T$$

(b). Show that this equation and LeChâtelier's Principle are consistent.

Answer: The plan is to parallel the approximations in Eqs. 18.4.9†-18.4.14† and *General Pattern ℘4*.

(a). Set $\Delta T \equiv T - T_o$. Following *General Pattern ℘4*, Eq. 3.5.13, for small changes in temperature, $TT_o \cong T_o^2$. Substitution into Eq. P18.29.1† gives:

$$\ln \frac{x_B}{x_{Bo}} = -\left(\frac{\Delta_{sol}H_B^\circ}{R}\right)\left(\frac{T_o - T}{T\,T_o}\right) = \left(\frac{\Delta_{sol}H_B^\circ}{RT_o^2}\right)\Delta T$$

For small changes in temperature, the change in solubility is small and $x_B/x_{Bo} \approx 1$. Using the Taylor series approximation, Table 1.5.3, $\ln x \approx x - 1$ near $x_o \approx 1$ gives:

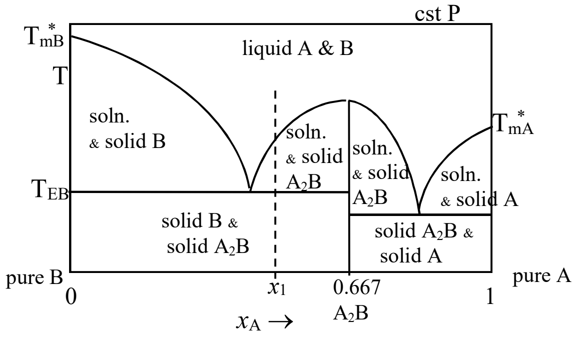
$$\frac{x_B}{x_{Bo}} - 1 = \left(\frac{\Delta_{sol}H_B^\circ}{RT_o^2}\right)\Delta T$$

Solving for x_B:

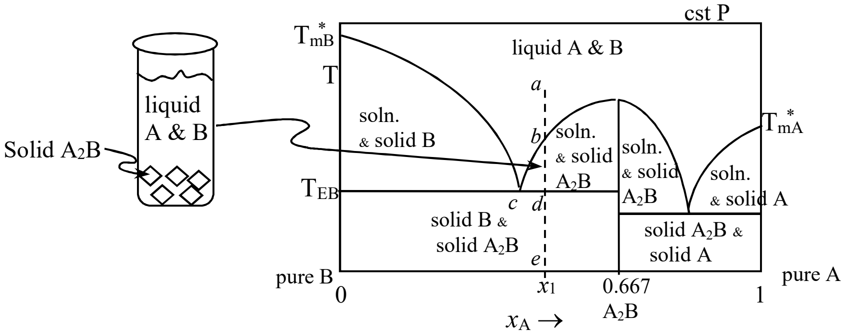
$$x_B = x_{Bo} + \left(\frac{\Delta_{sol}H_B^\circ\, x_{Bo}}{RT_o^2}\right)\Delta T \qquad \text{(ideal-dilute, small } \Delta T\text{)}$$

(b). If the enthalpy of solution is endothermic, the constant in parentheses is positive and the solubility increases with an increase in temperature. Think of the equilibrium solubility as a chemical reaction, $B(s) \rightleftarrows B(x_B)$. According to LeChâtelier's Principle, a reaction shifts in the endothermic direction with an increase in temperature. Increasing solubility corresponds to a shift to the right. The last equation and LeChâtelier's Principle are consistent.

32. Many binary solid-liquid phase diagrams are more complex than Figure 18.4.11. Some systems show the formation of a stable binary **compound** in the solid phase. Compounds typically have simple stoichiometries, such as A_2B, that are stabilized by strong intermolecular forces, like hydrogen bonding, or favorable crystal packing forces. The compound components are not covalently bound, and the compound doesn't exist in the liquid phase. An example of a compound in the phase diagram for NaCl in water is the dehydrate, $NaCl \cdot (H_2O)_2$. The solid-liquid phase diagram for a system with a stable solid-state compound, A_2B, is shown below. Analyzing a phase diagram that shows compound formation can be simplified by treating the compound as a hypothetical pure substance and dividing the phase diagram to either side as separate binary systems. Describe the phase transitions that occur along the cooling curve at the indicated composition, x_1.

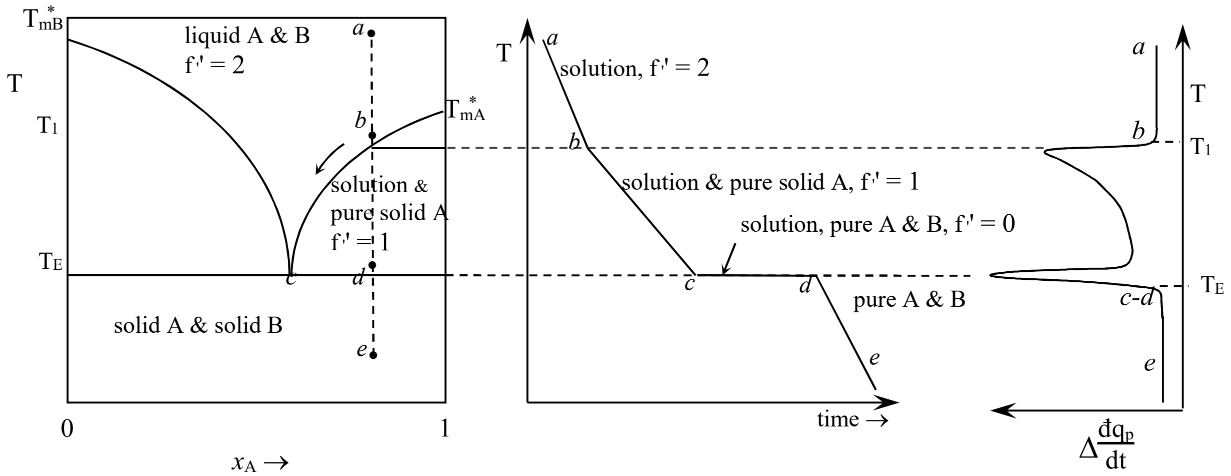


Answer: Start at high temperature, with solution only, point *a*. When the temperature drops to point *b*, solid compound A_2B begins to crystallize out of solution. The solution, which is also called the melt, becomes richer in B and the freezing point decreases. When the temperature drops to the eutectic temperature, between pure B and A_2B, solid A_2B begins to crystallize out of solution. The temperature remains constant until all the solution has solidified. The bulk composition is then at point *d*.

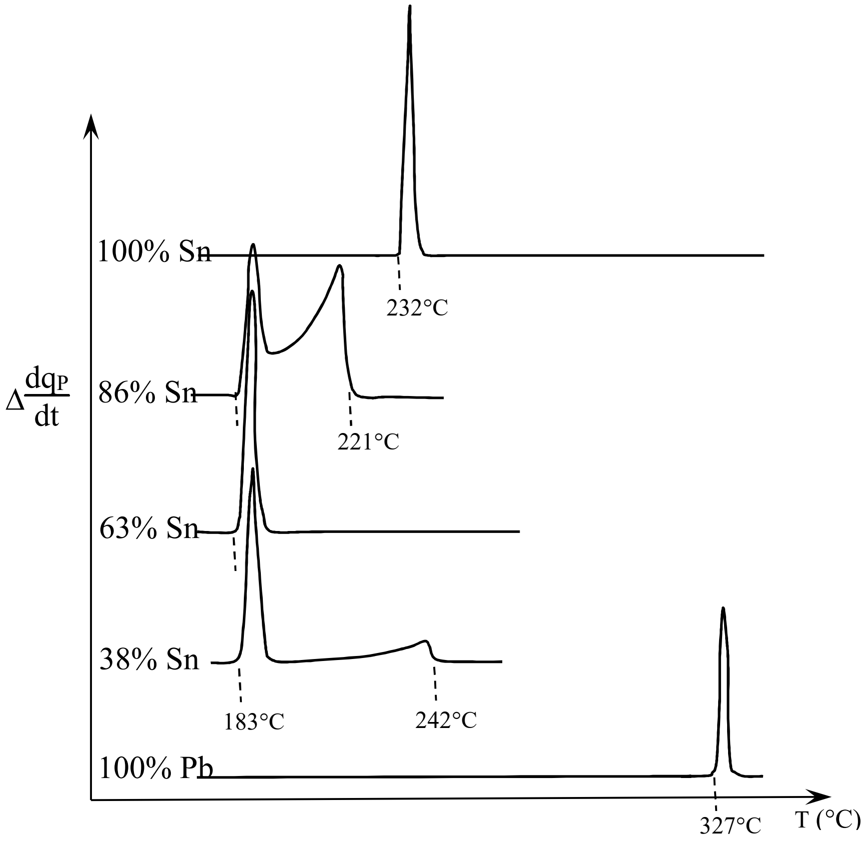


33. Relate the changes in the slopes of the segments on the cooling curve, Figure 18.4.12, and the widths of the peaks on the DSC melting curve, Figure 18.4.13, to the variances of the system at constant pressure. Discuss segments b-c and c-d.

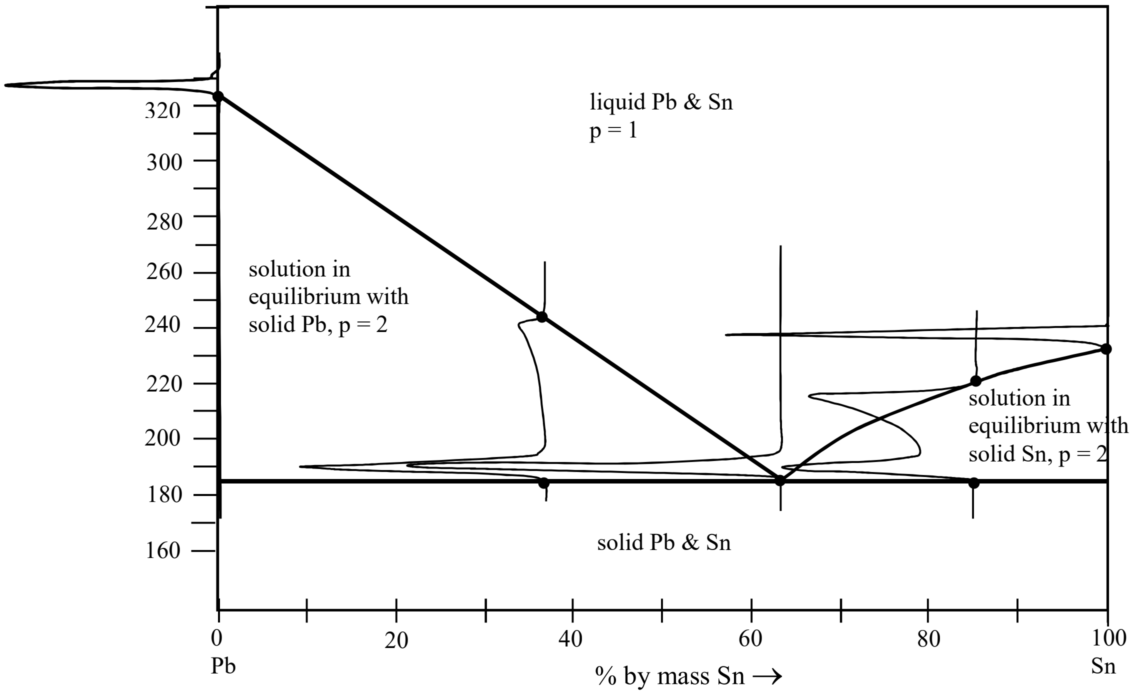
Answer: The corresponding regions and variances are diagrammed, below. For segment b-c the solution is in equilibrium with pure solid A. The variance of the system is f ' = 1. One intensive variable may be changed independently. For example, for a chosen composition, with freezing point of the solution is fixed. In segment b-c on the cooling curve, the temperature decreases as the solution become richer in B. The freezing point is depressed with increasing concentration of B in the solution. The corresponding melting peak in the DSC melting curve is broad. However, once the solution reaches the eutectic composition, the variance drops to f ' = 0, there are no independent variables. The temperature must then be fixed at the eutectic temperature. The cooling curve becomes flat at the eutectic temperature and the DSC melting peak at the eutectic temperature is narrow, comparable to the width of the melting peak of a pure substance. (The width of the eutectic melting peak is determined by instrument response times and the temperature scan rate.)



34. The following DSC melting thermograms were obtained from a range of starting compositions of Sn and Pb. The compositions are given as % by mass. The baselines of the thermograms are offset for clarity. Sketch the binary solid-liquid phase diagram. Use % by mass Sn as the composition axis, instead of mole fraction; % by mass gives a more convenient plot for this system.[7]



Answer: The sharp, low temperature transitions for the mixtures occur at the eutectic temperature. An easy way to think of building the phase diagram is to tilt the thermograms on their sides and replot them along the composition axis. Then connecting the melting temperatures by lines delineates the two-phase regions.



35. Find the variance for a gas in equilibrium with an aqueous solution of the gas. Give an expression for the general differential of the Gibbs energy, the change in Gibbs energy at constant temperature, and the change in Gibbs energy at constant temperature and pressure. Discuss the independent variables.

Answer: The two components are H_2O and the gas, c = 2. The two phases are the solution and the vapor, p = 2. The variances using Eq. 18.5.6 are:

$$f = c - p + 2 = 2 \qquad \text{at constant T: } f' = 1 \qquad \text{and at constant T \& P: } f'' = 0$$
$$D = c + p = 4 \qquad D' = 3 \qquad D'' = 2$$

Call the gas M; examples include methanol, CH_4, $CHCl_3$, O_2, and N_2. The change in Gibbs energy for a general process written in terms of all the possible terms is:

$$dG = - S\, dT + V\, dP + \mu_{H_2O}(x_{H_2O})\, dn_{H_2O,l} + \mu_{H_2O}(g)\, dn_{H_2O,g} + \mu_M(x_M)\, dn_{M,l} + \mu_M(g)\, dn_{M,g}$$
(with 4 independent)

The Gibbs Phase Rule points out that since the chemical potentials of each component are equal in the liquid and vapor, in addition to $x_{H_2O} + x_M = 1$ and $y_{H_2O} + y_M = 1$, there are only two degrees of freedom for the intensive variables. An equivalent way of noting this decrease in variance is that at equilibrium the vapor pressure of water is determined by Raoult's Law and the vapor phase pressure of the dissolved gas is given by Henry's Law. Following the allowed variance and arbitrarily focusing on the solution:

$$dG = - S\, dT + V\, dP + \mu_{H_2O}(x_{H_2O})dn_{H_2O} + \mu_M(x_M)dn_M \qquad (D = 4)$$
$$dG = V\, dP + \mu_{H_2O}(x_{H_2O})dn_{H_2O} + \mu_M(x_M)dn_M \qquad (\text{cst.T: } D' = 3)$$

$$dG = \mu_{H_2O}(x_{H_2O})dn_{H_2O} + \mu_M(x_M)dn_M \qquad \text{(cst. T\&P: D'' = 2)}$$

where $dn_{H_2O} = dn_{H_2O,l} + dn_{H_2O,g}$ and $dn_M = dn_{M,l} + dn_{M,g}$ (the chemical potential of the components in each phase are equal, so it doesn't matter which phase the components are in for calculating the overall Gibbs energy). The final expression for dG can often be written in various equivalent ways; however, f and D provide a check that you haven't included dependent terms.

36. Two partially miscible liquids, A and B, form a two-phase liquid system at equilibrium. One phase is mostly A with a small amount of B and the other phase is mostly B with a small amount of A. Consider only the liquid phases. Give an expression for the general differential of the Gibbs energy, the change in Gibbs energy at constant temperature, and the change in Gibbs energy at constant temperature and pressure. Discuss the independent variables. Most non-polar organic liquids and water are examples of this type of behavior; small amounts of water dissolve in the organic layer and small amounts of organic substance dissolve in the aqueous layer.

Answer: The two components are A and B, c = 2. The two phases are the solution rich in A, the α phase, and the solution rich in B, the β phase, so that p = 2. The variances are using Eq. 18.5.6:

$f = c - p + 2 = 2$ at constant T: $f' = 1$ and at constant T & P: $f'' = 0$
$D = c + p = 4$ $D' = 3$ $D'' = 2$

The change in Gibbs energy for a general process written in terms of all the possible terms is:

$$dG = -S\,dT + V\,dP + \mu_A(x_{A,\alpha})\,dn_{A,\alpha} + \mu_A(x_{A,\beta})\,dn_{A,\beta} + \mu_B(x_{B,\alpha})\,dn_{B,\alpha} + \mu_B(x_{B,\beta})\,dn_{B,\beta}$$
(with 4 independent)

with $x_{A,\alpha}$ the concentration of A in the alpha phase and $x_{A,\beta}$ the concentration of A in the beta phase. The Gibbs Phase Rule points out that since the chemical potentials of each component are equal in both liquid phases, in addition to $x_{A,\alpha} + x_{B,\alpha} = 1$, and $x_{A,\beta} + x_{B,\beta} = 1$, there are only two degrees of freedom for the intensive variables.

$$dG = -S\,dT + V\,dP + \mu_A(x_{A,\alpha})dn_A + \mu_B(x_{B,\alpha})dn_B \qquad (D = 4)$$
$$dG = V\,dP + \mu_A(x_{A,\alpha})dn_A + \mu_B(x_{B,\alpha})dn_B \qquad \text{(cst.T: D' = 3)}$$
$$dG = \mu_A(x_{A,\alpha})dn_A + \mu_B(x_{B,\alpha})dn_B \qquad \text{(cst. T\&P: D'' = 2)}$$

where $dn_A = dn_{A,\alpha} + dn_{A,\beta}$ and $dn_B = dn_{B,\alpha} + dn_{B,\beta}$ are the changes in total moles of A and B in both phases (the chemical potential of the components in each phase are equal, so it doesn't matter which phase the components are in for calculating the overall Gibbs energy). The final expression for dG can often be written in various equivalent ways; however, f and D provide a check that you haven't included dependent terms.

37. A system containing three components is univariant. How many phases are present?

Answer: The Gibbs Phase Rule, Eq. 18.5.6, determines the variance. For a univariant system, f = 1, and with c = 3:

$$f = c - p + 2$$
$$1 = 3 - p + 2 \qquad \text{giving} \quad p = 4$$

38. Show that for a pure substance the largest number of phases that can coexist is three.

Answer: For a pure substance c = 1. Since there are no composition variables, the only intensive variables are the temperature and pressure and the variance is f = 2. The Gibbs Phase Rule, Eq. 18.5.6, then determines the phases:

$$f = c - p + 2$$
$$2 = 1 - p + 2 \qquad \text{giving } p = 3$$

39. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). A champagne toast was used to celebrate the final stages of the construction of a transportation tunnel under the Thames River in London, in November 1827.[8] The celebration fell flat because at the higher ambient pressure in the tunnel, the Henry's Law solubility of the CO_2 in the wine increased, making the champagne taste flat. Participants also suffered gastric distress upon regaining ground level. This event is a practical example of Henry's Law.

(b). Soft drinks may be kept from "defizzing" by pumping air into the empty space above the soft drink in a partially filled bottle.

(c). Consider a two-phase region for a binary solid-liquid equilibrium system at constant pressure, with solution in equilibrium with pure solid A, Figure 18.4.12. At a fixed temperature, the solution composition may be any value along the tie line.

(d). A solution has a minimum freezing point (the eutectic temperature) because at the minimum temperature, the both the solute and the solvent have limited solubility in solution.

(e). The theory of ideal-dilute solutions doesn't take solute-solvent forces into account.

(f). The boiling point is elevated and the freezing point is depressed in a dilute solution of methanol in water.

(g). Two phases cannot be in equilibrium unless all components occur in each phase.

Answers: (a). False: Henry's Law, $p_{CO_2} = k_{H,CO_2}\, x_{CO_2}$, depends on the partial pressure of CO_2, not the total pressure. The partial pressure of CO_2 at equilibrium in a bottle of champagne is near 6 atm. The partial pressure of CO_2 in ambient air is 0.0003 atm.[9] The increased ambient pressure at the bottom of the tunnel does not significantly increase the CO_2 partial pressure in the atmosphere, compared to the 6 atm equilibrium partial pressure. Rather, the effect is caused by the kinetics of bubble formation. The kinetics of nucleation and bubble growth as the bubble rises in the solution is dependent on total pressure.[9] The correct statement is: the equilibrium solubility of CO_2 in beverages is essentially independent of total applied pressure of air. However, please see Eq. 17.1.30° for extreme changes in total pressure.

(b). False: pumping air into the empty space in a partially filled bottle increases the total pressure, but the partial pressure of CO_2 remains essentially unchanged. The partial pressure of CO_2 in the atmosphere is negligible in this regard, at 0.0003 atm. Henry's Law, $p_{CO_2} = k_{H,CO_2}\, x_{CO_2}$, depends on the partial pressure of CO_2, not the total pressure. The increase in total pressure does decrease the rate of bubble nucleation and bubble growth, but the equilibrium is unaffected. In addition, 80% of the transfer of CO_2 into the gas phase is by direct transfer from the surface of the solution (for further information see part (a) and Ref. 9). The correct statement: bottle-top pressure pumps do not prevent "defizzing" of soft drinks at equilibrium.

(c). False: the solution composition is at the solution end of the tie line, on the freezing point coexistence curve. The solid-phase composition is at the solid-phase end of the tie lie, which is pure A. The solution composition is fixed at a single value, subject to the system temperature. The corrected statement is: the overall system composition, z_B, may be any value along the tie line.

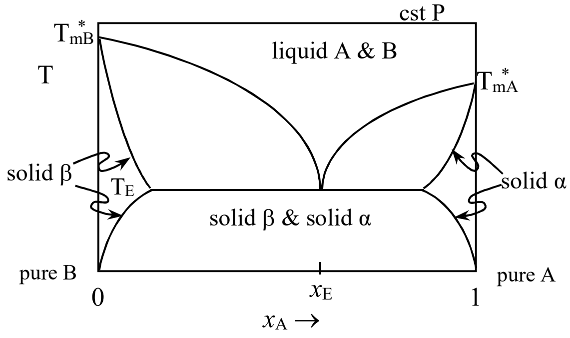
(d). True: thinking of the system from the perspective of freezing point depression, as the temperature of the solution is lowered, the solvent freezes out of solution. As the solute concentration increases the freezing point is depressed further. However, at some low temperature the solute also crystallizes out of solution, because the solute has limited solublility in the solution. At the eutectic temperature, both solute and solvent crystallize out of solution.

(e). False: The Henry's Law constant is the hypothetical vapor pressure of pure solute, assuming the forces are the same as between the solute and solvent. So, the solute-solvent forces are explicitly accounted for, in the dilute solution limit. Another way of seeing that the solute-solvent forces are carefully accounted for is to note that the Henry's Law constant for the solute is extrapolated from very dilute solution, where the only forces that affect the solute are the solute-solvent forces. Ideal-dilute solution theory does not take into account the concentration dependent changes as the forces shift from the solute-solvent forces in very dilute solution to solute-solute forces in pure solute, as $x_B \rightarrow 1$. The concentration dependent effects are resolved by the definition of activity in the next chapter. The correct statement is: ideal-dilute solution theory accounts for solute-solvent forces in the dilute solution limit, for which the only forces are the solute-solvent interaction.

(f). False/True: The freezing point is depressed in dilute methanol solutions. However, methanol is a volatile solute, so the colligative laws don't apply to the vapor above methanol-water solutions. Instead the binary liquid-vapor phase diagram is applicable, Figure 18.4.2, with water the less volatile component having the higher boiling point. At equilibrium the vapor pressures of methanol and water add, so the boiling point is lower for methanol-water solutions than pure water. The correct statement is: the boiling point is lowered and the freezing point is depressed in a dilute solution of methanol in water.

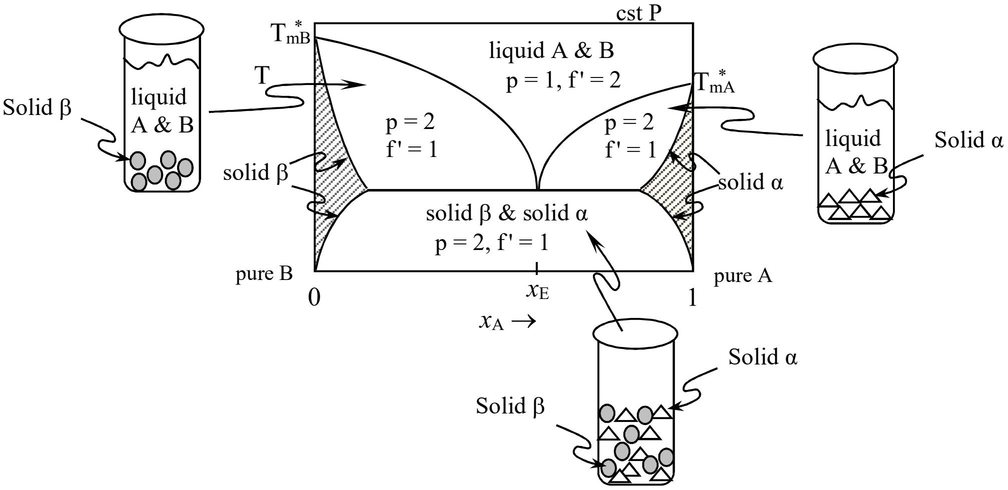
(g). True with a qualification: if two phases are in contact and a component occurs in one phase but not the other, then a concentration gradient will exist, and the component will diffuse into the other phase. The flux continues until the chemical potential of the component is equal in both phases. However, to be careful a qualification should be added: In the absence of a physical constraint, two phases cannot be in equilibrium unless all components occur in each phase. A semi-permeable membrane is such a constraint.

40. For many binary solid-liquid systems, the two solids are partially miscible. The solid phases consist of a phase rich in A with small amounts of B, the α phase, and a phase rich in B with small amounts of A, the β phase. Cooling a solution of A and B, with an initial concentration greater than the eutectic composition, freezes out solid α. Cooling a solution of A and B, with an initial concentration less than the eutectic composition, gives solid β. Below the eutectic temperature, solid β and solid α are in equilibrium. The compositions of the two solid phases depend on temperature. The phase diagram for a binary solid-liquid system with partial miscibility is shown below, at constant pressure. Describe the phases in equilibrium in each part of the phase diagram. Give the variance, f ', for each accessible region of the phase diagram.



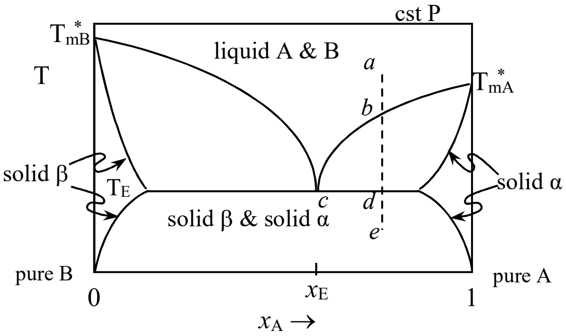
Answer: The plan is to base the description on Figure 18.5.2a and the Gibbs Phase Rule, Eq. 18.5.6. The experiment is at constant pressure, so we use f '.

At high temperatures, only the liquid phase exists, as a solution of A and B. With only one phase, p = 1 and f ' = c – p + 1 = 2 + 1 – 1 = 2. The temperature can vary over a wide range for each composition.

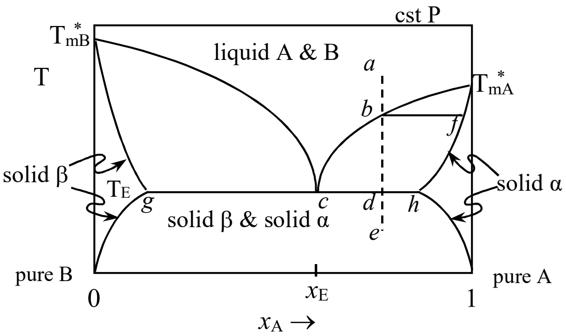


In the solid-liquid two-phase regions, with the solid and liquid in equilibrium, p = 2 and the variance at constant pressure is f ' = 2 – 2 + 1 = 1. On the left side of the phase diagram the solution is in equilibrium with the solid rich in B, solid β. On the right side the solution is in equilibrium with the A rich solid, solid α. At the eutectic temperature, the liquid phase, solid β, and solid α co-exist and p = 3 giving $f' = 2 - 3 + 1 = 0$. The eutectic temperature is an **invariant** point at constant pressure. Below the eutectic temperature, solid β and solid α are in equilibrium. The specific concentrations for the two solid phases are temperature dependent. The cross-hatched areas are not accessible starting from a homogeneous solution of A and B.

41. For many binary solid-liquid systems, the two solids are partially miscible. The solid phases consist of a phase rich in A with small amounts of B, the α phase, and a phase rich in B with small amounts of A, the β phase. Below the eutectic temperature, solid β and solid α are in equilibrium. The compositions of the two solid phases depend on temperature. The phase diagram for a binary solid-liquid system with partial miscibility is shown below, at constant pressure. Describe the phase changes that occur as the solution starting at point *a* is cooled to below the eutectic temperature, point *e*.



Answer: Cooling the solution of A and B starting at point *a*, the first phase change occurs when the temperature reaches the freezing point of the solution, point *b*. At point *b*, the solution is in equilibrium with solid α, with the composition given by the right side of the tie line at point *f*, in the diagram below. As solid α freezes out of solution, the solution composition becomes richer in B; the solution composition moves to the left on the co-existence curve and the freezing point of the solution decreases. The temperature continues to drop until the eutectic temperature is reached, point *c*. At the eutectic temperature, solid β crystallizes out of solution along with solid α. The temperature remains constant (the eutectic point is an invariant point at constant pressure), until the solution has completely frozen into a heterogeneous mixture of crystallites of solid α and solid β. The compositions of the two solid phases are at the ends of the tie line at the eutectic temperature, points *g* and *h*.



Below the eutectic temperature, the combined concentration of the solid phases is equal to the original solution concentration, point *d*, but no single phase has the composition at point *d*. The system continues to cool to point *e*. As the solution cools below the eutectic temperature, the composition of the solid phases at equilibrium change. However, establishing equilibrium is a very slow process in the solid state.

42. Consider a binary solid-liquid system with components that are completely immiscible in the solid phase, Figure 18.4.11. Below the eutectic temperature, only pure solid A and pure solid B are present. The general form of the Gibbs Phase Rule, $f = c - p + 2$, does not apply to this region because the components A and B don't occur in all the phases. Determine the variance in the two-phase solid region below the eutectic temperature for immiscible components.

Answer: There are only two intensive variables in the solid two-phase region: T and P. The concentrations are fixed, since the phases are pure. For the solid A phase $x_A = 1$ and for the solid B phase $x_B = 1$. The variance is then $f = 2$, accounting for the temperature and pressure variation. At constant pressure, $f' = 1$, and the system is univariant. Only the temperature may be varied at constant pressure. Please see Problems 39-40 for the more realistic case of partial miscibility.

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Chapter 19 Problems: Real Solutions

1. A solution of solvent A and solute B has relative forces A-A, B-B < A-B. Are the activity coefficients for the solvent less than one or greater than one?

Answer: The A-B forces are favorable giving negative deviations from ideality and $\gamma_A < 1$ for the solvent. We always assume a Raoult's Law standard state for the solvent.

2. The partial pressure of acetone over a solution of acetone in ether at 30°C is 0.120 bar at $x_{\text{acetone}} = 0.200$. The partial pressure of ether at this same concentration is 0.713 bar. Calculate the activity coefficients for ether and acetone given that vapor pressure of pure acetone is 0.377 bar and of pure ether is 0.861 bar.

Answer: On a Raoult's Law standard state basis, Eqs. 19.1.5 and 19.1.7, with $P^*_{\text{acetone}} = 0.377$ bar and $P^*_{\text{ether}} = 0.861$ bar, the activities are:

$$a_A = P_A/P_A^* = 0.120/0.377 = 0.318 \qquad \gamma_A = a_A/x_A = 0.318/0.200 = 1.59$$

$$a_E = P_E/P_E^* = 0.713/0.861 = 0.828 \qquad \gamma_E = a_E/x_E = 0.828/0.800 = 1.04$$

3. The pure vapor pressure of substance A is 28.2 torr. The mole fraction of A in the vapor above a solution is 0.0432 while the mole fraction of A in the solution is 0.672. Calculate the activity coefficient for A in this solution on a Raoult's Law basis. The total vapor pressure is 760.0 torr.

Answer: The plan is to use Dalton's Law to find the partial vapor pressure of A and then $a_A = P_A/P_A^*$.

Dalton's Law gives the partial vapor pressure of A in the gas phase:

$$P_A = y_A\, P = 0.0432\ (760 \text{ torr}) = 32.8 \text{ torr}$$

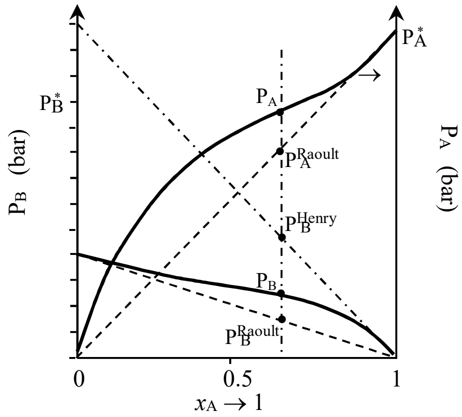
On a Raoult's Law standard state basis, Eqs. 19.1.5 and 19.1.7 give:

$$a_A = P_A/P_A^* = 32.8/28.2 = 1.16 \qquad \gamma_A = a_A/x_A = 1.16/0.672 = 1.73$$

Vapor phase composition data is easily obtained using gas-phase UV or IR absorption spectroscopy or gas chromatography.

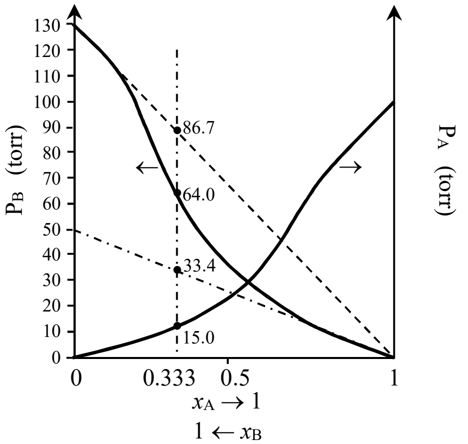
4. Under what circumstances can the activity coefficient of the solvent be greater than one, but in the same solution, the activity coefficient of the solute be less than one (or visa versa)?

Answer: The situation is likely when a Raoult's Law standard state is used for the solvent and a Henry's Law standard state is used for the solute. For example, if the solvent activity coefficient is greater than one, the solution has positive deviations from ideality, as in the figure below.



From the figure, for the solvent A, $P_A > P_A^{Raoult}$ giving $\gamma_A > 1$. For the solute B, $P_B < P_B^{Henry}$ giving $\gamma_B < 1$. At intermediate concentration, the behavior of each component is intermediate between Raoult's Law (for example, positive deviations) and Henry's Law (corresponding negative deviations).

5. (a). Calculate the activity coefficient for B at x_B =0.667 with a Raoult's Law and a Henry's Law standard state. (b). Characterize the relative forces, ε_{AB} versus $(\varepsilon_{AA}+ \varepsilon_{BB})/2$. (c). Find the vapor pressure of pure B and the Henry's Law constant for B from the plot. Find the Raoult's Law and Henry's Law predictions for the vapor pressure of B at x_B =0.667.



Answer: The plan is to note that $P_A = 15.0$ torr, $P_B = 64.0$ torr, $P_B^{Raoult} = 86.7$ torr, and $P_B^{Henry} =$ 33.4 torr at $x_B = 1 - x_A = 0.667$.

(a). Using Eq. 19.1.9 for a Raoult's Law standard state gives:

$$\gamma_B = P_B/P_B^{Raoult} = 64.0/86.7 = 0.738$$

Using Eq. 19.1.16 for a Henry's Law standard state gives:

$\gamma_B = P_B/P_B^{Henry} = 64.0/33.4 = 1.92$

At this intermediate concentration, the behavior of B is intermediate between Raoult's Law (with negative deviations) and Henry's Law (with positive deviations), as expected.

(b). Because the vapor pressures are less than the Raoult's Law predictions, this solution shows negative deviations from ideality; $|\varepsilon_{AB}| > |(\varepsilon_{AA} + \varepsilon_{BB})/2|$.

It is best to deal with magnitudes, since the forces are all attractive, ε_{AB}, ε_{AA}, $\varepsilon_{BB} < 0$. Using simple solution theory, noting Eq. 19.6.4, then ε_{AB} is more favorable than $(\varepsilon_{AA} + \varepsilon_{BB})$ so that $\varepsilon_{AB} < (\varepsilon_{AA} + \varepsilon_{BB})/2$ gives $\Delta_{sol}G < 0$.

(c). Visually, the vapor pressure of B at $x_B = 1$ is $P_B^* = 130.$ torr. The Raoult's Law prediction is:

$P_B^{Raoult} = x_B\, P_B^* = 0.667(130.\text{ torr}) = 86.7\text{ torr}$ as shown in the figure.

Visually, from the intersection of the Henry's Law line at $x_B = 1$, $k_{H,B} = 50.0$ torr. The Henry's Law prediction is:

$P_B^{Henry} = x_B\, k_{H,B} = 0.667(50.0\text{ torr}) = 33.4\text{ torr}$ as shown in the figure.

6. The partial vapor pressure of heptane above a solution of heptane and 1-bromobutane was 0.0885 bar for a heptane mole fraction of 0.4164. The vapor pressure of pure heptane is 0.187 bar. The Henry's Law constant for heptane was determined in Problem 18.13 to be k_H,heptane = 0.265 bar. Calculate the activity coefficients on both a Raoult's Law and Henry's Law basis.

Answer: On a Raoult's Law standard state basis, Eqs. 19.1.5 and 19.1.7 give:

$a_A = P_A/P_A^* = 0.0885/0.187 = 0.473$ $\gamma_A = a_A/x_A = 0.473/0.4164 = 1.14$

The solution has positive deviations from ideality, overall. On a Henry's Law standard state basis, using Eq. 19.1.14 for heptane as the solute B:

$a_B = P_B/k_{H,B} = 0.0885/0.265 = 0.334$ $\gamma_B = a_B/x_B = 0.334/0.4164 = 0.802$

The vapor pressure of heptane is less than that predicted from the dilute solution environment. The behavior of heptane is intermediate between Raoult's Law (positive deviations) and Henry's Law (negative deviations) as you might expect since the solution is intermediate in concentration.

7. The freezing point depression for a 10.00 % by weight solution of acetone in water is 3.29°C. Calculate the activity, activity coefficient, and osmotic coefficient. Calculate the osmotic pressure of the solution at 25°C assuming the activity coefficient and osmotic coefficient are constant over the given temperature range and the partial molar volume of the solvent is the pure molar volume. The molar mass of acetone is 58.05 g mol^{-1}. The enthalpy of fusion of water is 6.008 kJ mol^{-1}.

Answer: We follow Example 19.1.2. The mole fraction of the solvent, assuming 100.0 g of solution, is:

$$x_A = \frac{90.00\text{ g}/\mathfrak{M}_A}{90.00\text{ g}/\mathfrak{M}_A + 10.00\text{ g}/\mathfrak{M}_B} = \frac{90.0\text{ g}/18.0153\text{ g mol}^{-1}}{90.0\text{ g}/18.0153\text{ g mol}^{-1} + 10.00\text{ g}/58.05\text{ g mol}^{-1}} =$$

0.96667

The molality of the solute, assuming 100.0 g of solution, is:

$$m_B = \frac{10.00\text{ g}/\mathfrak{M}_B}{90.00\text{ g }(1\text{ kg}/1000\text{ g})} = \frac{10.0\text{ g}/58.05\text{ g mol}^{-1}}{90.0\text{ g }(1\text{ kg}/1000\text{ g})} = 1.914\text{ m}$$

Using Eq. 19.1.4 with the melting point of the solution, T = 273.15 K – 3.29 K = 269.86 K, and assuming a constant enthalpy of fusion:

$$\ln a_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) = -\frac{6.008\text{x}10^3\text{ J mol}^{-1}}{8.3145\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{269.86\text{ K}} - \frac{1}{273.15\text{ K}}\right) = -0.032252$$

$$a_A = 0.96826$$

The activity coefficient is $\gamma_A = a_A/x_A = 0.96826/0.96667 = 1.00164$.
The osmotic coefficient is given by Eq. 19.1.20 or directly using Eq. 19.1.23:

$$\phi = -(55.51\text{ mol kg}^{-1}\ln a_A)/m_B = \frac{\Delta_{fus}H_A}{R\,m_B/(55.51\text{ mol kg}^{-1})}\left(\frac{1}{T} - \frac{1}{T_m^*}\right)$$

$$= -55.51(-0.032252)/1.914\text{ m}$$

$$= 0.93538$$

The osmotic coefficient has a larger difference from one than the activity coefficient, as designed.

The pure molar volume of water is $V_A^* = \mathfrak{M}_A/d_{A,pure} = 18.069\text{ mL} = 0.018069\text{ L}$. The osmotic pressure can be calculated from Eq. 18.4.23† with the activity substituted or Eq. 19.1.24 using the osmotic coefficient:

$$\pi\,\bar{V}_A = -RT\ln a_A = -0.083145\text{ bar L K}^{-1}\text{ mol}^{-1}(298.15\text{ K})(-0.032252) \quad \text{giving}$$

$$\pi = 44.25\text{ bar} \qquad \text{alternatively:}$$

$$\pi\,\bar{V}_A = RT\,\phi\,m_B/(55.51\text{ mol kg}^{-1}) \qquad \text{giving} \quad \pi = 44.25\text{ bar}$$

The ideal prediction using Eq. 18.4.26† is 46.5 bar, which corresponds to a 5% error neglecting the activity coefficient. Electrolyte solutions show much larger deviations from ideality.

8. The freezing point depression for a 10.00 % by weight solution of $MgCl_2$ in water is 7.91°C. Calculate the activity, activity coefficient, and osmotic coefficient. Calculate the osmotic pressure of the solution at 25°C assuming the activity coefficient and osmotic coefficient are constant over the given temperature range and the partial molar volume of the solvent is the pure molar volume. The molar mass of $MgCl_2$ is 95.23 g mol^{-1}. The enthalpy of fusion of water is 6.008 kJ mol^{-1}.

Answer: We follow Example 19.1.2 with $m_B = \nu m_{MgCl_2}$ and $\nu = 3$. The mole fraction of the solvent, assuming 100.0 g of solution, is:

$$x_A = \frac{90.00\ \text{g}/\mathfrak{M}_A}{90.00\ \text{g}/\mathfrak{M}_A + 3(10.00\ \text{g}/\mathfrak{M}_B)} = \frac{90.0\ \text{g}/18.0153\ \text{g mol}^{-1}}{90.0\ \text{g}/18.0153\ \text{g mol}^{-1} + 3(10.00\ \text{g}/95.23\ \text{g mol}^{-1})}$$
$$= 0.94068$$

The molality of the solute particles, assuming 100.0 g of solution, is:

$$m_B = 3\left(\frac{10.00\ \text{g}/\mathfrak{M}_B}{90.00\ \text{g}\ (1\ \text{kg}/1000\ \text{g})}\right) = 3\left(\frac{10.0\ \text{g}/95.23\ \text{g mol}^{-1}}{90.0\ \text{g}\ (1\ \text{kg}/1000\ \text{g})}\right) = 3.5003\ \text{m}$$

Using Eq. 19.1.4 with the melting point of the solution, T = 273.15 K – 7.91 K = 265.24 K, and assuming a constant enthalpy of fusion:

$$\ln a_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) = -\frac{6.008\text{x}10^3\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{265.24\ \text{K}} - \frac{1}{273.15\ \text{K}}\right) = -0.078891$$
$$a_A = 0.92414$$

The activity coefficient is $\gamma_A = a_A/x_A = 0.92414/0.94068 = 0.98242$.
The osmotic coefficient is given by Eq. 19.1.20 or directly using Eq. 19.1.23:

$$\phi = -\ (55.51\ \text{mol kg}^{-1} \ln a_A)/m_B = \frac{\Delta_{fus}H_A}{R\ m_B/(55.51\ \text{mol kg}^{-1})}\left(\frac{1}{T} - \frac{1}{T_m^*}\right)$$
$$= -\ 55.51(-0.078891)/3.5003\ \text{m}$$
$$= 1.2511$$

The osmotic coefficient has a larger difference from one than the activity coefficient, as designed.

The pure molar volume of water is $V_A^* = \mathfrak{M}_A/d_{A,pure} = 18.069$ mL = 0.018069 L. The osmotic pressure can be calculated from Eq. 18.4.23† with the activity substituted or Eq. 19.1.24 using the osmotic coefficient:

$$\pi\ \bar{V}_A = -\ RT \ln a_A = -\ 0.083145\ \text{bar L K}^{-1}\ \text{mol}^{-1}(298.15\ \text{K})(\ -0.078891) \qquad \pi = 108.2\ \text{bar}$$
$$\pi\ \bar{V}_A = RT\ \phi\ m_B/(55.51\ \text{mol kg}^{-1}) \qquad \pi = 108.2\ \text{bar}$$

The ideal prediction using Eq. 18.4.26† is 83.9 bar, which corresponds to a 22% error neglecting the activity coefficient.

9. Eqs. 18.4.8†, 18.4.15†, and 19.1.4 assume the phase transition enthalpy of the solvent is constant. For careful determinations of the activity with large freezing point changes, the temperature dependence of the enthalpy of fusion should be taken into account: $\Delta_{fus}H_A(T) = \Delta_{fus}H_A(T_A^*) + \Delta_{fus}C_{p,A}\ (T - T_A^*)$. Use this temperature dependence to find a better approximation to Eq. 19.1.4 by completing the following steps.
(a). At equilibrium for a solid-liquid phase transition, the equivalence of the chemical potentials gives $\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$, which is the analog to Eq. 18.4.2†. Convert the last equation into the corresponding equation for a real solution. The Gibbs energy of fusion for the pure solvent is $\Delta_{fus}G_A = \mu_A^*(l) - \mu_A^*(s)$. Use the Gibbs-Helmholtz relationship, Eq. 16.3.12, to show:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = \frac{\Delta_{fus}H_A}{RT^2}$$

(b). Use the temperature dependence of the enthalpy to integrate this last equation from T_A^* to T. Note that $a_A = 1$ and $\ln a_A = 0$ at the pure standard melting point T_A^*. The result is:

$$\ln a_A = -\left(\frac{\Delta_{fus}H_A(T_A^*) - \Delta_{fus}C_{p,A}\, T_A^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_A^*}\right) + \frac{\Delta_{fus}C_{p,A}}{R} \ln(T/T_A^*)$$

Answer: (a). To convert the ideal solution equation to a real solution, we simply replace x_A with a_A. The difference in the chemical potentials gives: $\Delta_{fus}G_A = \mu_A^*(l) - \mu_A^*(s) = -RT \ln a_A$. Then the Gibbs-Helmholtz expression, Eq. 16.3.12, gives:

$$\left(\frac{\partial\left(\frac{\Delta_{fus}G_A}{T}\right)}{\partial T}\right)_P = -\frac{\Delta_{fus}H_A}{T^2}$$

Since $\ln a_A = -\Delta_{fus}G_A/RT$, dividing both sides of the last equation by $-R$ gives:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = \frac{\Delta_{fus}H_A}{RT^2}$$

(b). Integrating this last equation from T_A^* to T and using $\Delta_{fus}H_A(T) = \Delta_{fus}H_A(T_A^*) + \Delta_{fus}C_{p,A}\,(T - T_A^*)$:

$$\int_{\ln a_A(T_A^*)}^{\ln a_A(T)} d\ln a_A = \int_{T_A^*}^{T} \frac{\Delta_{fus}H_A(T_A^*)}{RT^2}\, dT + \int_{T_A^*}^{T} \frac{\Delta_{fus}C_{p,A}}{RT}\, dT - \int_{T_A^*}^{T} \frac{\Delta_{fus}C_{p,A}\, T_A^*}{RT^2}\, dT$$

Since at the pure standard melting point, $a_A = 1$ and $\ln a_A = 0$, the integral on the left is just $\ln a_A$ at the final temperature. The first integral on the right gives the standard form of the equation, Eq. 18.4.15†. The remaining two terms are the corrections:

$$\ln a_A = -\frac{\Delta_{fus}H_A(T_A^*)}{R}\left(\frac{1}{T} - \frac{1}{T_A^*}\right) + \frac{\Delta_{fus}C_{p,A}}{RT} \ln(T/T_A^*) + \frac{\Delta_{fus}C_{p,A}\, T_A^*}{R}\left(\frac{1}{T} - \frac{1}{T_A^*}\right)$$

Combining the first and last terms on the right gives the final result:

$$\ln a_A = -\left(\frac{\Delta_{fus}H_A(T_A^*) - \Delta_{fus}C_{p,A}\, T_A^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_A^*}\right) + \frac{\Delta_{fus}C_{p,A}}{R} \ln(T/T_A^*)$$

For water, $\Delta_{fus}H_A(T_A^*) = 6.008 \pm 0.004$ kJ mol^{-1}, $T_A^* = 273.15$ K, and $\Delta_{fus}C_{p,A} = 38.1 \pm 0.2$ J K^{-1} mol^{-1}. Substituting these values into equation 13 gives:

$$\ln a_A = 529.16\left(\frac{1}{T} - \frac{1}{273.15}\right) + 4.583 \ln(T/273.15)$$

So the result is actually easy to use.

10. Freezing point depression and boiling point elevation are used to determine the activity of the solvent at the measured phase transition temperature for the solution. We usually need to know the activity at 25°C. Find an expression for the temperature dependence of the activity of a substance by completing the following steps. (a). The chemical potential of the solvent in solution is $\mu_A(x_A) =$
$\mu_A^*(l) + RT \ln a_A$, Eq. 19.1.3. The partial molar Gibbs energy of solution for the solvent is $\Delta_{sol}\overline{G}_A = \mu_A(x_A) - \mu_A^*(l)$. Use the Gibbs-Helmholtz relationship, Eq. 16.3.12, to show:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = -\frac{\Delta_{sol}\overline{H}_A}{RT^2}$$

where $\Delta_{sol}\overline{H}_A$ is the partial molar enthalpy of solution. (b). Integrate this equation from T_1 to T_2. Assume the enthalpy of solution is constant over the temperature range. Show that the result is:

$$\ln\left(\frac{a_A(T_2)}{a_A(T_1)}\right) = -\left(\frac{\Delta_{sol}\overline{H}_A}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Answer: The plan is to use the same approach as the last problem, which is also based on the Gibbs-Helmholtz equation.

(a). The difference in the chemical potentials gives: $\Delta_{fus}\overline{G}_A = \mu_A(x_A) - \mu_A^*(l) = RT \ln a_A$. Then the Gibbs-Helmholtz expression, Eq. 16.3.12, gives:

$$\left(\frac{\partial\left(\frac{\Delta_{sol}\overline{G}_A}{T}\right)}{\partial T}\right)_P = -\frac{\Delta_{sol}\overline{H}_A}{T^2}$$

Since $\ln a_A = \Delta_{sol}\overline{G}_A/RT$, dividing both sides of the last equation by R gives:

$$\left(\frac{\partial \ln a_A}{\partial T}\right)_P = -\frac{\Delta_{sol}\overline{H}_A}{RT^2}$$

(b). Integrating this last equation from T_1 to T_2 and assuming $\Delta_{fus}\overline{H}_A$ is independent of temperature gives:

$$\int_{\ln a_A(T_1)}^{\ln a_A(T_2)} d \ln a_A = -\int_{T_1}^{T_2} \frac{\Delta_{sol}\overline{H}_A}{RT^2}\, dT$$

$$\ln\left(\frac{a_A(T_2)}{a_A(T_1)}\right) = \left(\frac{\Delta_{sol}\overline{H}_A}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For an ideal solution $\Delta_{sol}\overline{H}_A$ is zero, and the activity is then temperature independent. For real solutions, for narrow temperature ranges, the change in activity is often small. For large changes in temperature correction terms may be added to take into account the temperature dependence of the enthalpy of solvation, analogous to the approach in the last problem.

11. The osmotic coefficient for aqueous *n*-propanol solutions is: $\phi - 1 = a\, m_B^3 + b\, m_B^2 + c\, m_B$, with: $a = -4.73$ kg^3 mol^{-3}, $b = 2.21$ kg^2 mol^{-2}, and $c = -0.365$ kg mol^{-1} at 0°C, where m_B is the molality of *n*-propanol. Determine the activity coefficients for *n*-propanol and water at 0.100 m.

Answer: Doing the integral in Eq. 19.1.26 with the cubic polynomial gives:

$$\ln {}^m\gamma_B = \phi(m) - 1 + \int_0^m \left(\frac{a\, m_B^2 + b\, m_B}{m_B}\right) d\, m_B = \phi(m) - 1 + \frac{a}{3} m^3 + \frac{b}{2} m^2 + c\, m$$

For a 0.100 m solution: $\phi(m) - 1 = -4.73\, m^3 + 2.21\, m^2 + (-0.365)\, m = -0.1913$

$$\ln {}^m\gamma_B = (-0.1913) + (-4.73)\, m^3/3 + 2.21\, m^2/2 + (-0.365)\, m = -0.04616$$

giving ${}^m\gamma_B = 0.955$ on a molal basis. For water, using Eq. 19.1.21, the activity is:

$$\ln a_A = -\,\phi\, m_B/55.51 \text{ mol kg}^{-1} = (1 - 0.1913)\ 0.100 \text{ mol kg}^{-1}/55.51 \text{ mol kg}^{-1} = 1.457\text{x}10^{-3}$$
$$a_A = 1.001$$

The mole fractions for *n*-propanol and water are given by Eq. 2.2.13:

$$x_B = \frac{0.100 \text{ mol kg}^{-1}\ (1 \text{ kg})}{55.51 \text{ mol} + 0.100 \text{ mol kg}^{-1}\ (1 \text{ kg})} = 1.7982\text{x}10^{-3} \qquad \text{and } x_A = 1 - x_B = 0.99820$$

giving the activity coefficient for water as ${}^x\gamma_A = a_A/x_A = 1.001/0.99820 = 1.003$.

12. Find the overall solution activity in terms of the mean ionic activity coefficient and the solution molality, m, for: (a). KNO_3, (b). $CaCl_2$, (c). $LaCl_3$, (d). $CuSO_4$.

Answer: (a). Using Eq. 19.4.9, $m_+ = m_- = m$ for a 1:1 electrolyte:

$$a(KNO_3) = a_+\, a_- = \left(\frac{\gamma_\pm^2\, m_+\, m_-}{m^{\circ 2}}\right) = \left(\frac{\gamma_\pm^2\, m^2}{m^{\circ 2}}\right) = \gamma_\pm^2\, (m/m^\circ)^2$$

(b). Using Eq. 19.4.16, $m_+ = m_{Ca^{2+}} = m$ and $m_- = m_{Cl^-} = 2m$ for a 1:2 electrolyte:

$$a(CaCl_2) = a_{Ca^{2+}}\, a_{Cl^-}^2 = \left(\frac{\gamma_\pm^3\, (m)\, (2m)^2}{m^{\circ 3}}\right) = 4\, \gamma_\pm^3\, (m/m^\circ)^3$$

(c). For $LaCl_3$, $m_+ = m_{La^{3+}} = m$ and $m_- = m_{Cl^-} = 3m$ for a 1:3 electrolyte:

$$a(LaCl_3) = a_{La^{3+}}\, a_{Cl^-}^3 = \left(\frac{\gamma_\pm^4\, (m)\, (3m)^3}{m^{\circ 4}}\right) = 27\, \gamma_\pm^4\, (m/m^\circ)^4$$

(d). Using Eq. 19.4.9 for $CuSO_4$, $m_+ = m_- = m$ for a 1:1 electrolyte:

$$a(CuSO_4) = a_+\, a_- = \left(\frac{\gamma_\pm^2\, m_+\, m_-}{m^{\circ 2}}\right) = \left(\frac{\gamma_\pm^2\, m^2}{m^{\circ 2}}\right) = \gamma_\pm^2\, (m/m^\circ)^2$$

13. Find the ionic strength in terms of the molality, m, for the following strong electrolytes dissolved in pure water: (a). $CaCl_2$, (b). $LaCl_3$, (c). $CuSO_4$ (neglect any hydrolysis).

Answer: Using Eq. 19.4.22:

(a). For $CaCl_2$, $z_+ = 2$, $z_- = -1$, $m_{Ca^{2+}} = m$ and $m_{Cl^-} = 2$ m:

$$I = \tfrac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \tfrac{1}{2} [(2)^2 m + (-1)^2 (2m)]/m^\circ = 3\ m/m^\circ$$

(b). For $LaCl_3$, $z_+ = 3$, $z_- = -1$, $m_{La^{3+}} = m$ and $m_{Cl^-} = 3$ m:

$$I = \tfrac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \tfrac{1}{2} [(3)^2 m + (-1)^2 (3m)]/m^\circ = 6\ m/m^\circ$$

(b). For $CuSO_4$, $z_+ = 2$, $z_- = -2$, $m_{Cu^{2+}} = m$ and $m_{SO_4^{2-}} = m$:

$$I = \tfrac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \tfrac{1}{2} [(2)^2 m + (-2)^2 (m)]/m^\circ = 4\ m/m^\circ$$

Why did we specify that hydrolysis should be neglected? The sulfate ion can hydrolyze by:

$$SO_4^{2-} + H_2O \rightleftarrows HSO_4^- + OH^- \qquad K_b = K_w/K_{a,2} = 9.71\times10^{-13}$$

However, this equilibrium won't have a significant effect on the ionic strength. The hydrolysis will make the solution slightly basic, however.

14. Write the solubility product equilibrium expressions for the sparingly soluble salts: (a). Ag_2CrO_4, (b). $Cr(OH)_3$, (c). $Ca_3(PO_4)_2$.

Answer: Let m_s be the moles of salt dissolved per kg of solvent. Using Eq. 19.4.16:
(a). For Ag_2CrO_4, $m_+ = m_{Ag^+} = 2m_s$ and $m_- = m_{CrO_4^{2-}} = m_s$ for a 2:1 electrolyte:

$$K_{sp} = (a_{Ag^+})^2\, a_{CrO_4^{2-}} = \left(\frac{\gamma_\pm^3 (2m_s)^2 (m_s)}{m^{\circ 3}}\right) = 4\, \gamma_\pm^3\, (m_s/m^\circ)^3$$

(b). For $Cr(OH)_3$, $m_+ = m_{Cr^{3+}} = m_s$ and $m_- = m_{OH^-} = 3m_s$ for a 1:3 electrolyte:

$$K_{sp} = a_{Cr^{3+}}\, a_{OH^-}^3 = \left(\frac{\gamma_\pm^4 (m_s) (3m_s)^3}{m^{\circ 4}}\right) = 27\, \gamma_\pm^4\, (m_s/m^\circ)^4$$

(c). For $Ca_3(PO_4)_2$, $m_+ = m_{Ca^{2+}} = 3m_s$ and $m_- = m_{PO_4^{3-}} = 2m_s$ for a 3:2 electrolyte:

$$K_{sp} = (a_{Ca^{2+}})^3\, (a_{PO_4^{3-}})^2 = \left(\frac{\gamma_\pm^5 (3m_s)^3 (2m_s)^2}{m^{\circ 5}}\right) = 108\, \gamma_\pm^5\, (m_s/m^\circ)^5$$

15. Calculate the mean ionic activity coefficient for a 0.100 m aqueous solution of $CaCl_2$ at 25°C using the Debye-Hückel approximation.

Answer: The ionic strength for $CaCl_2$ is given in Problem 2a as I = 3 m/m°. For the given concentration:

$$I = 3\ m/m^\circ = 0.300$$

For $CaCl_2$, $z_+ = 2$ and $z_- = -1$. Using Eq. 19.4.23:

$$\ln \gamma_\pm = -1.171\ |z_+ z_-|\ I^{½} = -1.171\ |(2)(-1)|\ (0.300)^{½} = -1.2828$$

or $$\log \gamma_\pm = -0.509\ |z_+ z_-|\ I^{½} = -0.509\ |(2)(-1)|\ (0.300)^{½} = -0.55758$$

giving $\gamma_\pm = 0.277$.

16. Mercury pollution is an increasing problem in northern lakes. The source of the mercury is primarily coal combustion. Mercury compounds can be carried long distances by atmospheric aerosols. Calculate the solubility of mercury(I)chloride, Hg_2Cl_2, in pure water and in 0.0100 m KNO_3, $K_{sp} = 1.2\text{x}10^{-18}$. Remember that the dissociation is given by:

$$Hg_2Cl_2\ (s) \rightleftarrows Hg_2^{2+} + 2\ Cl^-$$

Answer: For Hg_2^{2+}, $z_+ = 2$, and for Cl^- $z_- = -1$. For this 1:2 electrolyte, $m_+ = m_{Hg22+} = m$ and $m_- = m_{Cl-} = 2m$. In pure water the ionic strength is given by:

$$I = ½ \sum z_i^2 \frac{m_i}{m^\circ} = ½\ [(2)^2\ m + (-1)^2\ (2m)]/m^\circ = 3\ m/m^\circ$$

However, we don't know the concentration of dissolved Hg_2Cl_2. We can estimate the solubility by neglecting the activity coefficients:

$$K_{sp} \approx [Hg_2^{2+}][Cl^-]^2 = (m_s/m^\circ)(2m_s/m^\circ)^2 = 4\ m_s^3$$

giving $m_s/m^\circ \approx (1.2\text{x}10^{-18}/4)^{1/3} \approx 6.694\text{x}10^{-7}$

With this approximate concentration, the ionic strength is $I = 3\ m/m^\circ = 2.008\text{x}10^{-6}$. Using the Debye-Hückel approximation gives the mean ionic activity coefficient:

$$\ln \gamma_\pm = -1.171\ |z_+ z_-|\ I^{½} = -1.171\ |(2)(-1)|\ (2.008\text{x}10^{-6})^{½} = -3.319\text{x}10^{-3}$$

or $$\log \gamma_\pm = -0.509\ |z_+ z_-|\ I^{½} = -0.509\ |(2)(-1)|\ (2.008\text{x}10^{-6})^{½} = -1.443\text{x}10^{-3}$$

giving $\gamma_\pm = 0.997$. The solubility in pure water is then:

$$K_{sp} = (a_{Hg22+})\ (a_{Cl-})^2 = \left(\frac{\gamma_\pm^3 (m_s)\ (2m_s)^2}{m^{\circ 3}}\right) = 4\ \gamma_\pm^3\ (m_s/m^\circ)^3$$

giving $m_s = m^\circ\ (1.2\text{x}10^{-18}/4/(0.997)^3)^{1/3} = 6.714\text{x}10^{-7}\ m$

The effect of the non-ideality is well within the limits of the experimental uncertainty. However, with the non-participating electrolyte, the ionic strength will be dominated by the 0.0100 m KNO_3:

$$I = ½\,[(2)^2\, m_{Hg_2^{2+}} + (-1)^2\,(2m_{Cl^-}) + (1)^2\, m_{K^+} + (-1)^2\, m_{NO_3^-}]/m° = 0.0100$$
$$I = ½\,[(2)^2\, 6.7\text{x}10^{-7} + (-1)^2\, 2\,(6.7\text{x}10^{-7}) + (1)^2\, 0.0100 + (-1)^2\, 0.0100]/m° = 0.0100$$

[For a 1:1, uni-positive-uni-positive electrolyte the ionic strength is equal to the molality.] The mean ionic activity coefficient in 0.0100 m KNO_3 is then:

$$\ln \gamma_\pm = -1.171\, |z_+ z_-|\, I^{½} = -1.171\, |(2)(-1)|\, (0.0100)^{½} = -0.2342$$

or $$\log \gamma_\pm = -0.509\, |z_+ z_-|\, I^{½} = -0.509\, |(2)(-1)|\, (0.0100)^{½} = -0.1018$$

giving $\gamma_\pm = 0.791$. The solubility in 0.0100 m KNO_3 is then:

$$m_s = m°\,(1.2\text{x}10^{-18}/4/(0.791)^3)^{1/3} = 8.46\text{x}10^{-7}\text{ m}$$

<u>17</u>. Write the acid dissociation equilibrium expressions in terms of the concentration of the undissociated acid, m_{HA}, the H^+ concentration, m_{H^+}, and the mean ionic activity coefficient, for the weak acids: (a). CH_3COOH, acetic acid (HOAc), (b). H_2S (for the first dissociation only).

Answers: The plan is to write the expression as you would for General Chemistry with $[H^+]$, $[A^-]$, and [HA] and then replace the concentrations by activities. The activity based acid dissociation constant is K_a. The acid dissociation constant written in terms of concentrations is called the effective equilibrium constant, $K_{a,eff}$, which is ionic strength dependent.

(a). For the dissociation: $HOAc\,(aq) \rightleftarrows H^+ + OAc^-$, $m_{H^+} = m_+ = m_-$:

$$K_{a,eff} = \frac{[H^+]\,[OAc^-]}{[HOAc]} \qquad K_a = \frac{(a_{H^+})(a_{OAc^-})}{a_{HOAc}} = \frac{\gamma_\pm^2\,(m_+/m°)(m_-/m°)}{m_{HA}/m°} = \frac{\gamma_\pm^2\,(m_{H^+}/m°)^2}{m_{HA}/m°}$$

Note that if the analytical concentration of the weak acid is $m_{HA,o}$ then at equilibrium $m_{HA} = m_{HA,o} - m_{H^+}$. The final $pH = -\log a_{H^+} = -\log(\gamma_\pm\, m_{H^+})$.

(b) For the dissociation: $H_2S\,(aq) \rightleftarrows H^+ + HS^-$, again $m_{H^+} = m_+ = m_-$ (neglecting further dissociation):

$$K_{a,eff} = \frac{[H^+]\,[HS^-]}{[H_2S]} \qquad K_{a,1} = \frac{(a_{H^+})(a_{HS^-})}{a_{H_2S}} = \frac{\gamma_\pm^2\,(m_+/m°)(m_-/m°)}{m_{H_2A}/m°} = \frac{\gamma_\pm^2\,(m_{H^+}/m°)^2}{m_{H_2A}/m°}$$

If the analytical concentration of the weak acid is $m_{H_2A,o}$ then at equilibrium $m_{H_2A} = m_{H_2A,o} - m_{H^+}$.

<u>18</u>. Using Eqs. 19.5.12, 19.5.18 and 19.5.19, derive Eq. 19.5.20.

Answer: The charge density is written in terms of κ by substituting Eq. 19.5.19 into Eq. 19.5.18:

$$\rho_i(r) = -\frac{\phi_i(r)e^2}{kT}\sum_{j=1}^{s} z_j^2\frac{N_j}{V} = -\varepsilon_r\varepsilon_o\ \phi_i(r)\ \kappa^2$$

Dividing by $\varepsilon(r) = \varepsilon_o\varepsilon_r$ for a uniform permittivity gives:

$$\frac{\rho_i(r)}{\varepsilon(r)} = -\kappa^2\ \phi_i(r)$$

and then substitution into Eq. 19.5.12 gives:

$$\frac{1}{r}\frac{\partial^2(r\ \phi_i(r))}{\partial r^2} = \kappa^2\ \phi_i(r)$$

Multiplying both sides of this equation by r gives Eq. 19.5.20:

$$\frac{\partial^2(r\,\phi_i(r))}{\partial r^2} = \kappa^2\ (r\ \phi_i(r))$$

19. Show that $\phi_i(r) = \frac{C}{r}\,e^{-\kappa r}$ is the solution to the Eq. 19.5.20.

Answer: With $(r\ \phi_i(r)) = C\,e^{-\kappa r}$, taking the second derivative on the left-hand side of Eq. 19.5.20 gives:

$$\frac{\partial^2(r\,\phi_i(r))}{\partial r^2} = \frac{\partial^2(C\,e^{-\kappa r})}{\partial r^2} = \kappa^2\ C\,e^{-\kappa r} = \kappa^2\ (r\,\phi_i(r))$$

The result is the right-hand side of Eq. 19.5.20, proving that $\phi_i(r)$ is a solution to the equation.

20. (a). Starting with Eq. 19.5.19, for an aqueous solution containing one pure electrolyte, show that:

$$\kappa^2 = \frac{e^2\ 1000\ \mathrm{L\ m^{-3}}\ d_o\ N_A\ m^\circ}{\varepsilon_r\varepsilon_o\,kT}\left(z_+^2\frac{m_+}{m^\circ} + z_-^2\frac{m_-}{m^\circ}\right) \qquad \text{P19.20.1}$$

(b). Given the definition of ionic strength in Eq. 19.5.25, show from Eq. P19.20.1 that:

$$\kappa = \sqrt{\frac{2\ e^2\ 1000\ \mathrm{L\ m^{-3}}\ d_o\ N_A\ m^\circ}{\varepsilon_r\varepsilon_o\,kT}}\ I^{1/2} \qquad \text{P19.20.2}$$

(c). Starting with Eq. P19.20.2 and $r_D = 1/\kappa$, prove that Eq. 19.5.7 gives the Debye length for aqueous solutions of unipositive-uninegative electrolytes, at concentration m molal, at 298.15 K. In Eq. 19.5.7 the constant is given as 305 pm; in your answer give the constant to at least four significant figures.
(d). Find the Debye length for a 0.0100 m and 0.100 m solution of KCl.

Answer: (a). From Eq. 19.5.23, solving for the concentration ratio:

$$\frac{N_j}{V} = 1000 \text{ L m}^{-3} \text{ d } N_A \, m_j$$

where d is the density of the solution. In dilute solution, the density of the solution is approximately the density of the pure solvent, $d \approx d_o$. The standard state concentration is introduced by multiplying and dividing each term in the concentration sum by m°. Substituting for the cationic and anionic terms for N_+/V and N_-/V in in terms of the molalities gives Eq. P19.20.1.

(b). From the definition of ionic strength, $(z_+^2\, m_+/m° + z_-^2\, m_-/m°) = 2I$, then taking the square root of Eq. P19.20.1 gives Eq. P19.20.2.

(c). The Debye length is $r_D = 1/\kappa$. For a unipositive-uninegative electrolyte I = m/m°. Using $e = 1.602177\text{x}10^{-19}$ C, $d = 0.997048$ g/cm^3, 1 g/cm^3 = 1 kg L^{-1}, $\varepsilon_o = 8.85419\text{x}10^{-12}$ J^{-1}C^{2}m^{-1}, $\varepsilon_r = 78.54$, $k = 1.38066\text{x}10^{-23}$ J K^{-1}, and T = 298.15K in Eq. P19.20.2 gives:

$$r_D = 1/\kappa = \frac{304.73 \text{ pm}}{(m/m°)^{½}}$$

(d). At m = 0.0100 m, r_D = 3050 pm = 30.5 Å while at 0.100 m, r_D = 964. pm = 9.64 Å.

21. Taking the limit as r → 0 of Eq. 19.5.27 using l'Hôpital's rule, prove that the electric potential at the central ion caused by the ionic atmosphere is given by Eq. 19.5.28.

22. Plot the screened Coulomb potential for a 0.0100 m and 0.100 m NaCl solution.

23. (a). Show that the charge density for the screened Coulomb potential can be written in terms of κ as:

$$\rho_i(r) = -\frac{q_i\,\kappa^2}{4\pi\, r}\, e^{-\kappa r}$$

(b). Find the maximum of the radial probability distribution for the charge density, $4\pi r^2 \rho_i$, in terms of κ.

Answer: The charge density is written in terms of κ by substituting Eq. 19.5.19 into Eq. 19.5.18:

$$\rho_i(r) = -\frac{\phi_i(r) e^2}{kT} \sum_{j=1}^{s} z_j^2 \frac{N_j}{V} = -\,\varepsilon_r\varepsilon_o\, \phi_i(r)\, \kappa^2$$

The screened Coulomb potential is given by Eq. 19.5.22; substitution gives:

$$\rho_i(r) = -\varepsilon_r\varepsilon_o\,\kappa^2\,\frac{q_i}{4\pi\varepsilon_o\varepsilon_r\,r}\,e^{-\kappa r} = -\,\frac{q_i\,\kappa^2}{4\pi\,r}\,e^{-\kappa r}$$

This result shows that the charge density has a sign opposite to the central charge. In other words, the charge density surrounding a cation is net negative. The radial probability distribution for the charge density is given by multiplying this last equation by $4\pi r^2$:

$$4\pi r^2\rho_i(r) = -\,q_i\,\kappa^2\,r\,e^{-\kappa r}$$

The maximum in the radial probability function is given by taking the derivative using the product rule:

$$\frac{d\,4\pi r^2\rho_i(r)}{dr} = -\,q_i\,\kappa^2\,[r\,(-\kappa)e^{-\kappa r} + e^{-\kappa r}] = 0$$

which gives the radius of maximum probability, r_D, the Debye length. Dividing by all the common factors gives:

$$[-\kappa\,r_D + 1] = 0 \qquad \text{or} \qquad \kappa = 1/r_D$$

as given in Eq. 19.5.7.

24. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). The ionic halo of an ion contains only ions of opposite charge.

(b). For a simple symmetric solution, the activity coefficient of the solute depends only on the mole fraction of the solvent. The deviatons from ideality are dominated by changes in solvent-solvent forces.

(c). For a fixed ionic strength, as the relative permittivity of the solvent increases, the Debye length increases, because the counter ions in the ionic halo are less tigthly held.

Answers: (a). False: the ionic atmopshere of a ion is determined by ions of both charges, from all sources, including supporting electrolytes and buffers. Near a central cation, the concentration of anions is greater than the bulk and the concentration of cations is less than the bulk, but both are present, Eq. 19.5.17. The correct statement is: The neighborhood near an ion is dominated by ions of opposite charge.

(b). False: While Eq. 19.2.7 is written only as a function of the mole fraction of the solvent, $x_A + x_B = 1$, so the mole fractions of the solvent and solute are directly related. Using $x_A = 1 - x_B$ gives:
$x_A^2 = (1 - x_B)^2 = 1 - 2\,x_B + x_B^2$ and the activity coefficient:

$$\ln\gamma_B = \frac{a}{RT}\,x_A^2 = \frac{a}{RT}\,(1 - 2\,x_B + x_B^2)$$

The dependence of $\ln\gamma_B$ on the concentration of B is quite strong. For example, starting with a solution with $x_B = 0.001$ and $x_A = 0.999$, doubling the concentration of B only changes the solvent concentration to $x_A = 0.998$, or a 0.2% change. The probability of a B-B contact, x_B^2, is quite small for dilute solution, but increases rapidly with increasing solute concentration. The correct statement is: For the solute in dilute solution, A-B forces dominate. As the solute concentration increases, for moderate concentrations, B-B forces dominate the change in activity coefficient for the solute.

(c). True: Solvents, or solvent mixtures, with high relative permittivity provide enhanced dielectric screening, weakening the ionic interactions. The counter ions around a central ion are less tightly held, expanding the ionic atmosphere. Electrostatic interactions are weaker in water than in hexane. One common binding motif in protein-substrate binding is the formation of salt bridges. Salt bridges are ion pairs commonly formed from positive and negative charged amino acid sidechains. Salt bridges are not stabilizing in aqueous solution. However, salt bridges that form in the interior of a protein are in a low permittivity environment that strengthens the electrostatic interaction. The relative permittivity inside a globular protein is often estimated as ~4.

Chapter 20 Problems: Chemical Equilibrium

1. Determine $\Delta_rG°$ at 298.2 K for the reaction: AgCl (s) $\rightleftarrows$ Ag^+ (aq) + Cl^- (aq). The K_{sp} for AgCl is $1.8\text{x}10^{-10}$.

Answer: Using $\Delta_rG° = -\ RT \ln K_a$:

$$\Delta_rG° = -\ 8.314\text{x}10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1}\ (298.2\ \text{K})\ \ln 1.8\text{x}10^{-10} = 55.63 \pm 0.13\ \text{kJ mol}^{-1}$$

assuming $K_{sp} = 1.8\text{x}10^{-10} \pm 0.1\text{x}10^{-10}$. Using significant figure rules you would expect only two significant figures in the result.

2. Nitrogen dioxide forms a dimer in the equilibrium: 2 NO_2 (g) $\rightleftarrows$ N_2O_4 (g). The standard state reaction Gibbs energy for the dimerization of NO_2 is -4.77 kJ mol^{-1} at 298.2 K. In a reaction mixture, the partial pressure of NO_2 is 0.332 bar and of N_2O_4 is 0.986 bar. Is the reaction at equilibrium, and if not what is the spontaneous direction for the reaction?

Answer: The plan is to calculate the equilibrium constant from $\Delta_rG°$ and then calculate the reaction quotient, Q, and compare.
The equilibrium constant is given by:

$$K_p = e^{-\Delta_rG°/RT} = e^{-(-4.77\text{x}10^3\ \text{J mol}^{-1})/(8.314\ \text{J K}^{-1}\text{mol}^{-1}\ 298.2\ \text{K})} = 6.84_8$$

The reaction quotient is: $Q = \dfrac{P_{N2O4}/P°}{(P_{NO2}/P°)^2} = \dfrac{0.986}{0.332^2} = 8.94_5$

Finally, $Q > K_p$; the reaction is not at equilibrium and the spontaneous direction is to the left, towards increased reactant, NO_2.

3. Under standard conditions, one of the steps in the photosynthetic production of glucose does not occur spontaneously:

fructose-6-P + glyceraldehyde-3-P $\rightleftarrows$ erythrose-4-P + xyulose-5-P

where $\Delta_rG°' = +6.28$ kJ mol^{-1} at 298.2 K. The "P" indicates the phosphorylated form of the sugar; fructose-6-P is fructose-6-phosphate. Can this reaction take place spontaneously in a chloroplast where the concentrations are: [fructose-6-P] = $53.0\text{x}10^{-5}$ M, [glyceraldehyde-3-P] = $3.20\text{x}10^{-5}$ M, [erythrose-4-P] = $2.00\text{x}10^{-5}$ M, and [xyulose-5-P] = $2.10\text{x}10^{-5}$ M ?

Answer: The prime for $\Delta_rG°'$ indicates pH = 7, the "biochemist's standard state." The reaction Gibbs energy under non-standard state conditions is given by Eq. 20.1.10:

$$\Delta_rG = \Delta_rG° + RT \ln Q = \Delta_rG° + RT \ln\left(\frac{[\text{erythrose-4-P}]/c° \; [\text{xyulose-5-P}]/c°}{[\text{fructose-6-P }]/c° \; [\text{glyceraldehyde-3-P}]/c°}\right)$$

where c° = 1 M, the standard state concentration. Substituting the given values:

$$\Delta_rG = +6.28 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1}(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln\left(\frac{(2.00\text{x}10^{-5})(2.10\text{x}10^{-5})}{(53.0\text{x}10^{-5})(3.20\text{x}10^{-5})}\right)$$
$$= +6.28 - 9.17 \text{ kJ mol}^{-1} = -2.89 \text{ kJ mol}^{-1}$$

The reaction is spontaneous under these conditions.

4. At 298.15 K the $\Delta_rG°$ for the dissociation of water to H^+ and OH^- is 79.89 kJ mol^{-1}. Calculate Δ_rG for the reaction conditions specified below.

$$H_2O\ (l) \rightleftarrows H^+\ (aq, a_{H+} = 1.005\text{x}10^{-7}) + OH^-\ (aq, a_{OH-} = 1.005\text{x}10^{-7})$$

Answer: The reaction Gibbs energy under non-standard state conditions is given by Eq. 20.1.10:

$$\Delta_rG = \Delta_rG° + RT \ln Q = \Delta_rG° + RT \ln[(a_{H+})(a_{OH-})]$$
$$= 79.89 \text{ kJ/mol} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln(1.010\text{x}10^{-14})$$
$$= 79.89 - 79.88_8 \text{ kJ mol}^{-1} = 0$$

The reaction conditions correspond to pH = 7.00, which is the equilibrium state for pure water at 298.15 K: $K_w = 1.01\text{x}10^{-14}$ at 298.15 K on a molal concentration basis. The reaction Gibbs energy at equilibrium should be zero.

5. In rivers and lakes, bacteria catalyze the oxidation of Fe(II) to Fe(III):

$$4\ Fe^{2+} + O_2(g) + 4\ H^+ \rightleftarrows 4\ Fe^{3+} + 2\ H_2O$$

with $\Delta_fG°(Fe^{2+}) = -78.90$ kJ mol^{-1}, $\Delta_fG°(Fe^{3+}) = -4.70$ kJ mol^{-1}, and $\Delta_fG°(H_2O) = -237.13$ kJ mol^{-1}. Calculate the reaction Gibbs energy for $m_{Fe2+} = 1.00\text{x}10^{-6}$ m, $m_{Fe3+} = 1.00\text{x}10^{-5}$m, $P_{O2} = 0.200$ bar, $m_{H+} = 1.00\text{x}10^{-6}$ m at 298.15 K (neglect activity coefficients).

Answer: The standard state reaction Gibbs energy is given by $\Delta_rG°$ = [Σproducts] – [Σreactants]:

$$\Delta_rG° = [2(-237.13 \text{ kJ mol}^{-1}) + 4(-4.70 \text{ kJ mol}^{-1})] - [4(-78.90 \text{ kJ mol}^{-1}) + (0) + 4(0)]$$
$$= -177.46 \text{ kJ mol}^{-1}$$

The reaction Gibbs energy under non-standard state conditions is given by Eq. 20.1.10:

$$\Delta_rG = \Delta_rG° + RT \ln Q = \Delta_rG° + RT \ln\left(\frac{(m_{Fe3+}/m°)^4}{(m_{Fe2+}/m°)^4\ (P_{O2}/P°)\ (m_{H+}/m°)^4}\right)$$

where m° = 1 m, the standard state concentration. Substituting the given values:

$$\Delta_rG = -177.46 + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln\left(\frac{(1.00\text{x}10^{-5})^4}{(1.00\text{x}10^{-6})^4(0.200)(1.00\text{x}10^{-6})^4}\right)$$

$$= -177.46 \text{ kJ mol}^{-1} + 163.80 \text{ kJ mol}^{-1} = -13.66 \text{ kJ mol}^{-1}$$

Note that the reaction pH can have a large influence of the spontaneity for redox reactions if the stoichiometric coefficient for the H^+ ion is large, as it is in this case.

6. The equilibrium constant for the dissociation $N_2O_4 \text{ (g)} \rightleftarrows 2 \text{ } NO_2 \text{ (g)}$ is $K_p = 0.146$ at 298.2 K. Assume that the initial amount of N_2O_4 is 0.300 mol with no initial NO_2. Find the equilibrium partial pressures for the dissociation assuming that the reaction is run under constant pressure conditions at (a) 0.500 bar and at (b) 5.00 bar. (c). Does the shift in equilibrium position with applied pressure agree with LeChâtelier's Principle?

Answer: The plan is to set up a table to calculate the mole fractions and partial pressures of N_2O_4 and NO_2 based on the extent of the reaction, ξ. The equilibrium expression is then constructed in terms of ξ, and the expression is solved for ξ. This problem is very similar to Example 20.2.1.

Let the initial moles of N_2O_4 be "a." The total moles at equilibrium will be:

$$n_{tot} = (a - \xi) + 2\,\xi = a + \xi \tag{1}$$

Next, a table for the moles of each reactant and product is constructed. Then the mole fractions using $Y_i = n_i/n_{tot}$ and the equilibrium partial pressures using Dalton's Law of pressures, $P_i = Y_i\, P$, are calculated:

$$\begin{array}{lll} & N_2O_4 \text{ (g)} \rightleftarrows & 2 \text{ } NO_2 \text{ (g)} \\ \text{moles} & a - \xi & 2\xi \\ Y_i & \dfrac{a-\xi}{a+\xi} & \dfrac{2\xi}{a+\xi} \\ P_i & \dfrac{a-\xi}{a+\xi}\,P & \dfrac{2\xi}{a+\xi}\,P \end{array} \tag{2}$$

where P is the total applied pressure. The equilibrium expression (law of mass action) is:

$$K_p = \frac{(P_{NO_2}/P°)^2}{P_{N_2O_4}/P°} = \frac{\left(\dfrac{2\xi}{a+\xi}\right)^2}{\left(\dfrac{a-\xi}{a+\xi}\right)}(P/P°) = \frac{4\xi^2}{(a+\xi)(a-\xi)}(P/P°) = \frac{4\xi^2}{a^2-\xi^2}(P/P°) \tag{3}$$

Notice the similarity to Eq. 20.2.7. To solve for the extent, divide both sides of the last equation by (P/P°):

$$\frac{4\xi^2}{a^2-\xi^2} = \frac{K_p}{(P/P°)} = K_x \tag{4}$$

The last equality results since $K_p = K_x\,(P/P°)^{\Delta_r n_g}$ with $\Delta_r n_g = 1$ for this dissociation. The solution to Eq. 4 is:

$$\xi = \left(\frac{K_x}{4+K_x}\right)^{1/2} a \tag{5}$$

(a). For P = 0.5 bar: $K_x = 0.292$ and $\xi = \left(\frac{0.292}{4+0.292}\right)^{½}$ 0.300 mol = 0.07825 mol

which gives a degree of dissociation of $\alpha = \xi/n_{tot} = 0.261$. The partial pressures using Eqs. 2 are:

$$P_{N_2O_4} = \frac{a-\xi}{a+\xi}P = \frac{0.300-0.07825}{0.300+0.07825}P = 0.2931 \text{ bar}$$

and $$P_{NO_2} = \frac{2\xi}{a+\xi}P = \frac{2(0.07825)}{a+0.07825}P = 0.2069 \text{ bar}$$

(b). For P = 5.00 bar: $K_x = 0.0292$ and $\xi = \left(\frac{0.0292}{4+0.0292}\right)^{½}$ 0.300 mol = 0.02554 mol

which gives a degree of dissociation of $\alpha = \xi/n_{tot} = 0.085$. The partial pressures using Eqs. 2 are:

$$P_{N_2O_4} = \frac{a-\xi}{a+\xi}P = \frac{0.300-0.07825}{0.300+0.07825}P = 4.215 \text{ bar}$$

and $$P_{NO_2} = \frac{2\xi}{a+\xi}P = \frac{2(0.07825)}{a+0.07825}P = 0.7845 \text{ bar}$$

(c). For a reaction with $\Delta_r n_g = 1$, the equilibrium extent should decrease with an increase in pressure, thus favoring the side of the reaction with the fewer moles of gas. The decrease in the degree of dissociation with pressure for this problem shows the expected result.

7. Calculate the equilibrium partial pressures at 298.2 K for the dimerization of NO_2: $2\,NO_2\,(g) \rightleftarrows N_2O_4\,(g)$. The standard state reaction Gibbs energy for the dimerization of NO_2 is -4.77 kJ mol^{-1} at 298.2 K. Assume the initial amount of NO_2 is 0.300 moles at a constant total pressure of 1.00 bar. [Hint: you may use successive approximations to solve for the equilibrium position.]

Answer: The plan is to set up a table to calculate the mole fractions and partial pressures of NO_2 and N_2O_4 based on the extent of the reaction, ξ. The equilibrium expression is then constructed in terms of ξ, and the expression is solved for ξ. The equilibrium constant is given by:

$$K_p = e^{-\Delta_r G°/RT} = e^{-(-4.77\text{x}10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1}\text{mol}^{-1}\ 298.2 \text{ K})} = 6.848$$

Let the initial moles of NO_2 be "a." The total moles at equilibrium will be:

$$n_{tot} = (a - 2\,\xi) + \xi = a - \xi$$

Next, set up a table for the moles of each reactant and product, the mole fractions using $Y_i = n_i/n_{tot}$, and the equilibrium partial pressures using Dalton's Law of pressures, $P_i = Y_i\,P$, with P the total pressure:

	$2\,NO_2$ (g)	⇄	N_2O_4 (g)
moles	$a - 2\xi$		ξ

Y_i	$\frac{a-2\xi}{a-\xi}$	$\frac{\xi}{a-\xi}$
P_i	$\frac{a-2\xi}{a-\xi}P$	$\frac{\xi}{a-\xi}P$

The equilibrium expression (law of mass action) is:

$$K_p = \frac{P_{N_2O_4}/P°}{(P_{NO_2}/P°)^2} = \frac{\left(\frac{\xi}{a-\xi}\right)}{\left(\frac{a-2\xi}{a-\xi}\right)^2}(P/P°)^{-1} = \frac{\xi(a-\xi)}{(a-2\xi)^2}(P/P°)^{-1} = \frac{a\xi-\xi^2}{(a-2\xi)^2}(P/P°)^{-1} \tag{1}$$

with P = 1 bar specified in the problem. This expression can be solved exactly using the quadratic expression:

$$(4K+1)\,\xi^2 - (4K+1)\,a\xi + Ka^2 = 0 \qquad \text{giving} \qquad \xi = \left(1 \pm \sqrt{\frac{1}{4K+1}}\right)\frac{a}{2} = 0.1218 \text{ mol}$$

However, successive approximations is often more time efficient. Using the values given:

$$K_p = \frac{0.300\,\xi - \xi^2}{(0.300-2\xi)^2} = 6.848 \tag{2}$$

As a basis for successive approximations, we need to solve this last equation for ξ in terms that also involve ξ. Two examples will show the idea. Solving the last equation for ξ:

$$(0.300-2\xi)^2 = \frac{0.300\,\xi - \xi^2}{6.848} \qquad \text{or} \qquad 0.300\,\xi - \xi^2 = 6.848\,(0.300-2\xi)^2 \tag{3}$$

$$\text{giving: } \xi = \tfrac{1}{2}\left(0.300 - \left(\frac{0.300\,\xi-\xi^2}{6.848}\right)^{1/2}\right) \qquad \text{or} \qquad \xi = \sqrt{0.300\,\xi - 6.848\,(0.300-2\xi)^2} \tag{4}$$

The next step is to guess an initial value. The extent of the reaction may vary from 0 to 0.300/2 moles. A short spreadsheet was written based on the first iteration formula in Eqs. 4 with an initial guess of 0.05 mol, below. The update formula for ξ in C8 is “=($C$3-SQRT(B8*($C$3-B8)/$C$4))/2”. The last column calculates the equilibrium constant using Eq. 2 with the updated value of ξ to check for accuracy. The approximation converges in three iterations. This update formula works for guesses from $\xi = 1.0\text{x}10^{-5}$ to 0.2999 mol. The range of initial guesses that leads, or converges, to the correct answer is called the convergence interval. Guesses outside the convergence interval either diverge or oscillate around the correct value.

A1	B	C	D
2			
3	a=	0.3	
4	Kp=	6.848	
5			
6	guess	updated	giving
7	extent	extent	Q
8	0.05	0.128638	12.0764
9	0.128638	0.121632	6.739764
10	0.121632	0.121857	6.852015
11	0.121857	0.121849	6.847854
12	0.121849	0.121849	6.848005

The second update formula from Eqs. 4 converges over the interval [0.115, 0.19]. Some rearrangements of Eq. 2 do not lead to update formulas that converge on the final result for any initial guess. The disadvantage of the successive approximations approach is that several rearrangements may need to be tried to find an update formula that converges rapidly.

For $\xi = 0.1218$ mol the corresponding partial pressures are:

$$P_{NO_2} = \frac{a - 2\xi}{a - \xi}\, P = \left(\frac{0.300 - 2(0.1218)}{0.300 - 0.1218}\right) 1.00 \text{ bar} = 0.3164 \text{ bar}$$

$$P_{N_2O_4} = \frac{\xi}{a - \xi}\, P = \left(\frac{0.1218}{0.300 - 0.1218}\right) 1.00 \text{ bar} = 0.6835 \text{ bar}$$

Checking the final results against the equilibrium constant gives $K_p = 0.6835/(0.3164)^2 = 6.838$

Method 2: A clever way to approach this problem is to first assume the reaction goes to completion, giving the moles of N_2O_4 as 0.150 mol. Then reversing the reaction gives the form of a dissociation: $N_2O_4\ (g) \rightleftarrows 2\ NO_2\ (g)$ with $K_p' = 1/K_p = 1/6.848 = 0.1460$. Then using Problem 6 Eq. 3, above:

$$K_p' = K_x\,(P/P°) = \frac{4\,\xi^2}{a^2 - \xi^2}\,(P/P°) = \frac{4\,\xi^2}{0.150^2 - \xi^2} = 0.1460$$

where "a" is now the amount of N_2O_4. Solving for the extent at equilibrium for the new direction gives $\xi = 0.0282$ mol, which results in the same final partial pressures as the more direct method.

8. Calculate the equilibrium partial pressures and the degree of dissociation for the reaction:

$$SO_2Cl_2\ (g) \rightleftarrows SO_2\ (g) + Cl_2\ (g)$$

The equilibrium constant is $K_p = 2.78$ at 110°C. Assume a constant total pressure of 0.500 bar with 2.00 moles of SO_2Cl_2, only, initially placed in the reaction vessel.

Answer: The plan is to note that the reaction is a A (g) $\rightleftarrows$ B (g) + C (g) dissociation, for which Eq. 20.2.7 and 20.2.8 apply.

Since $\Delta_r n_g = 1$ and $K_p = K_x\,(P/P°)^{\Delta_r n_g}$, $K_x = 2.78/0.500 = 5.56$. Using Eqs. 20.2.7 and 20.2.8 with the given parameters:

$$K_x = \frac{\xi^2}{2.00^2 - \xi^2} = 5.56 \quad \text{and} \quad \xi = \left(\frac{K_x}{1+K_x}\right)^{1/2} a = \left(\frac{5.56}{1 + 5.56}\right)^{1/2} 2.00 \text{ mol} = 1.841 \text{ mol}$$

We can check the result by substituting back in to calculate the resulting equilibrium constant given the extent of the reaction:

$$\text{check } K_x = \frac{\xi^2}{2.00^2 - \xi^2} = \frac{1.841^2}{2.00^2 - 1.841^2} = 5.55$$

which is close enough given round-off error. The degree of dissociation for this stoichiometry is then:

$$\alpha = \xi/a = 1.84_1/2.00 = 0.920$$

or 92% dissociated at equilibrium.

9. Consider a gas phase dissociation with the stoichiometry A (g) ⇄ B (g) + C (g). (a). Show that the equilibrium expression can be directly expressed in terms of the degree of dissociation as:

$$K_p = \frac{\alpha^2}{1-\alpha^2}\,(P/P°) \qquad \text{P20.9.1}$$

(b). Solve for the degree of dissociation.

Answer: At equilibrium:

	A (g) ⇄	B (g) +	C (g)
moles:	$a-\xi$	ξ	ξ
Y_i:	$\frac{a-\xi}{a+\xi}$	$\frac{\xi}{a+\xi}$	$\frac{\xi}{a+\xi}$
P_i:	$\frac{a-\xi}{a+\xi}P$	$\frac{\xi}{a+\xi}P$	$\frac{\xi}{a+\xi}P$

giving $n_{tot} = a-\xi+\xi+\xi = a+\xi$

where n_{tot} is the total moles of gases, $P_i = Y_i\,P$, and the total pressure is P. Substitution of the mole fractions into K_x gives:

$$K_p = \frac{(P_B/P°)\,(P_C/P°)}{(P_A/P°)} = \frac{\left(\frac{\xi}{a+\xi}\right)\left(\frac{\xi}{a+\xi}\right)}{\left(\frac{a-\xi}{a+\xi}\right)}\,(P/P°) = \frac{\xi^2}{a^2-\xi^2}\,(P/P°) \qquad 1$$

This result is the corresponding expression to Example 20.2.1, in terms of pressures. Eq. 1 can be expressed in terms of the degree of dissociation. Divide the numerator and denominator by the initial amount of reactant squared, a^2. Then use the definition of the degree of dissociation for this reaction, $\alpha = \xi/a$:

$$K_p = \frac{(\xi/a)^2}{1-(\xi/a)^2}\,(P/P°) = \frac{\alpha^2}{1-\alpha^2}\,(P/P°) \qquad 2$$

The total moles of gas is then determined by $n_{tot} = a + \xi = a(1+\alpha)$.

(b). To solve for the degree of dissociation, divide both sides of the last equation by (P/P°):

$$\frac{\alpha^2}{1-\alpha^2} = \frac{K_p}{(P/P°)} = K_x \qquad 3$$

The last equality results since $K_p = K_x\,(P/P°)^{\Delta_r n_g}$ with $\Delta_r n_g = 1$ for this dissociation. The solution to Eq. 3 is:

$$\alpha = \left(\frac{K_x}{1+K_x}\right)^{½} \tag{4}$$

10. For the reaction $H_2S\ (g) \rightleftarrows H_2\ (g) + ½\ S_2\ (g)$ the degree of dissociation of H_2S is 0.305 at 1125°C and 1.00 bar total pressure. Calculate K_p at 1125°C.

Answer: To determine the equilibrium expression for the reaction, let the initial moles of H_2S be "a" and the extent of the reaction be ξ. The total moles at equilibrium is:

$$n_{tot} = (a - \xi) + \xi + ½\ \xi = a + ½\ \xi$$

Next, set up a table for the moles of each reactant and product, the mole fractions using $Y_i = n_i/n_{tot}$, and the equilibrium partial pressures using Dalton's Law of pressures, $P_i = Y_i\ P$, with P the total pressure:

	$H_2S\ (g)$ $\rightleftarrows$	$H_2\ (g)$ +	$½\ S_2\ (g)$
moles	$a - \xi$	ξ	$½\ \xi$
Y_i	$\dfrac{a - \xi}{a + ½\ \xi}$	$\dfrac{\xi}{a + ½\ \xi}$	$\dfrac{½\ \xi}{a + ½\ \xi}$
P_i	$\dfrac{a - \xi}{a + ½\ \xi}\ P$	$\dfrac{\xi}{a + ½\ \xi}\ P$	$\dfrac{½\ \xi}{a + ½\ \xi}\ P$

The equilibrium expression (law of mass action) then simplifies to:

$$K_p = \frac{(P_{H_2}/P°)\ (P_{S_2}/P°)^{½}}{(P_{H_2S}/P°)} = \frac{\left(\dfrac{\xi}{a + ½\ \xi}\right)\left(\dfrac{½\ \xi}{a + ½\ \xi}\right)^{½}\ (P/P°)^{½}}{\left(\dfrac{a - \xi}{a + ½\ \xi}\right)} = \left(\frac{\xi}{a - \xi}\right)\left(\frac{½\ \xi}{a + ½\ \xi}\right)^{½}\ (P/P°)^{½}$$

Divide the numerator and denominator of each expression in parentheses by the initial moles of H_2S and then substitute the definition of the degree of dissociation, $\alpha = \xi/a$:

$$K_p = \left(\frac{\alpha}{1 - \alpha}\right)\left(\frac{½\ \alpha}{1 + ½\ \alpha}\right)^{½}(P/P°)^{½}$$

Substituting the given degree of dissociation:

$$K_p = \left(\frac{0.305}{1 - 0.305}\right)\left(\frac{½\ 0.305}{1 + ½\ 0.305}\right)^{½}\ 1.00^{½} = (0.4388)(0.1323)^{½} = 0.160$$

11. The K_p and K_x based equilibrium expressions are convenient to use for reactions at constant pressure. K_c based expressions are convenient for reactions at constant volume. Consider dissociation with the stoichiometry: $A\ (g) \rightleftarrows B\ (g) + C\ (g)$. Set up the K_p expression in terms of the extent of the reaction, ξ, as in Example 20.2.1. Show that the K_p expression reduces to:

$$K_c = \frac{(x/c^o)^2}{c_{Ao}/c^o - x/c^o}$$

where c_{Ao} is the initial concentration of A and x is the final concentration of B and C. Assume the reaction is run at constant volume.

Answer: The total moles of gas in the reaction mixture is: $n_{tot} = a - \xi + \xi + \xi = a + \xi$. The concentration of a constituent in the reaction mixture is $c_i = n_i/V$, with n_i moles of constituent i and V the total volume. The total pressure is determined by the total moles of gas:

$$P = n_{tot}\, RT/V = (a + \xi)\, RT/V \qquad 1$$

with the total volume V held constant. We next lay out the equilibrium state in terms of moles, mole fractions, and partial pressures. In the last step we substitute Eq. 1 for the total pressure and cancel the common factor:

$$\begin{array}{llll}
 & \text{A (g)} \rightleftarrows & \text{B (g)} \quad + & \text{C (g)} \\
\text{moles:} & a - \xi & \xi & \xi \\
X_i\text{:} & \dfrac{a-\xi}{a+\xi} & \dfrac{\xi}{a+\xi} & \dfrac{\xi}{a+\xi} \\
P_i\text{:} & \dfrac{a-\xi}{a+\xi}\,(P/P°) & \dfrac{\xi}{a+\xi}\,(P/P°) & \dfrac{\xi}{a+\xi}\,(P/P°) \\
P_i\text{:} & \dfrac{a-\xi}{V}\,(RT/P°) & \dfrac{\xi}{V}\,(RT/P°) & \dfrac{\xi}{V}\,(RT/P°)
\end{array} \qquad 2$$

The K_p expression is then:

$$K_p = \frac{(P_B/P°)\,(P_C/P°)}{(P_A/P°)} = \frac{(\xi/V)\,(\xi/V)}{(a-\xi)/V}\,(RT/P°) \qquad 3$$

Let c_{Ao} be the initial concentration of A with $c_{Ao} = a/V$ and let x be the final concentration of B and C with $x = \xi/V$. Substitution of these definitions into Eq. 3 gives:

$$K_p = \frac{x^2}{c_{Ao} - x}\,(RT/P°) \qquad 4$$

Multiply and divide through each concentration term by c^o and collect terms to ensure that the concentration based equilibrium constant is unitless:

$$K_p = \frac{(x/c^o)^2}{c_{Ao}/c^o - x/c^o}\,(c^o\, RT/P°) = K_c\,(c^o\, RT/P°) \qquad 5$$

Note that the result agrees with $K_p = K_c\,(c^o\,RT/P°)^{\Delta_r n_g}$ with $\Delta_r n_g = 1$ for this reaction. Dividing Eq. 5 by $(c^o\,RT/P°)$:

$$K_c = \frac{(x/c^o)^2}{c_{Ao}/c^o - x/c^o} \qquad 6$$

In other words, at constant volume, the position of equilibrium can be determined by solving the K_p or K_c expressions. Eq. 6 is the form for the equilibrium expression most commonly used in General Chemistry texts for this type of problem.

12. Calculate the equilibrium partial pressures and the degree of dissociation for the reaction:

$$SO_2Cl_2\ (g) \rightleftarrows SO_2\ (g) + Cl_2\ (g)$$

The equilibrium constant is $K_p = 2.78$ at 110.°C. Assume the reaction starts with 2.00 moles of SO_2Cl_2, only, initially placed in the reaction vessel with an initial pressure of 0.500 bar. Assume the reaction runs at constant volume (see Problem 8 for the constant pressure version of this problem).

Answer: The plan is to convert the initial amount of SO_2Cl_2 to the equivalent concentration and then use $K_c = (x/c^o)^2/(c_{Ao}/c^o - x/c^o)$. [In General Chemistry, you allowed K_c to have units and then $K_c = x^2/(c_{Ao} - x)$.]

For the given conditions, the volume and initial concentration of SO_2Cl_2 are:

$$V = n_{SO_2Cl_2}\, RT/P = 2.00\text{ mol}(0.08314\text{ L bar K}^{-1}\text{ mol}^{-1})(383.15\text{ K})/0.500\text{ bar} = 127.4\text{ L}$$

$$c_{Ao} = n_{SO_2Cl_2}/V = 2.00\text{ mol}/127.4\text{ L} = 0.01570\text{ mol L}^{-1}$$

Then using concentrations at equilibrium:

$$\begin{array}{llll} & SO_2Cl_2\ (g) \rightleftarrows & SO_2\ (g) + & Cl_2\ (g) \\ c_i: & c_{Ao} - x & x & x \end{array}$$

$$K_c = \frac{(x/c^o)^2}{c_{Ao}/c^o - x/c^o} \qquad (x/c^o)^2 + K_c\, x/c^o - K_c\, c_{Ao}/c^o = 0 \qquad x/c^o = \frac{-K_c \pm \sqrt{K_c^2 + 4\, K_c\, c_{Ao}/c^o}}{2}$$

Using $K_p = K_c\, (c^o\, RT/P^o)^{\Delta_r n_g}$ and $\Delta_r n_g = 1$ for this reaction:

$$K_c = \frac{2.78\ (1\text{ bar})}{0.08314\text{ L bar mol}^{-1}(383.15\text{ K})(1\text{ mol L}^{-1})} = 0.08726 = \frac{(x/c^o)^2}{0.01570\text{ mol L}^{-1} - x/c^o}$$

$$x = 0.013585\text{ mol L}^{-1}$$
$$c_{SO_2Cl_2} = (c_{Ao} - x) = (0.01570 - 0.013585\text{ mol L}^{-1}) = 0.00211\text{ mol L}^{-1}$$

Giving the final amounts and partial pressures:

$$n_{SO_2Cl_2} = (c_{Ao} - x)\, V = (0.00211\text{ mol L}^{-1})\ 127.4\text{ L} = 0.2690\text{ mol}$$
$$P_{SO_2Cl_2} = (c_{Ao} - x)\, RT = 0.00211\text{ mol L}^{-1}(0.08314\text{ L bar K}^{-1}\text{ mol}^{-1})(383.15\text{ K}) = 0.067\text{ bar}$$
$$n_{SO_2} = n_{Cl_2} = x\, V = 1.73\text{ mol}$$
$$P_{SO_2} = P_{Cl_2} = x\, RT = 0.433\text{ bar}$$

The final pressure is $P = P_{SO_2Cl_2} + P_{SO_2} + P_{Cl_2} = 0.933$ bar and the degree of dissociation is:

$$\alpha = n_{SO_2}/\ n_{SO_2Cl_2,o} = 1.73\text{ mol}/2.00\text{ mol} = 0.865$$

or equivalently: $\alpha = (n_{SO_2}/V)/(n_{SO_2Cl_2,o}/V) = x/c_{Ao} = 0.013585\text{ mol L}^{-1}/0.01570\text{ mol L}^{-1} = 0.865$.

Notice that the degree of dissociation is less than Problem 8, with a constant total pressure. The smaller degree of dissociation for the constant volume process is consistent with LeChâtelier's Principle, given $\Delta_r n_g = 1$ and the corresponding increase in pressure for this reaction. (See Problem 11 for more information on constant volume reactions.)

13. For the reaction $BeSO_4(s) \rightleftarrows BeO\ (s) + SO_3\ (g)$, $K_p = 1.71\text{x}10^{-19}$ at 400.0 K and $9.70\text{x}10^{-11}$ at 600.0 K. (a). Predict, without doing the numerical calculation, if the reaction is endothermic or exothermic. (b). Calculate $\Delta_r H°$ for this temperature range and $\Delta_r G°$ and $\Delta_r S°$ at 400.0 K.

Answer: The plan is to use LeChâtelier's Principle for part (a) and the integrated form of the van 't Hoff equation for two data points, Eq. 20.1.28, for part (b). Then the thermodynamic parameters are calculated using $\Delta_r G° = -RT \ln K_p$ and $\Delta_r G° = \Delta_r H° - T\,\Delta_r S°$ at 400.0 K.

(a). The equilibrium constant increases with temperature. In other words, the position of equilibrium shifts to the right, the forward direction, with an increase in temperature. The forward direction for the reaction, as written, must then be the endothermic direction.
(b). From Eq. 20.1.28, assuming $\Delta_r H°$ is constant over the temperature range:

$$\ln \frac{K_{p,T_2}}{K_{p,T_1}} = -\frac{\Delta_r H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{9.70\text{x}10^{-11}}{1.71\text{x}10^{-19}} = -\frac{\Delta_r H°}{8.314\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{600.0\text{ K}} - \frac{1}{400.0\text{ K}}\right)$$

$$\ln \frac{9.70\text{x}10^{-11}}{1.71\text{x}10^{-19}} = -\frac{\Delta_r H°}{8.314\text{ J K}^{-1}\text{ mol}^{-1}}\,(0.0016667 - 0.0025000)$$

$$20.156 = -\frac{\Delta_r H°}{8.314\text{ J K}^{-1}\text{ mol}^{-1}}\,(-8.333\text{x}10^{-4}\text{ K}^{-1})$$

$$\Delta_r H° = 2.011\text{x}10^{5}\text{ J mol}^{-1} = 201.1\text{ kJ mol}^{-1}$$

Remember to carry at least one extra significant figure than allowed for the $(1/T_2 - 1/T_1)$ term to avoid round-off error. The standard state reaction Gibbs energy and entropy at 400 K are then:

$$\Delta_r G° = -RT \ln K_p = -\ 8.3145\text{ J K}^{-1}\text{ mol}^{-1}\,(400.0\text{ K})\,(1\text{kJ}/1000\text{ J}) \ln 1.71\text{x}10^{-19}$$
$$= 143.7\text{ kJ mol}^{-1}$$

$$\Delta_r S° = \frac{\Delta_r H° - \Delta_r G°}{T} = \frac{(201.1\text{ kJ mol}^{-1} - 143.7\text{ kJ mol}^{-1})(1000\text{ J}/1\text{ kJ})}{400.0\text{ K}} = 144.\text{ J K}^{-1}\text{ mol}^{-1}$$
$$= 1.4\text{x}10^{2}\text{ J K}^{-1}\text{ mol}^{-1}$$

14. The autoprotolysis constant for water, K_w, is the equilibrium constant for the reaction:

$$H_2O\ (l) \overset{K_w}{\rightleftarrows} H^+\ (aq) + OH^-\ (aq)$$

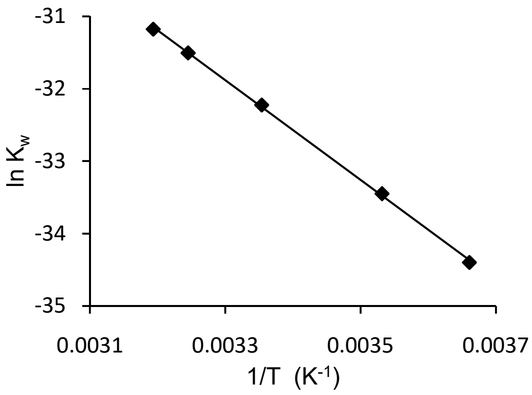
The temperature dependence for K_w is given in the table, below.[1] (a). Assume $\Delta_r H^\circ$ is constant. Calculate $\Delta_r H^\circ$ for this temperature range and $\Delta_r G^\circ$ and $\Delta_r S^\circ$ at 298.2 K. (b). Neutral pH is the pH that gives $a_{H^+} = a_{OH^-}$. Calculate the pH of a neutral solution at each temperature.

T (°C)	0.0	10.0	25.0	35.0	40.0
K_w	$1.15\text{x}10^{-15}$	$2.97\text{x}10^{-15}$	$1.01\text{x}10^{-14}$	$2.07\text{x}10^{-14}$	$2.88\text{x}10^{-14}$

Answer: First, don't forget to convert to kelvins. Eq. 20.1.31 shows a plot of ln K_w versus 1/T gives a slope of $-\Delta_r H^\circ/R$:

K_w	T (K)	1/T (K^{-1})	ln K
1.15E-15	273.15	0.003661	-34.399
2.97E-15	283.15	0.003532	-33.4502
1.01E-14	298.15	0.003354	-32.2262
2.07E-14	308.15	0.003245	-31.5086
2.88E-14	313.15	0.003193	-31.1784

slope	-6878.66	-9.18538	intercept
±	85.91525	0.292248	±
r^2	0.999532	0.033738	s(y)
F	6410.131	3	df
ss_{reg}	7.296323	0.003415	ss_{resid}



The corresponding $\Delta_r H^\circ$ is:

$$\Delta_r H^\circ = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (-6878.66 \text{ K}^{-1})(1\text{kJ}/1000 \text{ J}) = 57.2 \pm 0.7 \text{ kJ mol}^{-1}$$

From the data table at 298.15 K:

$$\Delta_r G^\circ = -RT \ln K_w = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) (1\text{kJ}/1000 \text{ J}) \ln 1.01\text{x}10^{-14}$$
$$= 79.89 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(57.2 \text{ kJ mol}^{-1} - 79.89 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})}{298.15 \text{ K}}$$
$$= -76.1 \pm 2.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

Notice that there is noticeable upward curvature to the plot, showing that the reaction enthalpy is temperature dependent for this range of temperatures. A more accurate estimation of $\Delta_r S^\circ$ would result from a curve fit to Eq. 20.1.36.

(b). From the equilibrium expression: $K_w = (a_{H^+})(a_{OH^-})$, or $pK_w = pH + pOH$. For a neutral solution pH = pOH. Neutral pH is then given by $pK_w/2$:

T (°C)	0.0	10.0	25.0	35.0	40.0
K_w	$1.15\text{x}10^{-15}$	$2.97\text{x}10^{-15}$	$1.01\text{x}10^{-14}$	$2.07\text{x}10^{-14}$	$2.88\text{x}10^{-14}$
pH=pOH	7.47	7.26	7.00	6.84	6.77

Notice that a neutral solution at body temperature is <u>not</u> pH = 7.

15. In the last problem for the autoprotolysis of water, we assumed that the reaction enthalpy was temperature independent. Assume the temperature dependence of the reaction enthalpy is given by $\Delta_r H^\circ_T = \Delta_r H^\circ_o + \Delta_r C_P\, T$, with $\Delta_r C_P = -186.6 \pm 2.7$ J K^{-1} mol. The temperature dependence of ln K is then just the first two terms of Eq. 20.1.36:

$$\ln K = -\frac{\Delta_r H^\circ_o}{RT} + \frac{\Delta_r C_P}{R} \ln T + c$$

where c is a constant. Calculate $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ at 298.2 K. A more complete table for the autoprotolysis constant for water, K_w, is given in the table, below.[1] [Hint: subtract $\Delta_r C_P \ln T$ from both sides of the above equation and plot ($\ln K - \Delta_r C_P \ln T$) along the vertical axis.]

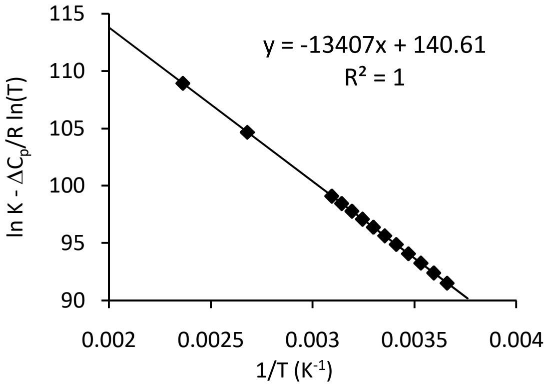
T (°C)	0.0	5.0	10.0	15.0	20.0	25.0	30.0
K_w	1.15x10^{-15}	1.88x10^{-15}	2.97x10^{-15}	4.57x10^{-15}	6.88x10^{-15}	1.01x10^{-14}	1.46x10^{-14}

T (°C)	35.0	40.0	45.0	50.0	100.0	150.0
K_w	2.07x10^{-14}	2.88x10^{-14}	3.94x10^{-14}	5.31x10^{-14}	5.43x10^{-13}	2.3x10^{-12}

Answer: As we did in the last problem, convert the temperature to kelvins and calculate ln K_w at each temperature. Then subtract $\Delta_r C_P \ln T$ from both sides of the above equation and plot ($\ln K - \Delta_r C_P \ln T$) along the vertical axis and 1/T along the horizontal axis:

$$\ln K - \frac{\Delta_r C_P}{R} \ln T \ = \ -\frac{\Delta_r H^\circ_o}{RT} + c$$

T(°C)	K	T (K)	1/T	ln K -ΔC$_p$/R ln T
0	1.15E-15	273.15	0.003661	91.505
5	1.88E-15	278.15	0.003595	92.404
10	2.97E-15	283.15	0.003532	93.261
15	4.57E-15	288.15	0.00347	94.085
20	6.88E-15	293.15	0.003411	94.880
25	1.01E-14	298.15	0.003354	95.643
30	1.46E-14	303.15	0.003299	96.385
35	2.07E-14	308.15	0.003245	97.101
40	2.88E-14	313.15	0.003193	97.793
45	3.94E-14	318.15	0.003143	98.462
50	5.31E-14	323.15	0.003095	99.110
100	5.43E-13	373.15	0.00268	104.664
150	2.30E-12	423.15	0.002363	108.930



slope	-134407.4	140.607	intercept
±	6.722926	0.021869	±
r^2	0.9999997	0.008509	s(y)
F	3977173	11	df
ss_{reg}	287.9829	0.000796	ss_{resid}

The curve fit results give:

$$\Delta_r H^\circ_o = -R \text{ slope} = 111.48 \pm 0.05 \text{ kJ mol}^{-1}$$

The corresponding reaction enthalpy at room temperature is:

$$\Delta_r H^\circ_T = \Delta_r H^\circ_o + \Delta_r C_p\, T = 111.48 \text{ kJ mol}^{-1} - 186.6 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})(1 \text{ kJ}/1000 \text{ J})$$
$$= 55.85 \pm 0.81 \text{ kJ mol}^{-1}$$

which matches the literature value of 55.84 kJ mol^{-1}. From the K_w table at 298.15 K:

$$\Delta_r G^\circ = -RT \ln K_w = -\,8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) (1\text{kJ}/1000 \text{ J}) \ln 1.01\text{x}10^{-14}$$
$$= 79.89 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(55.85 \text{ kJ mol}^{-1} - 79.89 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})}{298.15 \text{ K}}$$
$$= -80.6 \pm 2.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

The literature value for the reaction entropy is -80.66 J K^{-1} mol^{-1}. The agreement of our values with the literature should be considered to be fortuitous given the parameter uncertainties.

16. In the atmosphere NO and NO_2 approach equilibrium (see Ch. 5 Problems 10-12):

$$NO\ (g) + \tfrac{1}{2}\, O_2\ (g) \rightleftarrows NO_2(g)$$

Because NO and NO_2 are rapidly interconverted, the concentration of NO and NO_2 in the atmosphere are usually combined and quoted as $[NO_x]$. The equilibrium constant is $K_p = 1.168\text{x}10^5$ at 335.15 K and 4075. at 400.15 K. (a). Calculate the standard state reaction enthalpy at the average temperature, assuming the reaction enthalpy is constant over the temperature range. (b). Calculate the standard state reaction Gibbs energy and entropy at 335.15 K. (c). The molar constant pressure heat capacities are 29.844 J K^{-1} mol^{-1} for NO, 29.355 J K^{-1} mol^{-1} for O_2, and 37.20 J K^{-1} mol^{-1} for NO_2. Calculate $\Delta_rH°$, $\Delta_rS°$, and $\Delta_rG°$ at 298.15 K.

Answer: The plan is to use Eq. 20.1.28 to solve for $\Delta_rH°$ at the average temperature and $\Delta_rG° = -RT \ln K_p$ to find $\Delta_rG°$ at 335.15 K. $\Delta_rS°$ at 335.15 K is calculated from $\Delta_rG° = \Delta_rH° - T\,\Delta_rS°$. Then Δ_rC_p is used with Eqs. 8.5.5 and 13.3.7 to find $\Delta_rH°$ and $\Delta_rS°$ at 298.15 K. Finally, $\Delta_rG°$ at 298.15 K is calculated from $\Delta_rG° = \Delta_rH° - T\,\Delta_rS°$.

(a). Using the van 't Hoff equation for two data points, Eq. 20.1.28:

$$\ln \frac{K_{p,T_2}}{K_{p,T_1}} = -\frac{\Delta_rH°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{4075.}{1.168\text{x}10^5} = -\frac{\Delta_rH°}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{400.15\ \text{K}} - \frac{1}{335.15\ \text{K}}\right)$$

$$-3.3556 = -\frac{\Delta_rH°}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\,(0.00249906 - 0.00298374)$$

$$-3.3556 = -\frac{\Delta_rH°}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\,(-4.8468\text{x}10^{-4}\ \text{K}^{-1})$$

$$\Delta_rH° = -5.7564\text{x}10^4\ \text{J mol}^{-1} = -57.564\ \text{kJ mol}^{-1} \qquad \text{at average temperature 367.65 K}$$

(b). At 335.15 K: $\Delta_rG° = -RT \ln K_p$:

$$\Delta_rG° = -8.3145\ \text{J K}^{-1}\text{mol}^{-1}(1\ \text{kJ}/1000\ \text{J})(335.15\ \text{K}) \ln 1.168\text{x}10^5 = -32.515\ \text{kJ mol}^{-1}$$

$$\Delta_rS° = \frac{\Delta_rH° - \Delta_rG°}{T} = \frac{(-57.564\ \text{kJ mol}^{-1} - (-32.515\ \text{kJ mol}^{-1}))(1000\ \text{J}/1\ \text{kJ})}{335.15\ \text{K}} = -74.742\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(c). The reaction change in heat capacity is:

$$\Delta_rC_p = [37.20] - [29.844 + \tfrac{1}{2}\,(29.355)]\ \text{J K}^{-1}\ \text{mol}^{-1} = -7.322\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The reaction enthalpy corrected to 298.15 K from the average temperature for the experiment is:

$$\begin{aligned}\Delta_rH^o_{298\ K} &= \Delta_rH^o_{367\ K} + \Delta_rC_p\,\Delta T\\ &= -57.564\ \text{kJ mol}^{-1} + (-7.322\ \text{J K}^{-1}\ \text{mol}^{-1})(1\ \text{kJ}/1000\ \text{J})(298.15\ \text{K} - 367.65\ \text{K})\\ &= -57.055\ \text{kJ mol}^{-1}\end{aligned}$$

The reaction entropy at 298.15 K corrected from 335.15 K is:

$$\Delta_r S^o_{298\,K} = \Delta_r S^o_{367\,K} + \Delta_r C_p \ln(T_2/T_1)$$
$$= -74.742\ J\ K^{-1}\ mol^{-1} + (-7.322\ J\ K^{-1}\ mol^{-1})(1\ kJ/1000\ J)\ \ln(298.15/335.15)$$
$$= -74.742 + 0.8565\ J\ K^{-1}\ mol^{-1} = -73.885\ J\ K^{-1}\ mol^{-1}$$

The final standard state reaction Gibbs energy is then:

$$\Delta_r G° = \Delta_r H° - T\,\Delta_r S° = -57.055\ kJ\ mol^{-1} - (298.15\ K)(-73.885\ J\ K^{-1}\ mol^{-1})(1\ kJ/1000\ J)$$
$$\Delta_r G° = -35.03\ kJ\ mol^{-1}$$

17. The density at equilibrium for gas phase reaction mixtures can be used to calculate the equilibrium constant for the chemical reaction. Consider a gas phase dissociation with the stoichiometry A (g) ⇄ B (g) + C (g), giving at equilibrium (see Problem 9):

$$K_p = \frac{\xi^2}{a^2 - \xi^2}(P/P°) = \frac{(\xi/a)^2}{1 - (\xi/a)^2}(P/P°) = \frac{\alpha^2}{1 - \alpha^2}(P/P°) \qquad \text{(P20.9.1)}$$

Assume only A is initially placed in the reaction vessel. The total moles of gas is then determined by $n_{tot} = a + \xi = a(1 + \alpha)$. Now consider the density of the gas mixture. The total mass of the reaction mixture is constant, $w = a\mathfrak{M}_A$, where $\mathfrak{M}_A$ is the molar mass of reactant A. However, the total moles of gas changes as the reaction progresses, if $\Delta_r n_g \neq 0$. For a reaction at constant temperature and pressure, the change in moles of gas will cause a change in volume as the reaction progresses from the initial state. The density of the reaction gas mixture at equilibrium, assuming each constituent is ideal, is given by the ideal gas law:

$$d = w/V_{eq} = \frac{a\mathfrak{M}_A}{n_{tot}\,RT/P} = \frac{a\,\mathfrak{M}_A}{a(1+\alpha)\,RT/P} = \frac{1}{1+\alpha}\left(\frac{\mathfrak{M}_A\,P}{RT}\right) \qquad \text{P20.17.1°}$$

$COCl_2$ dissociates according to the reaction: $COCl_2\ (g) \rightleftarrows CO\ (g) + Cl_2\ (g)$. The density of the reaction mixture at equilibrium at 724. K and 1.00 bar total pressure is 1.16 g L^{-1}. Calculate the degree of dissociation, K_p, and $\Delta_r G°$ at 724. K.

Answer: The plan is to use Eq. P20.17.1° to find α, and then use Eq. 20.2.7 with $K_p = K_x\,P/P°$ and $\alpha = \xi/a$ to find K_p. Finally $\Delta_r G° = -RT \ln K_p$.

Solving Eq. P20.17.1° for the degree of dissociation gives:

$$\alpha = \left(\frac{\mathfrak{M}_A\,P}{d\,RT}\right) - 1 = \left(\frac{98.91\ g\ mol^{-1}\ 1.00\ bar}{1.16\ g\ L^{-1}\ 0.08314\ bar\ L\ K^{-1}\ mol^{-1}\ 724.\ K}\right) - 1 = 0.4166$$

The equilibrium expression is then given by Eq. 20.2.7. Then, $K_p = K_x\,(P/P°)^{\Delta_r n_g}$ with $\Delta_r n_g = 1$ for this dissociation. Substituting $K_p = K_x\,P/P°$, $\alpha = \xi/a$ and P = 1.00 bar gives:

$$K_p = \frac{\alpha^2}{1-\alpha^2}(P/P°) = \frac{0.4166^2}{1 - 0.4166^2} = 0.2100$$

See Problem 9 and Eq. P20.9.1 for a complete derivation of this last equation.

$$\Delta_r G° = -RT \ln K_p = -8.314\ J\ K^{-1}\ mol^{-1}\ (724.\ K)(1\ kJ/1000\ J)\ \ln 0.2100 = 9.39\ kJ\ mol^{-1}$$

18. The density of an equilibrium mixture of N_2O_4 (g) and NO_2 (g), at 1.00 bar pressure, is 3.62 g L^{-1} at 15.°C. Only N_2O_4 was initially placed in the reaction vessel. Calculate K_p and $\Delta_rG°$ at 15.°C. [Hint: write the equilibrium expression in terms of the degree of dissociation.]

Answer: The reaction is the dissociation of N_2O_4:

$$N_2O_4\,(g) \rightleftarrows 2\ NO_2\,(g)$$

See Problem 6 for the derivation of the equilibrium expression:

$$K_p = \frac{4\xi^2}{a^2 - \xi^2}\,(P/P°) \qquad 1$$

The degree of dissociation for this stoichiometry is $\alpha = \xi/a$. Dividing the numerator and denominator of the last equation by a^2 gives:

$$K_p = \frac{4(\xi/a)^2}{1 - (\xi/a)^2}\,(P/P°) = \frac{4\alpha^2}{1 - \alpha^2}\,(P/P°) \qquad 2$$

The total moles of gas is $n_{tot} = a + \xi = a(1 + \alpha)$. Now consider the density of the gas mixture. The total mass of the reaction mixture is constant, $w = a\ \mathfrak{M}_A$, where $\mathfrak{M}_A$ is the molar mass of reactant A. The total moles of gas changes as the reaction progresses if $\Delta_r n_g \neq 0$, giving a change in volume. The density of the reaction gas mixture at equilibrium, assuming each constituent is ideal, is given by the ideal gas law, $V_{eq} = n_{tot}\,RT/P$:

$$d = w/V_{eq} = \frac{a\mathfrak{M}_A}{n_{tot}\,RT/P} = \frac{a\ \mathfrak{M}_A}{a(1+\alpha)\,RT/P} = \frac{1}{1+\alpha}\left(\frac{\mathfrak{M}_A\,P}{RT}\right) \qquad 3°$$

where $\mathfrak{M}_A$ is the molar mass of reactant A, V_{eq} is the total volume at equilibrium, and P is the total applied pressure. Substituting in the given values and solving Eq. 3° for the degree of dissociation:

$$\alpha = \left(\frac{\mathfrak{M}_A\,P}{d\,RT}\right) - 1 = \left(\frac{92.02\ g\ mol^{-1}\ 1.00\ bar}{3.62\ g\ L^{-1}\ 0.08314\ bar\ L\ K^{-1}\ mol^{-1}\ 288.2\ K}\right) - 1 = 0.06082$$

The equilibrium constant is then given by Eq. 2 and P = 1.00 bar:

$$K_p = \frac{4\alpha^2}{1-\alpha^2}\,(P/P°) = \frac{4(0.06082)^2}{1 - 0.06082^2} = 0.01485$$

$$\Delta_rG° = -\,RT\ln K_p = -\,8.314\ J\ K^{-1}\ mol^{-1}\ (1\ kJ/1000J)(288.2\ K)\ \ln 0.01485$$
$$= 10.1\ kJ\ mol^{-1}$$

19. Create an Excel spreadsheet based on Eq. 20.1.21° to reproduce Figure 20.1.1. Assume the total pressure is constant at 1.00 bar and the standard state chemical potentials of A, B, C, and D are 6.24, 5.64, 2.78, and 2.22 kJ mol^{-1}, respectively. Assume 1.00 mol for A and B initially, with no C and D.

Answer: The spreadsheet used to produce Figures 20.1.1 and 20.1.2 is shown below.

species			A	B	C	D						
chem.potential			6.24	5.64	2.78	2.22	kJ/mol					
stoichiometry			-1	-1	1	1						
initial mol			1	1	0	0	mol					
T=	298.2	K	R=	8.314	J/K/mol		RT=	2.4792	kJ/mol			
K_p=	16.039		P_{tot}=	1	bar							
ξ (mol)	n_A	n_B	n_C	n_D	P_A	P_B	P_C	P_D	Q	Δ_rG	G°(pure)	G (kJ)
0	1	1	0	0	0.5	0.5	0	0	0		11.88	8.443
0.1	0.9	0.9	0.1	0.1	0.45	0.45	0.05	0.05	0.0123	-17.775	11.192	6.143
0.2	0.8	0.8	0.2	0.2	0.4	0.4	0.1	0.1	0.0625	-13.754	10.504	4.586
0.3	0.7	0.7	0.3	0.3	0.35	0.35	0.15	0.15	0.1837	-11.081	9.816	3.350
0.4	0.6	0.6	0.4	0.4	0.3	0.3	0.2	0.2	0.4444	-8.890	9.128	2.354
0.5	0.5	0.5	0.5	0.5	0.25	0.25	0.25	0.25	1	-6.880	8.44	1.566
0.6	0.4	0.4	0.6	0.6	0.2	0.2	0.3	0.3	2.25	-4.870	7.752	0.978
0.7	0.3	0.3	0.7	0.7	0.15	0.15	0.35	0.35	5.4444	-2.679	7.064	0.598
0.8	0.2	0.2	0.8	0.8	0.1	0.1	0.4	0.4	16	-0.006	6.376	0.458
0.9	0.1	0.1	0.9	0.9	0.05	0.05	0.45	0.45	81	4.015	5.688	0.639
1	0	0	1	1	0	0	0.5	0.5			5	1.563

The top section specifies the reaction stoichiometry for A + B $\rightleftarrows$ C + D, the given chemical potentials, and the initial conditions. The chemical potentials give the standard state reaction Gibbs energy using Eq. 15.4.17 and the equilibrium constant using Eq. 20.1.14 as $K_p = 16.0$. The partial pressures are determined by Dalton's Law of partial pressures, $P_i = Y_i\, P$, and then:

$$Q = \frac{(P_C/P°)\,(P_D/P°)}{(P_A/P°)\,(P_B/P°)} \qquad \Delta_rG = RT\ln(Q/K_p) \qquad G°(\text{pure}) = \sum n_i\,\mu_i°$$

and the Gibbs energy for each value of ξ from Eq. 20.1.21°. Notice that the minimum occurs for $\xi = 0.80$ where $Q = K_p = 16.0$.

20. Dissociations with the stoichiometries A $\rightleftarrows$ B + C and A $\rightleftarrows$ 2 B have significantly different equilibrium positions, given the <u>same</u> equilibrium constant and initial conditions. (a). First, assume the equilibrium constant for both reactions is $K_p = 1.33$ and the initial moles of reactant is 1.00 mol, with no initial products at 1.00 bar total pressure. Calculate the degree of dissociation for each reaction. (b). Qualitatively sketch diagrams of the form in Figure 20.1.1 and discuss the effect of the entropy of mixing in determining the difference in equilibrium position for the two reaction stoichiometries. (See also Problems 6, 8, and 9.)

Answer: (a). Since $\Delta_r n_g = 1$ for both reactions, $K_p = K_x\,(P/P°)^{\Delta_r n_g}$. Given the total pressure of 1.00 bar, $K_p = K_x$. Using Eq. 20.2.8 with $\alpha = \xi/a$, the degree of dissociation for the reaction A $\rightleftarrows$ B + C is given by Problem 9 Eq. 4:

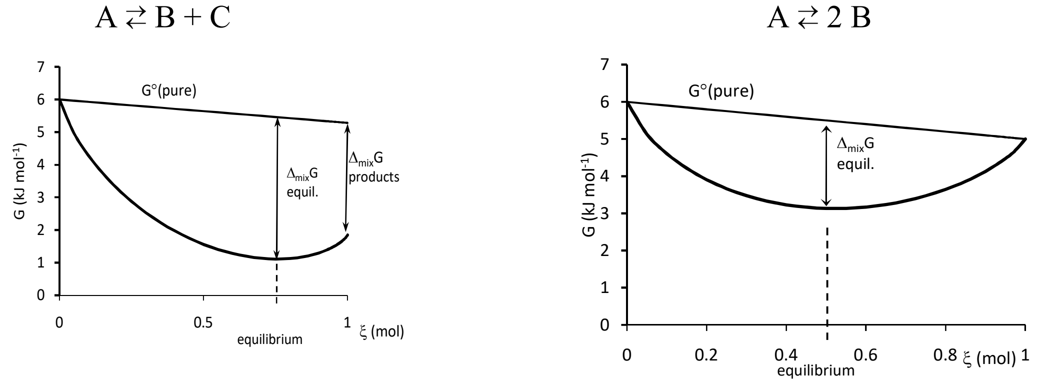
$$A \rightleftarrows B + C \qquad \alpha = \left(\frac{K_x}{1+K_x}\right)^{1/2} = \left(\frac{1.33}{1+1.33}\right)^{1/2} = 0.756$$

Using Problem 6 Eq. 5 for the reaction $A \rightleftarrows 2\,B$, the degree of dissociation is given by:

$$A \rightleftarrows 2\,B \qquad \alpha = \left(\frac{K_x}{4+K_x}\right)^{1/2} = \left(\frac{1.33}{4+1.33}\right)^{1/2} = 0.500$$

The extent of the reaction is significantly less for the stoichiometry $A \rightleftarrows 2\,B$. Why does this difference occur, even though the equilibrium constants are the same and $\Delta_r n_g = 1$ for both reactions?

(b). The difference in extent results because the reaction $A \rightleftarrows B + C$ has a favorable entropy and Gibbs energy of mixing for the products, while $A \rightleftarrows 2\,B$ does not. Since both reactions have the same equilibrium constant, the standard state reaction Gibbs energies are the same, $\Delta_r G° = -RT \ln K_p$. Sketches for the Gibbs energy versus reaction extent, corresponding to Figure 20.1.1, for the two reactions are shown below. Neither case has entropy of mixing for the reactants. There is a favorable entropy and Gibbs energy of mixing for intermediate reaction extents, so that the reactions don't run to completion in either case. The favorable entropy of mixing for the products pulls the position of equilibrium further to the right towards products for the $A \rightleftarrows B + C$ case.


$A \rightleftarrows B + C$ $\qquad$ $A \rightleftarrows 2\,B$

A rough sketch for this problem is sufficient; however, see the next problem for the Excel spreadsheet used to construct these figures.

21. Derive an expression for the Gibbs energy for the dissociation $A \rightleftarrows B + C$ as a function of the extent of the reaction. Your derivation will parallel Eqs. 20.1.16-20.1.21°, but for the new stoichiometry. Create an Excel spreadsheet based on your expression to produce a plot similar to Figure 20.1.1. Assume the total pressure is constant at 1.00 bar and the standard state chemical potentials of A, B, and C are 6.00, 2.95, and 2.34 kJ mol^{-1}, respectively. Assume 1.00 mol for A initially, with no B and C.

Answer: The initial amount of the reactant is n_{Ao}. Assume that we start with only reactant so that $n_{Bo} = 0$ and $n_{Co} = 0$. From the stoichiometry for this example, the mole amounts are:

$$n_A = n_{Ao} - \xi\,, \quad n_B = \xi\,, \quad n_C = \xi \qquad 1$$

The Gibbs energy at any point during the reaction is just the sum of the Gibbs energies for each product and reactant:

$$G = n_A\, \mu_A + n_B\, \mu_B + n_C\, \mu_C \qquad \text{(cst. T\&P)} \qquad 2$$

$$G = n_A \left[\mu_A^\circ + RT \ln\left(\frac{P_A}{P^\circ}\right)\right] + n_B \left[\mu_B^\circ + RT \ln\left(\frac{P_B}{P^\circ}\right)\right] + n_C \left[\mu_C^\circ + RT \ln\left(\frac{P_C}{P^\circ}\right)\right]$$

$$\text{(cst. T\&P, ideal gas)} \qquad 3^\circ$$

The partial pressures are expressed in terms of the mole fractions using Dalton's Law of partial pressures, $P_i = Y_i\, P$, with P the total pressure, $Y_i = n_i/n$, and $n = \Sigma\, n_i$. Collecting terms, as we did for Eqs. 20.1.17-20.1.19, gives:

$$\begin{aligned} G = {} & (n_A\, \mu_A^\circ + n_B\, \mu_B^\circ + n_C\, \mu_C^\circ) \\ & + n_A RT \ln Y_A + n_B RT \ln Y_B + n_C RT \ln Y_C \\ & + n_A RT \ln\left(\frac{P}{P^\circ}\right) + n_B RT \ln\left(\frac{P}{P^\circ}\right) + n_C RT \ln\left(\frac{P}{P^\circ}\right) \qquad \text{(cst. T\&P, ideal gas)} \qquad 4^\circ \end{aligned}$$

Using Eq. 20.1.20, $n = n_A + n_B + n_C$, and $G^\circ(\text{pure}) = (n_A\, \mu_A^\circ + n_B\, \mu_B^\circ + n_C\, \mu_C^\circ)$, we can simplify Eq. 4° to:

$$G = G^\circ(\text{pure}) + nRT\,(Y_A \ln Y_A + Y_B \ln Y_B + Y_C \ln Y_C) + nRT \ln\left(\frac{P}{P^\circ}\right)$$

$$\text{(cst. T\&P, ideal gas)} \qquad 5^\circ$$

The spreadsheet used to produce Figures 20.1.1 and 20.1.2 is shown below, but with the new stoichiometry and chemical potentials.

species		A	B	C		Δ_rG°			
chem.potential		6	2.95	2.34	kJ/mol	-0.71	kJ/mol		
stoichiometry		-1	1	1					
initial mol		1	0	0	mol				
T	298.2	K	R	8.31	J/K/mol		RT=	2.47923	kJ/mol
K_p =	1.332		P_{tot}=	1.00	bar				
ξ (mol)	n_A	n_B	n_C	P_{tot}	P_A	P_B	P_C	G°(pure)	G (kJ)
0	1	0	0	1	1	0	0	6.000	6
0.1	0.9	0.1	0.1	1.1	0.818	0.091	0.091	5.929	4.292
0.2	0.8	0.2	0.2	1.2	0.667	0.167	0.167	5.858	3.277
0.3	0.7	0.3	0.3	1.3	0.538	0.231	0.231	5.787	2.531
0.4	0.6	0.4	0.4	1.4	0.429	0.286	0.286	5.716	1.971
0.5	0.5	0.5	0.5	1.5	0.333	0.333	0.333	5.645	1.559
0.6	0.4	0.6	0.6	1.6	0.25	0.375	0.375	5.574	1.281
0.65	0.35	0.65	0.65	1.65	0.212	0.394	0.394	5.539	1.191
0.7	0.3	0.7	0.7	1.7	0.176	0.412	0.412	5.503	1.133
0.75	0.25	0.75	0.75	1.75	0.143	0.429	0.429	5.468	1.110
0.8	0.2	0.8	0.8	1.8	0.111	0.444	0.444	5.432	1.126
0.9	0.1	0.9	0.9	1.9	0.053	0.474	0.474	5.361	1.296
0.985	0.015	0.985	0.985	1.99	0.008	0.496	0.496	5.301	1.697
1	0	1	1	2	0	0.5	0.5	5.290	1.853

The top section specifies the reaction stoichiometry for A ⇄ B + C, the given chemical potentials, and the initial conditions. The chemical potentials give the standard state reaction Gibbs energy using Eq. 15.4.17 and the equilibrium constant using Eq. 20.1.14° as $K_p = 1.33$. The partial pressures are determined by Dalton's Law of partial pressures, $P_i = Y_i\, P$, and then:

$$G^\circ(\text{pure}) = \sum n_i\, \mu_i^\circ = (n_A\, \mu_A^\circ + n_B\, \mu_B^\circ + n_C\, \mu_C^\circ)$$

The Gibbs energy for each value of ξ is determined from Eq. 5. Notice that the minimum occurs for $\xi \cong 0.75$ as shown in Problem 20a. The plot of the Gibbs energy is shown in Problem 20.

22. Calculate the pH and degree of dissociation of 0.100 m acetic acid in water at 25°C using the Debye-Hückel approximation and $K_a = 1.75\text{x}10^{-5}$. (The acid dissociation constant is determined on a molal basis. Neglect the autoprotolysis of water.) Compare to the degree of dissociation calculated neglecting activity coefficients.

Answer: The dissociation is given by: HOAc (aq) ⇄ H^+ + OAc^-. Assume that the activity coefficient for undissociated acetic acid is one, since acetic acid is neutral. The analytical (nominal, undissociated) concentration of the weak acid is m_A. The activities for the ions are $a_{H+} = \gamma_\pm\, m_{H+}/m^\circ$ and $a_{OAc-} = \gamma_\pm\, m_{OAc-}/m^\circ$. However, by the 1:1 stoichiometry and neglecting the autoprotolysis of water, $m_{H+} = m_{OAc-}$. Let $x = m_{H+} = m_{OAc-}$. The value of x is the extent of the reaction measured as a molality. The acid dissociation reaction is:

$$\begin{array}{lllll} & \text{HOAc} & \rightleftarrows\ H^+ & + & OAc^- \\ \text{molality:} & m_A - x & \quad x & & x \\ \text{activity:} & (m_A - x)/m^\circ & \gamma_\pm\, x/m^\circ & & \gamma_\pm\, x/m^\circ \end{array}$$

$$K_a = \frac{(a_{H+})(a_{OH-})}{a_A} = \frac{\gamma_\pm^2\, (x/m^\circ)^2}{(m_A - x)/m^\circ} \qquad \text{giving} \qquad K_a^{eff} = \frac{x^2}{m_A - x} \qquad 1$$

where for convenience, we define the effective equilibrium constant as $K_a^{eff} = K_a/\gamma_\pm^2\, m^\circ$. Solving for x gives:

$$x^2 + K_a^{eff}\, x - K_a^{eff}\, m_A = 0 \qquad\qquad x = \frac{-K_a^{eff} \pm \sqrt{(K_a^{eff})^2 + 4\, K_a^{eff}\, m_A}}{2} \qquad 2$$

Neglecting activity coefficients, $K_a^{eff} \approx K_a$ and using the given values:

$$x = \frac{-1.75\text{x}10^{-5} \pm \sqrt{(1.75\text{x}10^{-5})^2 + 4(1.75\text{x}10^{-5})(0.100)}}{2} = 1.314\text{x}10^{-3}\ \text{m} \qquad (\text{ideal})\ 3^\circ$$

Only the positive root gives a positive concentration. The Debye-Hückel approximation depends on the ionic strength. However, the exact concentration of the ions is not known. However, since the degree of dissociation is so small, the activity coefficients will be close to one. We can use the ion concentrations that we calculate neglecting activity coefficients to approximate the ionic strength. Using the definition of ionic strength, Eq. 19.4.22:

$$I = \tfrac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \tfrac{1}{2}\, [(1)^2\, m + (-1)^2\, m]/m^\circ = m/m^\circ = 1.314\text{x}10^{-3} \qquad 4$$

This result is expected for a uni-positive:uni-negative electrolyte: $I = m/m°$. The mean ionic activity coefficient is calculated using Eq. 19.4.23:

$$\ln \gamma_\pm = -1.171\ |z_+ z_-|\ I^{½} = -1.171\ |(1)(-1)|\ (1.314\text{x}10^{-3})^{½} = -0.04245 \qquad 5$$

or

$$\log \gamma_\pm = -0.509\ |z_+ z_-|\ I^{½} = -0.509\ |(1)(-1)|\ (1.314\text{x}10^{-3})^{½} = -0.01845 \qquad 6$$

giving $\gamma_\pm = 0.9584$ and $K_a^{eff} = K_a/\gamma_\pm^2\, m° = 1.75\text{x}10^{-5}/(0.9584)^2 = 1.905\text{x}10^{-5}$ m. The molal extent using Eq. 2 is:

$$x = \frac{-1.905\text{x}10^{-5} \pm \sqrt{(1.905\text{x}10^{-5})^2 + 4(1.905\text{x}10^{-5})(0.100)}}{2} = 1.371\text{x}10^{-3}\ \text{m} \qquad 7$$

Given that $x = m_{H^+}$, the pH is calculated from the <u>activity</u>:

$$a_{H^+} = \gamma_\pm\, m_{H^+}/m° = 0.9584\ (1.371\text{x}10^{-3}) = 1.314\text{x}10^{-3}$$

$$pH = -\log a_{H^+} = 2.88$$

and the degree of dissociation is: $\alpha = x/m_A = 0.0137$ or 1.37% dissociated. The degree of dissociation neglecting activity coefficients, using Eq. 3°, is $\alpha = 0.0131$ for a 4% error.

23. Calculate the pH and degree of hydrolysis of 0.100 m ammonia in water at 25°C using the Debye-Hückel approximation and $K_b = 1.78\text{x}10^{-5}$. (The hydrolysis constant is determined on a molal basis. Neglect the autoprotolysis of water.) Compare to the degree of hydrolysis calculated neglecting activity coefficients.

Answer: The hydrolysis is given by: $NH_3\ (aq) + H_2O \rightleftarrows NH_4^+ + OH^-$. Assume that the activity coefficient for ammonia is one, since ammonia is neutral. The analytical (nominal, undissociated) concentration of the weak base is m_B. The activities for the ions are $a_{NH_4^+} = \gamma_\pm\, m_{NH_4^+}/m°$ and $a_{OH^-} = \gamma_\pm\, m_{OH^-}/m°$. However, by the 1:1 stoichiometry and neglecting the autoprotolysis of water, $m_{NH_4^+} = m_{OH^-}$. Let $x = m_{NH_4^+} = m_{OH^-}$. The value of x is the extent of the reaction measured as a molality. The hydrolysis reaction is:

	$NH_3\ (aq) + H_2O$	⇄	NH_4^+	+	OH^-
molality:	$m_B - x$		x		x
activity:	$(m_B - x)/m°$		$\gamma_\pm\, x/m°$		$\gamma_\pm\, x/m°$

$$K_b = \frac{(a_{NH_4^+})(a_{OH^-})}{a_B} = \frac{\gamma_\pm^2\,(x/m°)^2}{(m_B - x)/m°} \qquad \text{giving} \qquad K_b^{eff} = \frac{x^2}{m_B - x} \qquad 1$$

where for convenience, we define the effective equilibrium constant as $K_b^{eff} = K_b/\gamma_\pm^2\, m°$. Solving for x gives:

$$x^2 + K_b^{eff}\, x - K_b^{eff}\, m_B = 0 \qquad\qquad x = \frac{-K_b^{eff} \pm \sqrt{(K_b^{eff})^2 + 4\, K_b^{eff}\, m_B}}{2} \qquad 2$$

Neglecting activity coefficients, $K_b^{eff} \approx K_b$ and using the given values:

$$x = \frac{-1.78\text{x}10^{-5} \pm \sqrt{(1.78\text{x}10^{-5})^2 + 4(1.78\text{x}10^{-5})(0.100)}}{2} = 1.325\text{x}10^{-3}\text{ m} \qquad \text{(ideal)}\ 3^{o}$$

Only the positive root gives a positive concentration. The Debye-Hückel approximation depends on the ionic strength. However, the exact concentration of the ions is not known. However, since the degree of hydrolysis is so small, the activity coefficients will be close to one. We can use the ion concentrations that we calculate neglecting activity coefficients to approximate the ionic strength, Eq. 3°. Using the definition of ionic strength, Eq. 19.4.22:

$$I = ½ \sum z_i^2 \frac{m_i}{m°} = ½\ [(1)^2\ m + (-1)^2\ m]/m° = m/m° = 1.325\text{x}10^{-3} \qquad 4$$

This result is expected for a uni-positive:uni-negative electrolyte: I = m/m°. The mean ionic activity coefficient is calculated using Eq. 19.4.23:

$$\ln \gamma_\pm = -1.171\ |z_+\ z_-|\ I^{½} = -1.171\ |(1)(-1)|\ (1.325\text{x}10^{-3})^{½} = -0.04263 \qquad 5$$

or $$\log \gamma_\pm = -0.509\ |z_+\ z_-|\ I^{½} = -0.509\ |(1)(-1)|\ (1.325\text{x}10^{-3})^{½} = -0.01853 \qquad 6$$

giving $\gamma_\pm = 0.9583$ and $K_b^{eff} = K_a/\gamma_\pm^2\ m° = 1.78\text{x}10^{-5}/(0.9583)^2 = 1.938\text{x}10^{-5}$ m. The molal extent is:

$$x = \frac{-1.938\text{x}10^{-5} \pm \sqrt{(1.938\text{x}10^{-5})^2 + 4(1.938\text{x}10^{-5})(0.100)}}{2} = 1.382\text{x}10^{-3}\text{ m} \qquad 7$$

Given that $x = m_{OH^-}$ the pOH is calculated from the <u>activity</u>:

$$a_{OH^-} = \gamma_\pm\ m_{OH^-}/m° = 0.9583\ (1.382\text{x}10^{-3}) = 1.324\text{x}10^{-3}$$

$$pOH = -\log a_{OH^-} = 2.878 \qquad \text{and } pH = 13.995 - 2.878 = 11.12$$

and the degree of hydrolysis is: $\alpha = x/m_B = 0.0138$ or 1.38%. The degree of hydrolysis neglecting activity coefficients, using Eq. 3°, is $\alpha = 0.0132$ for a 4% error.

24. The K_{sp} for $PbCl_2$ in water is $1.70\text{x}10^{-5}$. (a). Calculate the solubility of $PbCl_2$ in pure water. (b). Show that the solubility of a 1:2 electrolyte with charges $z_+ = 2$ and $z_- = -1$ in a m-molal solution of $NaNO_3$ (or other uni-positive : uni-negative non-participating electrolyte) is given by:

$$m_s = 10^{0.509|z_+\ z_-|\ (m/m^o)^{½}} \left(\frac{K_{sp}}{4}\right)^{1/3}$$

Use the Debye-Hückel approximation at 25°C for the activity coefficients. Calculate the solubility of $PbCl_2$ in 0.100 m KNO_3.

Answer: The dissolution is $PbCl_2\ (s) \rightleftarrows Pb^{2+}\ (aq) + 2\ Cl^-\ (aq)$. Assume $PbCl_2$ is the only source of Cl^- ions, giving $m_{Cl^-} = 2\ m_{Pb^{2+}} = 2m_s$. The equilibrium expression is given by:

$$K_{sp} = (a_{Pb^{2+}})(a_{Cl^-})^2 = \gamma_\pm^3\ (m_{Pb^{2+}}/m^o)(m_{Cl^-}/m^o)^2 = \gamma_\pm^3\ (m_s/m^o)(2\ m_s/m^o)^2 = 4\ \gamma_\pm^3\ (m_s/m^o)^3 \qquad 1$$

(a). For $PbCl_2$ in pure water, first assume the activity coefficient is equal to one:

$$m_s \cong (1.70\text{x}10^{-5}/4)^{1/3}\ m^o = 0.01620\text{ m} \qquad \text{(ideal)} \qquad 2^o$$

We can use this concentration to approximate the ionic strength:

$$I = \tfrac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \tfrac{1}{2}\,[(2)^2\, m_s + (-1)^2\, 2\, m_s]/m^\circ = 3\, m_s/m^\circ = 0.04859 \qquad 3$$

and the mean-ionic activity coefficient for $PbCl_2$ is:

$$\log \gamma_\pm = -0.509\, |z_+\, z_-|\, I^{1/2} = \log \gamma_\pm = -0.509\, |(2)(-1)|\, (0.04859)^{1/2} = 0.5965 \qquad 4$$

$$\text{The solubility in pure water is } m_s = \left(\frac{K_{sp}}{4\gamma_\pm^3}\right)^{1/3} m^\circ \cong \left(\frac{1.70\text{x}10^{-5}}{4(0.5965)^3}\right)^{1/3} \cong 0.0272 \text{ m} \qquad 5$$

For more accurate calculations this new estimate of the solubility should be used in the spirit of successive approximations to calculate a new ionic strength, activity coefficient, and then more accurate solubility. Given that K_{sp} is uncertain to 6%, our current result is sufficient for comparison with part b.

(b). Assume that the ionic strength is dominated by the non-participating electrolyte. For a uni-positive : uni-negative electrolyte the ionic strength is given by the molality, $I = m/m^\circ$. The Debye-Hückel approximation correspondingly gives the activity coefficient of the sparingly soluble salt as:

$$\log \gamma_\pm = -0.509\, |z_+\, z_-|\, I^{1/2} \qquad \text{giving} \qquad \gamma_\pm = 10^{-0.509 |z_+\, z_-|\, (m/m^\circ)^{1/2}} \qquad 6$$

$$\text{Solving for the solubility gives: } m_s = \left(\frac{K_{sp}}{4\gamma_\pm^3}\right)^{1/3} = 10^{0.509 |z_+\, z_-|\, (m/m^\circ)^{1/2}} \left(\frac{K_{sp}}{4}\right)^{1/3} \qquad 7$$

For the specific case of $PbCl_2$ (s) in 0.100 m KNO_3, $I = 0.100$:

$$m_s = 10^{0.509 |(2)(-1)|\, (0.100)^{1/2}} \left(\frac{K_{sp}}{4}\right)^{1/3} m^\circ = (2.098)(0.01620 \text{ m}) = 0.0340 \text{ m} \qquad 8$$

or 210% of the ideal solubility, Eq. 2°, and 125% of the solubility in pure water, Eq. 5. The corresponding mean ionic activity coefficient in 0.100 m KNO_3 works out to $\gamma_\pm = 10^{-0.509|(2)(-1)|\, (0.100)^{1/2}} = 0.309$.

25. The K_{sp} for $PbCl_2$ in aqueous solution is $1.70\text{x}10^{-5}$ on a molal basis at 298.15 K. (a). Calculate the K_{sp} of $PbCl_2$ in pure water on a molarity concentration basis. (b). Calculate the K_{sp} of $PbCl_2$ on a molarity basis in a 0.200-M solution of KNO_3, assuming a very dilute solution. The density of 0.200 M KNO_3 is 0.9905 g mL^{-1}.

Answer: (a). For the solubility equilibrium $PbCl_2$ (s) ⇄ Pb^{2+} (aq) + 2 Cl^- (aq): $\Delta_r\nu = [1 + 2] - [0] = 3$, since the reactant is a solid. The solution is dilute, which allows the use of Eq. 20.3.12. Assume the solution density is the density of pure water at the same temperature, $d_{H_2O}^{25} = 0.99705$ g mL^{-1}, Table 2.2.1:

$$K_c = K_m\, (d_{soln}/1 \text{ g ml}^{-1})^{\Delta_r\nu} = 1.70\text{x}10^{-5}(0.99705)^3 = 1.685\text{x}10^{-5}$$

or only a 0.9% change.
(b). However, for the solubility in 0.200 M KNO_3:

$$K_c = K_m\,(d_{soln}/1\text{ g ml}^{-1})^{\Delta_r\nu} = 1.70\text{x}10^{-5}(0.9905)^3 = 1.652\text{x}10^{-5}$$

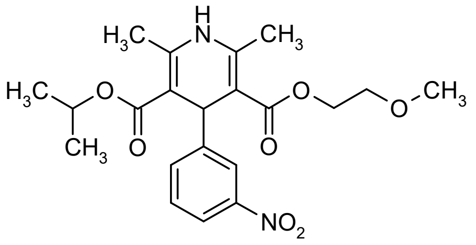
for a 3% difference.

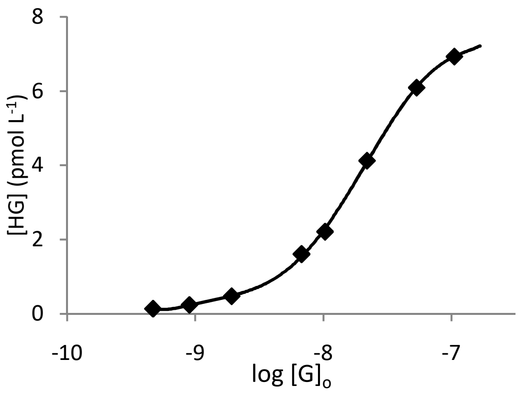
26. The hydrolysis of ammonia is given by: NH_3 (aq) + $H_2O \rightleftarrows NH_4^+ + OH^-$ with $K_b = 1.78\text{x}10^{-5}$ at 25°C on a molal basis. Calculate K_b on a molarity concentration basis. The density of 0.100 M ammonia is 0.994 g mL^{-1} at 25°C

Answer: For the hydrolysis $\Delta_r\nu = [1 + 1] - [1] = 1$, since water is kept on a mole fraction basis with $X_{H_2O} \cong 1$. Use of Eq. 20.3.12 with the solution density gives only a 0.6% difference in equilibrium constants:

$$K_c = K_m\,(d_{soln}/1\text{ g ml}^{-1})^{\Delta_r\nu} = 1.78\text{x}10^{-5}(0.994) = 1.769\text{x}10^{-5}$$

27. Nimodipine is a dihydropyridine calcium channel blocker that was developed for the treatment of high blood pressure:





This class of calcium channel blockers are antagonists that block the flow of Ca^{2+} ions out of cardiac muscle cells. A receptor site for nimodipine is found in the plasma membrane of striated muscle tissue, or sarcolemma. Isolated sarcolemma membranes were used in a binding study with tritium-labeled nimodipine. Tritiated-nimodipine was incubated with the purified membranes in the absence of Ca^{2+} ion and then filtered. The concentration of bound nimodipine was determined by liquid scintillation counting of the membranes trapped on the filters. Consider the membrane bound protein receptor as the host and nimodipine as the guest. The concentration of bound guest as a function of the total concentration of guest is given in the table below.[2] The effective concentration of the host membrane receptors is $[H]_o = 9.3 \pm 0.4$ pmol L^{-1}.

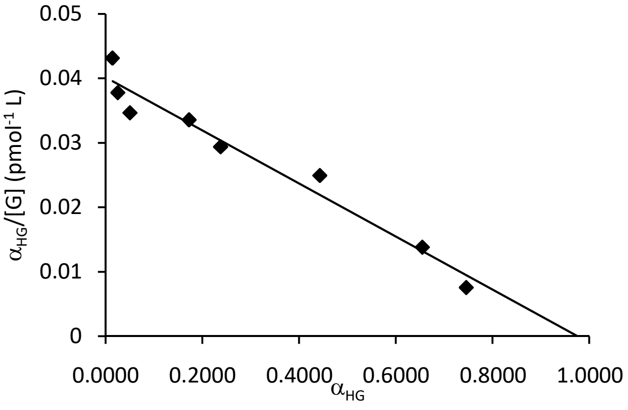
$[G]_o$ (pmol L^{-1})	0.468	0.9	1.92	6.75	10.3	21.9	53.4	105.4

[HG] (pmol L^{-1})	0.134	0.234	0.468	1.606	2.21	4.12	6.09	6.93

Answer: The plan is to determine the association constant from the Scatchard plot using Eq. 20.5.14. The free guest concentration is given by solving the mass balance: $[G] = [G]_o - [HG]$. The degree of association for the host is given by $\alpha_{HG} = [HG]/[H]_o$. A spreadsheet was developed to calculate [G], α_{HG}, and $\alpha_{HG}/[G]$ to form the Scatchard plot:

		$[H]_o$ =	9.3	pmol L^{-1}
$[G]_o$ (pmol L^{-1})	[HG] (pmol L^{-1})	[G] (pmol L^{-1})	α_{HG}	$\alpha_{HG}/[G]$ (pmol^{-1} L)
0.468	0.134	0.334	0.0144	0.04314
0.9	0.234	0.666	0.0252	0.03778
1.92	0.468	1.452	0.0503	0.03466
6.75	1.606	5.144	0.1727	0.03357
10.3	2.21	8.09	0.2376	0.02937
21.9	4.12	17.78	0.4430	0.02492
53.4	6.09	47.31	0.6548	0.01384
105.4	6.93	98.47	0.7452	0.00757

slope	-0.0411598	0.0401616	intercept
±	0.003408	0.0013577	±
r^2	0.9605001	0.0026033	s(y)
F	145.89902	6	df
ss$_{regression}$	0.0009888	4.0664E-05	ss$_{residual}$

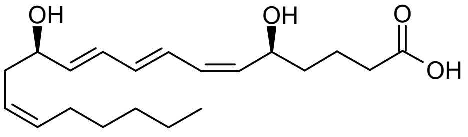


The association constant determined by the slope is 0.0412 pmol^{-1} L or:

$$K = 0.0412 \text{ pmol}^{-1}\text{ L}\left(\frac{1000 \text{ pmol}}{1 \text{ nmol}}\right) = 41.2 \text{ nmol}^{-1}\text{ L} = 41.2 \pm 3.4 \text{ nM}^{-1}$$

Even though the effective host concentration is very uncertain, you can verify by changing $[H]_o$ that the association constant that is determined from the slope is unaffected by the value of the total host concentration. The intercept should also give the association constant, but the value is strongly dependent on the total host concentration.

28. Leukotriene-B_4 is important in activating the inflammatory response:[3]



Developing leukotriene-B4 antagonists may be helpful in managing chronic obstructive pulmonary disease, severe asthma, rheumatoid arthritis, inflammatory bowel disease, and cystic fibrosis. A receptor site for leukotriene-B4 is a membrane bound protein in polymorphonuclear leukocytes, PMNLs. Isolated PMNL membranes were used in a binding study with radio-iodine labeled leukotriene-B4. The leukotriene was incubated with the purified membranes and then filtered. The concentration of bound leukotriene was determined by liquid scintillation counting of the membranes trapped on the filters. Consider the membrane bound protein receptor as the host and leukotriene-B4 as the guest. The concentration of bound guest as a function of the total concentration of guest is given in the table below.[3] The effective concentration of the host membrane receptors is $[H]_o = 33 \pm 12$ pmol L^{-1}.

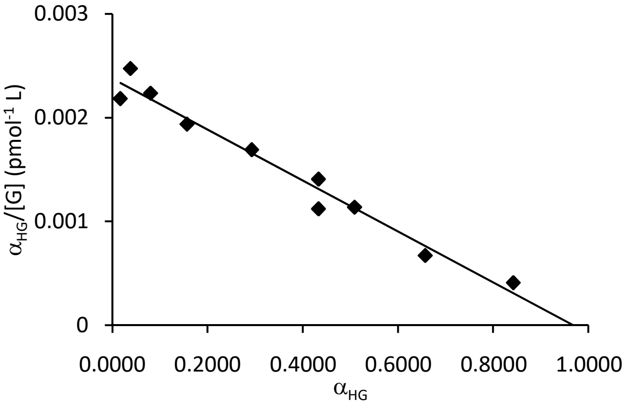
$[G]_o$ (pmol L^{-1})	8.33	16.7	38.7	86.4	183	322	401	464	1000	2080
[HG] (pmol L^{-1})	0.56	1.26	2.66	5.19	9.67	14.3	14.3	16.8	21.7	27.8

Answer: The plan is to determine the association constant from the Scatchard plot using Eq. 20.5.14. The free guest concentration is given by solving the mass balance: $[G] = [G]_o - [HG]$. The degree of association for the host is given by $\alpha_{HG} = [HG]/[H]_o$. A spreadsheet was developed to calculate [G], α_{HG}, and $\alpha_{HG}/[G]$ to form the Scatchard plot:

		$[H]_o$ =	33	pmol L^{-1}
$[G]_o$ (pmol L^{-1})	[HG] (pmol L^{-1})	[G] (pmol L^{-1})	α_{HG}	$\alpha_{HG}/[G]$ (pmol^{-1} L)
8.33	0.56	7.77	0.0170	0.00218
16.7	1.26	15.44	0.0382	0.00247
38.7	2.66	36.04	0.0806	0.00224
86.4	5.19	81.21	0.1573	0.00194
183	9.67	173.33	0.2930	0.00169
322	14.3	307.7	0.4333	0.00141
401	14.3	386.7	0.4333	0.00112
464	16.8	447.2	0.5091	0.00114
1000	21.7	978.3	0.6576	0.00067
2080	27.8	2052.2	0.8424	0.00041

The curve fit results are:

slope	-0.0024546	0.0023768	intercept
±	0.0001532	6.6721E-05	±
r^2	0.9697631	0.00012796	s(y)
F	256.57729	8	df
$ss_{regression}$	4.2011E-06	1.3099E-07	$ss_{residual}$



The association constant determined by the slope is 0.00245 pmol^{-1} L or:

$$K = 0.00245\ \text{pmol}^{-1}\ \text{L}\left(\frac{1000\ \text{pmol}}{1\ \text{nmol}}\right) = 2.45\ \text{nmol}^{-1}\ \text{L} = 2.45 \pm 0.15\ \text{nM}^{-1}$$

Even though the effective host concentration is very uncertain, you can verify by changing $[H]_o$ that the association constant that is determined from the slope is unaffected by the value of the total host concentration. The intercept should also give the association constant, but the value is strongly dependent on the total host concentration.

29. The organic dye eosin binds to the protein lysozyme. Binding to lysozyme quenches the fluorescence of the protein at 340 nm.[4] If I_H is the fluorescence intensity of the free form of lysozyme and I_{HG} is the fluorescence intensity of the bound form of the protein, then the observed intensity is the mole fraction weighted average:

$$I_{obs} = \alpha_H I_H + \alpha_{HG} I_{HG} = (1 - \alpha_{HG}) I_H + \alpha_{HG} I_{HG} = (I_{HG} - I_H)\, \alpha_{HG} + I_H \qquad \text{P20.29.1}$$

where α_H is the mole fraction of the free host protein, $\alpha_H = n_H/(n_H + n_{HG}) = [H]/[H]_o$, and α_{HG} is the mole fraction of the guest-host complex, $\alpha_{HG} = n_{HG}/(n_H + n_{HG}) = [HG]/[H]_o$. Solving Eq. P20.29.1 for the degree of association gives:

$$\alpha_{HG} = \frac{[HG]}{[H]_o} = \frac{I_H - I_{obs}}{I_H - I_{HG}} \qquad \text{P20.29.2}$$

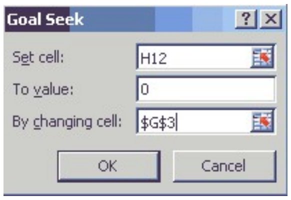
The fluorescence intensity of free lysozyme in buffer alone is $I_H = 1.541$. The fluorescence intensity, I_{obs}, as a function of the concentration of eosin with $[H]_o = 3.00\text{x}10^{-6}$ M lysozyme in each solution is:[4]

$[G]_o$ (M)	$5.00\text{x}10^{-6}$	$10.0\text{x}10^{-6}$	$20.0\text{x}10^{-6}$	$50.0\text{x}10^{-6}$
I_{obs}	1.198	1.064	0.855	0.494

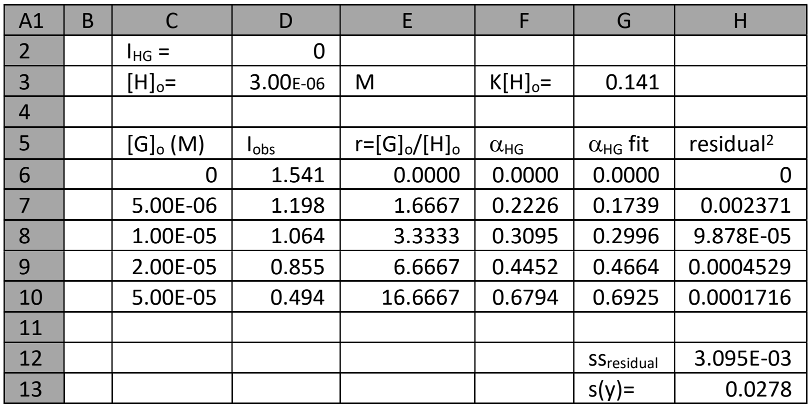
The fluorescence intensities are relative and in arbitrary units, which makes fluorescence intensity effectively unitless. Calculate the association constant of eosin with lysozyme. Assume that the fluorescence of lysozyme is negligible in the bound form, $I_{HG} \approx 0$. [Hints: a Scatchard plot is not appropriate for this experiment, because the free eosin concentration is not known. There is only one unknown, so use of a curve fitting program is not necessary. Using "goal seek" in a spreadsheet format is useful for finding the optimum value for an adjustable parameter in a non-linear equation.]

Answer: The plan is to use Eq. 20.5.22 for calculating the degree of association. A spreadsheet is constructed and then "goal seek" is used to find the value of $K[H]_o$ that best fits the data.

The spreadsheet is reproduced below. The raw data is in the first two columns. The guest-host ratio is then calculated, $r = [G]_o/[H]_o$, where the guest is eosin and the host is lysozyme. The degree of association is then determined from the fluorescence intensities: $\alpha_{HG} = (I_H - I_{obs})/(I_H - I_{HG})$. A value of $K[H]_o$ is guessed. Eq. 20.5.22 is then used to calculate the fit value for the degree of association based on the guessed value of $K[H]_o$, in the fifth column. The formula is: "`=((1+$G$3*(1+E6))-SQRT((1+$G$3*(1+E6))^2-4*$G$3^2*E6))/2/$G$3.`" The last column is the squared residual $(\alpha_{HG} - \alpha_{HG}\ \text{fit})^2$, which is used to judge the agreement of the experimental and modeled value based on the current guess for $K[H]_o$. The overall goodness of fit is determined by the sum of squared residuals in cell H12. The “goal seek” option under Data: What-if-analysis is then used to minimize the sum of squared residuals:



Set cell: H12
To value: 0
By changing cell: $G$3



A1	B	C	D	E	F	G	H
2		I_{HG} =	0				
3		$[H]_o$=	3.00E-06	M	$K[H]_o$=	0.141	
4							
5		$[G]_o$ (M)	I_{obs}	$r=[G]_o/[H]_o$	α_{HG}	α_{HG} fit	residual^2
6		0	1.541	0.0000	0.0000	0.0000	0
7		5.00E-06	1.198	1.6667	0.2226	0.1739	0.002371
8		1.00E-05	1.064	3.3333	0.3095	0.2996	9.878E-05
9		2.00E-05	0.855	6.6667	0.4452	0.4664	0.0004529
10		5.00E-05	0.494	16.6667	0.6794	0.6925	0.0001716
11							
12						$SS_{residual}$	3.095E-03
13						s(y)=	0.0278

The final optimized value is $K[H]_o = 0.141$ or $K = 4.7_0\text{x}10^4$. Biochemists often quote the results as dissociation constants and neglect to divide by the standard state concentrations in the equilibrium expression, which gives the dissociation constant with units: $K_D = 1/K = 2.1_3\text{x}10^{-5}$ = 21. µM. A standard goodness of fit criterion is the standard deviation of the y values, s_y or s(y). The y values in this problem are the α_{HG} values and $s_y = \sqrt{SS_{residual}/(n-1)}$. See the next problem for the error analysis.

30. Finding the optimum value for a single adjustable parameter in a non-linear equation is easily handled using the “goal seek” option in a spreadsheet, rather than using non-linear least squares curve fitting programs. However, the spreadsheet approach makes the determination of the uncertainty of the final fit value more involved than using non-linear least squares curve fitting algorithms. However, least squares curve fitting programs are often set up to fit two or more adjustable parameters, not just one parameter. The uncertainty for fitting procedures for a single parameter are easily handled using the following approach.

The general formula for propagation of errors for the two-parameter function f(x,y) is (Appendix 1):

$$\delta^2 f = \left(\frac{\partial f}{\partial x}\right)_y^2 \delta^2 x + \left(\frac{\partial f}{\partial y}\right)_x^2 \delta^2 y$$

Consider a non-linear function f(b,x), with the adjustable parameter b and independent variable x. The adjustable parameter is often an equilibrium constant and the x variable is a concentration or a mole ratio (see the previous problem). Let the value of the measured observables at a series of x values be $y_1 = f(b,x_1)$, $y_2 = f(b,x_2)$, $y_3 = f(b,x_3)$, … for n values of x. The y values are often absorbances, fluorescence intensities, or chemical shifts. The uncertain variables are the y_i values. The uncertainty in the fit parameter, b, is then given by:

$$\delta^2 b = \left(\frac{\partial b}{\partial y_1}\right)^2 \delta^2 y_1 + \left(\frac{\partial b}{\partial y_2}\right)^2 \delta^2 y_2 + \ldots$$

with the sum over all n data points. If we assume that the derivatives are all approximately equal, then the last equation reduces to:

$$\delta^2 b \approx \left(\frac{\partial b}{\partial y}\right)^2 \sum_{i=1}^{n} \delta^2 y_i \qquad \text{or} \qquad \left(\frac{\delta^2 b}{n-1}\right) \approx \left(\frac{\partial b}{\partial y}\right)^2 \left(\frac{\sum_{i=1}^{n} \delta^2 y_i}{n-1}\right)$$

Dividing both sides of the equation by n–1 converts the uncertainties to variances, s_b and s_y. Taking the square root and inverting the derivative gives:

$$s_b \approx \frac{1}{\left(\frac{\partial y}{\partial b}\right)} s_y$$

where $(\partial y/\partial b)$ is approximately evaluated numerically as the change in a typical y value for a small change in the fit parameter:

$$\left(\frac{\partial y}{\partial b}\right) = \frac{f(b+\delta b,x) - f(b,x)}{\delta b}$$

where x is a typical x-value and δb is a small change in the fit parameter. The derivative is easily calculated by finding the y-value for the optimal b-value , f(b,x), and then changing b by a small amount and finding the new y-value, $f(b+\delta b,x)$.

Using these last two equations, find the uncertainty in the association constant for the previous fluorescence quenching problem.

Answer: For the last problem the y_i values are the experimental α_{HG} values. The adjustable parameter is $b = K[H]_o$. The x values are the eosin concentrations. Focus on data point 3 for $x = 2.00\text{x}10^{-5}$ M eosin as a typical value, in the spreadsheet in the last problem. The fit value for $\alpha_{HG,3}$ is 0.4664 with $b = K[H]_o = 0.141$. Now change b to 0.142. The new value of $\alpha_{HG,3}$ is 0.4681. The derivative is then:

$$\left(\frac{\partial y}{\partial b}\right) = \frac{f(b+\delta b,x) - f(b,x)}{\delta b} = \frac{0.4681 - 0.4664}{0.001} = 1.70$$

The standard deviation of the y values from spreadsheet cell H13 is $s_y = 0.0278$, at the optimum value for $K[H]_o = 0.141$. The estimate for the uncertainty in the variable parameter $b = K[H]_o$ is then:

$$\delta b \approx \frac{1}{\left(\frac{\partial y}{\partial b}\right)} s_y = \frac{1}{1.70}(0.0278) = 0.0164 \qquad \text{or} \qquad \frac{0.0164}{0.141}\,100\% = 11.6\%$$

Giving the uncertainty in the association constant as $K = 4.7\text{x}10^4 \pm 0.5\text{x}10^4$. The dissociation constant is $K_D = 1/K = 2.13\text{x}10^{-5} \pm 0.25\text{x}10^{-5}$.

31. NMR is an important technique for measuring formation constants in guest-host chemistry. For example, if a given proton in the host shows a chemical shift difference between the free and bound forms, then the chemical shift of the proton is strongly concentration dependent. The dependence is due to changes in the mole fractions of the free and bound forms. Assume the reactions are rapid on the NMR time scale: rate > $1/\nu_o$ with ν_o the resonance frequency. If δ_H is the chemical shift of the free form of the host and δ_{HG} is the chemical shift of the bound form of the host, then the observed chemical shift is the mole fraction weighted average, assuming the reactions are rapid:

$$\delta_{obs} = \alpha_H\, \delta_H + \alpha_{HG}\, \delta_{HG}$$

where α_H is the mole fraction of the free host, $\alpha_H = n_H/(n_H + n_{HG}) = [H]/[H]_o$, and α_{HG} is the mole fraction of the guest-host complex, $\alpha_{HG} = n_{HG}/(n_H + n_{HG}) = [HG]/[H]_o$. Given that $\alpha_H + \alpha_{HG} = 1$, the observed chemical shift reduces to:

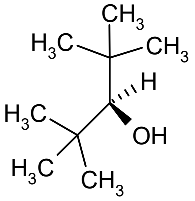
$$\delta_{obs} = (1 - \alpha_{HG})\, \delta_H + \alpha_{HG}\, \delta_{HG} = (\delta_{HG} - \delta_H)\, \alpha_{HG} + \delta_H$$

The mole fraction of the bound guest-host complex is calculated by Eq 20.5.22:

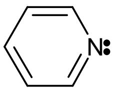
$$\delta_{obs} = (\delta_{HG} - \delta_H)\left(\frac{(1+K[H]_o\,(1+r)) - \sqrt{(1+K[H]_o\,(1+r))^2 - 4K^2[H]_o^2\, r}}{2K[H]_o}\right) + \delta_H$$

Although somewhat daunting looking, this equation is easily used in non-linear curve fitting with the "Nonlinear Least Squares Curve Fitting" applet on the text Web site and the companion CD. In particular, the guest and host can be a hydrogen-bonded pair. NMR is an important technique in studies of hydrogen bonding.

The formation of the hydrogen bond between the sterically crowded alcohol, below, and pyridine has been studied:[5]



2,2,4,4-tetramethyl-pentan-3-ol



pyridine

Consider the alcohol as the host and pyridine as the guest. The chemical shift of the alcohol hydrogen is given in the table, below, as a function of the concentration of pyridine in benzene solution. The alcohol concentration is fixed in each solution at 0.100 M. The chemical shift of the free alcohol is $\delta_H = 1.105$ ppm. The chemical shift difference, $(\delta_{HG} - \delta_H)$, and $K[H]_o$ are treated as the two variable parameters in the curve fitting. The binding constant is expected to be ≈1, since the formation of a single hydrogen bond is a weak interaction.

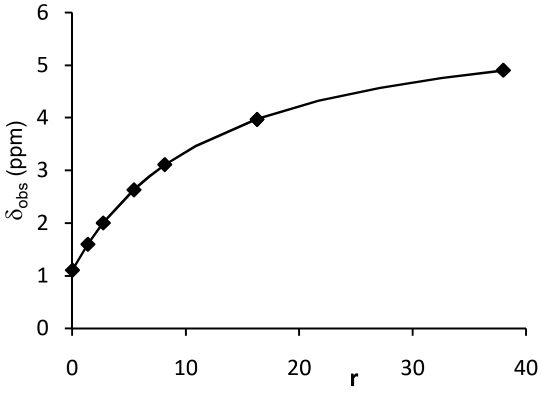
$[G]_o$ (M)	0	0.136	0.271	0.543	0.814	1.628	3.799
δ_{obs} (ppm)	1.105	1.594	2.000	2.630	3.111	3.970	4.901

Answer: The guest/host ratios, r, are calculated using the spreadsheet below and the r and δ_{obs} values are used in non-linear curve fitting using the "Nonlinear Least Squares Curve Fitting" applet on the text Web site and the companion CD. The fit function is listed in the applet as:

a{(1+b(1+x)) - sqrt[(1+b(1+x))^2 - 4(b^2)x]}/2b + c

where $a = \delta_{HG} - \delta_H$, $b = K[H]_o$, and $c = \delta_H$. The c value is treated as a fixed constant, c = 1.105 ppm. If initial guesses of a = 8 and b = 0.1 are used, the fit doesn't converge. After this first attempt, the non-converged fit values are listed by the applet as a = 4.96 and b = 0.8754, which are used as guesses for a second attempt that does converge. The results are listed and plotted below.

$[G]_o$ (M)	r	δ_{obs} (ppm)
0	0.000	1.105
0.136	1.357	1.594
0.271	2.713	2.000
0.543	5.427	2.630
0.814	8.140	3.111
1.628	16.281	3.970
3.799	37.989	4.901



```
======================   Results   =========================
 a= 4.9609 +- 0.043
 b= 0.087502 +- 0.000062
_______________________ Output Data _________________________
     x                     y               y(fit)      residual
  -0.0         1.105         1.102         0.003
   1.357       1.594         1.59388       0.00012
   2.713       2.0           2.00167      -0.00167
   5.427       2.63          2.63642      -0.00642
   8.14        3.111         3.10462       0.00638
  16.281       3.97          3.97322      -0.00322
  37.989       4.901         4.89762       0.00338
-------------------------------------------------------------
 sum of squared residuals= 0.0001156
 stand. dev. y values= 0.004808
 correlation between a & b= -0.9949
```

The value for the binding constant is $K = b/[H]_o = 0.08750/0.100 = 0.875$.

The between fit parameters correlation is very large, at -0.9949. Large between fit parameters correlations are a typical problem in guest-host chemistry for weak interactions. Authors support their results by independent measurements of the chemical shift of the completely complexed species, and by independent repetitions of the experiment.[5] Even so, there are often large inconsistencies between laboratories for the values of binding constants. The uncertainty obtained from the least squares fitting procedure underestimates the true uncertainty of the binding constant (you can prove this to yourself by changing the first chemical shift at $[G]_o = 0$ to 1.102 ppm and noting the difference in K, for example). Titration calorimetry is often used as an independent and, in most cases, more accurate method for determining binding constants. However, titration calorimetry is not applicable for all reactions.

32. Derive Eq. 20.5.23.

Answer: The plan is to recast the equilibrium expression in terms of $[H]_o$, $[G]_o$, and free guest, [G] using the mass balance. Then the equilibrium expression is used to solve for [G].

The mass balance equations are given by Eqs. 20.5.3 and 20.5.15:

$$[H]_o = [H] + [HG] \qquad (20.5.3)$$

$$[G]_o = [G] + [HG] \qquad (20.5.15)$$

Solving Eq. 20.5.15 for the complex concentration, [HG]:

$$[HG] = [G]_o - [G] \qquad 1$$

Solving Eq. 20.5.3 for the free host concentration and then using Eq. 1 for [HG] gives:

$$[H] = [H]_o - [HG] = [H]_o - [G]_o + [G] \qquad 2$$

Substitution of the mass balances into the equilibrium expression, Eq. 20.5.1, results in:

$$K = \frac{[G]_o - [G]}{([H]_o - [G]_o + [G])[G]} = \frac{[G]_o - [G]}{([H]_o - [G]_o)[G] + [G]^2} \qquad 3$$

Cross-multiplying and rearranging gives a quadratic expression:

$$K[G]^2 + (1 + K([H]_o - [G]_o))\,[G] - [G]_o = 0 \qquad 4$$

Substitution of the coefficients into the quadratic formula gives:

$$[G] = \frac{-(1+K([H]_o-[G]_o)) \pm \sqrt{(1+K([H]_o-[G]_o))^2 + 4K[G]_o}}{2K} \qquad 5$$

Only the positive root gives meaningful concentrations. To express [G] as a function of the mole ratio of the guest and host, multiply and divide the equilibrium constant by $[H]_o$ to give:

$$[G] = \frac{-(1+K[H]_o\,(1-[G]_o/[H]_o)) + \sqrt{(1+K[H]_o\,(1-[G]_o/[H]_o))^2 + 4K[H]_o\,[G]_o/[H]_o}}{2K[H]_o/[H]_o} \qquad 6$$

The mole ratio of the guest to host is $r \equiv [G]_o/[H]_o$ giving:

$$[G] = [H]_o \left(\frac{-(1+K[H]_o\,(1-r)) + \sqrt{(1+K[H]_o\,(1-r))^2 + 4K[H]_o\,r}}{2K[H]_o} \right) \tag{20.5.23}$$

33. Derive Eq. 20.5.24.

Answer: The plan is to recast the equilibrium expression in terms of $[H]_o$, $[G]_o$, and free host, [H] using the mass balance. Then the equilibrium expression is used to solve for [H].

The mass balance equations are given by Eqs. 20.5.3 and 20.5.15:

$$[H]_o = [H] + [HG] \tag{20.5.3}$$

$$[G]_o = [G] + [HG] \tag{20.5.15}$$

Solving Eq. 20.5.3 for the complex concentration, [HG]:

$$[HG] = [H]_o - [H] \tag{1}$$

Solving Eq. 20.5.15 for the free guest concentration and then using Eq. 1 for [HG] gives:

$$[G] = [G]_o - [HG] = [G]_o - [H]_o + [H] \tag{2}$$

Substitution of the mass balances into the equilibrium expression, Eq. 20.5.1, results in:

$$K = \frac{[H]_o - [H]}{[H]\,([G]_o - [H]_o + [H])} = \frac{[H]_o - [H]}{([G]_o - [H]_o)[H] + [H]^2} \tag{3}$$

Cross-multiplying and rearranging gives a quadratic expression:

$$K[H]^2 + (1 + K([G]_o - [H]_o))\,[H] - [H]_o = 0 \tag{4}$$

Substitution of the coefficients into the quadratic formula gives:

$$[H] = \frac{-(1+K([G]_o-[H]_o)) \pm \sqrt{(1+K([G]_o-[H]_o))^2 + 4K[H]_o}}{2K} \tag{5}$$

Only the positive root gives meaningful concentrations. To express [G] as a function of the mole ratio of the guest and host, multiply and divide the equilibrium constant by $[H]_o$ to give:

$$[H] = \frac{-(1+K[H]_o\,([G]_o/[H]_o - 1)) + \sqrt{(1+K[H]_o\,([G]_o/[H]_o - 1))^2 + 4K[H]_o}}{2K[H]_o/[H]_o} \tag{6}$$

The mole ratio of the guest to host is $r \equiv [G]_o/[H]_o$ giving:

$$[H] = [H]_o \left(\frac{-(1+K[H]_o\,(r-1)) + \sqrt{(1+K[H]_o\,(r-1))^2 + 4K[H]_o}}{2K[H]_o} \right) \tag{20.5.24}$$

34. An alternative form for the concentration of the guest-host complex often encountered in biochemical studies is based on the dissociation equilibria:

$$HG \rightleftarrows H + G \qquad\qquad K_D = \frac{[H]\,[G]}{[HG]}$$

where K_D is the dissociation constant. The relationship to the association constant and Eq. 20.5.1 is $K_D = 1/K$. (a). Show that the guest-host concentration is given by:

$$[HG] = \frac{([H]_o + [G]_o + K_D) - \sqrt{([H]_o + [G]_o + K_D)^2 - 4\,[H]_o\,[G]_o}}{2}$$

(b). Find the relationship in terms of the guest-host ratio, $r = [G]_o/[H]_o$.

Answer: The plan is to recast the equilibrium expression in terms of $[H]_o$, $[G]_o$, and the guest-host complex, [HG], using the mass balance. Then the equilibrium expression is used to solve for [HG].

The mass balance equations are given by Eqs. 20.5.3 and 20.5.15:

$$[H]_o = [H] + [HG] \qquad (20.5.3)$$
$$[G]_o = [G] + [HG] \qquad (20.5.15)$$

Solving Eqs. 20.5.3 and 20.5.15 for the free host and free guest concentrations:

$$[H] = [H]_o - [HG]$$
$$[G] = [G]_o - [HG]$$

Substitution of the mass balances into the dissociation equilibrium expression results in:

$$K_D = \frac{[H]\,[G]}{[HG]} = \frac{([H]_o - [HG])([G]_o - [HG])}{[HG]} = \frac{[H]_o[G]_o - ([H]_o + [G]_o)[HG] + [HG]^2}{[HG]}$$

Cross-multiplying and rearranging gives a quadratic expression:

$$[HG]^2 - ([H]_o + [G]_o + K_D)\,[HG] + [H]_o\,[G]_o = 0$$

Substitution of the coefficients into the quadratic formula gives:

$$[HG] = \frac{([H]_o + [G]_o + K_D) - \sqrt{([H]_o + [G]_o + K_D)^2 - 4\,[H]_o\,[G]_o}}{2}$$

Only the negative root gives meaningful concentrations. To express [HG] as a function of the mole ratio of the guest and host, factor out $[H]_o$ to give:

$$[HG] = [H]_o\,\frac{(1 + [G]_o/[H]_o + K_D/[H]_o) - \sqrt{(1 + [G]_o/[H]_o + K_D/[H]_o)^2 - 4\,[G]_o/[H]_o}}{2}$$

The mole ratio of the guest to host is $r \equiv [G]_o/[H]_o$ giving:

$$[H] = [H]_o\left(\frac{(1 + r + K_D/[H]_o) - \sqrt{(1 + r + K_D/[H]_o)^2 - 4\,r}}{2}\right)$$

The fit parameters for non-linear least-square curve fitting are $a = [H]_o$ and $b = K_D/[H]_o$.

35. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true, but too restrictive, give the more general statement.

(a). The relationship $\Delta_r G° = -RT \ln K_p$ shows that $\Delta_r G°$ is the reaction Gibbs energy at equilibrium.
(b). The position of equilibrium for a constant volume process is determined by the extent of the reaction, ξ.
(c). The position of equilibrium is unaffected by addition of an inert gas, such as helium, since the inert gas will not participate in the reaction.
(d). The position of equilibrium for the reaction types $2A \rightleftarrows B + C$ and $A + B \rightleftarrows C + D$ will be the same if the equilibrium constants are the same.
(e). The rate of the reaction $2A \rightarrow B + C$ increases with temperature so the equilibrium position of the reaction shifts to the right with an increase in temperature.
(f). The rate of the reaction $2A \rightarrow B + C$ is fast so the equilibrium constant for the reaction is large.

Answer: (a). False: The reaction Gibbs energy at equilibrium is zero. The standard state reaction Gibbs energy corresponds to each pure reactant and product under standard state conditions, $P° = 1$ bar. It is highly unlikely that the reaction will be at equilibrium with pure reactants and products for each substance at $P_i = 1$ bar, which is required to give $\Delta_r G° = 0$.
(b). True but too restrictive: The statement is true for constant V, P, and T. The statement should be: The position of equilibrium is determined by the extent of the reaction, ξ.
(c). The effect of an inert gas depends on the conditions. The statement is true for a constant volume reaction and false for a constant pressure problem if $\Delta_r n_g \neq 0$. At constant pressure the addition of an inert gas changes the volume of the system, lowering the partial pressure for each gaseous reactant and product. The statement also neglects changes in activity coefficients and the changes in chemical potentials of solids, liquids, and solutions for large changes in total pressure. The statement should be: The position of equilibrium for a reaction at constant volume is unaffected by addition of an inert gas, for moderate changes in total pressure.
(d). False: The reactant for $2A \rightleftarrows B + C$ has no entropy of mixing while the reactants in $A + B \rightleftarrows C + D$ do have an entropy of mixing. The favorable entropy of mixing for the reactants for $A + B \rightleftarrows C + D$ will lower the Gibbs energy of the reactants compared to the pure constituents and shift the position of equilibrium to the left compared to $2A \rightleftarrows B + C$. The statement should be: The position of equilibrium for the reaction $2A \rightleftarrows B + C$ will be to the right of the position of equilibrium for $A + B \rightleftarrows C + D$, assuming comparable equilibrium constants.
(e). False: don't confuse kinetic and equilibrium considerations. The equilibrium constant is the ratio of the forward and reverse overall reaction rates, $K_p = k_f/k_r$. Both forward and reverse reaction rates change with temperature. The equilibrium position can shift left or right with an increase in forward reaction rate. The correct statement is: The shift in equilibrium position with temperature is determined by the standard state reaction enthalpy.
(f). False: don't confuse kinetic and equilibrium considerations. The equilibrium constant is the ratio of the forward and reverse overall reaction rates, $K_p = k_f/k_r$. The reverse reaction rate can be faster than the forward reaction rate, which would make the equilibrium constant small.

36. The ITC titration of the enzyme ribonuclease A with the ligand 2'CMP is given in the table below. Consider ribonuclease A as the host and 2'CMP as the guest. The host concentration in the titration cell was 6.272×10^{-5} M, the guest concentration in the automated buret was

2.19×10^{-3} M, the titration cell volume was 1.4389 mL, and the titrant was added in 9.00 μL increments. The association constant was determined to be 6.99×10^{5} and the reaction enthalpy was -70.6 kJ mol^{-1} using non-linear curve fitting. (a). Calculate Δ_rG^o and Δ_rS^o . (b). Use the fit values to reproduce the titration curve. Neglect any corrections for exclusion of material from the constant volume titration cell (as discussed in the addendum). [Hint: construct a spreadsheet using Eq. 20.5.22. Show the titration curve with the calculated and experimental values, for comparision.]

i V_{inj} (μL)	9	18	27	36	45	54	63	72	81	90	99
q/n_{inj} (kJ mol^{-1})	-68.3	-67.3	-64.2	-56.3	-35.6	-14.6	-6.41	-3.61	-2.33	-1.64	-1.3

Answer: (a). $\Delta_rG^o = -\,RT \ln K = -33.4$ kJ mol^{-1} and:

$$\Delta_rS° = \frac{\Delta_rH° - \Delta_rG°}{T} = \frac{(\text{-70. 6 kJ mol}^{-1} - (\text{-33.4 kJ mol}^{-1}))(1000\text{ J/1 kJ})}{298.15\text{ K}} = \text{-125. J K}^{-1}\text{ mol}^{-1}$$

which completes the thermodynamic characterization of the reaction.

(b). The plan is to use Eqs. 20.6.3 and 20.6.4 to find $[G]_o$ and $r = [G]_o/[H]_o$. Eq. 20.5.22 is then used to find [HG]. Eqs. 20.6.5-20.6.7 are then used to calculate the enthalpy change per mole of added titrant at each step of the titration, which is compared to the experimental values.

The spreadsheet is:

A1	B	C	D	E	F	G	H	I	J
2									
3	host	$[H]_o$ =	6.272E-05	M	K=	6.99E+05			
4	titrant	$[G]_o$ =	2.190E-03	M	Δ_rH=	-70600	J/mol		
5	cell	V_{cell} =	1.4389	mL					
6	titrant add	V_{inj} =	9	uL					
7									
8	volume titrant:								
9	i V_{inj} (μL)	$[G]_o$	$r=[G]_o/[H]_o$	$1+K[H]_o(1+r)$	factor	[HG] (M)	$\Delta n_{HG,i}$ (mol)	q_i (mJ)	q_i/n_{inj} (kJ mol^{-1})
10	9	1.37E-05	0.218	54.416	35.805	1.33E-05	1.92E-08	-1.352	-68.613
11	18	2.74E-05	0.437	63.991	27.141	2.64E-05	1.88E-08	-1.325	-67.242
12	27	4.11E-05	0.655	73.566	19.356	3.88E-05	1.79E-08	-1.262	-64.003
13	36	5.48E-05	0.874	83.141	14.000	4.95E-05	1.54E-08	-1.085	-55.046
14	45	6.85E-05	1.092	92.716	14.167	5.62E-05	9.68E-09	-0.684	-34.684
15	54	8.22E-05	1.310	102.291	19.717	5.91E-05	4.14E-09	-0.292	-14.838
16	63	9.59E-05	1.529	111.865	27.571	6.03E-05	1.77E-09	-0.125	-6.343
17	72	1.10E-04	1.747	121.440	36.262	6.09E-05	9.10E-10	-0.064	-3.259
18	81	1.23E-04	1.966	131.015	45.311	6.13E-05	5.42E-10	-0.038	-1.940
19	90	1.37E-04	2.184	140.590	54.540	6.16E-05	3.56E-10	-0.025	-1.276
20	99	1.51E-04	2.402	150.165	63.870	6.17E-05	2.51E-10	-0.018	-0.900

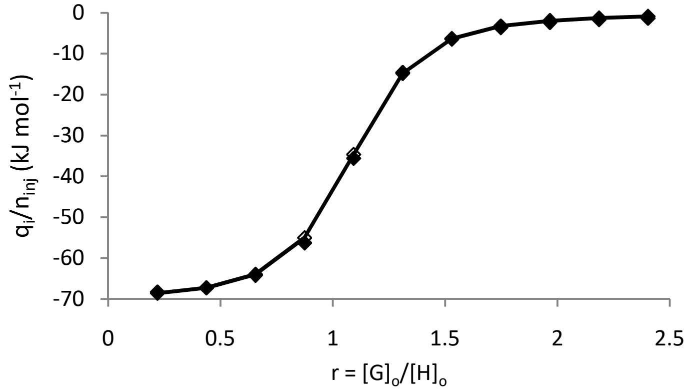
The terms in Eq. 20.5.22 were separated to make the calculations easier and to provide the opportunity to check for mistakes. The factor term is: $\text{factor} = \sqrt{(1+K[H]_o\,(1+r))^2 - 4K^2[H]_o^{\,2}\,r}$.

The formulas are:

C10: =B10/1000000*$D$4/$D$5*1000
D10: =C10/$D$3
E10: =1+$G$3*$D$3*(1+D10)
F10: =SQRT(E10^2-4*$G$3^2*$D$3^2*D10)
G10: =$D$3*((E10-F10)/2/$G$3/$D$3)
H10: =G10*$D$5/1000
H11: =(G11-G10)*$D$5/1000
I10: =H10*$G$4*1000

J10: =(I10/1000000)/($D$6/1000000*$D$4)

A plot of the modeled q_i/n_{inj} and experimental values is:



The modeled values are shown with outlined symbols and the experimental values are shown with solid symbols. The discrepancies are in part caused by neglecting the volume exclusion corrections.

37. Eq. 20.5.22 can be used directly in non-linear curve fitting for finding association constants from ITC titration curves. The results for each step in an ITC experiment are given by Eqs. 20.6.5-20.6.7. Consider the first two steps in the titration. The sum of the $q_{i,m}$ values for the first two steps gives, using Eqs. 20.6.6 and 20.6.7:

$$q_{tot} = q_{1,m} + q_{2,m} = q_2/n_{inj} + q_1/n_{inj} = (\Delta n_{HG,2} + \Delta n_{HG,2})\ \Delta_r H^o/n_{inj}$$

Then using Eq. 20.6.5 the total calorimetric enthalpy is given in terms of [HG] as:

$$q_{tot} = q_{1,m} + q_{2,m} = q_2/n_{inj} + q_1/n_{inj} = ([HG]_2 - [HG]_1 + [HG]_1 - [HG]_o)\ \Delta_r H^o\ V_{cell}/n_{inj}$$

$$q_{tot} = q_{1,m} + q_{2,m} = q_2/n_{inj} + q_1/n_{inj} = [HG]_2\ \Delta_r H^o\ V_{cell}/n_{inj}$$

since $[HG]_o = 0$. Solving for $[HG]_2\ \Delta_r H^o$ gives:

$$q_{tot}\ n_{inj}/V_{cell} = \Delta_r H^o\ [HG]_2$$

In a similar fashion, if we add the calorimetric enthalpies for the first n steps:

$$q_{tot}\ n_{inj}/V_{cell} = (q_{1,m} + q_{2,m} + \ldots + q_{2,n})\ n_{inj}/V_{cell} = \Delta_r H^o\ [HG]_n$$

Eq. 20.5.22 can then be used to calculate the concentration of the host-guest complex:

$$q_{tot}\left(\frac{n_{inj}}{V_{cell}\ [H]_o}\right) = \Delta_r H^o \left(\frac{(1+K[H]_o\ (1+r)) - \sqrt{(1+K[H]_o\ (1+r))^2 - 4K^2[H]_o^{\ 2}\ r}}{2K[H]_o}\right)$$

where r is the guest-host ratio at the nth step of the titration. The two adjustable parameters for curve fitting are $a = \Delta_r H^o$ and $b = K[H]_o$.

Use the data in the last problem to find the association constant and reaction enthalpy for the binding of ribonuclease A with 2'CMP.

Answer: The plan is to use Eqs. 20.6.3 and 20.6.4 to find $[G]_o$ and $r = [G]_o/[H]_o$. The value for $q_{tot}\ n_{inj}/(V_{cell}\ [H]_o)$ is then calculated as discussed in the problem introduction. The spreadsheet is:

A1	B	C	D	E	F	G
2						
3	host	$[H]_o$ =	6.272E-05	M		
4	titrant	$[G]_o$ =	2.190E-03	M		
5	cell	V_{cell} =	1.4389	mL		
6	titrant add	V_{inj} =	9	uL		
7						
8	volume titrant:					
9	i V_{inj} (μL)	$[G]_o$	exp (kJ mol^{-1})	$\Sigma q_i/n_{inj}$ (kJ mol^{-1})	$r=[G]_o/[H]_o$	Σq_i (J mol^{-1})
10	9	1.37E-05	-68.3	-68.3	0.218	-1.492E+04
11	18	2.74E-05	-67.3	-135.6	0.437	-2.961E+04
12	27	4.11E-05	-64.2	-199.8	0.655	-4.364E+04
13	36	5.48E-05	-56.3	-256.1	0.874	-5.593E+04
14	45	6.85E-05	-35.6	-291.7	1.092	-6.371E+04
15	54	8.22E-05	-14.6	-306.3	1.310	-6.690E+04
16	63	9.59E-05	-6.41	-312.71	1.529	-6.830E+04
17	72	1.10E-04	-3.61	-316.32	1.747	-6.908E+04
18	81	1.23E-04	-2.33	-318.65	1.966	-6.959E+04
19	90	1.37E-04	-1.64	-320.29	2.184	-6.995E+04
20	99	1.51E-04	-1.3	-321.59	2.402	-7.023E+04

The column labeled "exp" gives the experimental q_i/n_{inj} values from the calorimeter. The first $\Sigma q_i/n_{inj}$ column is the successive sum of the experimental enthalpies, $q_{tot} = \Sigma(q_i/n_{inj})$. The guest-host ratio is calculated using Eq. 20.6.4. The last column is the value for $q_{tot}\ n_{inj}/(V_{cell}\ [H]_o)$ in units of joules per mol for the reaction. Cell G10 is:

"=D10*1000*$D$4*$D$6*0.000001/$D$5/0.001/$D$3".

The final two columns are used as input in non-linear curve fitting using the "Nonlinear Least Squares Curve Fitting" applet on the text Web site and the companion CD. The fit function is:

a{(1+b(1+x)) - sqrt[(1+b(1+x))^2 - 4(b^2)x]}/2b + c

with fixed c = 0. The results are shown below.

```
==================   Results   =====================
 a= -71422 +- 188
 b= 39 +- 1.4
___________________ Output Data ____________________
    x        y           y(fit)      residual
   0.218   -14920.0      -15079.9659   159.9659
   0.437   -29610.0      -29893.45311  283.45311
   0.655   -43640.0      -43866.56378  226.56378
   0.874   -55930.0      -55853.66829  -76.33171
   1.092   -63710.0      -63439.95773 -270.04227
   1.31    -66900.0      -66841.80936  -58.19064
   1.529   -68300.0      -68357.87206   57.87206
   1.747   -69080.0      -69146.2291    66.2291
   1.966   -69590.0      -69621.5504    31.5504
   2.184   -69950.0      -69934.19432  -15.80568
   2.402   -70230.0      -70155.46303  -74.53697
----------------------------------------------------
 sum of squared residuals= 253900
 stand. dev. y values= 168
 correlation between a & b= 0.9463
```

The final results are $\Delta_r H^o = -71.42 \pm 0.19$ kJ mol^{-1} and

$$K = [H]_o\, b = 6.272\text{x}10^{-5}\ (39.) = 6.22\text{x}10^{5} \pm 0.22\text{x}10^{-5}$$

Notice that the between fit parameter correlation is high, but acceptable, at 0.9463. The results deviate from the values listed in the last problem, $K = 6.99\text{x}10^5$ and $\Delta_r H^o = -70.6$ kJ mol^{-1}, because we didn't correct for exclusion of material from the constant volume titration cell (as discussed in the addendum).

38. Comparison of Eqs. 20.1.17 and 20.1.5 might at first seem conflicting:

$$G = n_A\, \mu_A + n_B\, \mu_B + n_C\, \mu_C + n_D\, \mu_D \qquad (20.1.17)$$

$$\Delta_r G = c\, \mu_C + d\, \mu_D - a\, \mu_A - b\, \mu_B \qquad (20.1.5)$$

Derive Eq. 20.1.5 from Eq. 20.1.17, thus showing that the two equations are consistent. [Hint: remember that the reaction Gibbs energy is the Gibbs energy for the products minus the Gibbs energy for the reactants.]

Answer: Write the reaction as: $a\,A + b\,B \rightleftarrows c\,C\ \ d\,D$. We note using Eq. 3.1.4, $dn_i = \nu_i d\xi$, that as the reaction proceeds from reactants to products, for a given extent, n_i changes from:

$$n_i\text{:}\ \ n_{i,o} \rightarrow\ n_{i,o} + \nu_i\, \xi \qquad 1$$

where $n_{i,o}$ is the initial amount of constituent i. For the reaction run to completion:

$$\xi\text{: } 0 \rightarrow 1, \qquad n_A\text{:}\ \ n_{A,o} \rightarrow n_{A,o} - a \qquad n_B\text{:}\ \ n_{B,o} \rightarrow n_{B,o} - b$$

$$n_C\text{:}\ \ n_{C,o} \rightarrow n_{C,o} + c \qquad n_D\text{:}\ \ n_{D,o} \rightarrow n_{D,o} + d \qquad 2$$

Finally: $\Delta_r G = G_{products}(\xi{=}1) - G_{reactants}(\xi{=}0)$. Substituting Eqs. 2 into Eq. 20.1.17 at $\xi = 1$ and $\xi = 0$ gives:

$$\Delta_r G = G_{products} - G_{reactants}$$
$$= [(n_{A,o}- a)\mu_A + (n_{B,o}- b)\mu_B + (n_{C,o}+ c)\mu_C + (n_{D,o}+ d)\mu_D] - [n_{A,o}\, \mu_A + n_{B,o}\, \mu_B + n_{C,o}\, \mu_C + n_{D,o}\, \mu_D]$$

$$\Delta_r G = G_{products} - G_{reactants} = [c\, \mu_C + d\, \mu_D] - [a\, \mu_A + b\, \mu_B]$$

which is Eq. 20.1.5.

The alternative path is to note that both 20.1.17 and 20.1.5 result from integration of the total differential of the Gibbs energy, Eq. 20.1.2. Correspondingly, Eq. 20.1.17 is the Gibbs energy for the reaction mixture at some point during the reaction and $\Delta_r G$ is the change in Gibbs energy for the reaction of a-moles of A and b-moles of B to give c-moles of C and d-moles of D. Eq. 20.1.17 is valid at any point during the reaction, while Eq. 20.1.5 corresponds to the change for the reaction run to completion.

39. Calculate the equilibrium constant for the *anti*- to *gauche*-conformers for dichloroethane from $\Delta_r G^o$ and also the statistical approach. Use molecular mechanics to estimate of the difference in steric energy. Assume no significant change in vibrations between the two conformers.

Answer: The MMFF94x gas phase steric energy difference for *anti*- and *gauche*-dichloroethane is -5.143 kJ mol^{-1}. Using MM3, the difference is -4.325 kJ mol^{-1}. Just as for butane, Example 20.4.1, there are two equivalent *gauche*-conformers and one *anti*-conformer. The reaction entropy for the conformational change is, assuming no significant change in vibrations (or rotational constants):

$$\Delta_r S^\circ = S_{anti} - S_{gauche} = R \ln (1/2) = -5.763 \text{ J K}^{-1} \text{ mol}^{-1}$$

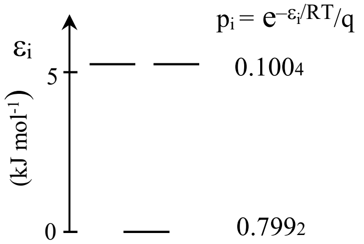
Then $\Delta_r G^\circ = G_{anti} - G_{gauche} = \Delta_r H^\circ - T\Delta_r S^\circ$ using the MMFF values gives:

$$\Delta_r G^\circ = -5.143 \text{ kJ mol}^{-1} - (298.2 \text{ K})(-5.763 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})$$
$$\Delta_r G^\circ = -3.425 \text{ kJ mol}^{-1} \text{ (MMFF) or } -2.607 \text{ kJ mol}^{-1} \text{ (MM3)}$$

$$\text{giving: } K = e^{-\Delta_r G^\circ/RT} = \frac{[anti]}{[gauche]} = 3.981 \text{ (MMFF) or } 2.862 \text{ (MM3)}$$

The *anti*-conformer has the lowest energy, which we assign as $\varepsilon_{anti} = 0$. Then the *gauche*-conformer has an energy $\varepsilon_{gauche} = 5.143$ kJ mol^{-1} above the *anti*-state using MMFF or $\varepsilon_{gauche} = 4.325$ kJ mol^{-1} using MM3. The table, below, gives the calculation for the probabilities using Eq. 20.4%.1 and the MMFF steric energy difference at 298.15 K.

Conformation	ε_i (kJ mol^{-1})	ε_i/RT	$e^{-\varepsilon_i/RT}$	$e^{-\varepsilon_i/RT}/q$
gauche	5.143	2.075	0.1256	0.1004
gauche	5.143	2.075	0.1256	0.1004
anti	0	0	1	0.7992
			q=1.2512	

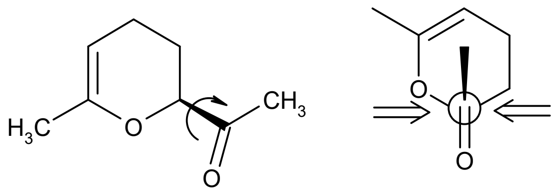


To calculate q we sum the weighting factors in column 4. Then we use q to calculate the probabilities in the last column. The ratio the *anti*- to *gauche*-probabilities is:

$$K = \frac{\Sigma \text{ probabilities for } anti}{\Sigma \text{ probabilities for } gauche} = \frac{0.7992}{0.1004 + 0.1004} = 3.981 \text{ (MMFF) or } 2.862 \text{ (MM3)}$$

There are roughly four molecules in the *anti*-conformation for every molecule in a *gauche*-conformation at 25°C, using the MMFF results.

40. The dimer of methylvinylketone is shown below, at left. The bond with free rotation is marked. Consider only the axial conformer for the –CO–CH_3 side chain. Calculate the equilibrium constant for the two low energy conformers. (b). Which face of the carbonyl is more susceptible to nucleophilic attack? Nucleophilic attack will be perpendicular to the trigonal plane of the sp^2 hybridized carbon, as shown by the arrows for one possible conformation at right. According to Cram's rule, the less hindered side is most susceptible to attack by nucleophiles. You may use molecular mechanics, semi-empirical AM1, *ab initio* HF/6-31G*, or B3LYP/6-31G* density functional methods to determine the energies.



Answer: The plan is to first determine the low energy conformers about the side-chain C-C bond to the ring. A conformational search around this bond can be done or several possible starting conformations can be minimized. The less sterically hindered side of the low energy conformer is noted. Space filling models are helpful in looking at steric influences.

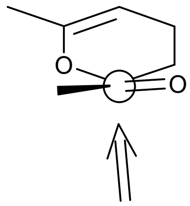
For this problem we will study just the axial conformer for the -CO-CH_3 side chain. The energy differences and Boltzmann weighting factors are given below using gas phase MMFF94x, MM3, AM1, HF/6-31G(d), and B3LYP/6-31G(d). The starting structures for the molecular orbital calculations were the MMFF minimized conformers. The equilibrium constant is given for the reaction written as: *anti* ⇄ *syn* , where the *anti* conformer is the low energy conformer:

$$K = [syn]/[anti]$$

The *anti*-conformer has the O–C–C=O dihedral near -144° and the *syn*- near -4° using MMFF.

	high ε (kJ mol^{-1})	low ε (kJ mol^{-1})	Δε (kJ mol^{-1})	$e^{-\Delta\varepsilon/RT}$	q	p_0	p_1	K
MMFF	81.7867	64.19009	17.5966	0.000826	1.000826	0.999175	0.000825	8.3×10^{-4}
MM3	61.8918	41.79398	20.0978	0.000301	1.000301	0.999699	0.000301	3.0×10^{-4}
AM1	-313.709	-319.661	5.95132	0.090639	1.090639	0.916894	0.083106	0.0906
HF	-1206787.	-1206799.	11.6751	0.009005	1.009005	0.991075	0.008925	9.0×10^{-3}
B3LYP	-1214304.	-1214315.	10.4392	0.014826	1.014826	0.985390	0.014610	0.0148

The favored direction of attack changes with conformation of the side chain. There are two low energy conformers; the lowest energy conformer of the axial isomer is shown below. The arrow shows the side of the carbonyl that is preferentially attacked by nucleophiles.



41. The next two problems develop a model for the equilibrium profile of NO in the lower troposphere. In the atmosphere, NO and NO_2 approach equilibrium (see Problem 16 and Ch. 5 Problems 10-12):

$$NO\ (g) + \tfrac{1}{2}\, O_2\ (g) \rightleftarrows NO_2(g) \qquad \text{P20.41.1}$$

In a given initial volume, let the number of moles of NO be "a", the moles of O_2 be "b", and the moles of other gases in the atmosphere be "n". These last contributions include primarily N_2 with small amounts of H_2O vapor, CO_2, and Ar. Assume that the initial amount of NO_2 is zero and the reaction runs at constant total pressure, P. To help simplify the relationships for the mole fractions, define $\alpha \equiv \xi/a$ as the fraction of NO oxidized, $r \equiv b/a$, and $q \equiv n/a$. Show that the equilibrium expression is:

$$K_p = \frac{\alpha}{1-\alpha}\left(\frac{1+r+q-\alpha/2}{r-\alpha/2}\right)^{1/2}(P/P°)^{-1/2} \qquad \text{P20.41.2°}$$

The concentration of NO_x in the atmosphere is typically in the ppm range. Correspondingly, r and q are much larger than α. Let $P_{NO,o}$ be the initial partial pressure of NO, before any oxidation occurs. Show that an excellent approximation is then:

$$K_{eff} \cong \frac{\alpha}{1-\alpha} \qquad \text{with } K_{eff} = K_p\left(\frac{r}{r+q}\right)^{1/2}(P/P°)^{1/2} \qquad (P_{NO,o} << P_{O_2}, P_{N_2}) \quad \text{P20.41.3°}$$

Answer: Assume that the initial amount of NO_2 is zero. The total moles at equilibrium is then:

$$n_{tot} = (a-\xi) + (b-\xi/2) + \xi + n = a + b + n - \xi/2 \qquad 1$$

The relationship of the mole amounts to the partial pressures is then:

$$\begin{array}{lccccc}
 & NO\,(g) & + & \tfrac{1}{2}O_2\,(g) & \rightleftarrows & NO_2\,(g) \\
\text{moles:} & a-\xi & & b-\xi/2 & & \xi \\
Y_i\text{:} & \dfrac{a-\xi}{a+b+n-\xi/2} & & \dfrac{b-\xi/2}{a+b+n-\xi/2} & & \dfrac{\xi}{a+b+n-\xi/2} \\
Y_i\text{:} & \dfrac{1-\alpha}{1+b/a+n/a-\alpha/2} & & \dfrac{b/a-\alpha/2}{1+b/a+n/a-\alpha/2} & & \dfrac{\alpha}{1+b/a+n/a-\alpha/2} \\
Y_i\text{:} & \dfrac{1-\alpha}{1+r+q-\alpha/2} & & \dfrac{r-\alpha/2}{1+r+q-\alpha/2} & & \dfrac{\alpha}{1+r+q-\alpha/2}
\end{array} \qquad 2$$

To obtain the final listed mole fractions, we divided by the moles of a in the numerator and denominator and substituted $\alpha = \xi/a$ to measure the degree of the reaction. α is the fraction of NO oxidized or alternatively the fraction of NO_2 formed. We then define $r \equiv b/a$ and $q \equiv n/a$. For the total pressure dependence, $\Delta_r n_g = -1/2$. The equilibrium expression is then:

$$K_p = \frac{(P_{NO_2}/P°)}{(P_{NO}/P°)(P_{O_2}/P°)^{1/2}} = K_x\,(P/P°)^{\Delta_r n_g} = \frac{\left(\dfrac{\alpha}{1+r+q-\alpha/2}\right)}{\left(\dfrac{1-\alpha}{1+r+q-\alpha/2}\right)\left(\dfrac{r-\alpha/2}{1+r+q-\alpha/2}\right)^{1/2}}(P/P°)^{-1/2}$$

$$= \frac{\alpha}{1-\alpha}\left(\frac{1+r+q-\alpha/2}{r-\alpha/2}\right)^{1/2}(P/P°)^{-1/2} \qquad \text{(P20.41.1°)}$$

The maximum value of α is 1 for the reaction as written. The concentration of NO in the atmosphere is typically in the ppm range. Then r and q are much larger than α. An excellent approximation is then to neglect the 1 and α terms to give:

$$K_p \cong \frac{\alpha}{1-\alpha}\left(\frac{r+q}{r}\right)^{1/2} (P/P°)^{-1/2} \qquad (P_{NO,o} << P_{O2}, P_{N2}) \qquad 3°$$

where $P_{NO,o}$ is the initial partial pressure of NO before oxidation. An effective equilibrium constant can then be defined to simplify the calculations:

$$K_{eff} \cong \frac{\alpha}{1-\alpha} \qquad \text{with} \qquad K_{eff} = K_p\left(\frac{r}{r+q}\right)^{1/2} (P/P°)^{1/2} \qquad (P20.41.2°)$$

The effective equilibrium constant, K_{eff}, is a constant at a given altitude.

42. Use Eq. P20.41.2° to determine the equilibrium partial pressure of NO up to an altitude of 2000 m in the troposphere. Use the barometric formula, Eqs. 1.3.16° and 1.3.17, to estimate the total pressure as a function of altitude. Assume that r and q are constant with altitude (that is, the atmosphere is well-mixed before any oxidation occurs). Assume also that the temperature in the troposphere decreases 6.0 K per 1000 m: the environmental lapse rate is $\gamma = -0.006$ K m^{-1}. For the oxidation, Eq. P20.41.1, $\Delta_rG° = -35.24$ kJ mol^{-1} and $\Delta_rH° = -57.07$ kJ mol^{-1}. Assume $\Delta_rH°$ is constant over the temperature range. Assume the temperature is 298.15 K and the total pressure is 1.00 bar at sea level. The initial partial pressure at sea level for O_2 is 0.200 bar and for NO is $1.00\text{x}10^{-5}$ bar (10 ppm) before any oxidation.

The barometric formula is derived assuming the temperature is constant at each altitude. However, for a realistic model, we also need to take into account the decrease in temperature with altitude. An easy way to take both pressure and temperature effects into account is to use an average temperature of 282.7 K with the barometric formula to calculate the pressure profile in the atmosphere. Separately, the variation of temperature is then determined using $\gamma = -0.006$ K m^{-1} starting at 298.2 K at sea level, h = 0.

Answer: The spreadsheet and the plot of the partial pressure of NO as a function of altitude are given below. The barometric formula, Eq. 1.3.16°, is used with the average molar mass of air of 28.8 g mol^{-1} and the average effective temperature in the lower troposphere of 282.7 K to calculate the pressure as a function of altitude in column D. The temperature profile in column E starts at 298.2 K and decreases -0.006 K m^{-1} as the altitude increases. The initial K_p at 298.2 K is calculated using $K_p = e^{-\Delta_rG°/RT} = 1.492\text{x}10^6$. The K_p at decreasing temperature (increasing altitude) is calculated using Eq. 20.1.29 and listed in column F:

$$K_{p,T2} = K_{p,T1}\, e^{\frac{-\Delta_rH°}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} = 1.492\text{x}10^6\, e^{\frac{-(-5.707\text{x}10^4 \text{J mol}^{-1})}{8.314 \text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{T_2}-\frac{1}{298.2 \text{ K}}\right)}$$

The molar ratio of O_2 to NO is given by the initial conditions at sea level:

$$r = b/a = n_{O2,o}/n_{NO,o} = (n_{O2,o}\, RT/V)/(n_{NO,o}\, RT/V) = P_{O2,o}/P_{NO,o}$$
$$= 0.200/1.00\text{x}10^{-5} = 2.00\text{x}10^4$$

where $n_{NO,o}$ is the initial amount of NO at sea level before any oxidation. The change in partial pressure of O_2 during the reaction is negligible. The partial pressure of N_2 and other minor constituents in air at sea level is given by Dalton's law of partial pressures: $P_{N_2} = P_{tot} - P_{O_2} - P_{NO} = (1.00 - 0.200 - 1.00\text{x}10^{-5})$ bar. The molar ratio of N_2 to NO from the initial conditions at sea level is $q = n/a = P_{N_2}/P_{NO} = 8.00\text{x}10^{4}$. The effective equilibrium constant at a given altitude is calculated using Eq. P20.41.2° assuming r and q are constant with altitude. The degree of reaction $\alpha = \alpha_{NO}$ is then calculated using Eq. P20.41.2° in column H. The partial pressure of NO is then given in column I using Problem 41 Eq. 2 for the mole fraction of NO:

$$P_{NO}(h) = \left(\frac{1-\alpha}{1+r+q-\alpha/2}\right) P(h)$$

where P(h) is the total pressure at the given altitude. Finally the accuracy of the calculation is checked by using the partial pressures to calculate Q at equilibrium, which should be equal to the equilibrium constant:

$$Q = \frac{(P_{NO_2}(h)/P^\circ)}{(P_{NO}(h)/P^\circ)(P_{O_2}(h)/P^\circ)^{1/2}}$$

A1	B	C	D	E	F	G	H	I	J
2	$\mathfrak{M}_{air}$	28.8	g mol^{-1}	$\Delta_r G^\circ$	-35.24	kJ mol^{-1}			
3	T	282.7	K	$\Delta_r H$	-57.07	kJ mol^{-1}			
4	R	8.3145	J K^{-1} mol^{-1}	$K_{p\ (298\ K)}$	1.492E+06				
5	g	9.8067	m s^{-1}	P_o(NO)	1.00E-05	bar			
6	Po	1	bar	P_o(O2)	0.2	bar			
7	γ	-0.006	K m^{-1}	r= b/a =	2.00E+04				
8				q= n/a =	8.00E+04	$(q+r/r)^{1/2}$ =	2.2361		
9									check K_p
10		h	P	T (K)	Kp	K_p*$(Pr/q+r)^{1/2}$	α_{NO}	P(NO)	Q
11		0	1	298	1.492E+06	6.672E+05	0.999998501	1.50E-11	1.492E+06
12		200	0.976	296.8	1.638E+06	7.236E+05	0.999998618	1.35E-11	1.638E+06
13		400	0.953	295.6	1.799E+06	7.853E+05	0.999998727	1.21E-11	1.799E+06
14		600	0.930	294.4	1.977E+06	8.530E+05	0.999998828	1.09E-11	1.977E+06
15		800	0.908	293.2	2.175E+06	9.272E+05	0.999998921	9.80E-12	2.175E+06
16		1000	0.887	292	2.395E+06	1.009E+06	0.999999009	8.79E-12	2.395E+06
17		1200	0.866	290.8	2.639E+06	1.098E+06	0.999999089	7.88E-12	2.639E+06
18		1400	0.845	289.6	2.910E+06	1.196E+06	0.999999164	7.06E-12	2.910E+06
19		1600	0.825	288.4	3.212E+06	1.305E+06	0.999999234	6.32E-12	3.212E+06
20		1800	0.806	287.2	3.547E+06	1.424E+06	0.999999298	5.66E-12	3.547E+06
21		2000	0.786	286	3.922E+06	1.555E+06	0.999999357	5.06E-12	3.922E+06

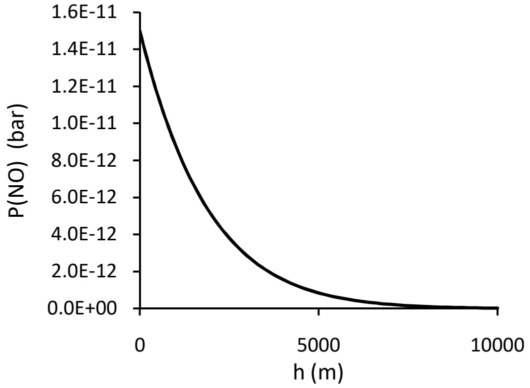


Figure P20.42.1: Equilibrium Partial Pressure of NO as a function of Altitude in the Troposphere.

The formulas are:
D12: “=$C$6*EXP(-$C$2/1000*$C$5*C12/$C$4/$C$3)”
E12: “=E11+$C$7*(C12-C11)”
F12: “=$F$4*EXP(-$F$3*1000/$C$4*(1/E12-1/$E$11))”
G12: “=F12*SQRT(D12)/$H$8”
H12: “=G12/(1+G12)”
I12: “=(1-H12)/(1+$F$7+$F$8-H12/2)*D12”
J12: “=($F$5*D12-I12)/I12/SQRT(0.2*D12)”

You can change the acceleration of gravity to zero to see the effect of temperature alone. The equilibrium shifts in the exothermic direction with increasing height, which favors NO_2 at altitude. You can change γ to zero to see the effect of pressure alone. The equilibrium shifts to the left with increasing height, which favors NO at altitude, although $\Delta_rG°$ is so negative that NO_2 remains the predominant species.

43. Consider the reaction $A + B \rightleftarrows C + D$ in solution from a thermodynamic perspective and from a kinetic perspective. The equilibrium constant is a function of the solution activities, but the rate law is conventionally written in terms of the concentrations:

$$K_a = \frac{a_C\, a_D}{a_A\, a_B} \qquad\qquad \upsilon = \frac{1}{V}\frac{d\xi}{dt} = k_f\,[A][B] - k_r[C][D]$$

(a). Use detailed balance to prove that the rate law is also expressible in terms of the solution activities:

$$\upsilon = \frac{1}{V}\frac{d\xi}{dt} = k_f'\; a_A\, a_B - k_r'\; a_C\, a_B$$

(b). Relate the two sets of rate constants, k_f and k_r with k_f' and k_r', given the activity coefficients for each species.

Answer: Detailed balance requires that the forward and reverse rates are equal for a reaction at equilibrium and that the ratio of the forward and reverse rate constants gives the equilibrium constant. Since the true thermodynamic equilibrium constant must be specified in terms of activities, the equilibrium constant that results from the kinetic rate law must also be written in terms of activities:

$$\upsilon = \frac{1}{V}\frac{d\xi}{dt} = k_f'\, a_A\, a_B - k_r'\, a_C\, a_B = 0 \qquad\qquad K_a = \frac{k_f'}{k_r'} = \frac{a_C\, a_D}{a_A\, a_B}$$

with $a_A = \gamma_A\,[A]$, $a_B = \gamma_B\,[B]$, etc.

(b). The rate constants for the reaction rate written in terms of concentration and in terms of activities are then related through the activity coefficients using:

$$\upsilon = \frac{1}{V}\frac{d\xi}{dt} = k_f'\,\gamma_A\gamma_B\,[A][B] - k_r'\,\gamma_C\gamma_D\,[C][D]$$

Comparing with the rate law in terms of concentrations gives:

$$\begin{array}{lccccc} \upsilon = \frac{1}{V}\frac{d\xi}{dt} = & k_f'\,\gamma_A\gamma_B & [A][B] & - & k_r'\,\gamma_C\gamma_D & [C][D] \\ & \uparrow & & & \uparrow & \\ \upsilon = \frac{1}{V}\frac{d\xi}{dt} = & k_f & [A][B] & - & k_r & [C][D] \end{array}$$

to give: $k_f = k_f'\,\gamma_A\gamma_B$ and $k_r = k_r'\,\gamma_C\gamma_D$.

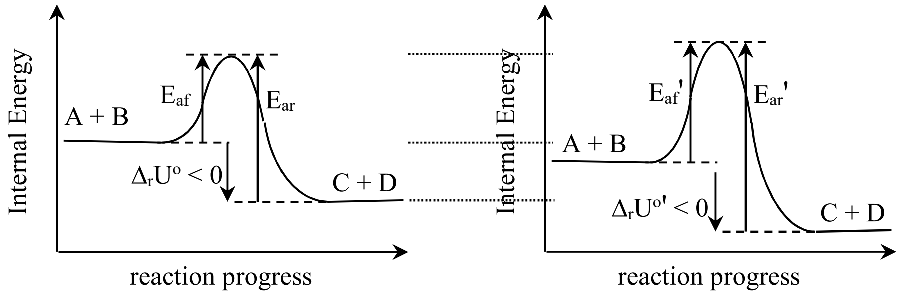
In other words, by convention for concentration based kinetic expressions, the activity coefficients of the reactants and products are incorporated into the rate constants. The corresponding true thermodynamic equilibrium constant is given by:

$$K_a = \frac{k_f'}{k_r'} = \left(\frac{\gamma_C\gamma_D}{\gamma_A\gamma_B}\right)\frac{k_f}{k_r}$$

As a case in point, we will use Debye-Hückel electrostatic theory to understand the kinetic salt effect in the chapter on molecular reaction dynamics. The energetic relationships are explored further in the next problem.

44. *Challenge Problem*: In the previous problem, we showed that the rate law for a reaction is best expressed in terms of activities, rather than concentrations, for consistency with detailed balance. However, by convention in concentration based kinetic expressions, the activity coefficients of the reactants and products are incorporated into the rate constants. The activity of a species deviates from the analytical concentration because of solute-solvent interactions. Rationalize the fact that solute-solvent interactions of the reactants and products have an effect on chemical reactions rates. However, be careful to separate thermodynamic and kinetic concerns. Assume that the kinetics follow Arrhenius behavior, and reason through the reaction profile, Figure 4.5.2.

Answer: We first must avoid using thermodynamic arguments to make a kinetic point. Consider a gas phase reaction and the same reaction in solution. For a particular example, assume an exothermic reaction and that the reactants and products are stabilized by solute-solvent forces while the transition state is destabilized by solute-solvent forces, as shown in the following figure.



(a). gas phase (b). in solution

We assume a constant volume process, so that the internal energy or Helmholtz energies are the appropriate thermodynamic variables. The parameters ofr the solution reaction are listed with primes, e.g. $\Delta_r U^{\circ\prime}$. First take the thermodynamic perspective. $\Delta_r U^\circ$ and $\Delta_r U^{\circ\prime}$ are independent of the transition state energy, and clearly have an effect on the equilibrium constant through $\Delta_r A^{\circ\prime} = \Delta_r U^{\circ\prime} - T\,\Delta_r S^{\circ\prime}$. The standard states are typically chosen as Henry's Law standard states for the reactants and products, and therefore include solute-solvent interactions. $\Delta_r U^{\circ\prime}$ is changed, compared to the gas phase, if the reactants and products are stabilized by solute-solvent interactions to a different extent. Now take the kinetic perspective.

Detailed balance requires that $E_{af} - E_{ar} = \Delta_r U^\circ$ for the gas phase reaction and $E_{af}' - E_{ar}' = \Delta_r U^{\circ\prime}$ for the solution phase reaction. The rates of the reaction, forward and reverse are strong functions of the activation energies. There are four possibilities:

1. For the particular example in the figure, if the reactants and products are stabilized by solute-solvent interactions and the transition state is destabilized, then the activation energies are increased and the reaction rates decrease.
2. However, if the reactants and products are stabilized by solute-solvent interactions and the transition state is also stabilized to a similar degree, then the activation energies are little changed.
3. Alternately, if the reactants and products are destabilized by solute-solvent interactions and the transition state is destabilized, then the activation energies are little changed.
4. Or, the final possibility is if the reactants and products are destabilized by solute-solvent interactions and the transition state is stabilized, then the activation energies are decreased and the reaction rates increase.

In any event, the effect of solute-solvent forces is to change the energies of the reactants and products, which in turn changes the activation energy: $E_{af} = E_{\text{transition-state}} - E_{\text{reactants}}$ and $E_{ar} = E_{\text{transition-state}} - E_{\text{products}}$. At thermodynamic equilibrium the transition-state energy cancels out:

$$\Delta_r U^\circ = E_{af} - E_{ar} = (E_{\text{transition-state}} - E_{\text{reactants}}) - (E_{\text{transition-state}} - E_{\text{products}}) = E_{\text{products}} - E_{\text{reactants}}$$

The activity coefficients then have an effect on both the thermodynamic equilibrium and the reaction rates through changes in energy or chemical potential of each reactant and product:

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i c_i$$

In summary, it matters little in the final effect if the rate law is written in terms of concentrations or activities; energetic interactions of the solutes with the solvent have an effect on the rates and equilibria of chemical reactions.

$$\upsilon = \frac{1}{V}\frac{d\xi}{dt} = k_f\,[A][B] - k_r[C][D] \qquad \text{or} \qquad \upsilon = \frac{1}{V}\frac{d\xi}{dt} = k_f'\,a_A\,a_B - k_r'\,a_C\,a_B$$

The kinetic changes are difficult to predict, however, because the effect of the solvent on the transition state must also be determined. Even if the transition state is traversed in a non-equilibrium, purely dynamical way, the effective activation energy still depends on the energies of the reactants and products. The energies of the reactants and products are altered by interactions with the solvent.

One deficiency in our argument is that we have considered energetic issues and have ignored entropic considerations. Certainly, solvation effects can have large entropic contributions. Entropic contributions to reaction rate constants are expressed primarily through the pre-exponential factor, A, in the Arrhenius expression $k_2 = A\,e^{-Ea/RT}$. Similar arguments can be framed through changes in the pre-exponential factors with entropic changes caused by solvation. The pre-exponential factor is referenced to the entropy of the reactants or products, for the forward and reverse reactions, respectively.

45. The temperature dependence of isomerization is conveniently followed by experimental techniques that have additive response of the two forms in equilibrium. The equilibrium constant of the two forms is given by:

$$A \rightleftarrows B \qquad \text{with} \qquad K = [B]/[A] \qquad \text{P20.45.1}$$

One example of an experimental technique with additive response is infrared spectroscopy. The wave number of an IR band is the mole fraction weighted average of the two forms:

$$\tilde{\nu}_{obs} = \tilde{\nu}_A\,x_A + \tilde{\nu}_B\,x_B \qquad \text{(additive response)} \qquad \text{P20.45.2}$$

where x_A and x_B are the mole fractions of A and B, respectively. The absorption wave numbers of the pure components are $\tilde{\nu}_A$ and $\tilde{\nu}_B$, respectively.

(a). Let the total analytical moles be a, with $n_A + n_B = a$, where n_A and n_B are the number of moles of A and B. The total volume of the solution is V. Show that the corresponding concentrations are related by [A] + [B] = [a], with concentrations in moles per liter.

(b). Show that the observed wave number is given in terms of the concentrations as:

$$\tilde{\nu}_{obs} = \tilde{\nu}_A\,\frac{[A]}{[a]} + \tilde{\nu}_B\,\frac{[B]}{[a]} \qquad \text{(additive response)} \qquad \text{P20.45.3}$$

(c). Using P20.43.1 show that the equilibrium concentrations are given by:

$$[A] = \frac{1}{1+K}\,[a] \qquad [B] = \frac{K}{1+K}\,[a] \qquad \text{P20.45.4}$$

(d). Using Eqs. P20.43.2-P20.43-4, show that the equilibrium constant is determined by:

$$K = \frac{\tilde{\nu}_{obs} - \tilde{\nu}_A}{\tilde{\nu}_B - \tilde{\nu}_{obs}} \qquad \text{(additive response)} \qquad \text{P20.45.5}$$

Answer: (a). The mole fractions and concentrations of the two forms are given by the numbers of moles of the two forms, n_A and n_B, and the total analytical moles, a:

$$x_A = n_A/a \qquad x_B = n_B/a \qquad n_A + n_B = a \quad \text{and } x_A + x_B = 1 \qquad 1$$

$$[A] = n_A/V \qquad [B] = n_B/V \qquad [a] = a/V \qquad 2$$

Substituting the concentrations into the mass balance, $n_A + n_B = a$, gives:

$$[A] + [B] = [a] \qquad 3$$

(b). The observed frequency can be written in terms of the concentrations of the two forms and the total analytical concentrations, [A], [B], [a], respectively using Eq. 20.45.2:

$$\tilde{\nu}_{obs} = \tilde{\nu}_A\, x_A + \tilde{\nu}_B\, x_B = \tilde{\nu}_A\, n_A/a + \tilde{\nu}_B\, n_B/a = \tilde{\nu}_A \frac{n_A/V}{a/V} + \tilde{\nu}_B \frac{n_B/V}{a/V} \qquad 4$$

$$\tilde{\nu}_{obs} = \tilde{\nu}_A \frac{[A]}{[a]} + \tilde{\nu}_B \frac{[B]}{[a]} \qquad (P20.45.3) \qquad 5$$

(c). From the mass balance, Eq. 3, [A] = [a] – [B] giving the equilibrium constant as:

$$K = \frac{[B]}{[a] - [B]} \qquad \text{solving for [B] gives:} \quad [B] = \frac{K}{1+K}[a] \qquad (P20.45.4) \qquad 6$$

Solving for [A] using the mass balance gives:

$$[A] = [a] - [B] = \left(1 - \frac{K}{1+K}\right)[a] = \frac{1}{1+K}[a] \qquad (P20.45.4) \qquad 7$$

(d). The observed frequency from Eqs. 5, 6, and 7 is then:

$$\tilde{\nu}_{obs} = \tilde{\nu}_A \frac{1}{1+K} + \tilde{\nu}_B \frac{K}{1+K} = \frac{\tilde{\nu}_A + \tilde{\nu}_B K}{1+K} \qquad 8$$

Cross multiplying by 1+K gives:

$$\tilde{\nu}_{obs} + \tilde{\nu}_{obs}K = \tilde{\nu}_A + \tilde{\nu}_B K \qquad \text{or} \qquad K = \frac{\tilde{\nu}_{obs} - \tilde{\nu}_A}{\tilde{\nu}_B - \tilde{\nu}_{obs}} \qquad (P20.45.5) \qquad 9$$

The last equation allows the equilibrium constants to be determined completely from the shift in the band frequency.

46. The infrared absorption of an intramolecular hydrogen-bonded amine (see Problem Ch. 10.13: N-[2-(dimethylamino)ethyl]-N-methylguanidium ion) as a function of temperature is at:

T (°C)	25.0	30.0	35.0	40.0	45.0
$\tilde{\nu}_{obs}$ (cm^{-1})	1520	1540	1548	1570	1573

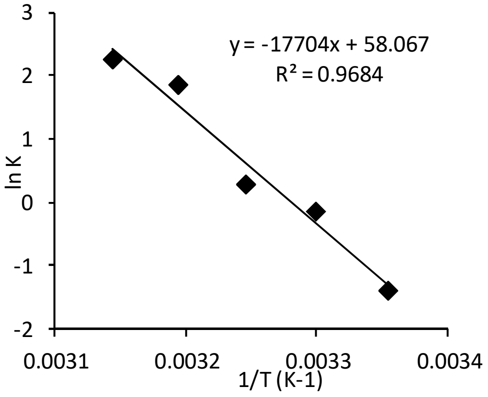
Equilibrium is established between the closed and open forms; the closed form is hydrogen-bonded and the open form is not hydrogen-bonded: C ⇄ O. The wave number of the closed form is: $\tilde{\nu}_C = 1505$ cm^{-1} and the open form is $\tilde{\nu}_O = 1580$ cm^{-1}. Using Eq. P20.45.5, determine the equilibrium constant and reaction Gibbs energy as a function of temperature.

Answer: The plan is to note that the equilibrium constant for an isomerization is determined completely from the observed band shifts using Eq. P20.45.5, while the linearized form of the temperature dependence is: ln K = $-\Delta_rH°/RT$ + ln c.

A spreadsheet was set up using Eq. P20.45.5 using the association of C $\rightleftarrows$ O with A $\rightleftarrows$ B:

T (K)	ν_{obs} (cm^{-1})	K	1/T (K^{-1})	ln K	$\Delta_rG°$ (kJ mol^{-1})
298.15	1520	0.2500	0.003354	-1.38629	3.437
303.15	1540	0.8750	0.003299	-0.13353	0.337
308.15	1548	1.3438	0.003245	0.295464	-0.757
313.15	1570	6.5000	0.003193	1.871802	-4.874
318.15	1573	9.7143	0.003143	2.273598	-6.014

slope	-17704	58.0673	intercept
±	1846.3	5.99645	±
r^2	0.9684	0.30777	s(y)
F	91.943	3	df
ss_{reg}	8.7092	0.28417	ss_{resid}



The reaction enthalpy is then determined from the slope of ln K vs. 1/T giving $\Delta_rH°$ = – slope(R) = 147. ± 15. kJ mol^{-1}. The reaction Gibbs energies are then given by $\Delta_rG° = -RT \ln K$. Assuming an uncertainty of ±2 cm^{-1} in the observed wave numbers, the uncertainty in the Gibbs energy is ± 0.005 kJ mol^{-1}. The reaction enthalpy is much larger than the hydrogen bond strength since proton transfer reactions accompany the formation of the hydrogen bond and shifts in pH occur with the changes in temperature.

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Chapter 21 Problems: Electrochemistry

1. Design an electrochemical cell with the net cell reaction: $Ag_2S\,(s) \rightleftarrows Ag^+\,(aq) + S^{2-}(aq)$.

Answer: The plan is to use a sparingly soluble salt electrode.
The electrode for Ag_2S as the sparingly soluble salt is the reduction at the cathode:

$$Ag_2S\,(s) + 2\,e^- \rightarrow 2\,Ag(s) + S^{2-} \qquad \text{(cathode)}$$

Subtracting the last reaction from the overall reaction gives the reaction at the anode:

$$2\,Ag \rightarrow 2\,Ag^+\,(aq) + 2\,e^- \qquad \text{(anode)}$$

The corresponding cell diagram is: $Ag|Ag_2S(s)|S^{2-}(aq)||Ag^+(aq)|Ag$
This overall reactrion is not a redox reaction, but with suitable electrodes, the reaction can be easily studied using electrochemical cell measurements.

2. For the reaction involving the reduced and oxidized forms of cyctochrome-c:

$$2\text{ cyctochrome-c}(Fe^{2+}) + \text{pyruvate} \rightarrow 2\text{ cytochrome-c}(Fe^{3+}) + \text{lactate}$$

Calculate the electrochemical cell voltage at 25°C if the lactate activity is 5.00 times the pyruvate activity and the cytochrome-c(Fe^{3+}) activity is 10.0 times the cyctochrome-c(Fe^{2+}) activity. For the pyruvate/lactate couple, $E^\circ_{red} = -0.19V$. For the cytochrome-c(Fe^{3+}),(Fe^{2+}) couple $E^\circ_{red} = 0.337V$. Two electrons are transferred in the process.

Answer: The Nernst Equation,Eq. 21.18, for the cell, with $z = 2$, is:

$$E_{cell} = E^\circ_{cell} - \frac{0.02569\text{ V}}{2} \ln\left(\frac{(a_{cc(Fe3+)})^2(a_{lactate})}{(a_{cc(Fe2+)})^2(a_{pyruvate})}\right) = -0.527\text{ V} - \frac{0.02569\text{ V}}{2} \ln((10.0)^2(5.00))$$

$$E_{cell} = -0.527\text{ V} - 0.02569\text{ V}/2\,(6.215) = -0.607\text{ V}$$

3. Calculate the standard state cell voltage, standard state reaction Gibbs energy, and equilibrium constant at 25°C for the reaction: $Zn_{(s)} + 2\,Fe^{3+} \rightarrow Zn^{2+} + 2\,Fe^{2+}$.

Answer: The cell reactions are given in Example 21.1.2. As written $z = 2$. The cathode is the reduction of Fe^{3+} to Fe^{2+}, and the anode the oxidation of Zn to Zn^{2+}. The cell potential is:

$$E^\circ_{cell} = E^\circ_R - E^\circ_L = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode}) = E^\circ_{red}(Fe^{3+},Fe^{2+}) - E^\circ_{red}(Zn^{2+},Zn)$$
$$= 0.771\text{ V} - (-0.762\text{ V}) = 1.533\text{ V}$$

$$\Delta_r G^\circ = -\,z\,F\,E^\circ_{cell} = -\,2(96485\text{ C mol}^{-1})(1.533\text{ V})(1\text{ kJ}/1000\text{ J}) = -295.8\text{ kJ mol}^{-1}$$

Remember that cell potentials are intensive, so they don't depend on the stoichiometric coefficients. Eqs. 21.1.9 give two equivalent ways to find the equilibrium constant:

$$\Delta_r G° = -2.958\text{x}10^5 \text{ J mol}^{-1} = -\text{ RT ln K}_a = -\text{ 8.3145 J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K}) \text{ ln K}_a$$

or $$E°_{cell} = 1.533 \text{ V} = \frac{RT}{zF} \ln K_a = \frac{0.02569 \text{ V}}{2} \ln K_a$$

$$K_a = 6.78\text{x}10^{51}$$

A cell voltage of 1.533 V, which sounds small, corresponds to a very large reaction Gibb energy and equilibrium constant.

4. Calculate the standard state cell voltage, standard state reaction Gibbs energy, and equilibrium constant at 25°C for the reaction:

$$3 \text{ Cu (s)} + 2 \text{ NO}_3^- \text{ (aq)} + 8 \text{ H}^+ \text{ (aq)} \rightarrow 3 \text{ Cu}^{2+} \text{ (aq)} + 2 \text{ NO (g)} + 4 \text{ H}_2\text{O (l)}$$

Answer: The plan is to determine which half-reaction serves as the cathode and which the anode, and then $\Delta_r G° = -zFE°_{cell}$ and either $\Delta_r G° = -RT \ln K$ or $E°_{cell} = (RT/zF) \ln K$.

The half-reactions are:

anode: $\text{Cu (s)} \rightarrow \text{Cu}^{2+} + 2 \text{ e}^-$ $\qquad E°_{red} = 0.339 \text{ V}$

cathode: $\text{NO}_3^- \text{ (aq)} + 4 \text{ H}^+ \text{ (aq) } 3\text{e}^- \rightarrow \text{NO (g)} + 2 \text{ H}_2\text{O (l)}$ $\qquad E°_{red} = 0.955 \text{ V}$

When balanced as given in this problem, $z = 6$ and the cell voltage is:

$$E°_{cell} = E°_R - E°_L = E°_{red}(\text{cathode}) - E°_{red}(\text{anode}) = 0.955 \text{ V} - 0.339 \text{ V} = 0.616 \text{ V}$$

Giving: $\Delta_r G° = -zFE°_{cell} = -6(96485 \text{ C mol}^{-1})(0.616 \text{ V}) = -3.566\text{x}10^5 \text{ J mol}^{-1} = -357. \text{ kJ mol}^{-1}$

$\Delta_r G° = -RT \ln K = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K}) \ln K$ giving $K = 2.98\text{x}10^{62}$

or $E°_{cell} = (RT/zF) \ln K = (0.025693 \text{ V}/6) \ln K$ giving $K = e^{6(0.616 \text{ V})/0.025693 \text{ V}} = 2.98\text{x}10^{62}$

This reaction is commonly illustrated in General Chemistry texts and done as a lecture demonstration. The NO produced oxidizes in air to form red NO_2 (g). A concentrated non-oxidizing acid, such as HCl and H_2SO_4 is insufficient to dissolve the Cu metal in a penny. Instead an oxidizing acid, such as HNO_3, is required.

5. For the cell Pt(H_2, 1bar)| HCl(m)| AgCl| Ag with m = 0.011195 m, the cell potential is E_{cell}= 0.45861 V. The standard cell potential for the silver/silver chloride electrode is $E°_{red}(\text{Cl}^-,\text{AgCl},\text{Ag}) = 0.2223$ V at 25°C. Calculate the mean ionic activity coefficient for 0.011195 m HCl.

Answer: The plan is to follow Example 21.2.4.

Using the Nernst equation, Eq. 21.1.8, for a unipositive-uninegative electrolyte, with $a_{HCL} = a_{H^+} a_{Cl^-} = \gamma_\pm^2 (m/m°)^2$, gives:

$$E_{cell} = E°_{cell} - (0.025693 \text{ V}) \ln \gamma_\pm^2 \left({}^{m}/_{m°}\right)^2$$

$$\ln \gamma_\pm = 2(E°_{cell} - E_{cell})/0.025693 - \ln {}^{m}/_{m°}$$

$$\ln \gamma_\pm = 2(0.2223 - 0.45861)/0.025693 - \ln 0.011195 = -0.094769$$

or $\gamma_\pm = 0.910$

6. For the cell $Zn|ZnSO_4\ (m)|PbSO_4\ (s)|Pb$ with m = 0.01000 m, the cell potential is E_{cell}= 0.55353 V. The standard cell potential is $E^{\circ}_{cell} = 0.412$ V at 25°C. Calculate the mean ionic activity coefficient for 0.01000 m $ZnSO_4$.

Answer: The plan is to write the Nernst equation for the cell reaction to determine the dependence of the cell potential on the activity of the common electrolyte, $ZnSO_4$.

The half-cell reactions are:

$$\begin{array}{l} Zn\ (s) \rightarrow Zn^{2+} + 2e^- \\ PbSO_4\ (s) + 2e^- \rightarrow Pb\ (s) + SO_4^{2-} \\ \hline Zn\ (s) + PbSO_4\ (s) \rightarrow Zn^{2+} + SO_4^{2-} + Pb\ (s) \end{array}$$

The number of electrons transferred for unit extent is $z = 2$. The Nernst expression considering all reactants and products is

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{2F} \ln\left(\frac{a_{Zn2+}\, a_{SO42-}\, a_{Pb}}{a_{Zn}\, a_{PbSO_4}}\right)$$

The pure solids are at unit activity, giving:

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{2F} \ln a_{Zn2+}\, a_{SO42-}$$

For this 1:1 electrolyte, $m_{Zn2+} = m_{SO42-} = m$, where m is the analytical concentration of $ZnSO_4$:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.025693\text{ V}}{2} \ln \gamma_{\pm}^2 \left({}^{m}/_{m^{\circ}}\right)^2 \qquad \text{or} \quad E_{cell} - E^{\circ}_{cell} = -0.025693\text{ V} \ln \gamma_{\pm}\, {}^{m}/_{m^{\circ}}$$

$$\ln \gamma_{\pm} = (E^{\circ}_{cell} - E_{cell})/0.025693 - \ln {}^{m}/_{m^{\circ}}$$

$$\ln \gamma_{\pm} = (0.412 - 0.55353)/0.025693 - \ln 0.01000 = -0.9033$$

or $\gamma_{\pm} = 0.405$

The Debye-Hückel approximation estimates $\gamma_{\pm} \cong 0.351$ (Extended Debye-Hückel estimates $\gamma_{\pm} \cong 0.463$).

7. (a). Find the standard reduction potential for the $Cl^-/Hg_2Cl_2/Hg$ electrode from the following data for the cell potential of $Pt|H_2|HCl\ (m)|Hg_2Cl_2\ (s)|Hg$ as a function of the concentration of HCl.[1] Assume unit fugacity (pressure) for H_2. (b). Calculate the mean ionic activity coefficient for 0.010947 m HCl.

m (mol kg^{-1})	0.0016077	0.0030769	0.0050403	0.0076938	0.010947
E_{cell} (V)	0.60080	0.56825	0.543665	0.522675	0.50532

Answer: The plan is to write the Nernst equation for the cell reaction to determine the dependence of the cell potential on the activity of the electrolyte, HCl.

(a). The half-cell reactions are:

$$\tfrac{1}{2}\,H_2\,(g) \rightarrow H^+ + e^-$$
$$\tfrac{1}{2}\,Hg_2Cl_2\,(s) + e^- \rightarrow Hg\,(s) + Cl^-$$
$$\overline{\tfrac{1}{2}\,Hg_2Cl_2\,(s) + \tfrac{1}{2}\,H_2\,(g) \rightarrow Hg\,(s) + H^+ + Cl^-}$$

The number of electrons transferred for unit extent is $z = 1$. The Nernst expression considering all reactants and products is

$$E_{cell} = E^\circ_{cell} - \frac{RT}{F} \ln\left(\frac{a_{Hg}\, a_{H^+}\, a_{Cl^-}}{a_{Hg_2Cl_2}\, f_{H_2}^{1/2}}\right)$$

The pure solid Hg_2Cl_2 and pure liquid Hg are at unit activity. We also assume that the H_2 gas is at unit fugacity, giving:

$$E_{cell} = E^\circ_{cell} - \frac{RT}{F} \ln a_{H^+}\, a_{Cl^-}$$

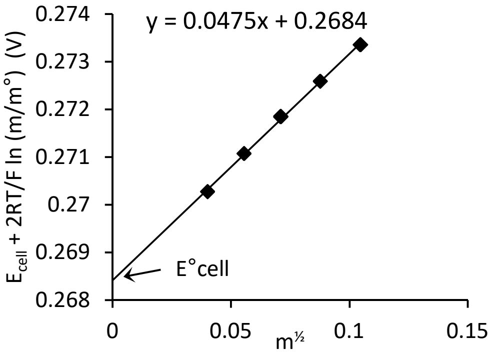
which is identical to Eq. 21.1.12. The extrapolation is then established following Eq. 21.1.17. An Excel spreadsheet was developed. The left-hand side of Eq. 21.1.17 is given in the column with the heading "LHS".

m (mol kg-1)	E_{cell} (V)	$m^{1/2}$	LHS (V)
0.0016077	0.6008	0.040096	0.270275
0.0030769	0.56825	0.055470	0.271077
0.0050403	0.543665	0.070995	0.271850
0.0076938	0.522675	0.087714	0.272591
0.010947	0.50532	0.104628	0.273355

slope	0.04754	0.26842	intercept
±	0.00098	0.00007	±
r^2	0.99873	0.00005	s(y)
F	2362.30	3	df
ss_{reg}	5.88E-06	7.47E-09	ss_{resid}

The data is plotted below. The standard hydrogen electrode reduction potential is defined as zero, giving the standard reduction potential for the $Cl^-/Hg_2Cl_2/Hg$ electrode as:

$$E^\circ_{cell} = E^\circ_{red}(Cl^-, Hg_2Cl_2, Hg) = 0.26842 \pm 0.00007\ V.$$



(b). Eq. 21.1.14 holds for a 1:1 electrolyte with $z = 1$. For 0.010947 m HCl:

$$E_{cell} = E^\circ_{cell} - \frac{2RT}{F} \ln \gamma_\pm\, {}^{m}/_{m^\circ} \qquad \ln \gamma_\pm = 2(E^\circ_{cell} - E_{cell})/0.025693 - \ln {}^{m}/_{m^\circ}$$

$$\ln \gamma_\pm = 2(0.26842 - 0.50532)/0.025693 - \ln 0.010947 = -0.096435$$

$$\gamma_\pm = 0.908$$

8. Tabulations of standard reduction potentials include temperature coefficients. The change in cell voltage with temperature for the Zn^{2+}/Zn electrode is $(\partial E^{\circ}_{red}/\partial T)_P = 0.119\ \text{mV K}^{-1}$ and for the Fe^{3+}/Fe^{2+} electrode is $1.175\ \text{mV K}^{-1}$. Calculate the reaction entropy at 25°C for the reaction: $Zn_{(s)} + 2\,Fe^{3+} \rightarrow Zn^{2+} + 2\,Fe^{2+}$. Check this value by repeating the calculation using Third Law absolute entropies for the reactants and products taken from the Data Tables in the appendix.

Answer: The cell reactions are given in Example 21.1.2. As written $z = 2$. The cathode is the reduction of Fe^{3+} to Fe^{2+}, and the anode is the oxidation of Zn to Zn^{2+}. The overall temperature coefficient is given in the same way as the overall cell voltage, right – left, or cathode – anode:

$$(\partial E^{\circ}_{cell}/\partial T)_P = 1.175\ \text{mV K}^{-1} - 0.119\ \text{mV K}^{-1} = 1.056\ \text{mV K}^{-1} = 1.056\text{x}10^{-3}\ \text{V K}^{-1}$$

Using Eq. 21.1.6 gives: $\left(\dfrac{\partial E_{cell}}{\partial T}\right)_P = \dfrac{\Delta_r S}{zF}$ or:

$$\Delta_r S^{\circ} = zF\left(\frac{\partial E_{cell}}{\partial T}\right)_P = 2(96485\ \text{C mol}^{-1})(\ 1.056\text{x}10^{-3}\ \text{V K}^{-1}) = 203.8\ \text{J K}^{-1}\ \text{mol}^{-1}$$

We can check this value using standard tabulations of the Third Law entropies. From the Data Tables in the appendix:

	$Zn_{(s)}$ +	$2\,Fe^{3+}$ →	Zn^{2+} +	$2\,Fe^{2+}$	units
S°	41.63	-315.9	-112.1	-137.7	$\text{J K}^{-1}\ \text{mol}^{-1}$

$$\Delta_r S^{\circ} = [-112.1 + 2(-137.7)] - [41.63 + 2(-315.9)]\ \text{J K}^{-1}\ \text{mol}^{-1} = 202.7\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The agreement is within experimental uncertainties and significant figure restrictions.

9. A zinc metal electrode is placed in a 0.1000 m $Zn(NO_3)_2$ aqueous solution. A platinum metal electrode is placed in a solution containing 0.3000 m $FeSO_4$ and 0.00100 m $Fe_2(SO_4)_3$. Assign the anode and cathode to give a Galvanic cell and determine the cell voltage at 25°C. Use the Debye-Hückel approximation to estimate the activity coefficients.

Answer: The plan is to follow Example 21.1.2.

Assume the cell is connected as given in Example 21.1.2. The corresponding cell potential is $E^{\circ}_{cell} = E^{\circ}_{R} - E^{\circ}_{L} = E^{\circ}_{red}(Fe^{3+},Fe^{2+}) - E^{\circ}_{red}(Zn^{2+},Zn) = 0.771 - (-0.762)\ \text{V} = 1.533\ \text{V}$. The voltage is positive, so the anode and cathode are assigned properly in the example. (Otherwise, all we need do is switch the half-cells). The Nernst equation then gives the cell voltage with $z = 2$ for:

$$Zn_{(s)} + Fe_2(SO_4)_3\ (0.00100\ \text{m}) \rightarrow Zn(NO_3)_2\ (0.1000\ \text{m}) + 2\,FeSO_4\ (0.3000\ \text{m})$$
$$Zn_{(s)} + 2\,Fe^{3+}\ (0.00200\ \text{m}) \rightarrow Zn^{2+}\ (0.1000\ \text{m}) + 2\,Fe^{2+}\ (0.3000\ \text{m})$$

For Fe^{3+}, $m_+ = 2\ \text{m}$ where m is the analytical concentration of $Fe_2(SO_4)_3$, giving:

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{zF}\ln\left(\frac{(a_{Zn^{2+}})\,(a_{Fe^{2+}})^2}{(a_{Fe^{3+}})^2}\right)$$

$$= E^{\circ}_{cell} - \frac{0.02569\text{ V}}{2}\ln\left(\frac{(\gamma_{\pm,Zn^{2+}})\,(0.1000)\,(\gamma_{\pm,Fe^{2+}})^2(0.3000)^2}{(\gamma_{\pm,Fe^{3+}})^2\,(0.00200)^2}\right)$$

The Debye-Hückel approximation, Eqs. 19.4.22-19.4.23, is then used to estimate the mean ionic activity coefficients. For the 0.1000 m $Zn(NO_3)_2$ solution with $m_+ = m$ and $m_- = 2m$, the ionic strength is:

$$I = ½ \sum z_i^2\, {}^{m_i}/_{m^\circ} = ½[(2)^2(0.100) + (-1)^2(0.200)] = 0.3000$$

and $\ln \gamma_\pm = -1.171\ |\ z_+ z_-\ |\ I^{½} = -1.171\ |(2)(-1)|(0.300)^{½} = -1.2828$ and $\gamma_{\pm,Zn^{2+}} = 0.2772$

For the cathode solution, the ionic strength includes both electrolytes: $m_{+,Fe^{2+}} = 0.3000$ m, $m_{+,Fe^{3+}} = 0.00200$ m, and $m_- = (0.3000 + 3(0.00100))$m including the SO_4^{2-} from both sources:

$$I = ½ \sum z_i^2\, {}^{m_i}/_{m^\circ} = ½[(2)^2(0.3000) + (3)^3(0.00200) + (-2)^2(0.30300)] = 1.2150$$

and $\ln \gamma_\pm = -1.171\ |\ z_+ z_-\ |\ I^{½} = -1.171\ |(2)(-2)|(1.2150)^{½} = -5.1630$ and $\gamma_{\pm,Fe^{2+}} = 5.7243\text{x}10^{-3}$

For $Fe_2(SO_4)_3$, the cathode solution has the same ionic strength, giving the activity coefficient:

$\ln \gamma_\pm = -1.171\ |\ z_+ z_-\ |\ I^{½} = -1.171\ |(3)(-2)|(1.2150)^{½} = -7.7445$ and $\gamma_{\pm,Fe^{3+}} = 4.3310\text{x}10^{-4}$

Giving the final cell potential:

$$E_{cell} = 1.533\text{ V} - \frac{0.02569\text{ V}}{2}\ln\left(\frac{(0.2772)\,(0.1000)\,(5.7243\text{x}10^{-3})^2(0.3000)^2}{(\,4.3310\text{x}10^{-4})^2\,(0.00200)^2}\right)$$

$$E_{cell} = 1.533\text{ V} - \frac{0.02569\text{ V}}{2}\ln(1.0895\text{x}10^{5})$$

$$E_{cell} = 1.533\text{ V} - 0.14899\text{ V} = 1.384\text{ V}$$

Even though the Fe^{3+} concentration is much less than the Fe^{2+} concentration, the activity coefficient for Fe^{3+} is smaller since Fe^{3+} has a greater charge and since the cations share the same solution and have the same ionic strength.

10. Sparingly soluble salt electrodes have the effect of "inverting" the sensitivity of the electrode from the metallic cation to the counter anion. Show that the $Pb^{2+}|PbSO_4(s)|Pb$ electrode can be used as a sulfate ion selective electrode. This electrode is the cathode in the lead-acid battery.

Answer: The half-reaction is : $PbSO_4\text{ (s)} + 2\text{ e}^- \rightarrow Pb\text{ (s)} + SO_4^{2-}$. The Nernst equation for the electrode half-reaction is, from Eq. 21.1.7:

$$E_{red} = E^{\circ}_{red}(SO_4^{2-},PbSO_4,Pb) - \frac{RT}{2F}\ln(a_{SO_4^{2-}})$$

The cell potential measurement is directly related to the SO_4^{2-} activity.

11. Calculate the solubility equilibrium constant for $PbSO_4$ from standard reduction potentials at 25°C. Ignore the hydrolysis of SO_4^{2-} to HSO_4^-.

Answer: The half-cell reaction for the $PbSO_4/Pb$ electrode and corresponding Nernst equation are: $PbSO_4\text{ (s)} + 2\text{ e}^- \rightarrow Pb\text{ (s)} + SO_4^{2-}$ with $z = 2$:

$$E_{red} = E^\circ_{red}(SO_4^{2-},PbSO_4,Pb) - \frac{RT}{2F}\ln a_{SO42-} \qquad 1$$

Alternately, the half-cell reaction can be considered as the two separate processes:

$$PbSO_4\text{ (s)} \rightleftarrows Pb^{2+} + SO_4^{2-} \qquad K_{sp} = a_{Pb2+}\, a_{SO42-} \qquad 2$$

$$Pb^{2+} + 2\text{ e}^- \rightarrow Pb\text{ (s)} \qquad E_{red} = E^\circ_{red}(Pb^{2+},Pb) - \frac{RT}{2F}\ln\left(\frac{1}{a_{Pb2+}}\right) \qquad 3$$

Solving the K_{sp} expression for the activity of the Pb^{2+} ion gives: $a_{Pb2+} = K_{sp}/a_{SO42-}$. Substituting for the Pb^{2+} activity into the Nernst equation for the Pb^{2+}/Pb metal electrode, Eq. 3, gives:

$$E_{red} = E^\circ_{red}(Pb^{2+},Pb) - \frac{RT}{2F}\ln(a_{SO42-}/K_{sp}) \qquad 4$$

Separating the factors in the logarithmic term gives:

$$E_{red} = E^\circ_{red}(Pb^{2+},Pb) - \frac{RT}{2F}\ln(1/K_{sp}) - \frac{RT}{2F}\ln a_{SO42-} \qquad 5$$

Comparing Eqs. 1 and 5 gives the standard reduction potential for the $PbSO_4/Pb$ electrode in terms of the Pb^{2+}/Pb metal electrode:

$$E^\circ_{red}(SO_4^{2-},PbSO_4,Pb) = E^\circ_{red}(Pb^{2+},Pb) - \frac{RT}{2F}\ln(1/K_{sp}) \qquad 6$$

Table 21.1.1 lists $E^\circ_{red}(Pb^{2+},Pb) = -0.126$ V and $E^\circ_{red}(SO_4^{2-},PbSO_4,Pb) = -0.3588$ V. Substitution into Eq. 5 gives:

$$-0.3588\text{ V} = -0.126\text{ V} - \frac{0.02569\text{ V}}{2}\ln(1/K_{sp})$$

giving $K_{sp} = e^{-2(-0.3588\,-\,-0.126)/0.02569} = 1.35\text{x}10^{-8}$

The literature value is $K_{sp} = 6.3\text{x}10^{-7}$. For simplicity, we neglected to include the equilibrium $HSO_4^{2-} \rightleftarrows SO_4^{2-} + H^+$, which has the $K_{a,2} = 1.03\text{x}10^{-2}$.

12. Show that the standard cell potential for $Ag|\ Ag^+||\ Br^-|\ AgBr|\ Ag$ is $E^\circ_{cell} = (RT/zF)\ln K_{sp}$. The K_{sp} for AgBr is $5.0\text{x}10^{-13}$ at 25°C. Calculate the cell voltage. Draw the physical cell.

Answer: The cell reactions are:

left, anode oxidation: $Ag\text{ (s)} \rightarrow Ag^+ + e^-$
right, cathode, reduction: $AgBr\text{ (s)} + e^- \rightarrow Ag\text{ (s)} + Br^-$

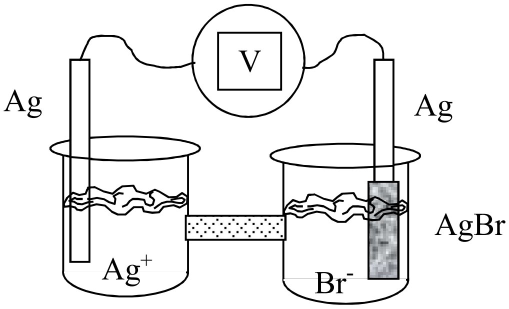
overall $AgBr\text{ (s)} \rightarrow Ag^+ + Br^-$

The standard state cell potential is given by $E^\circ_{cell} = E^\circ_R - E^\circ_L = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode})$:

$$E^\circ_{cell} = E^\circ_{red}(\text{Br}^-,\text{AgBr},\text{Ag}) - E^\circ_{red}(\text{Ag}^+,\text{Ag})$$

The standard reduction potential for the AgBr/Ag electrode can be written in terms of the Ag^+/Ag electrode following Eq. 21.2.6 as:

$$= E^\circ_{red}(\text{Ag}^+,\text{Ag}) - \frac{RT}{zF}\ln\frac{1}{K_{sp}} - E^\circ_{red}(\text{Ag}^+,\text{Ag})$$



The standard reduction potentials cancel:

$$E^\circ_{cell} = \frac{RT}{zF}\ln K_{sp}$$

Using the given K_{sp} with $z = 1$:

$$E^\circ_{cell} = \frac{RT}{zF}\ln K_{sp} = 0.02569\text{ V}\ln 5.0\text{x}10^{-13}$$
$$= -0.728\text{ V}$$

13. Given that the standard reduction potential for the reduction of oxygen is 1.229 V in acidic solution, calculate the standard reduction potential with a basic standard state, $a_{OH^-} = 1$:

acidic: $O_2\,(g) + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\circ_{red} = 1.229$ V
basic: $O_2\,(g) + 2\,H_2O\,(l) + 4\,e^- \rightarrow 4\,OH^-$ $E^\circ_{red} = ?$

Answer: The plan is to note that the acidic standard state is for $a_{H^+} = 1$ and the basic standard state is for $a_{H^+} = 1.008\text{x}10^{-14}$ since $K_w = 1.008\text{x}10^{-14}$ at 25°C.

The Nernst equation for the half reaction based on the acidic form is:

$$E = E^\circ_{red} - \frac{0.05917\text{ V}}{4}\log\frac{1}{P_{O_2}\,(a_{H^+})^4}$$

For the basic standard state $P_{O_2} = 1$ bar and $a_{OH^-} = 1$, giving $a_{H^+} = 1.008\text{x}10^{-14}$:

$$E^\circ_{red}(\text{basic}) = 1.229\text{ V} + (0.05917\text{ V})\log a_{H^+}$$
$$= 1.229\text{ V} + (0.05917\text{ V})\log 1.008\text{x}10^{-14} = 1.229\text{ V} - 0.8282\text{ V} = 0.401\text{ V}$$

as listed in standard reduction tabulations. Note that this half-cell corresponds to the reverse of the oxidation of water. See the next problem for the reduction of water to H_2 in basic solution.

14. Given that the standard reduction potential for the reduction of H^+ is defined as 0 V in acidic solution, calculate the standard reduction potential for water with a basic standard state, $a_{OH^-} = 1$:

acidic: $2\,H^+ + 2e^- \rightarrow H_2\,(g)$ $E^\circ_{red} \equiv 0$ V
basic: $2H_2O + 2e^- \rightarrow H_2\,(g) + 2OH^-$ $E^\circ_{red} = ?$

Answer: The plan is to note that the acidic standard state is for $a_{H^+} = 1$ and the basic standard state is for $a_{H^+} = 1.008\text{x}10^{-14}$ since $K_w = 1.008\text{x}10^{-14}$ at 25°C. Note also that the two half-reactions are related by the addition of 2 OH^- to each side of the acidic half-reaction.

The Nernst equation for the half reaction based on the acidic form is:

$$E = E^{\circ}_{red} - \frac{0.05917\ \text{V}}{2} \log \frac{P_{H2}}{(a_{H^+})^2}$$

For the basic standard state $P_{H2} = 1$ bar and $a_{OH^-} = 1$, giving $a_{H^+} = 1.008\text{x}10^{-14}$:

$$\begin{aligned} E^{\circ}_{red}(\text{basic}) &= 0\ \text{V} + (0.05917\ \text{V}) \log a_{H^+} \\ &= 0\ \text{V} + (0.05917\ \text{V}) \log 1.008\text{x}10^{-14} = 0\ \text{V} - 0.8282\ \text{V} = -0.8282\ \text{V} \end{aligned}$$

as listed in standard reduction tabulations. Note that this half-cell corresponds to the reduction of water under acidic and basic conditions. See the previous problem for the oxidation of water.

<u>15</u>. The standard reduction potential for the reduction of hypochlorite is +0.890 V under basic conditions, $a_{OH^-} = 1$. Calculate the standard reduction potential for hypochlorous acid with an acidic standard state, $a_{H^+} = 1$. The K_a for HClO is $3.0\text{x}10^{-8}$ and $K_w = 1.008\text{x}10^{-14}$ at 25°C. Notice that the products are different under acidic and basic conditions:

$$\begin{array}{ll} \text{basic: } OCl^- + H_2O\ (l) + 2\ e^- \rightarrow Cl^- + 2\ OH^- & E^{\circ}_{red} = +0.890\ \text{V} \\ \text{acidic: } 2\ HOCl + 2\ H^+ + 2\ e^- \rightarrow Cl_2\ (g) + 2\ H_2O\ (l) & E^{\circ}_{red} = ? \end{array}$$

Answer: The plan is to use the standard reduction potential of Cl_2 to give the desired chlorine species as the product, then note the acidic standard state is for $a_{H^+} = 1$. The hydrogen ion and hydroxide ion activities are related by the product $a_{H^+}\, a_{OH^-} = K_w$ with $K_w = 1.008\text{x}10^{-14}$ at 25°C.

The standard potential for the reduction of ClO^- to Cl_2 is obtained by converting the reduction potentials to reaction Gibbs energies and subtracting:

$$\begin{array}{lcr} & E^{\circ}_{red} & \Delta_rG^{\circ} \\ 2\ OCl^- + 2\ H_2O\ (l) + 4\ e^- \rightarrow 2\ Cl^- + 4\ OH^- & +0.890\ \text{V} & \Delta_rG^{\circ} = -4\ FE^{\circ}_{red} = -343.5\ \text{kJ mol}^{-1} \\ -\{Cl_2\ (g) + 2\ e^- \rightarrow 2\ Cl^-\} & +1.359\text{V} & -\{\Delta_rG^{\circ} = -2\ FE^{\circ}_{red} = -262.2\ \text{kJ mol}^{-1}\} \\ \hline 2\ OCl^- + 2\ H_2O\ (l) + 2\ e^- \rightarrow Cl_2 + 4\ OH^- & & \Delta_rG^{\circ} = -2\ FE^{\circ}_{red} = -81.\underline{3}\ \text{kJ mol}^{-1} \end{array}$$

The final cell potential for the combined half-cells is: $E^{\circ}_{red} = -(-81.\underline{3}\ \text{kJ mol}^{-1}/2F) = 0.421\text{V}$

The Nernst equation for the half reaction based on the basic form is:

$$E = E^{\circ}_{red}\ (\text{basic}) - \frac{0.05917\ \text{V}}{2} \log \frac{P_{Cl2}\, (a_{OH^-})^4}{(a_{OCl^-})^2}$$

The activity at the basic standard state for the hypochlorite ion is $a_{OCl^-} = 1$. The hydroxide activity in terms of H^+ is given as $a_{OH^-} = K_w/a_{H^+}$. The activity in terms of hypochlorus acid is given by:

$$K_a = \frac{a_{H^+}\, a_{OCl^-}}{a_{HOCl}} \qquad \text{or} \qquad a_{OCl^-} = \frac{K_a\, a_{HOCl}}{a_{H^+}}$$

Substitution of the activities for the hypochlorite ion and hydroxide ion give the basic solution Nernst equation as:

$$\begin{aligned} E &= E^\circ_{red}\,(\text{basic}) - \frac{0.05917\text{ V}}{2}\log\frac{P_{Cl2}\,(K_w/a_{H^+})^4}{(K_a\,a_{HOCl}/a_{H^+})^2} \\ &= E^\circ_{red}\,(\text{basic}) - \frac{0.05917\text{ V}}{2}\log\frac{P_{Cl2}\,K_w^4}{K_a^2\,(a_{HOCl})^2\,(a_{H^+})^2} \end{aligned}$$

For the acidic standard state $P_{Cl2} = 1$ bar, $a_{HOCl} = 1$, and $a_{H+} = 1$:

$$\begin{aligned} E^\circ_{red}(\text{acidic}) &= E^\circ_{red}\,(\text{basic}) - \frac{0.05917\text{ V}}{2}\log(K_w^4/K_a^2) \\ &= 0.421\text{V} - (0.05917\text{ V})\log[(1.008\text{x}10^{-14})^2/(3.0\text{x}10^{-8})] \\ &= 0.421\text{V} + 1.211\text{ V} = 1.630\text{ V} \end{aligned}$$

as listed in standard reduction potential tabulations.

<u>16</u>. Calculate the equilibrium membrane potential across a proton and water permeable membrane that separates a 0.00100 m and a 0.0100 m aqueous HCl solution (pH 3 and 2). Assume ideal dilute solutions with the partial molar volume of the solvent approximated as the pure molar volume $\bar{V}_{H2O} = V^*_{H2O} = 18.069\text{ mL mol}^{-1}$. The partial molar volume at infinite dilution for the proton is $\bar{V}_{H^+} = -0.28\text{ mL mol}^{-1}$ (based on $\bar{V}_{HCl} = 17.82\text{ mL mol}^{-1}$).[2,3] What fraction of the electric potential difference is driven by the osmotic pressure gradient? [If you calculate the osmotic pressure using molar concentrations, assume the density of the HCl solutions is 1.00 g mL^{-1}.]

Answer: The plan is to note that the osmotic pressure is given by Eq. 18.4.26† (or Eq. 18.4.30†) and the membrane potential by Eq. 21.2.13.

The more exact expression for osmotic pressure is based on the mole fraction of the solvent, Eq. 18.4.26†. The solvent mole fractions are given by Eq. 2.2.15:

$$x_{H2O}\,(0.001\text{ m}) = 1 - x_{H^+} - x_{Cl^-} \cong 1 - 2\,\frac{m_{HCl}\,(1\text{ kg})}{55.51\text{ mol}} = 1 - 3.603\text{x}10^{-5}$$

$$x_{H2O}\,(0.010\text{ m}) = 1 - 3.603\text{x}10^{-4}$$

Neglecting the activity coefficients for the solvent, the osmotic pressure is given by:

$$\Delta P_{eq} = \pi = -\,RT/\bar{V}_A\,\ln(a_{A,in}/a_{A,out})$$

$$\begin{aligned} \pi &= -0.083145\text{ L bar K}^{-1}\text{ mol}^{-1}(298.15\text{ K})/0.018069\text{ L mol}^{-1}\ln(0.999676) \\ &= 0.445\text{ bar} = 4.45\text{x}10^4\text{ Pa} \end{aligned}$$

Substitution into Eq. 21.2.13 gives:

$$\Delta\phi = \phi_{in} - \phi_{out} = -\frac{1}{z_+F}\,RT\,\ln(a_{H^+,in}/a_{H^+,out}) - \pi\bar{V}_{H^+}$$

$$\begin{aligned} \Delta\phi &= \phi_{(0.01\text{ m})} - \phi_{(0.001\text{ m})} \\ &= -\,0.025693\text{ V}\ln 10 - 4.45\text{x}10^4\text{ Pa}\,(-0.28\text{ mL mol}^{-1})(1\text{ m}^3/1\text{x}10^6\text{ mL}) \\ &= -0.05916\text{ V} + 0.0125\text{ V} = -0.0467\text{ V} \end{aligned}$$

The majority of the potential difference is driven by the direct concentration difference. The osmotic pressure contribution is 17% in magnitude. Note that Eq. 21.2.13 holds only if the membrane is permeable to just one ion.

Using Eq. 22.2.11 and assuming the density of the solutions is 1.00 g mL^{-1}, the molality and molarity are equal to three significant figures for these dilute solutions. Since HCl is a 1:1 strong electrolyte, the osmotic pressure is then:

$$\begin{aligned}\pi &= (c_{in} - c_{out})\ RT = (0.0200 - 0.00200\ \mathrm{mol\ L^{-1}})(0.083145\ \mathrm{bar\ L\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K}) \\ &= 0.446\ \mathrm{bar} = 4.46\mathrm{x}10^{4}\ \mathrm{Pa}\end{aligned}$$

which is within experimental error of the more approximate value used above. Using mole fractions, however, avoids needing to know the density of the solutions. The density of 0.0100 m HCl is approximately 1.000 g mL^{-1}, whereas pure water at 25°C is 0.99705 g mL^{-1}.

17. Give the oxidation states of chlorine in the species in the Latimer diagram, Eq. 21.4.1.

Answer: The oxidation states are listed in parentheses:

$$\underset{(+7)}{\mathrm{ClO_4^-}}\ \overset{1.226\ \mathrm{V}}{\overline{\qquad\quad}}\ \underbrace{\underset{(+5)}{\mathrm{ClO_3^-}}\ \overset{1.157\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(+3)}{\mathrm{HClO_2}}\ \overset{1.674\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(+1)}{\mathrm{HOCl}}\ \overset{1.630\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(0)}{\mathrm{Cl_2}}}_{1.458\ \mathrm{V}}\ \overset{1.360\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(-1)}{\mathrm{Cl^-}}$$

18. Give the oxidation states of nitrogen in the species in the Latimer diagram, Eq. 21.4.8.

Answer: The oxidation states are listed in parentheses:

$$\underbrace{\overbrace{\underset{(+5)}{\mathrm{NO_3^-}}\ \overset{0.773\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(+4)}{\mathrm{NO_2(g)}}\ \overset{1.108\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(+3)}{\mathrm{HNO_2}}\ \overset{0.984\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(+2)}{\mathrm{NO}}}^{0.955\ \mathrm{V}}}_{1.244\ \mathrm{V}\ \text{(continues to } \mathrm{N_2}\text{)}}$$

$$\underset{(+2)}{\mathrm{NO}}\ \overset{1.587\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(+1)}{\mathrm{N_2O}}\ \overset{1.769\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(0)}{\mathrm{N_2}}\ \overset{0.274\ \mathrm{V}}{\overline{\qquad\quad}}\ \underset{(-3)}{\mathrm{NH_4^+}}$$

Nitrogen is such a chemically and environmentally interesting element because nitrogen has the widest range of observed oxidation states for any non-metallic element. By comparison, only one oxidation state for phosphorus is environmentally significant, which in PO_4^{3-} and its polymers is +5.

19. The Latimer diagram for nitrogen oxides in given in Eq. 21.4.8. Is NO stable with respect to disproportionation under standard conditions at 25°C? What are the products of the disproportionation?

Answer: NO is unstable with respect to disproportionation under standard conditions at 25°C. The right-hand standard reduction potential is greater than the left-hand standard reduction potential giving either HNO_2 or NO_3^- as the oxidized product. For HNO_2 and N_2O as products:

$$\mathrm{HNO_2}\ \overset{0.984\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{NO}\ \overset{1.587\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{N_2O} \qquad 4\ \mathrm{NO}\ (g) + \mathrm{H_2O} \rightarrow 2\ \mathrm{HNO_2} + \mathrm{N_2O}\ (g)$$

$$E^\circ_{cell} = E_R - E_L = E^\circ_{red}(\mathrm{NO,N_2O}) - E^\circ_{red}(\mathrm{HNO_2,NO}) > 0$$

For NO_3^- and N_2O as products:

$$\mathrm{NO_3^-}\ \overset{0.955\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{NO}\ \overset{1.587\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{N_2O} \qquad 8\ \mathrm{NO}\ (g) + \mathrm{H_2O} \rightarrow 2\ \mathrm{NO_3^-} + 3\ \mathrm{N_2O} + 2\mathrm{H^+}$$

$$E^\circ_{cell} = E_R - E_L = E^\circ_{red}(\mathrm{NO,N_2O}) - E^\circ_{red}(\mathrm{NO_3^-,NO}) > 0$$

20. The Latimer diagram for manganese in acidic solution is given below at 25°C. Find the standard reduction potential for the reduction of permanganate ion, MnO_4^-, to Mn^{2+} from the potentials listed.

$$\mathrm{MnO_4^-}\ \overset{0.56\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{MnO_4^{2-}}\ \overset{2.26\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{MnO_2}\ (s)\ \overset{0.90\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{Mn^{3+}}\ \overset{1.56\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{Mn^{2+}}\ \overset{-1.182\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{Mn}\ (s)$$

$$|\underline{\hspace{4em}1.692\ \mathrm{V}\hspace{4em}}|\underline{\hspace{3em}1.230\ \mathrm{V}\hspace{3em}}|$$

Answer: The following two half cells add to give the desired reaction. The Gibbs energies add to give the Gibbs energy of the overall reaction:

	E°_{red}	Δ_rG°
$MnO_4^- + 4\ H^+ + 3e^- \rightarrow MnO_2\ (s) + 2\ H_2O$	1.69 V	$\Delta_rG^\circ = -\ 3\ FE^\circ_{red} = -489.2$ kJ mol^{-1}
$MnO_2\ (s) + 4\ H^+ + 2e^- \rightarrow Mn^{2+} + 2\ H_2O$	1.23 V	$\Delta_rG^\circ = -\ 2\ FE^\circ_{red} = -237.4$ kJ mol^{-1}
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$		$\Delta_rG^\circ = -\ 5\ FE^\circ_{red} = -726.6$ kJ mol^{-1}

After adding the Gibbs energies, the overall voltage is given by solving $\Delta_rG^\circ = -\ 5\ FE^\circ_{red}$:

$$E^\circ_{red} = \frac{\Delta G^\circ}{-\ 5\ F} = \frac{-726.6\mathrm{x}10^3\ \mathrm{J\ mol^{-1}}}{-\ 5\ (96485\ \mathrm{C\ mol^{-1}})} = 1.51\ \mathrm{V} \qquad \text{with } 1\ \mathrm{J} = 1\ \mathrm{C\ V}$$

21. The Latimer diagram for manganese in acidic solution is given below at 25°C. (a). Give the best oxidizing agent under standard conditions. (b). Give the best reducing agent. (c). Is Mn(s) a good oxidizing agent? (d). What are the products of the disproportionation of Mn^{3+} ?

$$\mathrm{MnO_4^-}\ \overset{0.56\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{MnO_4^{2-}}\ \overset{2.26\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{MnO_2}\ (s)\ \overset{0.90\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{Mn^{3+}}\ \overset{1.56\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{Mn^{2+}}\ \overset{-1.182\ \mathrm{V}}{\overline{\hspace{3em}}}\ \mathrm{Mn}\ (s)$$

$$|\underline{\hspace{4em}1.692\ \mathrm{V}\hspace{4em}}|\underline{\hspace{3em}1.230\ \mathrm{V}\hspace{3em}}|$$

Answers: (a). Give the best oxidizing agent under standard conditions: the most positive reduction potential is for MnO_4^{2-} . (b). Give the best reducing agent: the most negative reduction potential is for $Mn^{2+} + 2e^- \rightarrow Mn$, so Mn (s) is the best reducing agent. (c). Is Mn (s) a good oxidizing agent? No, metals don't have negative oxidation states in aqueous solution. For example, to act as an oxidizing agent a half reaction might be $Mn_{(s)} + e^- \rightarrow Mn^-$. (d). What are the products of the disproportionation of Mn^{3+} ? The products are the species on either side of Mn^{3+} giving the answers as MnO_2 (s) and Mn^{2+}.

22. Is chlorate ion a better oxidizing agent in acidic or basic solution? The product is either $HClO_2$ or ClO_2^- in acidic or basic solution, respectively.

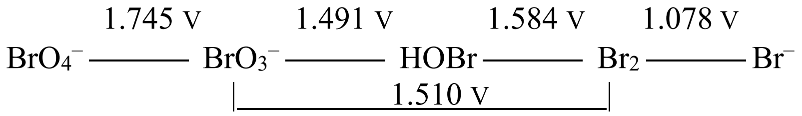
Answer: The plan is to compare the Latimer diagrams in Eqs. 21.4.1 and 21.4.2.
Under standard state conditions, and at pH close to standard state, the standard reduction potential for ClO_3^- is greater in acidic solution (1.157 V) than basic solution (0.271 V). Chlorate ion is a better oxidizing agent in acidic solution.

23. Given the following standard reduction potentials, construct the Latimer diagram:

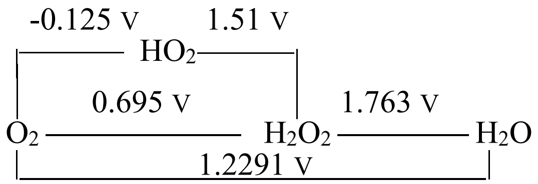
	E°_{red} (V)
$BrO_4^- + 2H^+ + 2e^- \rightarrow BrO_3^- + H_2O$	1.745 V
$BrO_3^- + 5H^+ + 4e^- \rightarrow HBrO + 2H_2O$	1.491 V
$BrO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2} Br_{2\,(l)} + 3H_2O$	1.510 V
$HOBr + H^+ + e^- \rightarrow \frac{1}{2} Br_{2\,(l)} + H_2O$	1.584 V
$Br_{2\,(l)} + 2e^- \rightarrow 2Br^-$	1.078 V

Answer: The highest oxidation state is listed at the left of the diagram by convention:

acidic solution:



24. The Latimer diagram for oxygen under acidic conditions is given below at 25°C. The Latimer diagram for chlorine is given in Eq. 21.4.1. Which chlorine species are stable in aqueous solution at pH 0. Assume the solution is deoxygenated.



Answer: The plan is to note that the only solvent related species in significant concentration in deoxygenated acidic solution are H_2O and H^+. We should consider the oxidation and reduction of each chlorine containing species. However, ClO_4^- can't be oxidized and Cl^- can't be reduced.
The two possible water decompositions are the reverse of the reduction half-reactions:

$$O_2\,(g) + 4H^+ + 4e^- \rightarrow 2\,H_2O \qquad E^\circ_{red} = 1.2291\text{ V}$$
$$H_2O_2 + 2\,H^+ + 2e^- \rightarrow 2\,H_2O \qquad E^\circ_{red} = 1.763\text{ V}$$

and the third possible half-reaction in aqueous solution is the reduction of H^+:

$$2H^+ + 2e^- \rightarrow H_2\,(g) \qquad E^\circ_{red} = 0.000\text{ V}$$

The oxidation of water occurs at the anode and the reduction of H^+ occurs at the cathode. The possible anode and cathode reactions involving chlorine species are conveniently summarized by the Latimer diagram:

$$\mathrm{ClO_4^-}\overset{1.226\text{ V}}{\text{———}}\underbrace{\mathrm{ClO_3^-}\overset{1.157\text{ V}}{\text{———}}\mathrm{HClO_2}\overset{1.674\text{ V}}{\text{———}}\mathrm{HOCl}\overset{1.630\text{ V}}{\text{———}}\mathrm{Cl_2}}_{1.458\text{ V}}\overset{1.360\text{ V}}{\text{———}}\mathrm{Cl^-}$$

For example consider chlorate ion, ClO_3^-. Chlorate can be oxidized or reduced giving the following possibilities:

$$E^\circ_{cell} = \qquad E^\circ_{cathode} \qquad - \qquad E^\circ_{anode}$$

$$E^\circ_{cell} = \left\{\begin{array}{c} 1.157\text{ V }(ClO_3^-) \\ \mathbf{1.458\text{ V }(ClO_3^-)} \\ 0.00\text{ V }(H^+) \end{array}\right\} - \left\{\begin{array}{c} \mathbf{1.226\text{ V }(ClO_3^-)} \\ 1.2291\text{ V }(H_2O) \\ 1.763\text{ V }(H_2O) \end{array}\right\} > 0$$

The maximum voltage results from choosing the largest standard reduction potential for the cathode and the smallest reduction potential for the anode. ClO_3^- is unstable with respect to diproportionation: $E^\circ_{cell} = 1.458 - 1.226\text{ V} = 0.232\text{ V}$. In addition, ClO_3^- is a sufficiently strong oxidizing agent to oxidize water to give Cl_2 and O_2: $E^\circ_{cell} = 1.458 - 1.2291\text{ V} = 0.229\text{ V}$. Thermodynamically the disproportionation is favored over the oxidation of water, however the kinetics of these processes is likely to determine the actual distribution of products. Overall then:

unstable with respect to disproportionation: ClO_3^-, $HClO_2$
oxidize water to O_2: ClO_3^-, $HClO_2$, $HOCl$, Cl_2 ($E^\circ_{red} > 1.2291$ V)
reduce water to H_2: none ($E^\circ_{red} < 0$)

Based on the listed half-reactions, the only thermodynamically stable species in aqueous 1.0 M H^+ are perchlorate and chloride ions: ClO_4^- and Cl^-.

25. The Latimer diagram for oxygen under acidic conditions is given in the previous problem. The Latimer diagram for manganese is given in Problem 20. Which manganese species are stable in aqueous solution at pH 0. Assume the solution is deoxygenated.

Answer: Referring to the previous problem, the two possible water decompositions are the reverse of the reduction half-reactions:

$$O_2\,(g) + 4H^+ + 4e^- \rightarrow 2\,H_2O \qquad E^\circ_{red} = 1.2291\text{ V}$$
$$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O \qquad E^\circ_{red} = 1.763\text{ V}$$

and the third possible half-reaction in aqueous solution is the reduction of H^+:

$$2H^+ + 2e^- \rightarrow H_2\,(g) \qquad E^\circ_{red} = 0.000\text{ V}$$

The oxidation of water occurs at the anode and the reduction of H^+ occurs at the cathode. The possible anode and cathode reactions involving manganese species are conveniently summarized by the Latimer diagram:

$$\begin{array}{ccccccccccc} & 0.56\text{ V} & & 2.26\text{ V} & & 0.90\text{ V} & & 1.56\text{ V} & & -1.182\text{ V} & \\ MnO_4^- & \text{———} & MnO_4^{2-} & \text{———} & MnO_2\,(s) & \text{———} & Mn^{3+} & \text{———} & Mn^{2+} & \text{———} & Mn\,(s) \\ | & \multicolumn{3}{c}{\underline{\qquad 1.692\text{ V}\qquad}} & | & \multicolumn{3}{c}{\underline{\qquad 1.230\text{ V}\qquad}} & | & & \end{array}$$

For example consider MnO_2. MnO_2 can be oxidized or reduced giving the following possibilities:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = \left\{\begin{array}{c} 0.90\text{ V }(MnO_2) \\ \mathbf{1.230\text{ V }(}MnO_2\mathbf{)} \\ 0.00\text{ V }(H^+) \end{array}\right\} - \left\{\begin{array}{c} 2.26\text{ V }(MnO_2) \\ \mathbf{1.2291}\text{ V }(H_2O) \\ 1.763\text{ V }(H_2O) \end{array}\right\} > 0$$

The maximum voltage results from choosing the largest standard reduction potential for the cathode and the smallest reduction potential for the anode. MnO_2 is stable with respect to diproportionation; for one example: $E^\circ_{cell} = 1.230 - 1.692\text{ V} = -0.462\text{ V}$. However, MnO_2 is just strong enough of an oxidizing agent to oxidize water to give Mn^{2+} and O_2: $E^\circ_{cell} = 1.230 - 1.2291\text{ V} = 0.001\text{ V}$. This small potential corresponds to an equilibrium constant of $K_a = 1.1$. Overall then:

unstable with respect to disproportionation: MnO_4^{2-}, Mn^{3+}
oxidize water to O_2: MnO_4^-, MnO_4^{2-}, MnO_2, Mn^{3+} ($E^\circ_{red} > 1.2291$ V)
reduce water to H_2: Mn ($E^\circ_{red} < 0$)

Based on the listed half-reactions, the only thermodynamically stable species in aqueous 1.0 M H^+ is Mn^{2+}.

<u>26</u>. Calculate the concentration polarization for $Zn^{2+} + 2\,e^- \rightarrow Zn\,(s)$ operating as the cathode with $c_o = [Zn^{2+}]_o = 1.00\times10^{-4}$ M, electrode area 5.00 cm^2, a depletion layer of 0.200 mm, 298.2 K, and the electrode current at 10.00 μamp. The limiting ionic conductivity of Zn^{2+} is $\lambda_+ = 10.56\text{ mS m}^2\text{ mol}^{-1}$. Neglect the activity coefficients.

Answer: Using Eq. 21.3.14, the ionic diffusion coefficient for Zn^{2+} ions at infinite dilution is:

$$D = \frac{RT}{F^2}\frac{\lambda_i}{|z_i|} = \frac{8.3145\text{ J K}^{-1}\text{ mol}^{-1}(298.15\text{ K})}{(96485\text{ C mol}^{-1})^2}\,\frac{10.56\times10^{-3}\text{ S m}^2\text{ mol}^{-1}}{2} = 1.406\times10^{-9}\text{ m}^2\text{ s}^{-1}$$

The concentration in mol m^{-3} is given by: $c_o = 1.00\times10^{-4}\text{ mol L}^{-1}\,(1000\text{ L}/1\text{ m}^3) = 0.100\text{ mol m}^{-3}$.

The electrode area in m^2 is: $A = 5.00\ cm^2\ (1m/100\ cm)^2 = 5.00x10^{-4}\ m^2$.

Using 21.3.12 to find the limiting current gives:

$$i_{\delta,max} = \frac{z_i\ FDA}{\delta}\ c_o = \frac{(2)(96485\ C\ mol^{-1})(1.406x10^{-9}\ m^2\ s^{-1})(5.00x10^{-4}\ m^2)}{0.200x10^{-3}\ m}\ 0.100\ mol\ m^{-3}$$
$$= 6.783x10^{-5}\ amp$$

Using Eq. 21.3.13, neglecting the activity coefficients, gives:

$$\eta = \frac{0.02569\ V}{2} \ln\left(1 - \frac{10.00x10^{-6}\ amp}{6.783x10^{-5}\ amp}\right) = \frac{0.02569\ V}{2}(-0.1595) = -0.00205\ V$$

27. Calculate the depletion layer thickness for a $Zn^{2+} + 2\ e^- \rightarrow Zn\ (s)$ electrode operating as the cathode with bulk concentration $c_o = [Zn^{2+}]_o = 1.00x10^{-5}$ M and electrode area 1.00 cm^2, at 298.2 K, if the electrode current is 10.00 μamp and the overvoltage is -0.0200 V. The limiting ionic conductivity of Zn^{2+} is $\lambda_+ = 10.56\ mS\ m^2\ mol^{-1}$. Neglect the activity coefficients.

Answer: Using Eq. 21.3.14, the ionic diffusion coefficient for Zn^{2+} ions at infinite dilution is:

$$D = \frac{RT}{F^2}\frac{\lambda_i}{|z_i|} = \frac{8.3145\ J\ K^{-1}\ mol^{-1}(298.15\ K)}{(96485\ C\ mol^{-1})^2}\ \frac{10.56\ x10^{-3}\ S\ m^2\ mol^{-1}}{2} = 1.406x10^{-9}\ m^2\ s^{-1}$$

The concentration in mol m^{-3} is: $c_o = 1.00x10^{-5}\ mol\ L^{-1}\ (1000\ L/1\ m^3) = 0.0100\ mol\ m^{-3}$.
The electrode area in m^2 is: $A = 1.00\ cm^2\ (1m/100\ cm)^2 = 1.00x10^{-4}\ m^2$.
Using 21.3.11, neglecting activity coefficients, gives:

$$c_o\ z_i\ FDA = 0.0100\ mol\ m^{-3}(2)(96485\ C\ mol^{-1})(1.406x10^{-9}\ m^2\ s^{-1})(1.00x10^{-4}\ m^2)$$
$$= 2.713x10^{-10}\ amp\ m$$

$$\eta = \frac{RT}{z_iF}\ln\left(1 - \frac{\delta\ i_\delta}{c_oz_i\ FDA}\right)$$

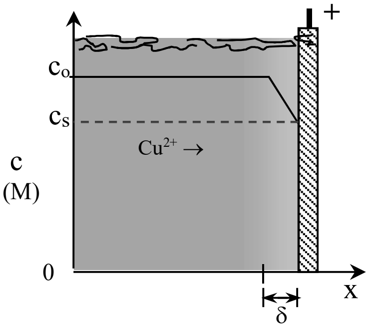
$$-0.0200\ V = \frac{0.02569\ V}{2}\ln\left(1 - \frac{\delta(10.00x10^{-6}\ amp)}{2.713x10^{-10}\ amp\ m}\right)$$

Giving the diffusion depletion layer thickness as:

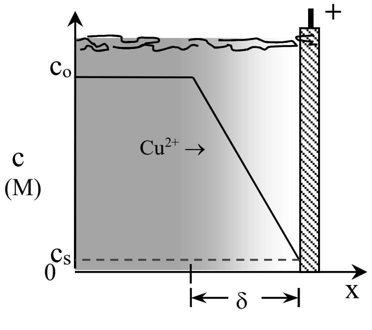
$$0.2108 = (1 - \delta(3.686x10^4\ m^{-1})) \qquad \text{or}\ \ \delta = 2.141x10^{-5}\ m = 0.0214\ mm$$

28. (a). What is the concentration of the electroactive species at the surface of the electrode in a Galvanic cell when the electrode current is equal to the limiting current? (b). Roughly sketch the concentration profile of the electroactive species in an unstirred solution for a Galvanic cell at two different times: a time shortly after current first flows and at a later time. (c). Give two ways to decrease concentration polarization.

Answer: (a). At the limiting current, the surface concentration is zero. (b). The concentration profiles for short and long times are sketched below. (c). For a given current, increasing the bulk concentration, the electrode area, and vigorous stirring decreases concentration polarization. Stirring decreases the thickness of the depletion layer by convection.

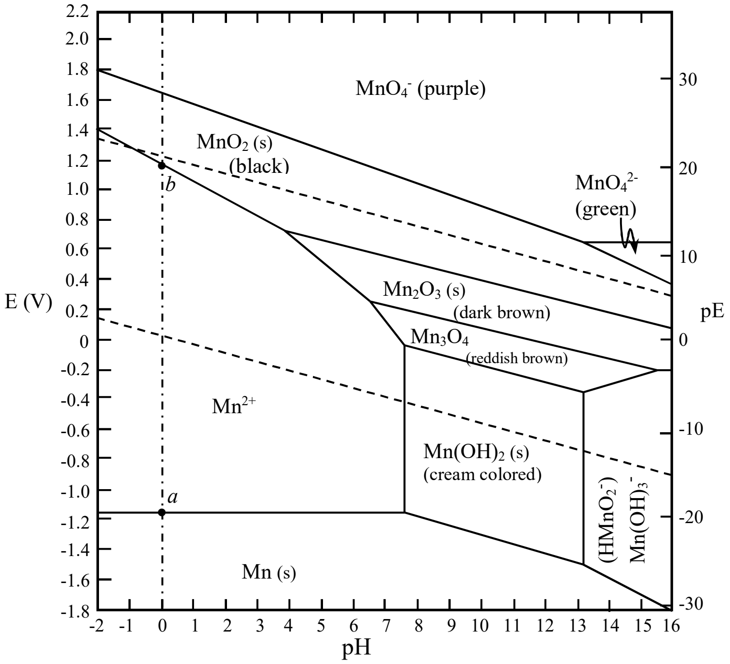


short time after initiation of current



long times

29. The Pourbaix diagram for manganese is shown below:



(a). Circle the point on the diagram that corresponds to the standard reduction potential for the Mn^{2+}, Mn couple and the point for the MnO_2, Mn^{2+} couple.
(b). Is the reaction that takes you from the Mn^{2+} region of the diagram to the MnO_2 region of the diagram pH dependent? How do you know from the diagram?
(c). Look up the standard reduction potential and the balanced half-cell reaction for the MnO_2, Mn^{2+} couple. Verify the pH dependence that you found in part (b).
(d). Label the vertical axis of the diagram with several pE values so that you can read the vertical axis using either volts or pE.
(e). What is the H^+ activity and the electron activity (calculated from the pE) where Mn^{2+}, $Mn(OH)_2$ (s), and Mn(s) are all three at equilibrium?

(f). Is Mn metal stable in water or will Mn metal react with water?

Answer: (a). The standard reduction potential for the Mn^{2+}, Mn couple is labeled (*a*) and the point for the MnO_2, Mn^{2+} couple is labeled (*b*) in the diagram above.
(b). The reduction of MnO_2 to Mn^{2+} is pH dependent. The line between the two regions has a finite slope.
(c). The reduction potential and balanced half-cell reaction for the MnO_2, Mn^{2+} couple is pH dependent, since the half-reaction involves H^+:

$$MnO_2\,(s) + 4\,H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \qquad E^{\circ}_{red} = 1.230\ V$$

(d). Given pE = 30.00, $E_H = 0.05917\ V\ pE = 1.78\ V$. The pE axis is included on the plot, above.
(e). The E_H and pH where Mn^{2+}, $Mn(OH)_2$ (s), and Mn(s) are all three at equilibrium, as read from the figure, is $E^{\circ}_{red}(Mn^{2+}, Mn) = -1.18\ V$ and pH = 7.6. The corresponding pE is -19.94. The H^+ activity is $a_{H+} = 10^{-pH} = 2.5x10^{-8}$, the electron activity is $a_{e-} = 10^{-pE} = 8.71x10^{19}$.
(f). The Mn metal region of the diagram lies completely below the dotted line for the reduction of water to form hydrogen gas. Mn metal is not stable in aqueous solution and reacts with water with the Mn^{2+}, Mn couple at the anode:

$$Mn + 2H^+ \rightarrow Mn^{2+} + H_2\,(g) \qquad E^{\circ}_{cell} = E^{\circ}_{red}(\text{cathode}) - E^{\circ}_{red}(\text{anode}) = 1.182\ V$$

30. Show that the pH dependence of the solubility of $Fe(OH)_2$ is governed by the equilibrium expression: $K_2 = a_{Fe2+}/(a_{H+})^2$ with $K_2 = K_{sp}/K_w{}^2 = 7.9x10^{-16}/(1.01x10^{-14})^2 = 7.7x10^{12}$ for the reaction:

$$Fe(OH)_2\,(s) + 2\,H^+ \rightleftarrows Fe^{2+} + 2\,H_2O$$

Calculate the equilibrium pH assuming $a_{Fe2+} = 1.00$ and verify the value on Figure 21.4.2.

Answer: The plan is to combine the K_{sp} expression for $Fe(OH)_2$ with the K_w expression for the autoprotolysis of water.
The solubility and autoprotolysis equilibria are given by:

$$Fe(OH)_2\,(s) \overset{K_{sp}}{\rightleftarrows} Fe^{2+} + 2\,OH^- \qquad H_2O \overset{K_w}{\rightleftarrows} H^+ + OH^-$$

When reactions add, the equilibrium constants multiply. Reversing the last reaction and multiplying by two with addition to the solubility equilibrium gives the overall reaction:

$$\begin{array}{ll} Fe(OH)_2\,(s) \rightleftarrows Fe^{2+} + 2\,OH^- & K = K_{sp} \\ 2\,H^+ + 2\,OH^- \rightleftarrows 2\,H_2O & K = 1/K_w^2 \\ \hline Fe(OH)_2\,(s) + 2\,H^+ \rightleftarrows Fe^{2+} + 2\,H_2O & K_2 = K_{sp}/K_w^2 \end{array}$$

The designation as K_2 is arbitrary and simply references reaction 2 in Eq. 21.4.14. The equilibrium expression is then:

$$K_2 = K_{sp}/K_w^2 = \frac{a_{Fe2+}}{(a_{H+})^2}$$

At $a_{Fe^{2+}} = 1.00$ the pH is then: $\quad \mathrm{pH} = -½ \log\left(\frac{a_{Fe^{2+}}}{K_2}\right) = 6.44$

31. Show that the pH dependence of the solubility of $Fe(OH)_3$ is governed by the equilibrium expression: $K_3 = a_{Fe^{3+}}/(a_{H^+})^3$ with $K_3 = K_{sp}/K_w^3 = 1.6\text{x}10^{-39}/(1.01\text{x}10^{-14})^3 = 1.55\text{x}10^3$ for the reaction:

$$Fe(OH)_3\,(s) + 3\,H^+ \rightleftarrows Fe^{3+} + 3\,H_2O$$

Calculate the equilibrium pH assuming $a_{Fe^{3+}} = 1.00$ and verify the value on Figure 21.4.2.

Answer: The plan is to combine the K_{sp} expression for $Fe(OH)_3$ with the K_w expression for the autoprotolysis of water.

The solubility and autoprotolysis equilibria are given by:

$$Fe(OH)_3\,(s) \overset{K_{sp}}{\rightleftarrows} Fe^{3+} + 3\,OH^- \qquad\qquad H_2O \overset{K_w}{\rightleftarrows} H^+ + OH^-$$

When reactions add, the equilibrium constants multiply. Reversing the last reaction and multiplying by three with addition to the solubility equilibrium gives the overall reaction:

$$\begin{array}{ll} Fe(OH)_3\,(s) \rightleftarrows Fe^{3+} + 2\,OH^- & K = K_{sp} \\ 3\,H^+ + 3\,OH^- \rightleftarrows 3\,H_2O & K = 1/K_w^3 \\ \hline Fe(OH)_3\,(s) + 3\,H^+ \rightleftarrows Fe^{3+} + 3\,H_2O & K_3 = K_{sp}/K_w^3 \end{array}$$

The designation as K_3 is arbitrary and simply references reaction 3 in Eq. 21.4.14. The equilibrium expression is then:

$$K_3 = K_{sp}/K_w^3 = \frac{a_{Fe^{3+}}}{(a_{H^+})^3}$$

At $a_{Fe^{3+}} = 1.00$ the pH is: $\quad \mathrm{pH} = -\,{}^1/_3 \log\left(\frac{a_{Fe^{3+}}}{K_3}\right) = 1.06$

32. Find the slopes of the cell potential versus pH for the reaction lines in the Pourbaix diagram, Figure 21.4.2, for:

(a). $Fe(OH)_3\,(s) + 3H^+ + e^- \rightleftarrows Fe^{2+} + 3\,H_2O$ and (b). $Fe(OH)_2\,(s) + 2\,H^+ + 2\,e^- \rightarrow Fe\,(s) + 2\,H_2O$

Qualitatively verify the relative magnitudes of the slopes shown in the diagram.

Answer: The plan is to start with the Nernst equation for the Fe^{3+}, Fe^{2+} couple for the first half-reaction and then the Fe^{2+}, Fe couple for the second half-reaction. The metal-ion activities are given by Eqs. 21.4.17 and 21.4.16, respectively.

(a). For $Fe(OH)_3$, the reduction half-reaction is $Fe^{3+} + e^- \rightarrow Fe^{2+}$ with the Nernst equation:

$$E = E^\circ_{red}(Fe^{3+},Fe^{2+}) - (0.05917\text{ V}) \log \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

The activity of Fe^{3+} is given by Eq. 21.4.17 (see also the previous problem), $a_{Fe^{3+}} = K_3\,(a_{H^+})^3$:

$$E = E^\circ_{red}(Fe^{3+},Fe^{2+}) - (0.05917\text{ V}) \log \frac{a_{Fe^{2+}}}{K_3\,(a_{H^+})^3}$$

$$= \left[E^\circ_{red}(Fe^{3+},Fe^{2+}) - (0.05917\text{ V}) \log 1/K_3\,\right] - (0.05917\text{ V}) \log \frac{a_{Fe^{2+}}}{(a_{H^+})^3}$$

Assuming that $a_{Fe^{2+}} = 1.00$ gives:

$$E = E^\circ_{red}(Fe(OH)_3,Fe^{2+}) - 3(0.05917\text{ V})\,pH$$

The slope for the reduction of $Fe(OH)_3$ is –3(0.05917 V) = -0.1775 V
(b). For $Fe(OH)_2$, the reduction half-reaction is $Fe^{2+} + 2e^- \rightarrow Fe\,(s)$ with the Nernst equation:

$$E = E^\circ_{red}(Fe^{2+},Fe) - \frac{0.05917\text{ V}}{2} \log \frac{1}{a_{Fe^{2+}}}$$

The activity of Fe^{2+} is given by Eq. 21.4.16 (see also Problem 29), $a_{Fe^{2+}} = K_2\,(a_{H^+})^2$:

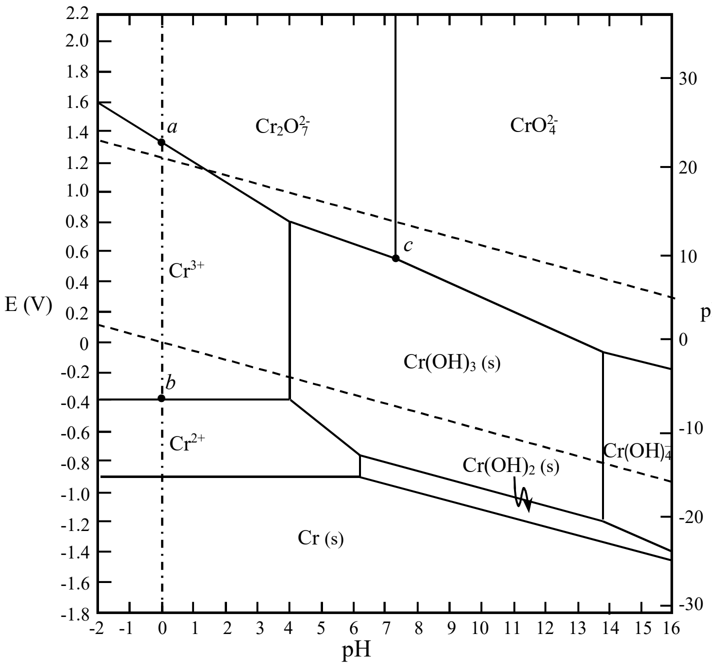
$$E = E^\circ_{red}(Fe^{3+},Fe^{2+}) - (0.05917\text{ V}) \log \frac{1}{K_2\,(a_{H^+})^2}$$

$$= \left[E^\circ_{red}(Fe^{2+},Fe) - \frac{0.05917\text{ V}}{2} \log 1/K_2\,\right] - \frac{0.05917\text{ V}}{2} \log \frac{1}{(a_{H^+})^2}$$

$$= E^\circ_{red}(Fe(OH)_2,Fe) - (0.05917\text{ V})\,pH$$

The slope for the reduction of $Fe(OH)_2$ is –0.05917 V. Note in Figure 21.4.2 that the slope of line 4, for $Fe(OH)_3$ reduction, is three times that of line 7, for $Fe(OH)_2$ reduction. As a short-cut, note the slope is given by –0.05917 n_p/z, where n_p is the number of protons in the balanced reaction as reactants.

<u>33</u>. The Pourbaix diagram for chromium is shown below.



(a). Circle the point on the diagram that corresponds to the standard reduction potential for the $Cr_2O_7^{2-}$, Cr^{3+} couple and the point for the Cr^{3+}, Cr^{2+} couple.
(b). Is the reaction that takes you from the CrO_4^{2-} region of the diagram to the $Cr(OH)_3$ region of the diagram pH dependent? How do you know from the diagram?
(c). Look up the standard reduction potential and the balanced half-cell reaction for the CrO_4^{2-}, $Cr(OH)_3$ couple. Verify the pH dependence that you found in part (b).
(d). Calculate the pE that corresponds to $E_H = 2.20$ V.
(e). What is the H^+ activity and the electron activity where $Cr_2O_7^{2-}$, CrO_4^{2-}, and $Cr(OH)_3$ (s) are all three at equilibrium?
(f). Is Cr^{2+} ion stable in water or will Cr^{2+} ion react with water? If there is a reaction, give the balanced reaction in acidic solution and the standard cell voltage.

Answer: (a). The standard reduction potential for the $Cr_2O_7^{2-}$, Cr^{3+} couple is labeled (*a*) and the point for the Cr^{3+}, Cr^{2+}couple is labeled (*b*) in the diagram above.
(b). The reduction of CrO_4^{2-} to $Cr(OH)_3$ is pH dependent. The line between the two regions has a finite slope.
(c). The reduction potential and balanced half-cell reaction for the CrO_4^{2-}, $Cr(OH)_3$ couple is pH dependent, since the half-reaction involves OH^-, giving the pH dependence from pH = 14 – pOH:

$$CrO_4^{2-} + 4\ H_2O + 3e^- \rightarrow Cr(OH)_3\ (s) + 5\ OH^- \qquad E^\circ_{red} = -0.12\ V$$

Notice that the line for this reaction gives the voltage at pH = 14 as $E^\circ_{red} = -0.12$ V.
(d). Given $E_H = 2.20$ V, $pE = E_H/0.05917\ V = 37.181$.
(e). The E_H and pH where $Cr_2O_7^{2-}$, CrO_4^{2-}, and $Cr(OH)_3$ (s) are all three at equilibrium, as read from the figure at point *c*, is $E_H = +0.54$ V and pH = 7.3. The corresponding pE is 9.1. The H^+ activity is $a_{H^+} = 10^{-pH} = 5x10^{-8}$, the electron activity is $a_{e^-} = 10^{-pE} = 7.5x10^{-10}$.
(f). The Cr^{2+} region of the diagram lies completely below the line for the reduction of water to form hydrogen gas. The Cr^{2+} ion not stable in aqueous solution and reacts with water with the Cr^{3+}, Cr^{2+} couple at the anode:

$$2\ Cr^{2+} + 2H^+ \rightarrow 2\ Cr^{3+} + H_2\ (g) \qquad E^\circ_{cell} = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode}) = 0.42\ V$$

Note also that Cr metal is also not stable in water. How do you explain the use of chromium electroplating to resist corrosion on metal automobile parts? Chromium metal reacts with oxygen in air to form a tough oxide coating, Cr_2O_3, that acts as a kinetic barrier for the reduction of water by the underlying metal to give hydrogen gas.

<u>34</u>. Find the slope of the pE vs. pH line for the reduction of $Cr_2O_7^{2-}$ to Cr^{3+}. Compare to the Pourbaix diagram in the Problem 33.

Answer: The plan is to write the Nernst equation for the $Cr_2O_7^{2-}$, Cr^{3+} couple.
The balanced half-cell is:

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O \qquad E^\circ_{red} = 1.36\ V$$

giving the Nernst equation: $E = E^\circ_{red}(Cr_2O_7^{2-}, Cr^{3+}) - \frac{0.05917\ V}{6} \log \frac{(a_{Cr3+})^2}{a_{Cr2O72-}\ (a_{H+})^{14}}$

Separating out the pH dependent term gives:

$$E = E^\circ_{red}(Cr_2O_7^{2-}, Cr^{3+}) - \frac{0.05917\ V}{6} \log \frac{(a_{Cr3+})^2}{a_{Cr2O72-}} - \frac{14(0.05917\ V)}{6} \log \frac{1}{a_{H+}}$$

$$= E^\circ_{red}(Cr_2O_7^{2-}, Cr^{3+}) - \frac{0.05917\ V}{6} \log \frac{(a_{Cr3+})^2}{a_{Cr2O72-}} - \frac{14(0.05917\ V)}{6}\ pH$$

The slope of the E_H vs. pH curve is then $-14(0.05917\ V)/6 = -0.1381\ V$, which is the steepest pH dependence in the figure. As a short-cut, note the slope is given by $-0.05917\ n_p/z$, where n_p is the number of protons in the balanced reaction as reactants.

35. Calculate the equilibrium pH for the conversion of dichromate to chromate with $a_{Cr2O72-} = a_{CrO42-} = 1.00$:

$$Cr_2O_7^{2-} + H_2O \rightleftarrows 2\ CrO_4^{2-} + 2\ H^+$$

Compare to the chromium Pourbaix diagram in the Problem 33. Note the following equilibrium constants:

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{2-} \qquad K_{a2} = 3.2\text{x}10^{-7}$$

$$2\ HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O \qquad K_{assoc} = 40.$$

Answer: The plan is to combine the acid dissociation reaction and the association to give the overall dissociation process, written in terms of the H^+ activity.

When reactions add, the equilibrium constants multiply. Doubling the acid dissociation, reversing the association, and adding the resultant equilibria gives the desired dissociation:

$$2\ HCrO_4^- \rightleftarrows 2H^+ + 2\ CrO_4^{2-} \qquad K = K_{a2}^2$$

$$Cr_2O_7^{2-} + H_2O \rightleftarrows 2\ HCrO_4^- \qquad K = 1/K_{assoc}$$

$$Cr_2O_7^{2-} + H_2O \rightleftarrows 2\ CrO_4^{2-} + 2\ H^+ \qquad K = K_{a2}^2/K_{assoc} = (3.2\text{x}10^{-7})^2/40. = 2.56\text{x}10^{-15}$$

The equilibrium expression is then: $K_{a2}^2/K_{assoc} = \frac{(a_{CrO42-})^2(a_{H+})^2}{a_{Cr2O72-}}$

Assuming $a_{Cr2O72-} = a_{CrO42-} = 1.00$ gives the equilibrium H^+ activity as:

$$a_{H+} = \sqrt{K_{a2}^2/K_{assoc}} = 5.05\text{x}10^{-8} \quad \text{or} \quad pH = 7.30$$

Note the vertical line separating $Cr_2O_7^{2-}$ and CrO_4^{2-} in the chromium Pourbaix diagram in Problem 33 is at pH = 7.30.

36. Find the slopes of the cell potential versus pH for the reaction lines in the chromium Pourbaix diagram, Problem 33, for:

(a). $\mathrm{Cr(OH)_2\,(s) + 2\,H^+ + 2e^- \rightleftarrows Cr\,(s) + 2\,H_2O}$
(b). $\mathrm{Cr(OH)_3\,(s) + H^+ + 1\,e^- \rightarrow Cr(OH)_2\,(s) + H_2O}$

Qualitatively verify the relative magnitudes of the slopes shown in the diagram.

Answer: The plan is to start with the Nernst equation for the $\mathrm{Cr^{2+}}$, Cr couple for the first half-reaction and then the $\mathrm{Cr^{3+}}$, $\mathrm{Cr^{2+}}$ couple for the second half-reaction. The metal-ion activities are obtained using solubility equilibria, in the same way as Eqs. 21.4.17 and 21.4.16, respectively.
(a). For $\mathrm{Cr(OH)_2}$, the reduction half-reaction is $\mathrm{Cr^{2+} + 2e^- \rightarrow Cr\,(s)}$, with the Nernst equation:

$$E = E^{\circ}_{\mathrm{red}}(\mathrm{Cr^{2+},Cr}) - \frac{0.05917\ \mathrm{V}}{2} \log \frac{1}{a_{\mathrm{Cr2+}}} \tag{1}$$

The solubility and autoprotolysis equilibria are given by (see Problem 29):

$$\overset{K_{sp}(\mathrm{Cr(OH)_2})}{\mathrm{Cr(OH)_2\,(s) \rightleftarrows Cr^{2+} + 2\,OH^-}} \qquad\qquad \overset{K_w}{\mathrm{H_2O \rightleftarrows H^+ + OH^-}} \tag{2}$$

Reversing the autoprotolysis reaction and multiplying by two with addition to the solubility equilibrium gives the overall reaction:

$$\begin{array}{ll} \mathrm{Cr(OH)_2\,(s) \rightleftarrows Cr^{2+} + 2\,OH^-} & K = K_{sp}(\mathrm{Cr(OH)_2}) \\ \mathrm{2\,H^+ + 2\,OH^- \rightleftarrows 2\,H_2O} & K = 1/K_w^2 \\ \hline \mathrm{Cr(OH)_2\,(s) + 2\,H^+ \rightleftarrows Cr^{2+} + 2\,H_2O} & K_2 = K_{sp}(\mathrm{Cr(OH)_2})/K_w^2 \end{array} \tag{3}$$

The equilibrium expression is then:

$$K_2 = K_{sp}(\mathrm{Cr(OH)_2})/K_w^2 = \frac{a_{\mathrm{Cr2+}}}{(a_{\mathrm{H+}})^2} \qquad \text{with} \qquad a_{\mathrm{Cr2+}} = K_2\,(a_{\mathrm{H+}})^2 \tag{4}$$

Substitution of the $\mathrm{Cr^{2+}}$ activity into the Nernst equation, Eq. 1, gives:

$$E = E^{\circ}_{\mathrm{red}}(\mathrm{Cr^{2+},Cr}) - \frac{0.05917\ \mathrm{V}}{2} \log \frac{1}{K_2\,(a_{\mathrm{H+}})^2} \tag{5}$$

$$= \left[E^{\circ}_{\mathrm{red}}(\mathrm{Cr^{2+},Cr}) - \frac{0.05917\ \mathrm{V}}{2} \log 1/K_3\,\right] - \frac{0.05917\ \mathrm{V}}{2} \log \frac{1}{(a_{\mathrm{H+}})^2} \tag{6}$$

$$= E^{\circ}_{\mathrm{red}}(\mathrm{Cr(OH)_2,Cr}) - (0.05917\ \mathrm{V})\ \mathrm{pH} \tag{7}$$

The slope for the reduction of $\mathrm{Cr(OH)_2}$ is -0.05917 V.

(b). For $\mathrm{Cr(OH)_3}$, the reduction half-reaction is $\mathrm{Cr^{3+} + e^- \rightarrow Cr^{2+}}$ with the Nernst equation:

$$E = E^{\circ}_{\mathrm{red}}(\mathrm{Cr^{3+},Cr^{2+}}) - (0.05917\ \mathrm{V}) \log \frac{a_{\mathrm{Cr2+}}}{a_{\mathrm{Cr3+}}} \tag{8}$$

The activity of $\mathrm{Cr^{2+}}$ is given by Eq. 4. To obtain the activity of $\mathrm{Cr^{3+}}$, the solubility and autoprotolysis equilibria are given by (see Problem 30):

$$Cr(OH)_3\,(s) \overset{K_{sp}(Cr(OH)_3)}{\rightleftarrows} Cr^{3+} + 3\,OH^- \qquad H_2O \overset{K_w}{\rightleftarrows} H^+ + OH^- \qquad 9$$

Reversing the autoprotolysis and multiplying by three with addition to the solubility equilibrium gives the overall reaction:

$$\begin{array}{ll} Cr(OH)_3\,(s) \rightleftarrows Cr^{3+} + 2\,OH^- & K = K_{sp}(Cr(OH)_3) \\ 3\,H^+ + 3\,OH^- \rightleftarrows 3\,H_2O & K = 1/K_w^3 \\ \hline Cr(OH)_3\,(s) + 3\,H^+ \rightleftarrows Cr^{3+} + 3\,H_2O & K_3 = K_{sp}(Cr(OH)_3)/K_w^3 \end{array} \qquad 10$$

The equilibrium expression is then:

$$K_3 = K_{sp}(Cr(OH)_3)/K_w^3 = \frac{a_{Cr^{3+}}}{(a_{H^+})^3} \qquad \text{with} \qquad a_{Cr^{3+}} = K_3\,(a_{H^+})^3 \qquad 11$$

Substitution of the Cr^{2+} and Cr^{3+} activities, Eqs. 4 and 11, into the Nernst equation, Eq. 8, gives:

$$E = E^{\circ}_{red}(Cr^{3+},Cr^{2+}) - (0.05917\text{ V}) \log \frac{K_{sp}(Cr(OH)_2)/K_w^2\,(a_{H^+})^2}{K_{sp}(Cr(OH)_3)/K_w^3\,(a_{H^+})^3} \qquad 12$$

$$= \left[E^{\circ}_{red}(Cr^{3+},Cr^{2+}) - (0.05917\text{ V}) \log(K_w\,K_{sp}(Cr(OH)_2)/K_{sp}(Cr(OH)_3))\right] - (0.05917\text{ V}) \log \frac{1}{a_{H^+}}$$

$$= E^{\circ}_{red}(Cr(OH)_3,Cr(OH)_2) - (0.05917\text{ V})\text{ pH} \qquad 13$$

The slope for the reduction of $Cr(OH)_3$ to $Cr(OH)_2$ is –0.05917 V, which is the same as for $Cr(OH)_2$. Note in the chromium Pourbaix diagram in Problem 33, the slopes of the lines separating the $Cr(OH)_3$, $Cr(OH)_2$, and Cr (s) regions are equal and the dependence on pH is weak compared to the other pH dependent boundaries.

<u>37</u>. Calculate the equilibrium pH for the conversion of $Cr(OH)_3$ to $Cr(OH)_4^-$ with $a_{Cr(OH)_4^-} = 1.00$:

$$Cr(OH)_3\,(s) + OH^- \rightleftarrows Cr(OH)_4^-$$

Compare to the chromium Pourbaix diagram in Problem 33. Note the following solubility product and cumulative formation equilibrium constants:

$$\begin{array}{ll} Cr(OH)_3\,(s) \rightleftarrows Cr^{3+} + 3\,OH^- & K_{sp} = 1.6\text{x}10^{-30} \\ Cr^{3+} + 4\,OH^- \rightleftarrows Cr(OH)_4^- & K_4 = 8.\text{x}10^{29} \end{array}$$

Answer: The plan is to add the reactions and multiply the equilibrium constants.
Simply adding the given reactions gives:

$$\begin{array}{ll} Cr(OH)_3\,(s) \rightleftarrows Cr^{3+} + 3\,OH^- & K_{sp} = 1.6\text{x}10^{-30} \\ Cr^{3+} + 4\,OH^- \rightleftarrows Cr(OH)_4^- & K_4 = 8.\text{x}10^{29} \\ \hline Cr(OH)_3\,(s) + OH^- \rightleftarrows Cr(OH)_4^- & K = K_{sp}\,K_4 = 1.6\text{x}10^{-30}\; 8.\text{x}10^{29} = 1.28 \end{array}$$

The equilibrium expression is: $K_{sp}\,K_4 = \dfrac{a_{Cr(OH)_4^-}}{a_{OH^-}}$

For $a_{\mathrm{Cr(OH)_4^-}} = 1.00$ the hydroxide ion activity is: $a_{\mathrm{OH^-}} = \dfrac{1}{K_{sp}\,K_4} = 0.78$

The corresponding pH is 13.9, as shown in the Pourbaix diagram in Problem 33. The problem could also have been solved directly in terms of the hydrogen ion activity:

$$\begin{array}{ll} \mathrm{Cr(OH)_3\,(s) \rightleftarrows Cr^{3+} + 3\,OH^-} & K_{sp} = 1.6\mathrm{x}10^{-30} \\ \mathrm{Cr^{3+} + 4\,OH^- \rightleftarrows Cr(OH)_4^-} & K_4 = 8.\mathrm{x}10^{29} \\ \mathrm{H_2O \rightleftarrows H^+ + OH^-} & K_w = 1.008\mathrm{x}10^{-14} \\ \hline \mathrm{Cr(OH)_3\,(s) + H_2O \rightleftarrows Cr(OH)_4^- + H^+} & K = K_{sp}\,K_4\,K_w \end{array}$$

with the equilibrium expression: $K = K_{sp}\,K_4\,K_w = a_{\mathrm{Cr(OH)_4^-}}\,a_{\mathrm{H^+}}$

and $K_{sp}\,K_4\,K_w = 1.6\mathrm{x}10^{-30}\;8.\mathrm{x}10^{29}\;1.008\mathrm{x}10^{-14} = 1.29\mathrm{x}10^{-14}$

38. *Challenge Problem*: Find the slope of the cell potential vs. pH line for the reduction of $\mathrm{CrO_4^{2-}}$ to $\mathrm{Cr(OH)_4^-}$. Compare to the chromium Pourbaix diagram in Problem 33.

Answer: The plan is to write the Nernst equation for the $\mathrm{CrO_4^{2-}}$, $\mathrm{Cr(OH)_3}$ couple and then rearrange using the equilibrium expression for $\mathrm{Cr(OH)_3\,(s) + OH^- \rightleftarrows Cr(OH)_4^-}$.

The tabulated standard reduction half-cell in basic solution is:

$$\mathrm{CrO_4^{2-} + 4\,H_2O + 3e^- \rightarrow Cr(OH)_3\,(s) + 5\,OH^-} \qquad E^\circ_{red} = -0.12\text{ V}$$

giving the Nernst equation: $E = E^\circ_{red}(\mathrm{CrO_4^{2-}, Cr(OH)_3}) - \dfrac{0.05917\text{ V}}{3}\log\dfrac{(a_{\mathrm{OH^-}})^5}{a_{\mathrm{CrO_4^{2-}}}}$

The conversion from solid $\mathrm{Cr(OH)_3}$ to $\mathrm{Cr(OH)_4^-}$ is through the equilibria (see previous problem):

$$\begin{array}{ll} \mathrm{Cr(OH)_3\,(s) \rightleftarrows Cr^{3+} + 3\,OH^-} & K_{sp} = 1.6\mathrm{x}10^{-30} \\ \mathrm{Cr^{3+} + 4\,OH^- \rightleftarrows Cr(OH)_4^-} & K_4 = 8.\mathrm{x}10^{29} \\ \hline \mathrm{Cr(OH)_3\,(s) + OH^- \rightleftarrows Cr(OH)_4^-} & K = K_{sp}\,K_4 = 1.6\mathrm{x}10^{-30}\;8.\mathrm{x}10^{29} = 1.28 \end{array}$$

The corresponding equilibrium expression is: $K_{sp}\,K_4 = \dfrac{a_{\mathrm{Cr(OH)_4^-}}}{a_{\mathrm{OH^-}}}$

Solving this last equation for the hydroxide activity gives: $a_{\mathrm{OH^-}} = \dfrac{a_{\mathrm{Cr(OH)_4^-}}}{K_{sp}\,K_4}$

Substituting this expression for one of the hydroxide activities in the Nernst equation introduces the dependence on the $\mathrm{Cr(OH)_4^-}$ activity:

$$E = E^\circ_{red}(\mathrm{CrO_4^{2-}, Cr(OH)_3}) - \frac{0.05917\text{ V}}{3}\log\frac{a_{\mathrm{Cr(OH)_4^-}}\,(a_{\mathrm{OH^-}})^4}{K_{sp}\,K_4\,a_{\mathrm{CrO_4^{2-}}}}$$

Using $a_{\mathrm{OH^-}} = K_w/a_{\mathrm{H^+}}$ introduces the hydrogen ion activity:

$$E = E^\circ_{red}(\mathrm{CrO_4^{2-}, Cr(OH)_3}) - \frac{0.05917\text{ V}}{3}\log\frac{K_w^4\,a_{\mathrm{Cr(OH)_4^-}}}{K_{sp}\,K_4\,a_{\mathrm{CrO_4^{2-}}}(a_{\mathrm{H^+}})^4}$$

Separating out the pH dependent term gives:

$$E = E^\circ_{red}(CrO_4^{2-}, Cr(OH)_3) - \frac{0.05917\ V}{3}\log\frac{K_w^4\ a_{Cr(OH)_4^-}}{K_{sp}\ K_4\ a_{CrO_4^{2-}}} - \frac{4(0.05917\ V)}{3}\log\frac{1}{a_{H^+}}$$

$$= E^\circ_{red}(\ CrO_4^{2-}, Cr(OH)_3) - \frac{0.05917\ V}{3}\log\frac{K_w^4\ a_{Cr(OH)_4^-}}{K_{sp}\ K_4\ a_{CrO_4^{2-}}} - \frac{4(0.05917\ V)}{3}\ pH$$

The slope of the E_H vs. pH curve is then –4(0.05917 V)/3 = -0.0789 V, which is shown in the chromium Pourbaix diagram.

As noted in Problems 31 and 33, as a short-cut, the slope is given by –0.05917 n_p/z, where n_p is the number of protons in the balanced reaction as reactants. Starting with the balanced reaction in basic solution, converting $Cr(OH)_3$ to $Cr(OH)_4^-$, and adding H^+ ions to both sides gives:

$$\begin{array}{l} CrO_4^{2-} + 4\ H_2O + 3e^- \rightarrow Cr(OH)_4^- + 4\ OH^- \\ \qquad + 4\ H^+ \qquad\qquad\qquad\qquad + 4\ H^+ \\ \hline CrO_4^{2-} + 4\ H^+ + 3e^- \rightarrow Cr(OH)_4^-\ (s) \end{array}$$

giving $n_p/z = 4/3$. This last half-cell is a bit misleading, since it applies in basic solution where $a_{H^+} \cong 10^{-14}$, but the result is rigorous and useful for this purpose.

39. The construction of a Frost diagram is straight-forward from the Latimer diagram. The corresponding half-reactions are written with the number of electrons transferred equal to the change in oxidation state. For the nitrogen example, Figure 21.4.3:

Ox. States	Reaction	E°_{red} (V)	zE°_{red} (V) ref. to N_2
+5→+4	$NO_3^- + 2H^+ + e^- \rightarrow NO_2\ (g) + H_2O$	0.773	6.221
+4→+3	$NO_2\ (g) + H^+ + e^- \rightarrow HNO_2$	1.108	5.448
+3→+2	$HNO_2 + H^+ + e^- \rightarrow NO\ (g) + H_2O$	0.984	4.340
+2→+1	$NO\ (g) + H^+ + e^- \rightarrow \frac{1}{2}\ N_2O + \frac{1}{2}\ H_2O$	1.587	3.356
+1→ 0	$\frac{1}{2}\ N_2O + H^+ + e^- \rightarrow \frac{1}{2}\ N_2 + \frac{1}{2}\ H_2O$	1.769	1.769
0	$N_2\ (g)$	0	0
0→-1	$\frac{1}{2}\ N_2\ (g) + 2H^+ + H_2O + e^- \rightarrow NH_3OH^+$	-1.83	1.83
-1→-2	$NH_3OH^+ + \frac{1}{2}\ H^+ + e^- \rightarrow \frac{1}{2}\ N_2H_5^+ + H_2O$	1.40	0.43
-2→-3	$\frac{1}{2}\ N_2H_5^+ + {}^3/_2\ H^+ + e^- \rightarrow NH_4^+$	1.250	-0.82

Cell potentials don't add for a sequence of electron transfer reactions, but Gibbs energies do. For a given half-reaction i, $\Delta_r G^\circ_i = -z_i F E^\circ_{red,i}$. The sum starts with the element as the reference, with oxidation number i = 0. For species j with oxidation number z_j and standard reduction potential to the reference $E^\circ_{red,j}$, the sum of the half-cell Gibbs energies is equivalent to a sum of $z_i E^\circ_{red,i}$ values. With N_2 as the reference oxidation state:

$$z_j\ E^\circ_{red,j} = -\frac{\sum_{i=0}^{j} \Delta_r G^\circ_i}{F} = -\ (G^\circ_j - G^\circ_{N_2})/F = \sum_{i=0}^{j} z_i\ E^\circ_{red,i} \qquad (j > \text{reference})$$

In other words, the $z_i\, E^\circ_{red,i}$ values are added, starting at the element, as in the table above. The equation holds for oxidation numbers greater than the reference. For oxidation numbers less than the reference, the Gibbs energies of the given oxidation state and the reference are given in the opposite order from the sum:

$$\frac{\sum_{i=0}^{j} \Delta_r G^\circ_j}{F} = (G^\circ_{N_2} - G^\circ_j)/F \qquad (j < \text{reference})$$

because N_2 is on the reactant side of the reaction arrows instead of the product side. An overall negative sign is needed for the sum, as applied in the table above:

$$z_j\, E^\circ_{red,j} = -\,(G^\circ_j - G^\circ_{N_2})/F = -\sum_{i=0}^{j} z_i\, E^\circ_{red,i} \qquad (j < \text{reference})$$

The Latimer diagram for phosphorous at 25°C is given below.

$$\mathrm{H_3PO_4} \overset{-0.933\text{ V}}{\text{———}} \mathrm{H_4P_2O_6} \overset{0.380\text{ V}}{\text{———}} \mathrm{H_3PO_3} \overset{-0.499\text{ V}}{\text{———}} \mathrm{H_3PO_2} \overset{-0.508\text{ V}}{\text{———}} \mathrm{P_4} \overset{-0.063\text{ V}}{\text{———}} \mathrm{PH_3}$$

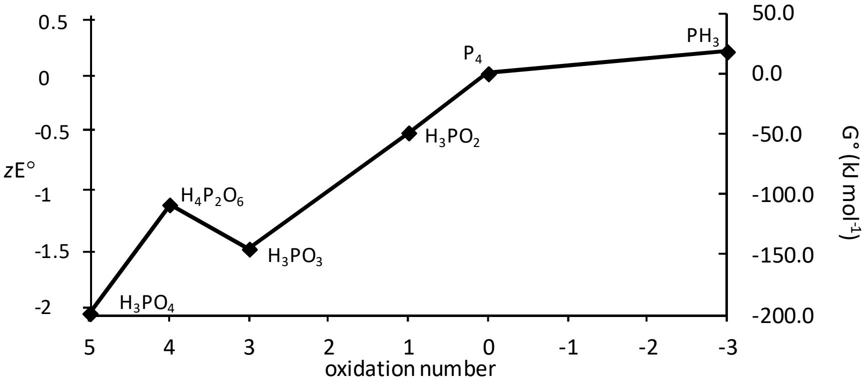
(a). Construct the Frost diagram.
(b). What is the most stable oxidation state for phosphorus under standard state conditions in aqueous solution?
(c). Which species are good reducing agents? What species can act as oxidizing agents?
(d). Which species are unstable with respect to disproportionation?

Answer: (a). The Latimer diagram and corresponding oxidation states are:[4]

$$\underset{(+5)}{\mathrm{H_3PO_4}} \overset{-0.933\text{ V}}{\text{———}} \underset{(+4)}{\mathrm{H_4P_2O_6}} \overset{0.380\text{ V}}{\text{———}} \underset{(+3)}{\mathrm{H_3PO_3}} \overset{-0.499\text{ V}}{\text{———}} \underset{(+1)}{\mathrm{H_3PO_2}} \overset{-0.508\text{ V}}{\text{————}} \underset{(0)}{\mathrm{P_4}} \overset{-0.063\text{ V}}{\text{————}} \underset{(-3)}{\mathrm{PH_3}}$$

The successive zE° values add starting from P_4 as the reference. The zE° and reaction Gibbs energies add as follows:

	ox. state	E_{red}° (V)	zE° (V)	G° (kJ mol^{-1})
H_3PO_4	5	-0.933	-2.059	-198.7
$H_4P_2O_6$	4	0.38	-1.126	-108.6
H_3PO_3	3	-0.499	-1.506	-145.3
H_3PO_2	1	-0.508	-0.508	-49.0
P_4	0	0	0	0.0
PH_3	-3	-0.063	0.189	18.2



(b). The most stable oxidation state for phosphorus under standard state conditions in aqueous solution is +5, for H_3PO_4.
(c). All species except for H_3PO_4 are good reducing agents. Phosphorus acid can act as a reducing agent if H_3PO_4 is the product. The only species that can act as an oxidizing agent is pyrophosphorous acid, $H_4P_2O_6$, but only with H_3PO_3 as a product.
(d). Using the Latimer diagram, $H_4P_2O_6$ and P_4 are unstable with respect to disproportionation. The Frost diagram can also be used for the prediction. If the *z*E° value for a species lies above the line joining the adjacent oxidized and reduced forms, then the species is unstable with respect to disproportionation. The *z*E° value for $H_4P_2O_6$ lies above the line joining the values for H_3PO_4 and H_3PO_3, making $H_4P_2O_6$ unstable with respect to disproportionation. The *z*E° value for P_4 lies above the line joining the values for H_3PO_2 and PH_3, making P_4 unstable with respect to disproportionation.

<u>40</u>. The Latimer diagram for carbon at pH 7 and 25°C is shown below.[4] Draw the Frost diagram for carbon. The zE° and chemical potential of the element is usually set to zero, as the reference. However, since elemental carbon will not appear in your diagram, use CO_2 as the reference.

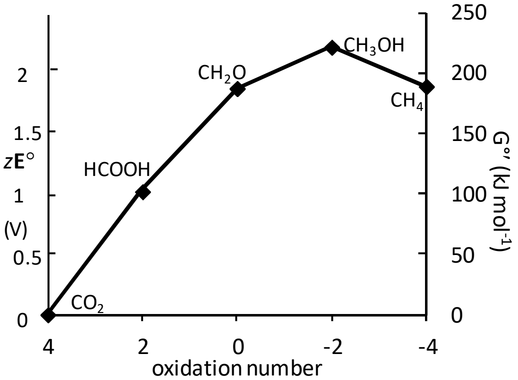
-0.486 V -0.004 V
-0.528 V -0.443 V -0.177 V 0.169 V
CO_2 (g) —— HCOOH —— CH_2O —— CH_3OH —— CH_4 (g)
-0.383 V
-0.2448 V

Answer: The oxidation states are determined for each species as:

-0.486 V -0.004 V
-0.528 V -0.443 V -0.177 V 0.169 V
CO_2 (g) —— HCOOH —— CH_2O —— CH_3OH —— CH_4 (g)
(+4) (+2) (0) (-2) (-4)
-0.383 V
-0.2448 V

The Gibbs energy for CO_2 is set to 0 kJ mol^{-1}. The sums and plot are completed in the following spreadsheet:

	oxid. state	$E^{\circ\prime}_{red}$	$zE^{\circ\prime}$ (V)	$G^{\circ\prime}$ (kJ mol^{-1})
CO_2 (g)	4	0	0	0
HCOOH	2	-0.528	1.056	101.9
CH_2O	0	-0.443	1.943	187.5
CH_3OH	-2	-0.177	2.297	221.6
CH_4 (g)	-4	0.169	1.960	189. 1



For example, the values for acetaldehyde, CH_2O, are given by:

$$-\Sigma z_i E_i^{\circ\prime} = 0 + 2(0.528 \text{ V}) + 2(0.443 \text{ V}) = 1.943 \text{ V}$$

$$G^{\circ\prime}_{CH_2O} = F\,(-\Sigma z_i E_i^{\circ\prime}) = 96485(1.943 \text{ V}) = 187.5 \text{ kJ mol}^{-1}$$

CO_2 has the minimum chemical potential of carbon containing species. Any chemical conversions of CO_2 require the input of energy. CO_2 is at the bottom of the chemical reactivity ladder. The conversion of CO_2 to acetaldehyde, CH_2O, is representative of the process of photosynthesis (see the next problem).

41. The Latimer diagram for carbon is given in the previous problem. In this problem, we make the connection between biological processes and the corresponding redox potentials. Acetaldehyde, CH_2O, and glucose have the same empirical formula; glucose is $(CH_2O)_6$. Cell potentials and reaction Gibbs energies for acetaldehyde are representative of glucose and glucose polymers, on a per carbon atom basis. Similarly, formic acid, HCOOH, and methanol, CH_3OH, are representative of organic acids and alcohols, respectively, on a per carbon atom basis. Use the standard reduction potentials in the Latimer diagram for carbon to find the half-cell potentials and reaction Gibbs energies at pH 7 for the following representative biological processes, written as reduction half-cells:

(a). Methane fermentation: $CO_2\ (g) + 8\ H^+ + 8\ e^- \rightarrow CH_4\ (g) + 2\ H_2O$
(b). Fermentation: $CH_2O\ (l) + 4\ H^+ + 4\ e^- \rightarrow CH_3OH\ (l)$
(c). Photosynthesis: $CO_2\ (g) + 4\ H^+ + 4\ e^- \rightarrow CH_2O(\ l)$

Answer: The half-cell potentials are directly given by individual steps in the Latimer diagram:

(a). Methane fermentation: $CO_2\ (g) + 8\ H^+ + 8\ e^- \rightarrow CH_4\ (g) + 2\ H_2O$
$E^{\circ\prime}_{red} = -0.2448$ V $\qquad \Delta_r G^{\circ\prime} = -zFE^{\circ\prime}_{red} = -189.0$ kJ mol^{-1}

(b). Alcoholic fermentation: $CH_2O\ (l) + 4\ H^+ + 4\ e^- \rightarrow CH_3OH\ (aq)$
$E^{\circ\prime}_{red} = -0.177$ V $\qquad \Delta_r G^{\circ\prime} = -zFE^{\circ\prime}_{red} = -68.31$ kJ mol^{-1}

(c). Photosynthesis: $CO_2\ (g) + 4\ H^+ + 4\ e^- \rightarrow CH_2O\ (aq)$

$$E^{\circ\prime}_{red} = -0.486\ V \qquad \Delta_r G^{\circ\prime} = -zFE^{\circ\prime}_{red} = -188.0\ kJ\ mol^{-1}$$

In biological systems, these reactions are catalyzed by microbes, and in the case of photosynthesis by photosynthetic microbes and plants.

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4. S. G. Bratsch, "Standard Electrode Potentials and Temperature Coefficients in Water at 298 K," *J. Phys. Chem. Ref. Data*, **1989**, *18(1)*, 1-20.

Chapter 22 Problems: Linear Non-equilibrium Thermodynamics

1. For a closed system and PV work only, describe why the second, lost-work term in Eq. 22.1.5 always gives the change in entropy production as greater than zero for an isothermal process (established by contact of the system with the surroundings acting as a constant temperature bath).

Answer: The plan is to apply the reasoning in Sec. 13.1 to Eq. 22.1.5:

$$\frac{dS_{tot}}{dt} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right)\frac{đq}{dt} + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right)\frac{dV}{dt}$$

The second term involving P, P_{ext}, and V relates the pressure of the system, P, to the external pressure, P_{ext}. The difference in pressure, $P - P_{ext}$, is the pressure gradient between the system and the surroundings. This PV term is always positive for a spontaneous process. For an isothermal process, with the system in contact with the surroundings acting as a constant temperature reservoir, $T = T_{surr}$ giving the first term as zero. Assume the pressure of the system is greater than the external pressure. The pressure gradient is then positive, $P - P_{ext} > 0$. Our experience shows that the system will expand in a spontaneous process giving $dV > 0$. The product of $(P - P_{ext})/T$ and dV is positive. Now, consider a process with the system pressure less than the external pressure, $P < P_{ext}$. The system will contract in a spontaneous process giving $dV < 0$. However, the pressure gradient is also negative, $P - P_{ext} < 0$, so the product of $(P - P_{ext})/T$ and dV is still positive. In either case, the entropy increases for these spontaneous isothermal processes, $dS > 0$. On the other hand, if the system pressure and the external pressure are equal, the pressure gradient is zero and the entropy change is zero, $dS = 0$, for an isothermal process. With no pressure gradient, the system is at equilibrium and no process occurs.

The second term is often called the **lost work** term. The PdV portion gives the work done by a reversible process. The $P_{ext}dV$ portion gives the actual work done by the spontaneous process. The difference, $PdV - P_{ext}dV$, is always positive. The difference is the lost work between the reversible and real process. In other words, to "pay" for an increase in entropy, some work is lost.

2. Reproduce Figure 22.1.1. Use the parameters in the caption and assume that the heat capacity of coffee is that of pure water. Assume a density of 1.00 g mL^{-1}.

Answer: The plan is to use Eq. 7.2.18 to find the temperature difference and Eq. 22.1.7 to find the entropy production as a function of time.

For convenience in the following table the entropy production is converted to mJ K^{-1} s^{-1} to enable a common axis with ΔT. The formula for the temperature difference in D10 is:

=($D$6-$G$6)*EXP(-$G$4/$G$3*C10)

The formula for the entropy production in E10 is:

=$G$4*($D$6-$G$6)^2/$G$6^2*EXP(-2*$G$4/$G$3*C10)*1000

The total entropy is determined by finite difference integration. F9 is set to zero. F10 is:

=F9+E9*(C10-C9)/1000

where E9 is the height of the current "rectangle" and C10-C9 is the width of the rectangle and the integral is the sum of the areas of the preceding rectangles. F11 and subsequent cells in the column continues the pattern: F11 is:

=F10+E10*(C11-C10)/1000

A1	B	C	D	E	F	G	H
2							
3		$\mathcal{K}$	1.14	J s^{-1} K^{-1} m^{-1}	Cp	836.8	J K^{-1}
4		$\mathcal{A}$	0.015	m^2	$\mathcal{K}\mathcal{A}/\delta$	5.7	J $K^{-1}s^{-1}$
5		δ	3.00E-03	m			
6		T_o	310	K	T_{surr}	298	K
7							
8	t (min)	t (sec)	ΔT (K)	dS_{tot}/dt (mJ K^{-1} s^{-1})	S_{tot} (J K^{-1})		
9	0	0	12.000	9.243	0.000		
10	0.5	30	9.782	6.142	0.277		
11	1	60	7.974	4.081	0.462		
12	1.5	90	6.500	2.712	0.584		
13	2	120	5.299	1.802	0.665		
14	2.5	150	4.320	1.198	0.719		
15	3	180	3.521	0.796	0.755		
16	3.5	210	2.870	0.529	0.779		
17	4	240	2.340	0.351	0.795		

5. With reference to Table 13.7.1, evaluate the entropy production for isothermal reversible, isothermal irreversible, adiabatic reversible, adiabatic irreversible, and a constant pressure expansion of an ideal gas. For the irreversible expansions, assume a constant external pressure, P_{ext}. Assume a closed system with no chemical reactions. In each case, specify the forces and fluxes that are zero in each case.

Answer: Consider first dS_{tot} and the overall change in the total entropy for a process. The forces are determined by the temperature and pressure gradients. The processes are summarized in the table below.

For an isothermal process the temperature gradient is zero: $\left(\frac{1}{T} - \frac{1}{T_{surr}}\right) = 0$

For an adiabatic process, $đq = 0$ and the heat flux is then zero, $đq/dt = 0$.

For a reversible process, $P = P_{ext}$ and the pressure gradient is zero: $\left(\frac{P}{T} - \frac{P_{ext}}{T}\right) = 0$

For an isothermal expansion of an ideal gas against a constant external pressure, $P/T = nR/V$:

$$dS_{tot} = \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) dV = \frac{P}{T}\,dV - \frac{P_{ext}}{T}\,dV = \frac{nR}{V}\,dV - \frac{P_{ext}}{T}\,dV$$

and the PV work term integrates for an overall process to give:

$$\int dS_{tot} = \int_{V_1}^{V_2} \frac{nR}{V}\,dV - \int_{V_1}^{V_2} \frac{P_{ext}}{T}\,dV = nR \ln\frac{V_2}{V_1} - \frac{P_{ext}\Delta V}{T} \qquad \text{(isothermal, } P = P_{ext}\text{)}$$

For an adiabatic expansion of an ideal gas against a constant external pressure, $dU = đw$. For any process in an ideal gas $dU = C_v dT$. Then for a constant external pressure, $C_v\,dT = -\,P_{ext}\,dV$. Solving for dV:

$$dV = -\frac{C_v}{P_{ext}}\,dT$$

Using this last equation and P/T = nR/V in the entropy production gives:

$$dS_{tot} = \left(\frac{P}{T} - \frac{P_{ext}}{T}\right) dV = \frac{P}{T}\,dV - \frac{P_{ext}}{T}\,dV = \frac{P}{T}\,dV - \frac{C_v}{P_{ext}}\frac{P_{ext}}{T}\,dT = \frac{P}{T}\,dV - \frac{C_v}{T}\,dT$$

Integrating gives: $\Delta S_{tot} = nR \ln\frac{V_2}{V_1} + C_v \ln\frac{T_2}{T_1}$ (irr.adiabatic)

Finally for the last process, a constant pressure expansion for a change in temperature from T_1 to T_2, the pressure gradient is zero leaving:

$$dS_{tot} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right) đq$$

For an ideal gas at constant pressure $đq = đq_p = C_p\,dT$ giving:

$$dS_{tot} = \left(\frac{C_p}{T} - \frac{C_p}{T_{surr}}\right) dT$$

Integrating the result for a constant T_{surr} gives:

$$\Delta S_{tot} = \int_{T_1}^{T_2} \frac{C_p}{T}\,dT - \int_{T_1}^{T_2} \frac{C_p}{T_{surr}}\,dT = C_p \ln\frac{T_2}{T_1} - \frac{C_p}{T_{surr}}\Delta T \qquad (\text{cst. } P = P_{ext})$$

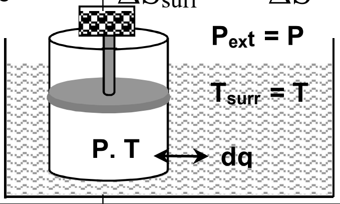
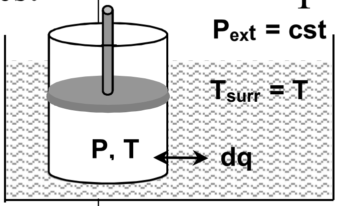
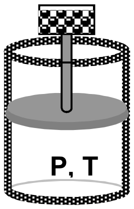
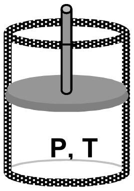
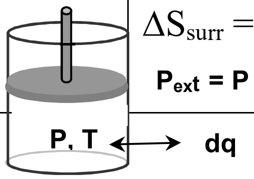
For the entropy production, instead of integrating over the complete process, the evolution of entropy is followed as a function of time:

$$\frac{dS_{tot}}{dt} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right)\frac{đq}{dt} + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right)\frac{dV}{dt}$$

The result depends on the heat flux as a function of time and the volume change as a function of time. However, the final results are the same as given in the table and as derived above. Reversible processes give no entropy production. For an adiabatic process the heat flux is zero. For constant volume processes in closed systems the entropy production is entirely from the heat flux.

Entropy and the Surroundings – Ideal Gas

System	Surroundings	Universe $dS_{univ} = dS + dS_{surr}$
$dS = \frac{dU}{T} + \frac{P}{T}dV$	$dS_{surr} = -\frac{dq}{T_{surr}}$	$dS_{tot} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right)đq + \left(\frac{P}{T} - \frac{P_{ext}}{T}\right)dV$
$\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ $\Delta S = C_P \ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$	$\Delta S_{surr} = -\frac{q}{T_{surr}}$	$\Delta S_{tot} = \Delta S + \Delta S_{surr}$

System	Surroundings	Universe $dS_{univ} = dS + dS_{surr}$
Isothermal reversible $T = T_{surr}$ $\Delta S = nR\ln\frac{V_2}{V_1}$	$\Delta S_{surr} = -\Delta S$  	$\Delta S_{tot} = 0$ $dS_{tot} = \left(\frac{1}{T} - \cancelto{0}{\frac{1}{T_{surr}}}\right)đq + \left(\frac{P}{T} - \cancelto{0}{\frac{P_{ext}}{T}}\right)dV$
Isothermal irreversible $T = T_{surr}$ $P_{ext} = cst$ $\Delta S = nR\ln\frac{V_2}{V_1}$	$\Delta S_{surr} = -\frac{P_{ext}\Delta V}{T}$  	$\Delta S_{univ} = nR\ln\frac{V_2}{V_1} - \frac{P_{ext}\Delta V}{T}$ $dS_{tot} = \left(\frac{1}{T} - \cancelto{0}{\frac{1}{T_{surr}}}\right)đq + \left(\frac{P}{T} - \overset{\nwarrow}{\frac{P_{ext}}{T}}\right)dV$
Adiabatic reversible $\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ $= 0$	$\Delta S_{surr} = 0$  	$\Delta S_{tot} = 0$ $dS_{tot} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right)\cancelto{0}{đq} + \cancelto{0}{\left(\frac{P}{T} - \frac{P_{ext}}{T}\right)}dV$
Adiabatic irreversible $P_{ext} = cst$ $\Delta S = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ $C_V (T_2 - T_1) = -P_{ext}(V_2 - V_1)$	$\Delta S_{surr} = 0$  	$\Delta S_{tot} = C_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$ $dS_{tot} = \left(\frac{1}{T} - \frac{1}{T_{surr}}\right)\cancelto{0}{đq} + \left(\frac{P}{T} - \overset{\nwarrow}{\frac{P_{ext}}{T}}\right)dV$ $dV = -\frac{C_v}{P_{ext}}dT$
Constant $P = P_{ext}$ $\Delta S = C_P \ln\frac{T_2}{T_1}$  	$\Delta S_{surr} = -\frac{C_P\Delta T}{T_{surr}}$	$\Delta S_{tot} = C_P \ln\frac{T_2}{T_1} - \frac{C_P\Delta T}{T_{surr}}$