Problem 1.4. "Twice as hot" on the Celsius (or Fahrenheit) scale would make no sense, because the zero point is chosen arbitrarily. There's no fundamental sense, for instance, in which 2°C is twice as hot as 1°C. But if we measure temperatures from absolute zero, then "twice as hot" makes perfect sense: the melting point of lead is twice room temperature; the sun's surface is 20 times room temperature; and so on. This is another good reason to use kelvin temperatures.

Problem 1.5. I was taught to leave the thermometer in my mouth for at least three minutes. However, the bulb of the thermometer must come most of the way up to body temperature within 10 or 20 seconds; waiting three minutes is necessary only because we want a reading that is accurate to within a fraction of a degree. The numerical value of the "relaxation time" could therefore be anywhere from 10 or 20 seconds to three minutes, depending on exactly how we define it.

Problem 1.6. On a cold morning, when I step from the bathroom rug into the tub for my shower, the tub feels a lot colder to my feet than the rug. Yet they must be at essentially the same temperature, since they've been right next to each other all night long in a room that is pretty well insulated from the weather. In fact the rug is just as cold as the tub, but it sucks heat out of my feet much more slowly due to its relatively poor thermal contact and low heat capacity. For another example, see the quote on page 48.

Problem 1.7. (Thermal expansion of liquids.)

(a) The mercury thermometer from my medicine cabinet has a roughly cylindrical bulb that measures 4 mm in diameter by 5 mm long. Its volume is therefore about 60 mm^3. Under a 1°C temperature increase, this much mercury should increase in volume by

$$\Delta V = \beta \cdot V \cdot \Delta T = (1.81 \times 10^{-4}\ \mathrm{K}^{-1})(60\ \mathrm{mm}^3)(1\ \mathrm{K}) = 0.011\ \mathrm{mm}^3.$$

The expansion, however, takes place inside a narrow tube with a length of 8.5 mm (the length of a 1°C increment on the scale) and unknown cross-sectional area. Assuming that the tube is cylindrical, its radius would have to be

$$r = \sqrt{\frac{\Delta V}{\pi \ell}} = \sqrt{\frac{0.011\ \mathrm{mm}^3}{\pi (8.5\ \mathrm{mm})}} = 0.02\ \mathrm{mm},$$

so its diameter would be only 0.04 mm. No wonder it's so hard to see the column of mercury, even with the optical magnification of the glass!

(b) As the water in a lake cools, the densest water will sink to the bottom and the less dense water will rise to the top. Below 4°C, this means that the *warmer* water will sink while the *cooler* water rises. The first water to freeze will therefore be at the top; and since ice is even less dense, the ice floats on the surface. This ice then insulates the rest of the water from the cold weather, so even during a long, cold winter, only the smallest ponds freeze completely from top to bottom.

If the thermal expansion coefficient of water were always positive, then the coldest water in a lake would always be at the bottom, so ice would form first at the bottom.

If ice were also more dense than liquid water, the lake would freeze from the bottom up. Without the insulating layer of ice on top, many lakes would freeze completely, and any fish in these lakes would be frozen along with them. (If ice were still less dense than water, I suppose bits of ice would form at the bottom and then float to the surface.)

Problem 1.8. (Thermal expansion of solids.)

(a) Let's say the annual temperature extremes are −30 and +40 Celsius, for a total variation of 70 K. Under this variation, the change in length of a 1-km steel bridge would be

$$\Delta L = \alpha L\, \Delta T = (1.1 \times 10^{-5}\ \mathrm{K}^{-1})(1000\ \mathrm{m})(70\ \mathrm{K}) = 0.77\ \mathrm{m} = 77\ \mathrm{cm}.$$

To be safe, I'd design the bridge to accomodate at least a meter of thermal expansion.

(b) The two metals in the coil have different thermal expansion coefficients, so as the temperature increases, one expands more than the other, causing the coil to coil further and turn.

(c) Imagine a rectangular solid with dimensions L_x, L_y, and L_z. When the temperature increases, the solid expands in all three dimensions:
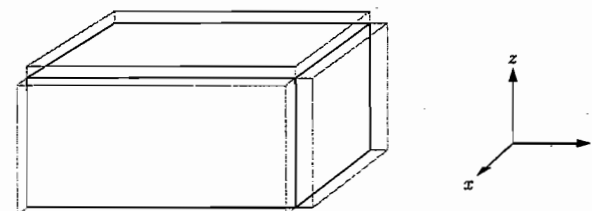
Assuming that the expansion is infinitesimal, we consider it to be equivalent to adding the three shaded slabs to the volume of the solid, neglecting the corner strips omitted from the diagram. Then the volume increase is

$$\Delta V = (\Delta L_x)L_y L_z + (\Delta L_y)L_x L_z + (\Delta L_z)L_x L_y.$$

Writing each ΔL in terms of the appropriate linear expansion coefficient, this becomes

$$\Delta V = (\alpha_x L_x\, \Delta T)L_y L_z + (\alpha_y L_y\, \Delta T)L_x L_z + (\alpha_z L_z\, \Delta T)L_x L_y$$
$$= (\alpha_x + \alpha_y + \alpha_z)V\, \Delta T.$$

Comparing to the definition of the volume expansion coefficient β, we see that this result has the same form, with $\beta = \alpha_x + \alpha_y + \alpha_z$.

Alternatively, we can rewrite the definitions of α and β in terms of derivatives:

$$\alpha = \frac{1}{L}\frac{dL}{dT}; \qquad \beta = \frac{1}{V}\frac{dV}{dT}.$$

(Technically, these should be partial derivatives, with pressure held fixed.) With the aid of the product rule, the derivation is now nothing but symbol-pushing:

$$\beta = \frac{1}{V}\frac{dV}{dT} = \frac{1}{V}\frac{d}{dT}(L_x L_y L_z) = \frac{1}{V}\left[\frac{dL_x}{dT}L_y L_z + \frac{dL_y}{dT}L_x L_z + \frac{dL_z}{dT}L_x L_y\right]$$

$$= \frac{1}{V}\left[(\alpha_x L_x)L_y L_z + (\alpha_y L_y)L_x L_z + (\alpha_z L_z)L_x L_y\right]$$

$$= \frac{1}{V}\left[\alpha_x + \alpha_y + \alpha_z\right]L_x L_y L_z = \alpha_x + \alpha_y + \alpha_z.$$

Problem 1.9. For a mole of air at room temperature and atmospheric pressure,

$$V = \frac{nRT}{P} = \frac{(1\ \text{mol})(8.31\ \text{J/mol·K})(300\ \text{K})}{10^5\ \text{N/m}^2} = 0.025\ \text{m}^3 = 25\ \text{liters}.$$

Problem 1.10. Consider an "average" room measuring 4 meters square by 3 meters high. The number of air molecules (at room temperature and atmospheric pressure) is

$$N = \frac{PV}{kT} = \frac{(10^5\ \text{N/m}^2)(4\ \text{m})(4\ \text{m})(3\ \text{m})}{(1.38 \times 10^{-23}\ \text{J/K})(300\ \text{K})} = 1.2 \times 10^{27} \approx 10^{27}.$$

(That's about 2000 moles.)

Problem 1.11. Since the rooms are connected by an open door, the pressure must be the same in each room; if it weren't, air would rush from one room into the other. Also we're told that the volume of each room is the same. Now look at the ideal gas law: $PV = NkT$. The left-hand-side is the same for both rooms, so Room B, which has a smaller T, must have a *larger* N, hence a larger mass of air.

Problem 1.12. The volume per molecule for an ideal gas at room temperature and atmospheric pressure is

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23}\ \text{J/K})(300\ \text{K})}{10^5\ \text{N/m}^2} = 4.1 \times 10^{-26}\ \text{m}^3 = 41\ \text{nm}^3.$$

If we imagine each molecule being in a cube of this volume, then the width of the cube would be the cube root of this number, 3.5 nm. This is then a good estimate of the average distance between neighboring molecules. The diameter of a molecule like N_2 or H_2O, on the other hand, is only a few ångstroms, about ten times smaller than this average distance.

Problem 1.13. In each case we merely need to determine the total number of protons plus neutrons in one molecule (or for the solids, one atom). Since a mole of protons or neutrons has a mass of one gram, this same number is the mass of the sample in grams.

(a) Water is H_2O; each hydrogen atom has just a single proton while the oxygen has 8 protons and 8 neutrons, so we have 18 nucleons total, and a mole of water therefore has a mass of 18 grams.

(b) Each nitrogen atom has 7 protons and 7 neutrons, so an N_2 molecule has 28 nucleons and a mole of them therefore has a mass of 28 grams.

(c) The atomic mass of lead is 207 (a weighted average over several common isotopes), so a mole of lead has a mass of 207 g.

(d) A quartz "molecule" has 28 nucleons in the silicon atom and 32 in the two oxygen atoms, for a total of 60, so a mole of quartz has a mass of 60 g.

Problem 1.14. For a mole of pure N_2, the mass would be 28 g; for O_2, the mass would be 32 g; and for Ar, the mass would be 40 g. For the mixture found in dry air, therefore, the mass would be the weighted average:

$$M = (0.78)(28\ g) + (0.21)(32\ g) + (0.01)(40\ g) = 28.96\ g \approx 29.0\ g.$$

Problem 1.15. The upward buoyant force on the balloon is equal to the weight of the air displaced. Assuming that this force is approximately in balance with gravity, we can write

$$\rho_0 V g = (M + \rho V)g \qquad \text{or} \qquad \rho_0 - \rho = M/V,$$

where ρ_0 is the density of the surrounding air, V is the volume of the balloon, and M is the mass of the unfilled balloon and payload, and ρ is the density of the air inside the balloon. According to the ideal gas law, the density of air is

$$\rho = \frac{mn}{V} = \frac{mP}{RT},$$

where m is the mass of one mole of air (29 g, as shown in the previous problem). This formula applies either inside or outside the balloon, with the same pressure in both places but different temperatures. Therefore the balance of forces implies

$$\frac{mP}{RT_0} - \frac{mP}{RT} = \frac{M}{V},$$

where T is the temperature inside the balloon and T_0 is the temperature outside. A bit of algebra then yields

$$\frac{1}{T} = \frac{1}{T_0} - \frac{M}{m}\frac{R}{PV}.$$

Let's assume an outside air temperature of 290 K, and atmospheric pressure. The volume of the balloon can be estimated from Figure 1.1: Comparing to the heights of the people standing underneath, I estimate the balloon in the foreground to have a diameter of about 50 feet or 15 meters, and therefore a volume of $\frac{4}{3}\pi r^3 = 1770\ \text{m}^3$. The mass of the unfilled balloon and payload is assumed to be 500 kg, so the previous expression evaluates to

$$\frac{1}{T} = \frac{1}{290\ \text{K}} - \frac{500\ \text{kg}}{0.029\ \text{kg}}\frac{8.31\ \text{J/K}}{(10^5\ \text{N/m}^2)(1770\ \text{m}^3)} = \frac{1}{290\ \text{K}} - \frac{1}{1235\ \text{K}} = \frac{1}{379\ \text{K}}.$$

Thus the temperature inside the balloon must be about 379 K or just over 100°C. (Thanks to Chuck Niederriter for informing me that this is indeed a typical operating temperature.) Assuming this temperature, the mass of the air inside the balloon should be roughly

$$M_{\text{air}} = mn = \frac{mPV}{RT} = \frac{(0.029\ \text{kg})(10^5\ \text{N/m}^2)(1770\ \text{m}^3)}{(8.31\ \text{J/K})(379\ \text{K})} = 1600\ \text{kg},$$

more than three times the mass of the unfilled balloon and payload!

Problem 1.16. (The exponential atmosphere.)
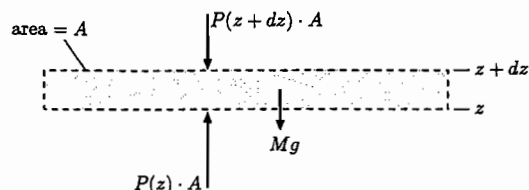
(a) Mechanical equilibrium requires that the vertical forces balance:

$$P(z+dz) \cdot A + Mg = P(z) \cdot A, \quad \text{or} \quad P(z+dz) - P(z) = -\frac{Mg}{A},$$

where A is the area of the slab and M is its total mass. Plugging in $M = \rho A\, dz$, canceling the A's, and dividing through by dz gives

$$\frac{P(z+dz) - P(z)}{dz} = -\rho g \quad \text{or} \quad \frac{dP}{dz} = -\rho g.$$

(b) The density of the gas is $\rho = M/V = Nm/V = Pm/kT$, where m is the average molecular mass and in the last step I've used the ideal gas law. Thus the differential equation becomes

$$\frac{dP}{dz} = -\frac{mg}{kT} P.$$

(c) The function $P(z)$ is one whose derivative is some constant (namely $-mg/kT$) times itself. The function Ae^{az} has this property, where $a = -mg/kT$ and A is an arbitrary constant whose interpretation is the value of P when $z = 0$ (since $e^0 = 1$). Thus the solution is

$$P(z) = P(0)\, e^{-mgz/kT}.$$

The density $\rho(z)$ is just m/kT times $P(z)$, so it has the same exponential form with a different constant out in front. The constant, $P(0) \cdot m/kT$, must be $\rho(0)$ because the exponential again equals 1 at $z = 0$.

(d) I'll take $z = 0$ at sea level so that $P(0) = 1$ atm. I'll also take $T = 280$ K as an average temperature at the locations given. Air is 80% nitrogen (N_2), so the mass of a molecule in kilograms is about $.028/N_A$, hence the quantity kT/mg is roughly $RT/(.028 \text{ kg})(9.8 \text{ N/kg}) = 8500$ meters or about 28,000 feet. (This is the height at which the pressure has fallen to $1/e$ atmospheres.) Plugging in the elevations given, I find for Ogden (4700 feet), $P = e^{-.17}$ atm $= .84$ atm; Leadville (10500 feet), $P = .69$ atm; Mt. Whitney (14,500 feet), $P = .59$ atm; Mt. Everest (29,000 feet), $P = .35$ atm.

Problem 1.17. (The virial expansion.)

(a) Truncating the virial expansion after the second term, we have

$$PV = nRT\left(1 + \frac{B(T)}{(V/n)}\right).$$

For given values of P, T, and B, this is a quadratic equation for V/n. However, it is reasonable to assume that the second term on the right-hand side is small compared to the first, so we can find V/n accurately enough from the ideal gas law. At 100 K and 1 atm,

$$\frac{V}{n} = \frac{RT}{P} = \frac{(8.315 \text{ J/mol} \cdot \text{K})(100 \text{ K})}{1.013 \times 10^5 \text{ Pa}} = 0.00823 \text{ m}^3/\text{mol}.$$

Therefore the correction term under these conditions is

$$\frac{B(T)}{V/n} = \frac{-160 \times 10^{-6} \text{ m}^3/\text{mol}}{0.00823 \text{ m}^3/\text{mol}} = -0.019.$$

In other words, the volume of the gas is about 2% less than the ideal gas law would predict (or at a given volume, the pressure is 2% less). Repeating the calculation for the other temperatures, I find:

T	$B/(V/n)$
100	-0.019
200	-0.0021
300	-0.00017
400	$+0.00027$
500	$+0.00041$
600	$+0.00043$

Notice that at reasonably high temperatures, the correction to the ideal gas law is less than one part in a thousand (at atmospheric pressure).

(b) Attractive forces between molecules should reduce the pressure of a gas, yielding a negative second virial coefficient, while repulsive forces should increase the pressure, leading to a positive second virial coefficient. Apparently the forces between molecules can be either attractive or repulsive, with attractive forces dominating at low temperatures and repulsive forces dominating at high temperatures. Does this make sense? I think so. Molecules attract each other weakly when they're close but not "touching." At low temperatures, they'll be moving slowly enough for this attraction to have a significant effect on the pressure. But when molecules collide head-on, they repel each other strongly. At high temperatures, when the molecules are moving very fast, this should be the more significant effect.

(c) Solving the van der Waals equation for P, then factoring out nRT/V on the right-hand side, puts it into the form

$$PV = nRT\left(\frac{1}{1 - nb/V} - \frac{an}{RTV}\right).$$

Problem 1.27. Temperature increase with no heat added: The resistor in the previous problem provides an example; it gets hot as the battery supplies energy in the form of work (not heat). Other examples would be "heating" a cup of tea in the microwave, or compressing air to pump up a bicycle tire, or simply rubbing your hands together. Heat input with no increase in temperature: I can think of two types of examples. The first is a phase change, like boiling a pot of water on the stove. Heat is constantly flowing in, but the temperature of the water remains at 100°C (or at whatever the boiling temperature is at your altitude). The second type of example is when the system does work on its surroundings to compensate for the energy put in as heat. For instance, you could have a gas in a cylinder with a flame under it, while letting the piston out fast enough that the gas actually cools.

Problem 1.28. Let's say we have 200 g of water, initially at 20°C. Then the total energy required to bring it to 100° is (200)(80) calories or 67,000 J. The microwaves pump in 600 J per second, so the total time required should be (67,000 J)/(600 J/s) = 110 seconds, or about two minutes. (This coincides roughly with my experience.)

There is no heat involved in this process because heat is a spontaneous flow of energy from a hot object to a cold object. In this case there is no hotter object from which heat is flowing into the water. (If anything, heat is flowing *out* of the water into the cup and the surrounding air.) The transfer of energy from the magnetron into the water is classified as electromagnetic *work*.

Problem 1.29. The 5° temperature increase of the water requires the input of energy: specifically, 5 calories per gram, or 1000 calories total (4200 J). This energy *could* have entered as heat, but it also could have entered as work, for instance, by someone vigorously stirring or shaking the water. So the answer is that I can conclude *nothing* about how much heat was added to the water. (Probably the amount of heat added was no greater than 1000 cal, since there's no easy way for the water to *lose* energy by doing work. But it's not impossible, and it's certainly permitted by the first law of thermodynamics.)

Problem 1.30. For this experiment I used about an ounce of water in an eight-ounce plastic bottle that was small enough to hold between my fingers and thumb for rapid shaking. I was able to shake it back and forth about four times per second, with the water traveling about a foot during each half-shake or about eight feet total per second. Using the water's average speed to compute the kinetic energy that gets converted to thermal energy, I would then predict for each half-shake

$$mc\,\Delta T = \frac{1}{2}mv^2 \quad \text{or} \quad \Delta T = \frac{v^2}{2c} = \frac{1}{2(4200 \text{ J/kg·°C})}\left(\frac{0.3 \text{ m}}{0.125 \text{ s}}\right)^2 = 0.00069°C.$$

With eight half-shakes per second, the temperature rise after one minute should therefore be about 0.3°C. What I actually found upon trying the experiment three times, shaking for three to five minutes each time, was a pretty consistent temperature rise of 1.0°C per minute. However, my theoretical calculation could be on the low side because I used only the average speed of the water, when perhaps I should have used the maximum speed. Also, as a control I tried simply holding the bottle in my hand for a few minutes, and this

produced a temperature increase of between 0.3 and 0.5°C per minute simply from the heat of my fingers. To do the experiment more accurately it would probably be best to use a bit more water, and to wear gloves or otherwise insulate the system from the heat of my fingers. But I've already demonstrated that kinetic energy can be converted to thermal energy, producing a temperature increase of the expected order of magnitude.

Problem 1.31. (A helium expansion example.)

(a)
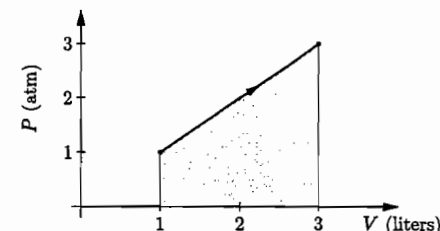
(b) The work done is minus the area under the graph (shaded). The easiest way to compute this area is to note that the average pressure during the process is 2 atm, so

$$W = -\overline{P}\,\Delta V = -(2 \text{ atm})(2 \text{ liters}) \approx -(2 \times 10^5 \text{ Pa})(2 \times 10^{-3} \text{ m}^3) = -400 \text{ J}.$$

The minus sign indicates that 400 J of work is done *by* the gas on its surroundings.

(c) Each helium atom has three degrees of freedom, so at any point the thermal energy of the helium is $U = \frac{3}{2}NkT = \frac{3}{2}PV$. The change in energy during this process is

$$\Delta U = \frac{3}{2}\left[P_f V_f - P_i V_i\right] = \frac{3}{2}\left[(3 \text{ atm})(3 \text{ liters}) - (1 \text{ atm})(1 \text{ liter})\right]$$
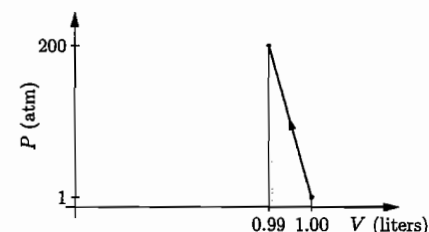$$= 12 \text{ liter} \cdot \text{atm} = 1200 \text{ J}.$$

(d) By the first law,

$$Q = \Delta U - W = 1200 \text{ J} - (-400 \text{ J}) = 1600 \text{ J}.$$

This amount of heat *enters* the gas.

(e) To cause such an increase in pressure (and temperature) as the gas expands, you must provide heat, for instance, by holding a flame under the cylinder and letting the piston out slowly enough to allow the pressure to rise as desired.

Problem 1.32. (Compressing water.)

Problem 1.40. (Dry adiabatic lapse rate.)

(a) Starting from the first law and setting $Q = 0$,

$$dU = Q + W = W = -P\, dV.$$

For an ideal gas, $U = \frac{f}{2}NkT$, so

$$\frac{f}{2}Nk\, dT = -P\, dV. \tag{1.35}$$

In this equation there are three variables—T, V, and P. In this problem we want to eliminate V in favor of T and P. One way to do this is to start with the ideal gas law and consider a small change in each side of the equation:

$$d(PV) = Nk\, dT.$$

The left-hand side is $P\, dV + V\, dP$, by the product rule for derivatives, so

$$P\, dV = Nk\, dT - V\, dP = Nk\, dT - \frac{NkT}{P}dP,$$

where I've used the ideal gas law again in the last step. Therefore equation 1.35 becomes

$$\frac{f}{2}Nk\, dT = -Nk\, dT + \frac{NkT}{P}dP.$$

Canceling the Nk and collecting terms gives

$$\frac{f+2}{2}dT = \frac{T}{P}dP, \qquad \text{or} \qquad \frac{dT}{dP} = \frac{2}{f+2}\frac{T}{P}.$$

(You can also derive this differential equation from the solutions for T and P in terms of V, equations 1.39 and 1.40.)

(b) The result of part (a) can be written

$$dT = \frac{2}{f+2}\frac{T}{P}dP;$$

this is the change in temperature under an infinitesimal adiabatic change in pressure dP. If this change occurs because the air mass is rising a distance dz, and if the vertical forces on it are balanced throughout this process, then the result of Problem 1.16(b) tells us that

$$dP = -\frac{mg}{kT}P\, dz,$$

where m is the average mass of an air molecule. Therefore the change in temperature is

$$dT = -\frac{2}{f+2}\frac{T}{P}\frac{mg}{kT}P\, dz = -\frac{2}{f+2}\frac{mg}{k}dz,$$

and the temperature gradient is

$$\frac{dT}{dz} = -\frac{2}{f+2}\frac{mg}{k} = -\frac{2}{f+2}\frac{Mg}{R},$$

where M is the molar mass of air, 29 g/mol. Plugging in $f = 5$ and $g = 9.8$ N/kg, the numerical value comes out to

$$\frac{dT}{dz} = -\frac{2}{7}\frac{(.029\text{ kg})(9.8\text{ N/kg})}{8.315\text{ J/mol}\cdot\text{K}} = -.0098\text{ K/m} = -9.8\text{ K/km}.$$

Problem 1.41. (Measuring a heat capacity.)

(a) The heat gained by the water is

$$m_w c_w(\Delta T)_w = (250\text{ g})(4.186\text{ J/g}\cdot\text{°C})(4\text{°C}) = 4186\text{ J}.$$

(b) The heat lost by the metal must be the same as the heat lost by the water, 4186 J, since there are no other energy transfers going on and energy must be conserved.

(c) The heat capacity of the chunk of metal must therefore be

$$C_m = \frac{Q}{\Delta T_m} = \frac{-4186\text{ J}}{-76\text{°C}} = 55\text{ J/°C}.$$

(d) The specific heat capacity is the heat capacity per unit mass,

$$c_m = \frac{C_m}{m_m} = \frac{55\text{ J/°C}}{100\text{ g}} = 0.55\text{ J/g}\cdot\text{°C}.$$

Problem 1.42. The heat lost by the water should be approximately equal to the heat gained by the pasta. Therefore,

$$m_w c_w(T_w - T_f) = m_p c_p(T_f - T_p),$$

where w stands for water, p for pasta, and f for the common final temperature. Solving for T_f gives

$$T_f = \frac{m_w c_w T_w + m_p c_p T_p}{m_w c_w + m_p c_p}$$

$$= \frac{(1500\text{ g})(4.186\text{ J/g}\cdot\text{°C})(100\text{°C}) + (340\text{ g})(1.8\text{ J/g}\cdot\text{°C})(25\text{°C})}{(1500\text{ g})(4.186\text{ J/g}\cdot\text{°C}) + (340\text{ g})(1.8\text{ J/g}\cdot\text{°C})} = 93.3\text{°C}.$$

So we would expect the water temperature to drop by nearly 7°C, assuming that equilibration happens faster than the stove can provide any significant additional heat. To prevent the water temperature from dropping so much, it might be wise to use a bigger pot of water.

Problem 1.43. Suppose we have 18 g of water, which makes exactly one mole. The total heat capacity is $18 \cdot 4.186$ J/K, so the heat capacity per molecule is

$$\frac{C}{N} = \frac{18 \cdot 4.186\text{ J/K}}{6.02 \times 10^{23}} = 1.25 \times 10^{-22}\text{ J/K} = 9.07\, k.$$

If all the thermal energy were stored in quadratic degrees of freedom, then each would get a heat capacity of $k/2$, so there would have to be 18 degrees of freedom per molecule—an unrealistically large number. In fact, much of the thermal energy is stored in the energy of intermolecular interactions, and these energies are not quadratic functions of position.

Problem 5.9. According to equation 5.24, the slope of a graph of G vs. T at fixed P should be minus the entropy. Therefore the slope is always negative, and becomes steeper as T and S increase. When the substance undergoes a phase transformation, its entropy increases abruptly, so the slope of the graph of G should be discontinuous. The graph at right shows all these features qualitatively.
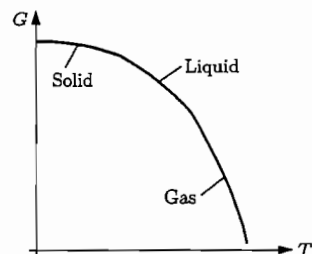
Problem 5.10. From the relation $(\partial G/\partial T)_P = -S$, we can write the change in G as $\partial G = -S\, dT$. The table on page 405 lists the entropy of a mole of water under standard conditions as 69.91 J/K, so the change in G from 25°C to 30°C is

$$dG = -(69.91 \text{ J/K})(5 \text{ K}) = -349.6 \text{ J}.$$

In other words, the Gibbs free energy is about 350 J lower at 30°C than at 25°C. If we now imagine increasing the pressure at fixed temperature, the relation $(\partial G/\partial P)_T = V$ tells us that $dG = V\, dP$, where V is the volume of a mole of water, 18.07×10^{-6} m³. Raising the pressure therefore increases G. To produce an increase of 349.6 J, we would need to increase the pressure by

$$dP = \frac{dG}{V} = \frac{349.6 \text{ J}}{18.07 \times 10^{-6} \text{ m}^3} = 1.93 \times 10^7 \text{ Pa} = 193 \text{ bars}.$$

The moral of the story is that temperature changes tend to have much larger effects on G than pressure changes, at least within the realm of conditions familiar to us in everyday life.

Problem 5.11. (Hydrogen fuel cell at 75°C.)

(a) Under an "infinitesimal" temperature change dT, the Gibbs free energy changes by $dG = -S dT$. Taking $dT = 50$ K and looking up the room-temperature entropies, we obtain (for a mole of each substance)

$$\text{H}_2: \quad G = 0 - (131 \text{ J/K})(50 \text{ K}) = -6550 \text{ J};$$
$$\text{O}_2: \quad G = 0 - (205 \text{ J/K})(50 \text{ K}) = -10250 \text{ J};$$
$$\text{H}_2\text{O}: \quad G = -237000 \text{ J} - (70 \text{ J/K})(50 \text{ K}) = -240500 \text{ J}.$$

(Of course, the entropies are not constant over this temperature interval, so it would be better to first estimate the entropy of each substance in the middle of the interval, at 323 K, and use that value instead of the room-temperature value. For H$_2$, the increase in entropy between 298 K and 323 K is approximately $C_P \ln(T_f/T_i) = (29 \text{ J/K}) \ln(323/298) = 2.3$ J/K. The entropies of the O$_2$ and H$_2$O are likewise only slightly greater at 323 K.)

(b) At 75°C, ΔG for the reaction is

$$G_{\text{H}_2\text{O}} - G_{\text{H}_2} - \tfrac{1}{2}G_{\text{O}_2} = -240500 \text{ J} + 6550 \text{ J} + 5125 \text{ J} = -229 \text{ kJ}.$$

Thus, the maximum electrical work done by the cell is only 229 kJ (per mole of hydrogen consumed), about 3.5% less than the room-temperature value of 237 kJ. Why the difference? The reacting gases have a lot of entropy, which must be gotten rid of by dumping waste heat into the environment. At the higher temperature, we need to dump *more* waste heat to get rid of this entropy, so less of the energy is left to perform electrical work.

Problem 5.12. (Maxwell relations.) Starting with the function $U(S,V)$, we assume that this function is well enough behaved that the mixed second derivatives are equal:

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right).$$

But the thermodynamic identity for U, $dU = T\, dS - P\, dV$, tells us that $(\partial U/\partial S)_V = T$ and $(\partial U/\partial V)_S = -P$. Plugging in these quantities gives us our first Maxwell relation,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.$$

Next, consider the enthalpy H, which due to the thermodynamic identity $dH = T\, dS + V\, dP$ is best considered a function of S and P. Equality of the mixed second derivatives tells us that

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right).$$

But by the thermodynamic identity for H, $(\partial H/\partial S)_P = T$ and $(\partial H/\partial P)_S = V$. Plugging in these quantities gives us a Maxwell relation for H,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.$$

The Helmholtz free energy, due to its thermodynamic identity $dF = -S\, dT - P\, dV$, is most naturally considered a function of T and V. The equality of mixed second derivatives is therefore

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right).$$

But the thermodynamic identity for F tells us that $(\partial F/\partial T)_V = -S$ and $(\partial F/\partial V)_T = -P$. Plugging in these values gives a third Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

Finally, consider the Gibbs free energy, $G(T,P)$. The relevant equality of mixed second derivatives is

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right).$$

Problem 7.35. (Doped semiconductors.)

(a) We saw in Problem 7.33 that for pure silicon at room temperature, the number of electrons excited from the valence band into the conduction band is on the order of 10^{16} per cubic meter, or 10^{10} per cubic centimeter. On the other hand, in Problem 7.5 we saw that for silicon doped with 10^{17} phosphorus atoms per cubic centimeter, nearly every P atom contributes an electron to the conduction band (at room temperature). Therefore, it should be a good approximation to entirely neglect the electrons excited from the valence band, as in Problem 7.5. Under this assumption, the chemical potential is as calculated in Problem 7.5(b):

$$\mu = -kT \ln\left(\frac{2V}{N_c v_Q}\right) = -kT \ln\left(\frac{2V}{x N_d v_Q}\right),$$

where the energy zero-point is taken to be ϵ_c (the bottom of the conduction band). Here N_c is the number of conduction electrons, equal to the number of donor impurities (N_d) times the dimensionless fraction x that was calculated in Problem 7.5(d):

$$x = \frac{1}{2y}(\sqrt{1+4y} - 1), \qquad y = (0.0036)\frac{e^{1/t}}{t^{3/2}}, \qquad t = \frac{kT}{I},$$

where I is the donor ionization energy, 0.044 eV. The number 0.0036, calculated for silicon doped with 10^{17} phosphorus atoms per cm^3, also comes up in the formula for μ:
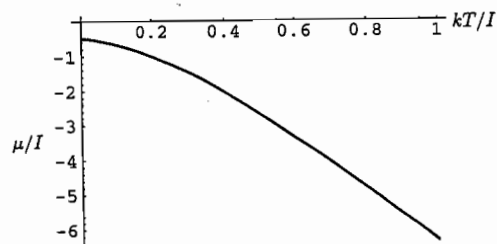
$$\frac{N_d v_Q}{V} = \frac{0.0036}{t^{3/2}}.$$

Therefore we can write the formula for μ as

$$\frac{\mu}{I} = -t \ln\left(\frac{2t^{3/2}}{(0.0036)x}\right).$$

To plot this function, I used the following *Mathematica* code, which produced the graph below:

```
y[t_] := 0.0036 * Exp[1/t] / t^1.5
x[t_] := (Sqrt[1+4y[t]] - 1) / (2y[t])
Plot[-t*Log[2*t^1.5/(0.0036*x[t])],{t,0,1}]
```


Notice that at $T = 0$, $\mu = -I/2$, halfway between the bottom of the conduction band and the energy of the electrons bound to the donor ions. As the temperature increases, the chemical potential drops, just as for an ordinary ideal gas.

(b) The conduction electrons can be treated as an ordinary ideal gas as long as the 1 in the denominator of the Fermi-Dirac distribution is negligible compared to the exponential function, $e^{(\epsilon-\mu)/kT}$, for all ϵ in the conduction band. This is the same as saying that $\epsilon - \mu \gg kT$ for all ϵ in the conduction band, so a sufficient condition is $\epsilon_c - \mu \gg kT$. In the limit $T \to 0$ this condition definitely holds, since $\epsilon_c - \mu$ goes to a nonzero constant, $I/2$, in this limit. Note also that $\epsilon_c - \mu$ is at least this large at any temperature; furthermore, from the graph in part (a) we see that $\epsilon_c - \mu$ is at least four times greater than kT over the entire range of temperatures plotted. This range includes room temperature, at which $kT = 0.026$ eV so $kT/I = 0.026/0.044 = 0.59$; at this temperature, $\epsilon_c - \mu$ is slightly greater than $3I$, about 5 times greater than kT. Since $e^5 \approx 150$, approximating the Fermi-Dirac distribution by the Boltzmann distribution within the conduction band should be accurate to about the 1% level.

(c) At temperatures around room temperature or lower, the number of valence electrons excited to the conduction band will be quite negligible compared to the number from donor ions, as discussed in part (a). (Actually, the number is even less than in a pure semiconductor, since the chemical potential is considerably higher in this case, implying that occupancies in the valence band are even closer to 1.) At higher temperatures, though, the number of conduction electrons from donor impurities saturates at 10^{17} per cm^3, while the number excited from the valence band continues to rise. At what temperature will this number equal 10^{17} per cm^3? To make a crude estimate, let's go back to the simplified model of a pure semiconductor used in Problem 7.33. There we calculated that at room temperature, pure silicon contains about 10^{10} conduction electrons per cm^3. If we double the temperature to 600 K, the exponential factor increases to

$$e^{-\Delta\epsilon/2kT} = 2.3 \times 10^{-5},$$

about 40,000 times greater than at 300 K. The quantum volume also decreases by a factor of $2^{3/2} = 2.8$, the combined effect is to increase the density of conduction electrons by only a factor of about 10^5. At 900 K, however, the exponential factor increases to 8.1×10^{-4}, greater than at 300 K by a factor of 1.5×10^6. Factor in the decrease in the quantum volume, $(900/300)^{3/2} = 5.2$, and we obtain an increase in the number of conduction electrons by a factor of nearly 10^7, as desired. Of course, all this assumes that the chemical potential is at the midpoint between the valence and conduction bands. In a doped semiconductor, as we've just seen, the chemical potential is considerably higher at relatively low temperatures. But for our phosphorus-in-silicon example, a temperature of 900 K implies $kT/I = 1.76$, at which the chemical potential should drop below ϵ_c by more than 12 times the ionization energy (extrapolating from the graph in part (a)). That puts μ pretty near the center of the band gap, as needed.

Problem 7.36. (Magnetization of a degenerate Fermi gas.)

(a) In the paramagnetic systems studied in Chapters 3 and 6, every elementary dipole was free to flip its spin from up to down—there were no restrictions from states already being occupied. But in a degenerate Fermi gas, most electrons can't flip from one spin alignment to the other, because the state with opposite spin alignment is already occupied by another electron. Only near the Fermi energy are there a significant