Problem 5.22. Show that equation 5.40 is in agreement with the explicit formula for the chemical potential of a monatomic ideal gas derived in Section 3.5. Show how to calculate μ° for a monatomic ideal gas.

Problem 5.23. By subtracting μN from U, H, F, or G, one can obtain four new thermodynamic potentials. Of the four, the most useful is the **grand free energy** (or **grand potential**),

$$\Phi \equiv U - TS - \mu N.$$

(a) Derive the thermodynamic identity for Φ, and the related formulas for the partial derivatives of Φ with respect to T, V, and μ.

(b) Prove that, for a system in thermal and diffusive equilibrium (with a reservoir that can supply both energy and particles), Φ tends to decrease.

(c) Prove that $\Phi = -PV$.

(d) As a simple application, let the system be a single proton, which can be "occupied" either by a single electron (making a hydrogen atom, with energy -13.6 eV) or by none (with energy zero). Neglect the excited states of the atom and the two spin states of the electron, so that both the occupied and unoccupied states of the proton have zero entropy. Suppose that this proton is in the atmosphere of the sun, a reservoir with a temperature of 5800 K and an electron concentration of about 2×10^{19} per cubic meter. Calculate Φ for both the occupied and unoccupied states, to determine which is more stable under these conditions. To compute the chemical potential of the electrons, treat them as an ideal gas. At about what temperature would the occupied and unoccupied states be equally stable, for this value of the electron concentration? (As in Problem 5.20, the prediction for such a small system is only a probabilistic one.)

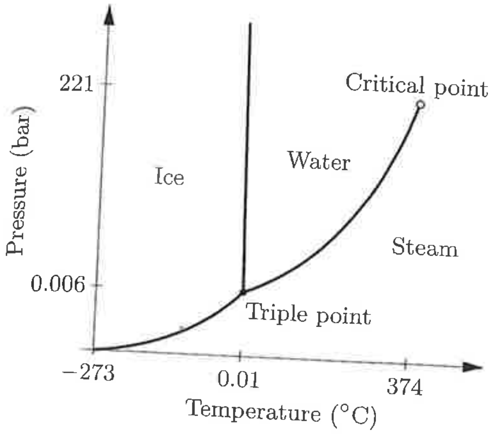
5.3 Phase Transformations of Pure Substances

A **phase transformation** is a discontinuous change in the properties of a substance, as its environment is changed only infinitesimally. Familiar examples include melting ice and boiling water, either of which can be accomplished with only a very small change in temperature. The different forms of the substance—in this case ice, water, and steam—are called **phases**.

Often there is more than one variable that can affect the phase of a substance. For instance, you can condense steam either by lowering the temperature or by raising the pressure. A graph showing the equilibrium phases as a function of temperature and pressure is called a **phase diagram**.

Figure 5.11 shows a qualitative phase diagram for H_2O, along with some quantitative data on its phase transformations. The diagram is divided into three regions, indicating the conditions under which ice, water, or steam is the most stable phase. It's important to realize, though, that "metastable" phases can still exist; for instance, liquid water can be "supercooled" below the freezing point yet remain a liquid for some time. At high pressures there are actually several different phases of ice, with differing crystal structures and other physical properties.

The lines on a phase diagram represent conditions under which two different phases can coexist in equilibrium; for instance, ice and water can coexist stably at

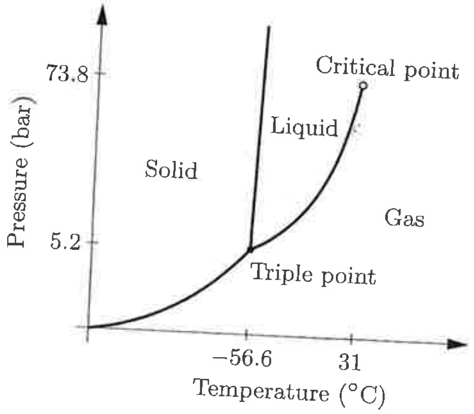


T (°C)	P_v (bar)	L (kJ/mol)
−40	0.00013	51.16
−20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).

0°C and 1 atm (≈ 1 bar). The pressure at which a gas can coexist with its solid or liquid phase is called the **vapor pressure**; thus the vapor pressure of water at room temperature is approximately 0.03 bar. At $T = 0.01°\text{C}$ and $P = 0.006$ bar, all three phases can coexist; this point is called the **triple point**. At lower pressures, liquid water cannot exist (in equilibrium): ice "sublimates" directly into vapor.

You have probably observed sublimation of "dry ice," frozen carbon dioxide. Evidently, the triple point of carbon dioxide lies above atmospheric pressure; in fact it is at 5.2 bars. A qualitative phase diagram for carbon dioxide is shown in Figure 5.12. Another difference between CO_2 and H_2O is the slope of the solid-liquid phase boundary. Most substances are like carbon dioxide: Applying more pressure *raises* the melting temperature. Ice, however, is unusual: Applying



T (°C)	P_v (bar)
−120	0.0124
−100	0.135
−80	0.889
−78.6	1.000
−60	4.11
−56.6	5.18
−40	10.07
−20	19.72
0	34.85
20	57.2
31	73.8

Figure 5.12. Phase diagram for carbon dioxide (not to scale). The table gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Data from Lide (1994) and Reynolds (1979).

pressure *lowers* its melting temperature. We will soon see that this is a result of the fact that ice is less dense than water.

The liquid-gas phase boundary always has a positive slope: If you have liquid and gas in equilibrium and you raise the temperature, you must apply *more* pressure to keep the liquid from vaporizing. As the pressure increases, however, the gas becomes more dense, so the difference between liquid and gas grows less. Eventually a point is reached where there is no longer any discontinuous change from liquid to gas. This point is called the **critical point**, and occurs at 374°C and 221 bars for H_2O. The critical point of carbon dioxide is more accessible, at 31°C and 74 bars, while that of nitrogen is at only 126 K and 34 bars. Close to the critical point, it's best to hedge and simply call the substance a "fluid." There's no critical point on the solid-liquid phase boundary, since the distinction between solids and liquids is a qualitative issue (solids having crystal structure and liquids having randomly arranged molecules), not just a matter of degree. Some materials made of long molecules can, however, form a **liquid crystal** phase, in which the molecules move around randomly as in a liquid but still tend to be oriented parallel to each other.

Helium has the most exotic phase behavior of any element. Figure 5.13 shows the phase diagrams of the two isotopes of helium, the common isotope ^{4}He and the rare isotope ^{3}He. The boiling point of ^{4}He at atmospheric pressure is only 4.2 K, and the critical point is only slightly higher, at 5.2 K and 2.3 bars; for ^{3}He these parameters are somewhat lower still. Helium is the only element that remains a liquid at absolute zero temperature: It *will* form a solid phase, but only at rather high pressures, about 25 bars for ^{4}He and 30 bars for ^{3}He. The solid-liquid phase boundary for ^{4}He is almost horizontal below 1 K, while for ^{3}He this boundary has a *negative* slope below 0.3 K. Even more interesting, ^{4}He has two distinct liquid phases: a "normal" phase called helium I, and a **superfluid**

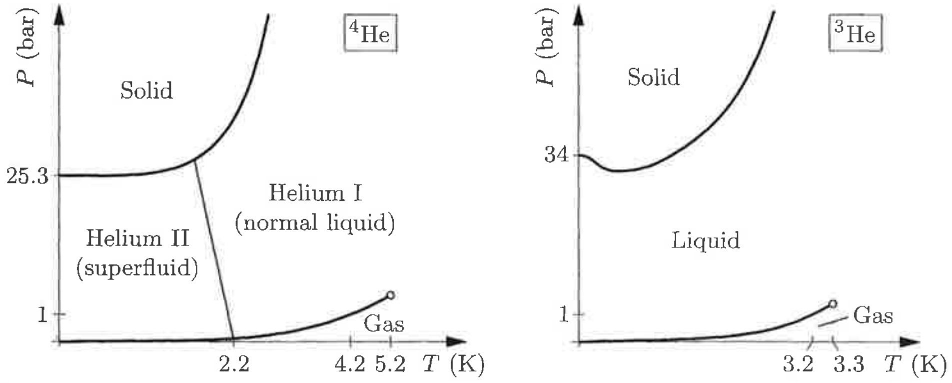


Figure 5.13. Phase diagrams of ^{4}He (left) and ^{3}He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ^{3}He below 3 mK.

phase, below about 2 K, called helium II. The superfluid phase has a number of remarkable properties including zero viscosity and very high thermal conductivity. Helium-3 actually has two distinct superfluid phases, but only at temperatures below 3 mK.

Besides temperature and pressure, changing other variables such as composition and magnetic field strength can also cause phase transformations. Figure 5.14 shows phase diagrams for two different magnetic systems. At left is the diagram for a typical **type-I superconductor**, such as tin or mercury or lead. The superconducting phase, with zero electrical resistance, exists only when both the temperature and the external magnetic field strength are sufficiently low. At right is the diagram for a **ferromagnet** such as iron, which has *magnetized* phases pointing either up or down, depending on the direction of the applied field. (For simplicity, this diagram assumes that the applied field always points either up or down along a given axis.) When the applied field is zero, phases that are magnetized in both directions can coexist. As the temperature is raised, however, the magnetization of both phases becomes weaker. Eventually, at the **Curie temperature** (1043 K for iron), the magnetization disappears completely, so the phase boundary ends at a critical point.*

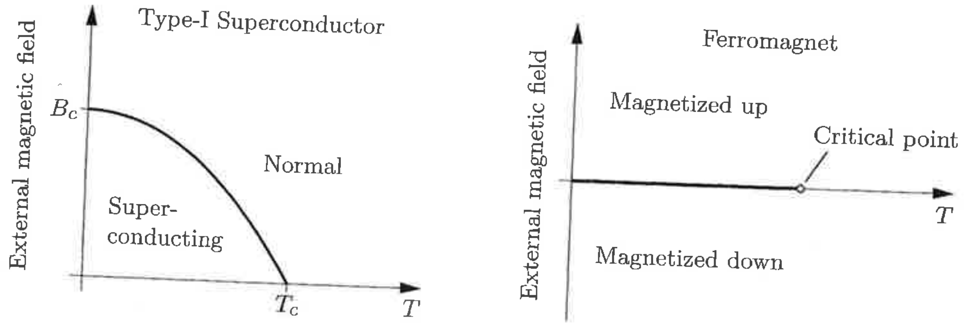


Figure 5.14. Left: Phase diagram for a typical type-I superconductor. For lead, $T_c = 7.2$ K and $B_c = 0.08$ T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis.

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*For several decades people have tried to classify phase transformations according to the abruptness of the change. Solid-liquid and liquid-gas transformations are classified as "first-order," because S and V, the *first* derivatives of G, are discontinuous at the phase boundary. Less abrupt transitions (such as critical points and the helium I to helium II transition) used to be classified as "second-order" and so on, depending on how many successive derivatives you had to take before getting a discontinuous quantity. Because of various problems with this classification scheme, the current fashion is to simply call all the higher-order transitions "continuous."

Diamonds and Graphite

Elemental carbon has two familiar phases, diamond and graphite (both solids, but with different crystal structures). At ordinary pressures the more stable phase is graphite, so diamonds will spontaneously convert to graphite, although this process is extremely slow at room temperature. (At high temperatures the conversion proceeds more rapidly, so if you own any diamonds, be sure not to throw them into the fireplace.*)

The fact that graphite is more stable than diamond under standard conditions is reflected in their Gibbs free energies: The Gibbs free energy of a mole of diamond is greater, by 2900 J, than the Gibbs free energy of a mole of graphite. At a given temperature and pressure, the stable phase is always the one with the lower Gibbs free energy, according to the analysis of Section 5.2.

But the difference of 2900 J is for standard conditions, 298 K and atmospheric pressure (1 bar). What happens at higher pressures? The pressure dependence of the Gibbs free energy is determined by the volume of the substance,

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \tag{5.41}$$

and since a mole of graphite has a greater volume than a mole of diamond, its Gibbs free energy will grow more rapidly as the pressure is raised. Figure 5.15 shows a graph of G vs. P for both substances. If we treat the volumes as constant (neglecting the compressibility of both substances), then each curve is a straight line. The slopes are $V = 5.31 \times 10^{-6}$ m^3 for graphite and $V = 3.42 \times 10^{-6}$ m^3 for diamond. As you can see, the two lines intersect at a pressure of about 15 kilobars. Above this very high pressure, diamond should be more stable than graphite. Apparently,

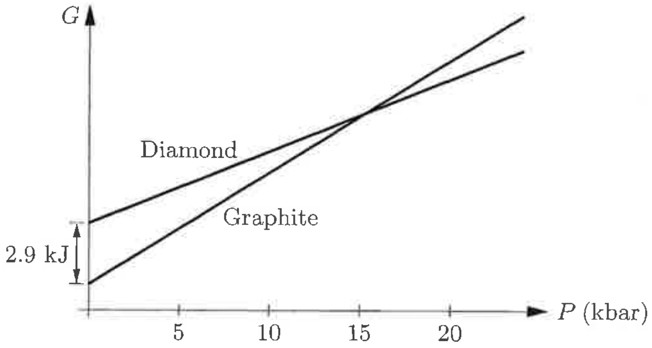

Figure 5.15. Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases.

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*The temperature required to convert diamond to graphite quickly is actually quite high, about 1500°C. But in the presence of oxygen, either diamond or graphite will easily burn to form carbon dioxide.

natural diamonds must form at very great depths. Taking rock to be about three times as dense as water, it's easy to estimate that underground pressures normally increase by 3 bars for every 10 meters of depth. So a pressure of 15 kbar requires a depth of about 50 kilometers.

The temperature dependence of the Gibbs free energies can be determined in a similar way, using the relation

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S. \tag{5.42}$$

As the temperature is raised the Gibbs free energy of either substance decreases, but this decrease is more rapid for graphite since it has more entropy. Thus, raising the temperature tends to make graphite more stable relative to diamond; the higher the temperature, the more pressure is required before diamond becomes the stable phase.

Analyses of this type are extremely useful to geochemists, whose job is to look at rocks and determine the conditions under which they formed. More generally, the Gibbs free energy is the key to attaining a quantitative understanding of phase transformations.

Problem 5.24. Go through the arithmetic to verify that diamond becomes more stable than graphite at approximately 15 kbar.

Problem 5.25. In working high-pressure geochemistry problems it is usually more convenient to express volumes in units of kJ/kbar. Work out the conversion factor between this unit and m^3.

Problem 5.26. How can diamond ever be more stable than graphite, when it has less entropy? Explain how at high pressures the conversion of graphite to diamond can increase the *total* entropy of the carbon plus its environment.

Problem 5.27. Graphite is more compressible than diamond.

(a) Taking compressibilities into account, would you expect the transition from graphite to diamond to occur at higher or lower pressure than that predicted in the text?

(b) The isothermal compressibility of graphite is about 3×10^{-6} bar^{-1}, while that of diamond is more than ten times less and hence negligible in comparison. (Isothermal compressibility is the fractional reduction in volume per unit increase in pressure, as defined in Problem 1.46.) Use this information to make a revised estimate of the pressure at which diamond becomes more stable than graphite (at room temperature).

Problem 5.28. Calcium carbonate, $CaCO_3$, has two common crystalline forms, calcite and aragonite. Thermodynamic data for these phases can be found at the back of this book.

(a) Which is stable at earth's surface, calcite or aragonite?

(b) Calculate the pressure (still at room temperature) at which the other phase should become stable.

Problem 5.29. Aluminum silicate, Al_2SiO_5, has three different crystalline forms: kyanite, andalusite, and sillimanite. Because each is stable under a different set of temperature-pressure conditions, and all are commonly found in metamorphic rocks, these minerals are important indicators of the geologic history of rock bodies.

(a) Referring to the thermodynamic data at the back of this book, argue that at 298 K the stable phase should be kyanite, regardless of pressure.

(b) Now consider what happens at fixed pressure as we vary the temperature. Let ΔG be the difference in Gibbs free energies between any two phases, and similarly for ΔS. Show that the T dependence of ΔG is given by

$$\Delta G(T_2) = \Delta G(T_1) - \int_{T_1}^{T_2} \Delta S(T)\, dT.$$

Although the entropy of any given phase will increase significantly as the temperature increases, above room temperature it is often a good approximation to take ΔS, the *difference* in entropies between two phases, to be independent of T. This is because the temperature dependence of S is a function of the heat capacity (as we saw in Chapter 3), and the heat capacity of a solid at high temperature depends, to a good approximation, only on the number of atoms it contains.

(c) Taking ΔS to be independent of T, find the range of temperatures over which kyanite, andalusite, and sillimanite should be stable (at 1 bar).

(d) Referring to the room-temperature heat capacities of the three forms of Al_2SiO_5, discuss the accuracy the approximation ΔS = constant.

Problem 5.30. Sketch qualitatively accurate graphs of G vs. T for the three phases of H_2O (ice, water, and steam) at atmospheric pressure. Put all three graphs on the same set of axes, and label the temperatures 0°C and 100°C. How would the graphs differ at a pressure of 0.001 bar?

Problem 5.31. Sketch qualitatively accurate graphs of G vs. P for the three phases of H_2O (ice, water, and steam) at 0°C. Put all three graphs on the same set of axes, and label the point corresponding to atmospheric pressure. How would the graphs differ at slightly higher temperatures?

The Clausius-Clapeyron Relation

Since entropy determines the temperature dependence of the Gibbs free energy, while volume determines its pressure dependence, the shape of any phase boundary line on a PT diagram is related in a very simple way to the entropies and volumes of the two phases. Let me now derive this relation.

For definiteness, I'll discuss the phase boundary between a liquid and a gas, although it could just as well be any other phase boundary. Let's consider some fixed amount of the stuff, say one mole. At the phase boundary, this material is equally stable as a liquid or a gas, so its Gibbs free energy must be the same, whether it is in either phase:

$$G_l = G_g \qquad \text{at phase boundary.} \tag{5.43}$$

(You can also think of this condition in terms of the chemical potentials: If some liquid and some gas are in diffusive equilibrium with each other, then their chemical potentials, i.e., Gibbs free energies per molecule, must be equal.)

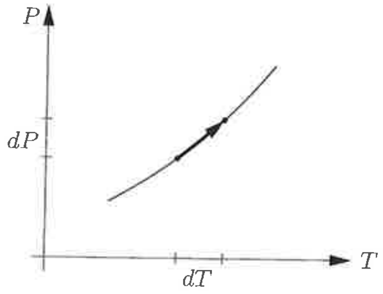

Figure 5.16. Infinitesimal changes in pressure and temperature, related in such a way as to remain on the phase boundary.

Now imagine increasing the temperature by dT and the pressure by dP, in such a way that the two phases remain equally stable (see Figure 5.16). Under this change, the Gibbs free energies must remain equal to each other, so

$$dG_l = dG_g \qquad \text{to remain on phase boundary.} \tag{5.44}$$

Therefore, by the thermodynamic identity for G (equation 5.23),

$$-S_l\,dT + V_l\,dP = -S_g\,dT + V_g\,dP. \tag{5.45}$$

(I've omitted the $\mu\,dN$ terms because I've already assumed that the total amount of stuff is fixed.) Now it's easy to solve for the slope of the phase boundary line, dP/dT:

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}. \tag{5.46}$$

As expected, the slope is determined by the entropies and volumes of the two phases. A large difference in entropy means that a small change in temperature can be very significant in shifting the equilibrium from one phase to the other. This results in a steep phase boundary curve, since a large pressure change is then required to compensate the small temperature change. On the other hand, a large difference in volume means that a small change in pressure can be significant after all, making the phase boundary curve shallower.

It's often more convenient to write the difference in entropies, $S_g - S_l$, as L/T, where L is the (total) latent heat for converting the material (in whatever quantity we're considering) from liquid to gas. Then equation 5.46 takes the form

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V}, \tag{5.47}$$

where $\Delta V = V_g - V_l$. (Notice that, since both L and ΔV are extensive, their ratio is intensive—independent of the amount of material.) This result is known as the **Clausius-Clapeyron relation**. It applies to the slope of any phase boundary line on a PT diagram, not just to the line separating liquid from gas.

As an example, consider again the diamond-graphite system. When a mole of diamond converts to graphite its entropy increases by 3.4 J/K, while its volume increases by 1.9×10^{-6} m^3. (Both of these numbers are for room temperature; at higher temperatures the difference in entropy is somewhat greater.) Therefore the slope of the diamond-graphite phase boundary is

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{3.4\ \mathrm{J/K}}{1.9\times10^{-6}\ \mathrm{m}^3} = 1.8\times10^6\ \mathrm{Pa/K} = 18\ \mathrm{bar/K}. \tag{5.48}$$

In the previous subsection I showed that at room temperature, diamond is stable at pressures above approximately 15 kbar. Now we see that if the temperature is 100 K higher, we need an additional 1.8 kbar of pressure to make diamond stable. *Rapid* conversion of graphite to diamond requires still higher temperatures, and correspondingly higher pressures, as shown in the phase diagram in Figure 5.17. The first synthesis of diamond from graphite was accomplished at approximately 1800 K and 60 kbar. Natural diamonds are thought to form at similar pressures but somewhat lower temperatures, at depths of 100–200 km below earth's surface.*

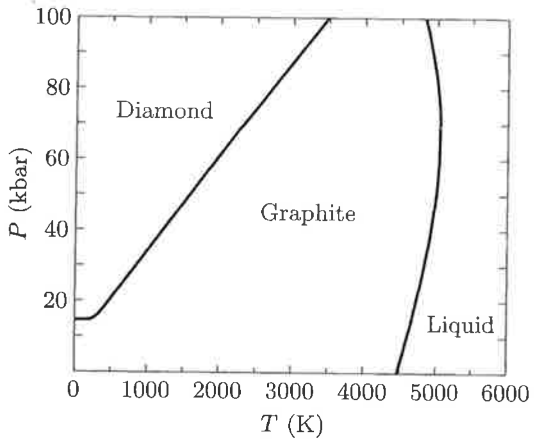

Figure 5.17. The experimental phase diagram of carbon. The stability region of the gas phase is not visible on this scale; the graphite-liquid-gas triple point is at the bottom of the graphite-liquid phase boundary, at 110 bars pressure. From David A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).

Problem 5.32. The density of ice is 917 kg/m^3.

(a) Use the Clausius-Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.

(b) How much pressure would you have to put on an ice cube to make it melt at −1°C?

(c) Approximately how deep under a glacier would you have to be before the weight of the ice above gives the pressure you found in part (b)? (Note that the pressure can be greater at some locations, as where the glacier flows over a protruding rock.)

(d) Make a rough estimate of the pressure under the blade of an ice skate, and calculate the melting temperature of ice at this pressure. Some authors have claimed that skaters glide with very little friction because the increased pressure under the blade melts the ice to create a thin layer of water. What do you think of this explanation?

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*For more on the formation of natural diamonds and the processes that bring them near earth's surface, see Keith G. Cox, "Kimberlite Pipes," *Scientific American* **238**, 120–132 (April, 1978).

Problem 5.33. An inventor proposes to make a heat engine using water/ice as the working substance, taking advantage of the fact that water expands as it freezes. A weight to be lifted is placed on top of a piston over a cylinder of water at 1°C. The system is then placed in thermal contact with a low-temperature reservoir at −1°C until the water freezes into ice, lifting the weight. The weight is then removed and the ice is melted by putting it in contact with a high-temperature reservoir at 1°C. The inventor is pleased with this device because it can seemingly perform an unlimited amount of work while absorbing only a finite amount of heat. Explain the flaw in the inventor's reasoning, and use the Clausius-Clapeyron relation to prove that the maximum efficiency of this engine is still given by the Carnot formula, $1 - T_c/T_h$.

Problem 5.34. Below 0.3 K the slope of the ^{3}He solid-liquid phase boundary is negative (see Figure 5.13).

(a) Which phase, solid or liquid, is more dense? Which phase has more entropy (per mole)? Explain your reasoning carefully.

(b) Use the third law of thermodynamics to argue that the slope of the phase boundary must go to zero at $T = 0$. (Note that the ^{4}He solid-liquid phase boundary is essentially horizontal below 1 K.)

(c) Suppose that you compress liquid ^{3}He adiabatically until it becomes a solid. If the temperature just before the phase change is 0.1 K, will the temperature after the phase change be higher or lower? Explain your reasoning carefully.

Problem 5.35. The Clausius-Clapeyron relation 5.47 is a differential equation that can, in principle, be solved to find the shape of the entire phase-boundary curve. To solve it, however, you have to know how both L and ΔV depend on temperature and pressure. Often, over a reasonably small section of the curve, you can take L to be constant. Moreover, if one of the phases is a gas, you can usually neglect the volume of the condensed phase and just take ΔV to be the volume of the gas, expressed in terms of temperature and pressure using the ideal gas law. Making all these assumptions, solve the differential equation explicitly to obtain the following formula for the phase boundary curve:

$$P = (\text{constant}) \times e^{-L/RT}.$$

This result is called the **vapor pressure equation**. Caution: Be sure to use this formula only when all the assumptions just listed are valid.

Problem 5.36. Effect of altitude on boiling water.

(a) Use the result of the previous problem and the data in Figure 5.11 to plot a graph of the vapor pressure of water between 50°C and 100°C. How well can you match the data at the two endpoints?

(b) Reading the graph backwards, estimate the boiling temperature of water at each of the locations for which you determined the pressure in Problem 1.16. Explain why it takes longer to cook noodles when you're camping in the mountains.

(c) Show that the dependence of boiling temperature on altitude is very nearly (though not exactly) a linear function, and calculate the slope in degrees Celsius per thousand feet (or in degrees Celsius per kilometer).

Problem 5.37. Use the data at the back of this book to calculate the slope of the calcite-aragonite phase boundary (at 298 K). You located one point on this phase boundary in Problem 5.28; use this information to sketch the phase diagram of calcium carbonate.

Problem 5.38. In Problems 3.30 and 3.31 you calculated the entropies of diamond and graphite at 500 K. Use these values to predict the slope of the graphite-diamond phase boundary at 500 K, and compare to Figure 5.17. Why is the slope almost constant at still higher temperatures? Why is the slope zero at $T = 0$?

Problem 5.39. Consider again the aluminosilicate system treated in Problem 5.29. Calculate the slopes of all three phase boundaries for this system: kyanite-andalusite, kyanite-sillimanite, and andalusite-sillimanite. Sketch the phase diagram, and calculate the temperature and pressure of the triple point.

Problem 5.40. The methods of this section can also be applied to reactions in which one set of solids converts to another. A geologically important example is the transformation of albite into jadeite + quartz:

$$\mathrm{NaAlSi_3O_8} \longleftrightarrow \mathrm{NaAlSi_2O_6} + \mathrm{SiO_2}.$$

Use the data at the back of this book to determine the temperatures and pressures under which a combination of jadeite and quartz is more stable than albite. Sketch the phase diagram of this system. For simplicity, neglect the temperature and pressure dependence of both ΔS and ΔV.

Problem 5.41. Suppose you have a liquid (say, water) in equilibrium with its gas phase, inside some closed container. You then pump in an inert gas (say, air), thus raising the pressure exerted on the liquid. What happens?

(a) For the liquid to remain in diffusive equilibrium with its gas phase, the chemical potentials of each must change by the same amount: $d\mu_l = d\mu_g$. Use this fact and equation 5.40 to derive a differential equation for the equilibrium vapor pressure, P_v, as a function of the total pressure P. (Treat the gases as ideal, and assume that none of the inert gas dissolves in the liquid.)

(b) Solve the differential equation to obtain

$$P_v(P) = P_v(P_v) \cdot e^{(P-P_v)V/NkT},$$

where the ratio V/N in the exponent is that of the *liquid.* (The quantity $P_v(P_v)$ is just the vapor pressure in the absence of the inert gas.) Thus, the presence of the inert gas leads to a slight increase in the vapor pressure: It causes more of the liquid to evaporate.

(c) Calculate the percent increase in vapor pressure when air at atmospheric pressure is added to a system of water and water vapor in equilibrium at 25°C. Argue more generally that the increase in vapor pressure due to the presence of an inert gas will be negligible except under extreme conditions.

Problem 5.42. Ordinarily, the partial pressure of water vapor in the air is less than the equilibrium vapor pressure at the ambient temperature; this is why a cup of water will spontaneously evaporate. The ratio of the partial pressure of water vapor to the equilibrium vapor pressure is called the **relative humidity**. When the relative humidity is 100%, so that water vapor in the atmosphere would be in diffusive equilibrium with a cup of liquid water, we say that the air is **saturated**.* The **dew point** is the temperature at which the relative humidity would be 100%, for a given partial pressure of water vapor.

(a) Use the vapor pressure equation (Problem 5.35) and the data in Figure 5.11 to plot a graph of the vapor pressure of water from 0°C to 40°C. Notice that the vapor pressure approximately doubles for every 10° increase in temperature.

(b) The temperature on a certain summer day is 30°C. What is the dew point if the relative humidity is 90%? What if the relative humidity is 40%?

Problem 5.43. Assume that the air you exhale is at 35°C, with a relative humidity of 90%. This air immediately mixes with environmental air at 10°C and unknown relative humidity; during the mixing, a variety of intermediate temperatures and water vapor percentages temporarily occur. If you are able to "see your breath" due to the formation of cloud droplets during this mixing, what can you conclude about the relative humidity of your environment? (Refer to the vapor pressure graph drawn in Problem 5.42.)

Problem 5.44. Suppose that an unsaturated air mass is rising and cooling at the dry adiabatic lapse rate found in Problem 1.40. If the temperature at ground level is 25°C and the relative humidity there is 50%, at what altitude will this air mass become saturated so that condensation begins and a cloud forms (see Figure 5.18)? (Refer to the vapor pressure graph drawn in Problem 5.42.)

Problem 5.45. In Problem 1.40 you calculated the atmospheric temperature gradient required for unsaturated air to spontaneously undergo convection. When a rising air mass becomes saturated, however, the condensing water droplets will give up energy, thus slowing the adiabatic cooling process.

(a) Use the first law of thermodynamics to show that, as condensation forms during adiabatic expansion, the temperature of an air mass changes by

$$dT = \frac{2}{7}\frac{T}{P}\,dP - \frac{2}{7}\frac{L}{nR}\,dn_w,$$

where n_w is the number of moles of water vapor present, L is the latent heat of vaporization per mole, and I've set $\gamma = 7/5$ for air. You may assume that the H_2O makes up only a small fraction of the air mass.

(b) Assuming that the air is always saturated during this process, the ratio n_w/n is a known function of temperature and pressure. Carefully express dn_w/dz in terms of dT/dz, dP/dz, and the vapor pressure $P_v(T)$. Use the Clausius-Clapeyron relation to eliminate dP_v/dT.

(c) Combine the results of parts (a) and (b) to obtain a formula relating the temperature gradient, dT/dz, to the pressure gradient, dP/dz. Eliminate

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*This term is widely used, but is unfortunate and misleading. Air is not a sponge that can hold only a certain amount of liquid; even "saturated" air is mostly empty space. As shown in the previous problem, the density of water vapor that can exist in equilibrium has almost nothing to do with the presence of air.

The van der Waals Model

To understand phase transformations more deeply, a good approach is to introduce a specific mathematical model. For liquid-gas systems, the most famous model is the **van der Waals equation**,

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT, \tag{5.49}$$

proposed by Johannes van der Waals in 1873. This is a modification of the ideal gas law that takes molecular interactions into account in an approximate way. (Any proposed relation among P, V, and T, like the ideal gas law or the van der Waals equation, is called an **equation of state**.)

The van der Waals equation makes two modifications to the ideal gas law: adding aN^2/V^2 to P and subtracting Nb from V. The second modification is easier to understand: A fluid can't be compressed all the way down to zero volume, so we've limited the volume to a minimum value of Nb, at which the pressure goes to infinity. The constant b then represents the minimum volume occupied by a molecule, when it's "touching" all its neighbors. The first modification, adding aN^2/V^2 to P, accounts for the short-range attractive forces between molecules when they're not touching (see Figure 5.19). Imagine freezing all the molecules in place, so that the only type of energy present is the negative potential energy due to molecular attraction. If we were to double the density of the system, each molecule would then have twice as many neighbors as before, so the potential energy due to all its interactions with neighbors would double. In other words, the potential energy associated with a single molecule's interactions with all its neighbors is proportional to the density of particles, or to N/V. The *total* potential energy associated with all molecules' interactions must then be proportional to N^2/V, since there are N molecules:

$$\text{total potential energy} = -\frac{aN^2}{V}, \tag{5.50}$$

where a is some positive constant of proportionality that depends on the type of molecules. To calculate the pressure, imagine varying the volume slightly while holding the entropy fixed (which isn't a problem if we've frozen all thermal motion); then by the thermodynamic identity, $dU = -P\,dV$ or $P = -(\partial U/\partial V)_S$. The contribution to the pressure from just the potential energy is therefore

$$P_{\text{due to p.e.}} = -\frac{d}{dV}\left(-\frac{aN^2}{V}\right) = -\frac{aN^2}{V^2}. \tag{5.51}$$

If we add this negative pressure to the pressure that the fluid would have in the

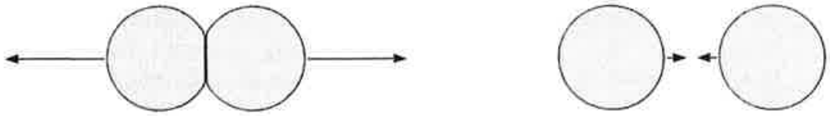


Figure 5.19. When two molecules come very close together they repel each other strongly. When they are a short distance apart they attract each other.

absence of attractive forces (namely, $NkT/(V-Nb)$), we obtain the van der Waals equation,

$$P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}. \tag{5.52}$$

While the van der Waals equation has the right properties to account for the qualitative behavior of real fluids, I need to emphasize that it is nowhere near exact. In "deriving" it I've neglected a number of effects, most notably the fact that as a gas becomes more dense it can become inhomogeneous on the microscopic scale: Clusters of molecules can begin to form, violating my assertion that the number of neighbors a molecule has will be directly proportional to N/V. So throughout this section, please keep in mind that we won't be making any accurate quantitative predictions. What we're after is qualitative understanding, which can provide a starting point if you later decide to study liquid-gas phase transformations in more depth.

The constants a and b will have different values for different substances, and (since the model isn't exact) will even vary somewhat for the same substance under different conditions. For small molecules like N_2 and H_2O, a good value of b is about $6 \times 10^{-29}\ \text{m}^3 \approx (4\ \text{Å})^3$, roughly the cube of the average width of the molecule. The constant a is much more variable, because some types of molecules attract each other much more strongly than others. For N_2, a good value of a is about $4 \times 10^{-49}\ \text{J}\cdot\text{m}^3$, or $2.5\ \text{eV}\cdot\text{Å}^3$. If we think of a as being roughly the product of the average interaction energy times the volume over which the interaction can act, then this value is fairly sensible: a small fraction of an electron-volt times a few tens of cubic ångstroms. The value of a for H_2O is about four times as large, because of the molecule's permanent electric polarization. Helium is at the other extreme, with interactions so weak that its value of a is 40 times less than that of nitrogen.

Now let us investigate the consequences of the van der Waals model. A good way to start is by plotting the predicted pressure as a function of volume for a variety of different temperatures (see Figure 5.20). At volumes much greater than Nb the isotherms are concave-up, like those of an ideal gas. At sufficiently high

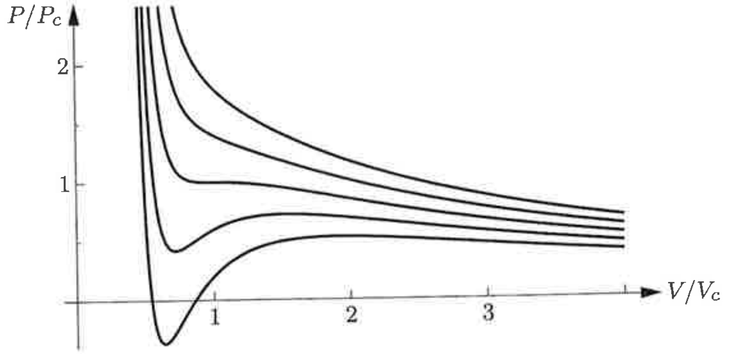


Figure 5.20. Isotherms (lines of constant temperature) for a van der Waals fluid. From bottom to top, the lines are for 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c, the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point; in these units the minimum volume (Nb) is 1/3.

temperatures, reducing the volume causes the pressure to rise smoothly, eventually approaching infinity as the volume goes to Nb. At lower temperatures, however, the behavior is much more complicated: As V decreases the isotherm rises, falls, and then rises again, seeming to imply that for some states, compressing the fluid can cause its pressure to decrease. Real fluids don't behave like this. But a more careful analysis shows that the van der Waals model doesn't predict this, either.

At a given temperature and pressure, the true equilibrium state of a system is determined by its Gibbs free energy. To calculate G for a van der Waals fluid, let's start with the thermodynamic identity for G:

$$dG = -S\,dT + V\,dP + \mu\,dN. \tag{5.53}$$

For a fixed amount of material at a given, fixed temperature, this equation reduces to $dG = V dP$. Dividing both sides by dV then gives

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{N,T}. \tag{5.54}$$

The right-hand side can be computed directly from the van der Waals equation (5.52), yielding

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}. \tag{5.55}$$

To integrate the right-hand side, write the V in the numerator of the first term as $(V - Nb) + (Nb)$, then integrate each of these two pieces separately. The result is

$$G = -NkT\ln(V-Nb) + \frac{(NkT)(Nb)}{V-Nb} - \frac{2aN^2}{V} + c(T), \tag{5.56}$$

where the integration constant, $c(T)$, can be different for different temperatures but is unimportant for our purposes. This equation allows us to plot the Gibbs free energy for any fixed T.

Instead of plotting G as a function of volume, it's more useful to plot G vertically and P horizontally, calculating each as a function of the parameter V. Figure 5.21 shows an example, for the temperature whose isotherm is shown alongside. Although the van der Waals equation associates some pressures with more than one volume, the thermodynamically stable state is that with the lowest Gibbs free energy; thus the triangular loop in the graph of G (points 2-3-4-5-6) corresponds to unstable states. As the pressure is gradually increased, the system will go straight from point 2 to point 6, with an abrupt decrease in volume: a phase transformation. At point 2 we should call the fluid a gas, because its volume decreases rapidly with increasing pressure. At point 6 we should call the fluid a liquid, because its volume decreases only slightly under a large increase in pressure. At intermediate volumes between these points, the thermodynamically stable state is actually a combination of part gas and part liquid, still at the transition pressure, as indicated by the straight horizontal line on the PV diagram. The curved portion of the isotherm that is cut off by this straight line correctly indicates what the allowed states *would* be if the fluid were homogeneous; but these homogeneous states are unstable, since

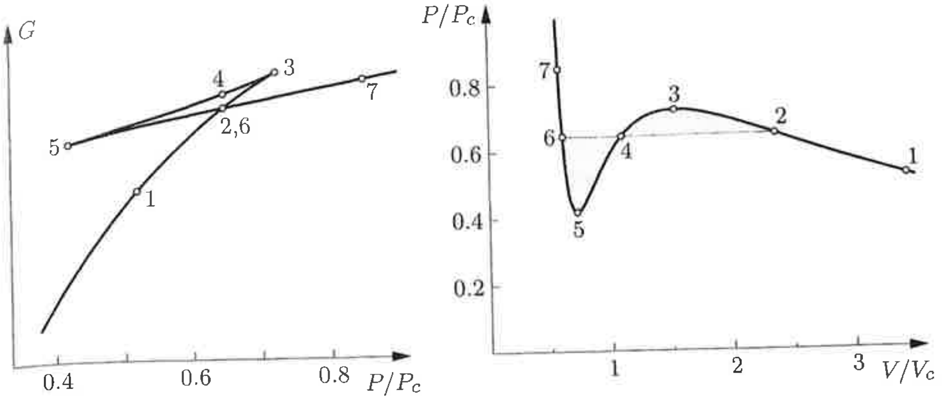


Figure 5.21. Gibbs free energy as a function of pressure for a van der Waals fluid at $T = 0.9T_c$. The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable.

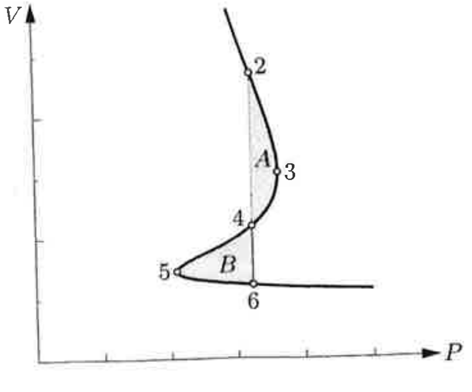
there is always another state (gas or liquid) at the same pressure with a lower Gibbs free energy.

The pressure at the phase transformation is easy enough to determine from the graph of G, but there is a clever method of reading it straight off the PV diagram, without plotting G at all. To derive this method, note that the net change in G as we go around the triangular loop (2-3-4-5-6) is zero:

$$0 = \int_{\text{loop}} dG = \int_{\text{loop}} \left(\frac{\partial G}{\partial P}\right)_T dP = \int_{\text{loop}} V\, dP. \tag{5.57}$$

Written in this last form, the integral can be computed from the PV diagram, though it's easier to turn the diagram sideways (see Figure 5.22). The integral from point 2 to point 3 gives the entire area under this segment, but the integral from point 3 to point 4 cancels out all but the shaded region A. The integral from 4 to 5 gives minus the area under that segment, but then the integral from 5 to 6 adds back all but the shaded region B. Thus the entire integral equals the area

Figure 5.22. The same isotherm as in Figure 5.21, plotted sideways. Regions A and B have equal areas.



of A minus the area of B, and if this is to equal zero, we conclude that the two shaded regions must have equal areas. Drawing the straight line so as to enclose equal areas in this way is called the **Maxwell construction**, after James Clerk Maxwell.

Repeating the Maxwell construction for a variety of temperatures yields the results shown in Figure 5.23. For each temperature there is a well-defined pressure, called the **vapor pressure**, at which the liquid-gas transformation takes place; plotting this pressure vs. temperature gives us a prediction for the entire liquid-gas phase boundary. Meanwhile, the straight segments of the isotherms on the PV diagram fill a region in which the stable state is a combination of gas and liquid, indicated by the shaded area.

But what about the *high*-temperature isotherms, which rise monotonically as V decreases? For these temperatures there is no abrupt transition from low-density states to high-density states: no phase transformation. The phase boundary therefore disappears above a certain temperature, called the **critical temperature**, T_c. The vapor pressure just at T_c is called the **critical pressure**, P_c, while the corresponding volume is called the **critical volume**, V_c. These values define the **critical point**, where the properties of the liquid and gas become identical.

I find it remarkable that a model as simple as the van der Waals equation predicts *all* of the important qualitative properties of real fluids: the liquid-gas phase transformation, the general shape of the phase boundary curve, and even the critical point. Unfortunately, the model fails when it comes to numbers. For example, the experimental phase boundary for H_2O falls more steeply from the critical point than does the predicted boundary shown above; at $T/T_c = 0.8$, the measured vapor pressure is only about $0.2P_c$, instead of $0.4P_c$ as predicted. More

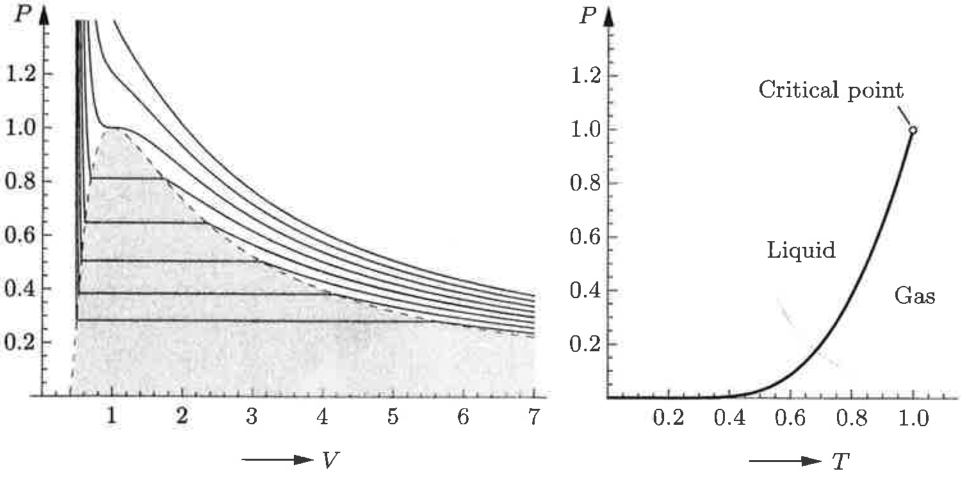


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values.