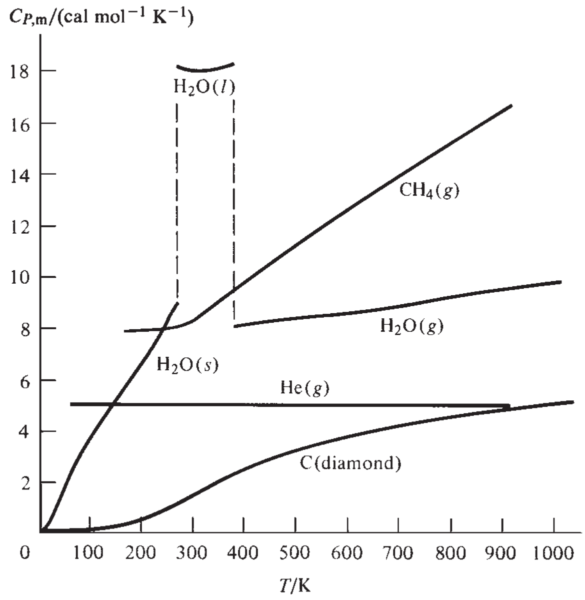
Figure 2.15

$C_{P,m}$ at 1 atm versus T for several substances; s, l, and g stand for solid, liquid, and gas.



The heat capacities $C_{P,m} = (\partial H_m/\partial T)_P$ and $C_{V,m} = (\partial U_m/\partial T)_V$ are measures of how much energy must be added to a substance to produce a given temperature increase. The more ways (translation, rotation, vibration, intermolecular interactions) a substance has of absorbing added energy, the greater will be its $C_{P,m}$ and $C_{V,m}$ values.

2.12 PROBLEM SOLVING

Trying to learn physical chemistry solely by reading a textbook without working problems is about as effective as trying to improve your physique by reading a book on body conditioning without doing the recommended physical exercises.

If you don't see how to work a problem, it often helps to carry out these steps:

1. List all the relevant information that is given.
2. List the quantities to be calculated.
3. Ask yourself what equations, laws, or theorems connect what is known to what is unknown.
4. Apply the relevant equations to calculate what is unknown from what is given.

Although these steps are just common sense, they can be quite useful. The point is that problem solving is an active process. Listing the given information and the unknown quantities and actively searching for relationships that connect them gets your mind working on the problem, whereas simply reading the problem over and over may not get you anywhere. In listing the given information, it is helpful to *translate the words in the problem into equations.* For example, the phrase "adiabatic process" is translated into $dq = 0$ and $q = 0$; "isothermal process" is translated into $dT = 0$ and $T =$ constant.

In steps 1 and 2, sketches of the system and the process may be helpful. In working a problem in thermodynamics, one must have clearly in mind which portion of the universe is the system and which is the surroundings. The nature of the system should be noted—whether it is a perfect gas (for which many special relations hold), a nonideal gas, a liquid, a solid, a heterogeneous system, etc. Likewise, be aware of the kind of process involved—whether it is adiabatic, isothermal (T constant), isobaric (P constant), isochoric (V constant), reversible, etc.

Of course, the main hurdle is step 3. Because of the many equations in physical chemistry, it might seem a complex task to find the right equation to use in a problem. However, there are relatively few equations that are best committed to memory. These are usually the most fundamental equations, and usually they have fairly simple forms. For example, we have several equations for mechanically reversible *P-V* work in a closed system: $dw_{rev} = -P\,dV$ gives the work in an infinitesimal reversible process; $w_{rev} = -\int_1^2 P\,dV$ gives the work in a finite reversible process; the work in a constant-pressure process is $-P\,\Delta V$; the work in an isothermal reversible process in a perfect gas is $w = nRT \ln (V_1/V_2)$. The only one of these equations worth memorizing is $dw_{rev} = -P\,dV$, since the others can be quickly derived from it. Moreover, rederiving an equation from a fundamental equation reminds you of the conditions under which the equation is valid. *Do not memorize unstarred equations.* Readers who have invested their time mainly in achieving an understanding of the ideas and equations of physical chemistry will do better than those who have spent their time memorizing formulas.

Many of the errors students make in thermodynamics arise from using an equation where it does not apply. To help prevent this, many of the equations have the conditions of validity stated next to them. *Be sure the equations you are using are applicable to the system and process involved.* For example, students asked to calculate q in a reversible isothermal expansion of a perfect gas sometimes write "$dq = C_P\,dT$ and since $dT = 0$, we have $dq = 0$ and $q = 0$." This conclusion is erroneous. Why? (See Prob. 2.63.)

If you are baffled by a problem, the following suggestions may help you. (*a*) Ask yourself what given information you have not yet used, and see how this information might help solve the problem. (*b*) Instead of working forward from the known quantities to the unknown, try working backward from the unknown to the known. To do this, ask yourself what quantities you must know to find the unknown; then ask yourself what you must know to find these quantities; etc. (*c*) Write down the definition of the desired quantity. For example, if a density is wanted, write $\rho \equiv m/V$ and ask yourself how to find m and V. If an enthalpy change is wanted, write $H \equiv U + PV$ and $\Delta H = \Delta U + \Delta(PV)$ and see if you can find ΔU and $\Delta(PV)$. (*d*) In analyzing a thermodynamic process, ask yourself which state functions stay constant and which change. Then ask what conclusions can be drawn from the fact that certain state functions stay constant. For example, if V is constant in a process, then the *P-V* work must be zero. (*e*) Stop working on the problem and go on to something else. The solution method might occur to you when you are not consciously thinking about the problem. A lot of mental activity occurs outside of our conscious awareness.

When dealing with abstract quantities, it often helps to take specific numerical values. For example, suppose we want the relation between the rates of change dn_A/dt and dn_B/dt for the chemical reaction A + 2B → products, where n_A and n_B are the moles of A and B and t is time. Typically, students will say either that $dn_A/dt = 2\,dn_B/dt$ or that $dn_A/dt = \frac{1}{2}dn_B/dt$. (Before reading further, which do you think is right?) To help decide, suppose that in a tiny time interval $dt = 10^{-3}$ s, 0.001 mol of A reacts, so that $dn_A = -0.001$ mol. For the reaction A + 2B → products, find the corresponding value of dn_B and then find dn_A/dt and dn_B/dt and compare them.

In writing equations, a useful check is provided by the fact that *each term in an equation must have the same dimensions.* Thus, an equation that contains the expression $U + TV$ cannot be correct, because U has dimensions of energy = mass × length^2/time^2, whereas TV has dimensions of temperature × volume = temperature × length^3. From the definitions (1.25) and (1.29) of a derivative and a partial derivative, it follows that $(\partial z/\partial x)_y$ has the same dimensions as z/x. The definitions (1.52) and (1.59) of indefinite and definite integrals show that $\int f\,dx$ and $\int_a^b f\,dx$ have the same dimensions as fx.

When writing equations, do not mix finite and infinitesimal changes in the same equation. Thus, an equation that contains the expression $P\,dV + V\,\Delta P$ must be wrong because dV is an infinitesimal change and ΔP is a finite change. If one term in an equation contains a single change in a state function, then another term that contains only state functions must contain a change. Thus, an equation cannot contain the expression $PV + V\,\Delta P$ or the expression $PV + V\,dP$.

As to step 4, performing the calculations, errors can be minimized by carrying units of all quantities as part of the calculation. *Make sure you are using a self-consistent set of units.* Do not mix joules and kilojoules or joules and calories or joules and cm^3 atm in the same equation. If you are confused about what units to use, a strategy that avoids errors is to express all quantities in SI units. *Inconsistent use of units is one of the most common student errors in physical chemistry.*

Express your answer with the proper units. *A numerical answer with no units is meaningless.*

In September 1999, the $125 million U.S. Mars Climate Orbiter spacecraft was lost. It turned out that the engineers at Lockheed Martin sent data on the thrust of the spacecraft's thrusters to scientists at the Jet Propulsion Laboratory in units of pounds-force, but the JPL scientists assumed the thrust was in units of newtons, and so their programming of rocket firings to correct the trajectory produced an erroneous path that did not achieve orbit (*New York Times,* Oct. 1, 1999, p. A1). You don't have to be a rocket scientist to mess up on units.

On July 23, 1983, Air Canada Flight 143 ran out of fuel at 28,000 feet altitude and only halfway to its destination. When the plane had been refueled in Ottawa, the plane's on-board fuel gauge was not working. Captain Robert Pearson knew that the plane needed 22,000 kg of fuel for the trip. The fuel-truck gauge read in liters, so Pearson asked the mechanic for the density of the fuel. He was told "1.77." Pearson assumed this was 1.77 kg/L, and used this figure to calculate the volume of the fuel needed. The plane was a new Boeing 767, and in line with Canada's conversion to metric units, its fuel load was measured in kilograms, in contrast to older planes, which used pounds. The mechanic was used to dealing with fuel loads in pounds (lb), so the figure of 1.77 he gave was actually 1.77 lb/L, which is 0.80 kg/L. Because of this miscommunication due to omission of units, Pearson requested a bit less than half the fuel volume he needed and took off with 22,000 pounds of fuel instead of 22,000 kg.

Although the plane was out of fuel, an emergency electric generator (the ram air turbine) that uses the air stream resulting from the plane's speed to supply power to the plane's hydraulic system gave Pearson some control of the plane. Also, emergency battery power kept a few of the plane's instrument-panel gauges working. Pearson was an experienced glider pilot and flew the plane for 17 minutes after it ran out of fuel. He headed for an abandoned Canadian Air Force base at Gimli. Approaching Gimli, he realized the plane was coming in too high and too fast for a safe landing, so he executed a maneuver used with gliders to lose speed and altitude; this maneuver had never been tried with a commercial jet, but it worked. When the plane reached the runway, the crew saw people on the runway—the abandoned runway was being used for car races. The crew used a backup system to drop the landing gear; the nose wheel got stuck partway down and collapsed on landing; the scraping of the nose along the ground, together with Pearson's application of the brakes, brought the plane to a stop before it reached the people on the runway. There were no fatalities and only a few minor injuries when the passengers evacuated the plane.

Express the answer to the proper number of significant figures. Use a calculator with keys for exponentials and logarithms for calculations. After the calculation is completed, it is a good idea to check the entire solution. If you are like most of us, you are probably too lazy to do a complete check, but it takes only a few seconds to check that the sign and the magnitude of the answer are physically reasonable. Sign errors are especially common in thermodynamics, since most quantities can be either positive or negative.

A solutions manual for problems in this textbook is available.