

5

Free Energy and Chemical Thermodynamics

The previous chapter applied the laws of thermodynamics to cyclic processes: the operation of engines and refrigerators whose energy and entropy are unchanged over the long term. But many important thermodynamic processes are not cyclic. Chemical reactions, for example, are constrained by the laws of thermodynamics but do not end with the system in the same state where it started.

The purpose of the present chapter is to apply the laws of thermodynamics to chemical reactions and other transformations of matter. One complication that arises immediately is that these transformations most often occur in systems that are not isolated but are interacting with their surroundings, thermally and often mechanically. The energy of the system itself is usually not fixed; rather its *temperature* is held fixed, through interaction with a constant-temperature environment. Similarly, in many cases it is not the volume of the system that is fixed but rather the pressure. Our first task, then, is to develop the conceptual tools needed to understand constant-temperature and constant-pressure processes.

5.1 Free Energy as Available Work

In Section 1.6 I defined the **enthalpy** of a system as its energy plus the work needed to make room for it, in an environment with constant pressure P :

$$H \equiv U + PV. \quad (5.1)$$

This is the total energy you would need, to create the system out of nothing and put it in such an environment. (Since the initial volume of the system is zero, $\Delta V = V$.) Or, if you could completely annihilate the system, H is the energy you could recover: the system's energy plus the work done by the collapsing atmosphere.

Often, however, we're not interested in the total energy needed or the total energy that can be recovered. If the environment is one of constant temperature,

the system can extract heat from this environment for free, so all *we* need to provide, to create the system from nothing, is any additional *work* needed. And if we annihilate the system, we generally can't recover all its energy as work, because we have to dispose of its entropy by dumping some heat into the environment.

So I'd like to introduce two more useful quantities that are related to energy and analogous to H . One is the **Helmholtz free energy**,

$$F \equiv U - TS. \quad (5.2)$$

This is the total energy needed to create the system, minus the heat you can get for free from an environment at temperature T . This heat is given by $T\Delta S = TS$, where S is the system's (final) entropy; the more entropy a system has, the more of its energy can enter as heat. Thus F is the energy that must be provided as work, if you're creating the system out of nothing.* Or if you annihilate the system, the maximum energy that comes out as work is F , since you have to dump some heat, equal to TS , into the environment in order to get rid of the system's entropy. The *available*, or "free," energy is F .

The word "work" in the previous paragraph means *all* work, including any that is done automatically by the system's surroundings. If the system is in an environment with constant pressure P and constant temperature T , then the work *you* need to do to create it, or the work you can recover when you destroy it, is given by the **Gibbs free energy**,

$$G \equiv U - TS + PV. \quad (5.3)$$

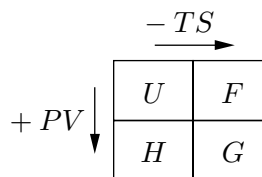
This is just the system's energy, minus the heat term that's in F , plus the atmospheric work term that's in H (see Figure 5.1).



Figure 5.1. To create a rabbit out of nothing and place it on the table, the magician need not summon up the entire enthalpy, $H = U + PV$. Some energy, equal to TS , can flow in spontaneously as heat; the magician must provide only the difference, $G = H - TS$, as work.

*In the context of creating a system, the term *free* energy is a misnomer. The energy that comes for free is TS , the term we *subtracted* to get F . In this context, F should be called the *costly* energy. The people who named F were instead thinking of the reverse process, where you annihilate the system and recover F as work.

Figure 5.2. To get H from U or G from F , add PV ; to get F from U or G from H , subtract TS .



The four functions U , H , F , and G are collectively called **thermodynamic potentials**. Figure 5.2 shows a diagram that I use to remember the definitions.

Usually, of course, we deal with processes that are much less dramatic than the creation or annihilation of an entire system. Then instead of F and G themselves, we want to look at the *changes* in these quantities.

For any change in the system that takes place at constant temperature T , the change in F is

$$\Delta F = \Delta U - T \Delta S = Q + W - T \Delta S, \quad (5.4)$$

where Q is the heat added and W is the work done on the system. If no *new* entropy is created during the process, then $Q = T \Delta S$, so the change in F is precisely equal to the work done on the system. If new entropy *is* created, then $T \Delta S$ will be greater than Q , so ΔF will be less than W . In general, therefore,

$$\Delta F \leq W \quad \text{at constant } T. \quad (5.5)$$

This W includes *all* work done on the system, including any work done automatically by its expanding or collapsing environment.

If the environment is one of constant pressure, and if we're not interested in keeping track of the work that the environment does automatically, then we should think about G instead of F . For any change that takes place at constant T and P , the change in G is

$$\Delta G = \Delta U - T \Delta S + P \Delta V = Q + W - T \Delta S + P \Delta V. \quad (5.6)$$

Again, the difference $Q - T \Delta S$ is always zero or negative. Meanwhile, W includes the work done by the environment, $-P \Delta V$, plus any “other” work (such as electrical work) done on the system:

$$W = -P \Delta V + W_{\text{other}}. \quad (5.7)$$

This $P \Delta V$ cancels the one in equation 5.6, leaving

$$\Delta G \leq W_{\text{other}} \quad \text{at constant } T, P. \quad (5.8)$$

Because free energy is such a useful quantity, values of ΔG for an enormous variety of chemical reactions and other processes have been measured and tabulated. There are many ways to measure ΔG . The easiest conceptually is to first measure ΔH for the reaction, by measuring the heat absorbed when the reaction takes place at constant pressure and no “other” work is done. Then calculate ΔS from

the entropies of the initial and final states of the system, determined separately from heat capacity data as described in Sections 3.2 and 3.4. Finally, compute

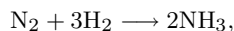
$$\Delta G = \Delta H - T \Delta S. \quad (5.9)$$

Values of ΔG for the formation of selected compounds and solutions (at $T = 298$ K and $P = 1$ bar) are given in the table at the back of this book. You can compute ΔG values for other reactions by imagining first that each reactant is converted to elemental form and then that these elements are converted into the products.

As with U and H , the actual *value* of F or G is unambiguous only if we include *all* the energy of the system, including the rest energy (mc^2) of every particle. In everyday situations this would be ridiculous, so instead we measure U from some other convenient but arbitrary reference point, and this arbitrary choice also fixes the zero points for H , F , and G . *Changes* in these quantities are unaffected by our choice of reference point, and changes are all we usually talk about anyway, so in practice we can often avoid choosing a reference point.

Problem 5.1. Let the system be one mole of argon gas at room temperature and atmospheric pressure. Compute the total energy (kinetic only, neglecting atomic rest energies), entropy, enthalpy, Helmholtz free energy, and Gibbs free energy. Express all answers in SI units.

Problem 5.2. Consider the production of ammonia from nitrogen and hydrogen,



at 298 K and 1 bar. From the values of ΔH and S tabulated at the back of this book, compute ΔG for this reaction and check that it is consistent with the value given in the table.

Electrolysis, Fuel Cells, and Batteries

As an example of using ΔG , consider the chemical reaction



the electrolysis of liquid water into hydrogen and oxygen gas (see Figure 5.3). Assume that we start with one mole of water, so we end with a mole of hydrogen and half a mole of oxygen.

According to standard reference tables, ΔH for this reaction (at room temperature and atmospheric pressure) is 286 kJ. This is the amount of heat you would get out if you burned a mole of hydrogen, running the reaction in reverse. When we *form* hydrogen and oxygen out of water, we need to put 286 kJ of energy into the system in some way or other. Of the 286 kJ, a small amount goes into pushing the atmosphere away to make room for the gases produced; this amount is $P \Delta V = 4$ kJ. The other 282 kJ remains in the system itself (see Figure 5.4). But of the 286 kJ needed, must we supply all as work, or can some enter as heat?

To answer this question we must determine the change in the system's entropy. The measured and tabulated entropy values for one mole of each species are

$$S_{\text{H}_2\text{O}} = 70 \text{ J/K}; \quad S_{\text{H}_2} = 131 \text{ J/K}; \quad S_{\text{O}_2} = 205 \text{ J/K}. \quad (5.11)$$



Figure 5.3. To separate water into hydrogen and oxygen, just run an electric current through it. In this home experiment the electrodes are mechanical pencil leads (graphite). Bubbles of hydrogen (too small to see) form at the negative electrode (left) while bubbles of oxygen form at the positive electrode (right).

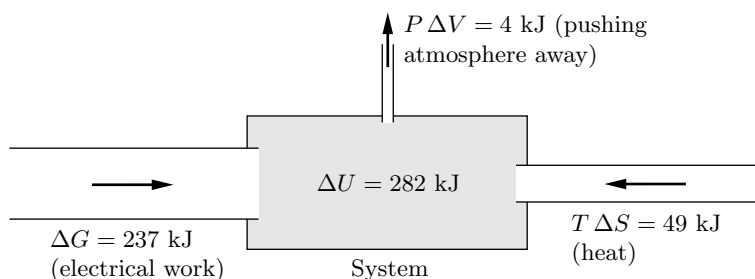


Figure 5.4. Energy-flow diagram for electrolysis of one mole of water. Under ideal conditions, 49 kJ of energy enter as heat ($T\Delta S$), so the electrical work required is only 237 kJ: $\Delta G = \Delta H - T\Delta S$. The difference between ΔH and ΔU is $P\Delta V = 4$ kJ, the work done to make room for the gases produced.

Subtract 70 from $(131 + \frac{1}{2} \cdot 205)$ and you get +163 J/K—the system’s entropy *increases* by this amount. The maximum amount of heat that can enter the system is therefore $T\Delta S = (298 \text{ K})(163 \text{ J/K}) = 49 \text{ kJ}$. The amount of energy that must enter as electrical work is the difference between 49 and 286, that is, 237 kJ.

This number, 237 kJ, is the change in the system’s Gibbs free energy; it is the minimum “other” work required to make the reaction go. To summarize the computation,

$$\begin{aligned} \Delta G &= \Delta H - T \Delta S, \\ 237 \text{ kJ} &= 286 \text{ kJ} - (298 \text{ K})(163 \text{ J/K}). \end{aligned} \quad (5.12)$$

For convenience, standard tables (like the one at the back of this book) generally include ΔG values, saving you from having to do this kind of arithmetic.

We can also apply ΔG to the reverse reaction. If you can combine hydrogen and oxygen gas to produce water in a controlled way, you can, in principle, extract 237 kJ of electrical work for every mole of hydrogen consumed. This is the principle

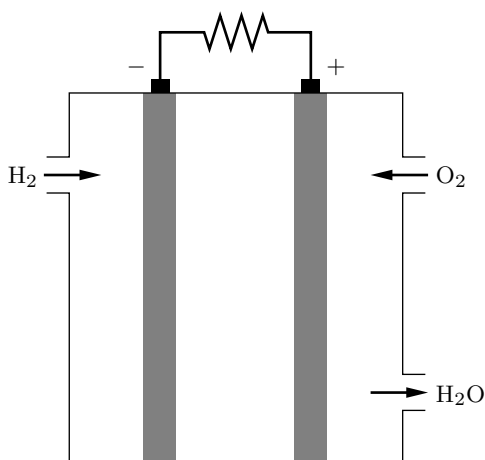
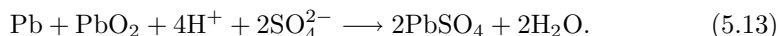


Figure 5.5. In a hydrogen fuel cell, hydrogen and oxygen gas pass through porous electrodes and react to form water, removing electrons from one electrode and depositing electrons on the other.

of the **fuel cell** (see Figure 5.5), a device that might replace the internal combustion engine in future automobiles.* In the process of producing this electrical work, the fuel cell will also expel 49 kJ of waste heat, in order to get rid of the excess entropy that was in the gases. But this waste heat is only 17% of the 286 kJ of heat that would be produced if you burned the hydrogen and tried to run a heat engine from it. So an ideal hydrogen fuel cell has an “efficiency” of 83%, much better than any practical heat engine. (In practice, the waste heat will be more and the efficiency less, but a typical fuel cell still beats almost any engine.)

A similar analysis can tell you the electrical energy output of a **battery**, which is like a fuel cell but has a fixed internal supply of fuel (usually not gaseous). For example, the familiar lead-acid cell used in car batteries runs on the reaction



According to thermodynamic tables, ΔG for this reaction is -394 kJ/mol, at standard pressure, temperature, and concentration of the solution. So the electrical work produced under these conditions, per mole of metallic lead, is 394 kJ. Meanwhile, ΔH for this reaction is -316 kJ/mol, so the energy that comes out of the chemicals is actually *less* than the work done, by 78 kJ. This extra energy comes from heat, absorbed from the environment. Along with this heat comes some entropy, but that’s fine, since the entropy of the products is greater than the entropy of the reactants, by $(78 \text{ kJ})/(298 \text{ K}) = 260 \text{ J/K}$ (per mole). These energy flows are shown in Figure 5.6. When you *charge* the battery, the reaction runs in reverse, taking the system back to its initial state. Then you have to put the 78 kJ of heat back into the environment, to get rid of the excess entropy.

You can also calculate the *voltage* of a battery or fuel cell, provided that you know how many electrons it pushes around the circuit for each molecule that reacts. To determine this number, it helps to look at the chemistry in more detail. For a

*See Sivan Kartha and Patrick Grimes, “Fuel Cells: Energy Conversion for the Next Century,” *Physics Today* **47**, 54–61 (November, 1994).

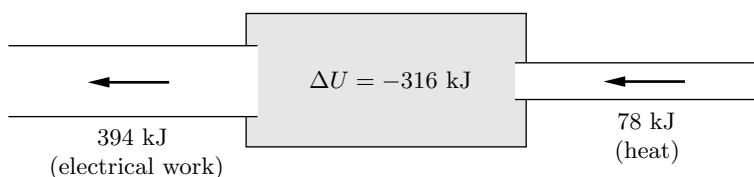
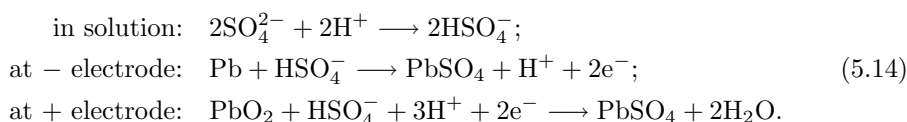


Figure 5.6. Energy-flow diagram for a lead-acid cell operating ideally. For each mole that reacts, the system's energy decreases by 316 kJ and its entropy increases by 260 J/K. Because of the entropy increase, the system can absorb 78 kJ of heat from the environment; the maximum work performed is therefore 394 kJ. (Because no gases are involved in this reaction, volume changes are negligible so $\Delta U \approx \Delta H$ and $\Delta F \approx \Delta G$.)

lead-acid cell, the reaction (5.13) takes place in three steps:



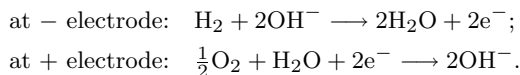
Thus, two electrons are pushed around the circuit each time the full reaction occurs. The electrical work produced *per electron* is

$$\frac{394 \text{ kJ}}{2 \cdot 6.02 \times 10^{23}} = 3.27 \times 10^{-19} \text{ J} = 2.04 \text{ eV}. \tag{5.15}$$

But 1 volt is just the voltage needed to give each electron 1 eV of energy, so the cell has a voltage of 2.04 V. In practice the voltage may be slightly different, because the concentrations used are different from the standard concentration (one mole per kilogram of water) assumed in thermodynamic tables. (By the way, a car battery contains six lead-acid cells, giving a total of about 12 V.)

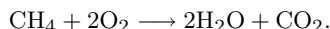
Problem 5.3. Use the data at the back of this book to verify the values of ΔH and ΔG quoted above for the lead-acid reaction 5.13.

Problem 5.4. In a hydrogen fuel cell, the steps of the chemical reaction are



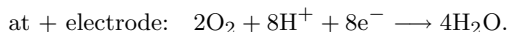
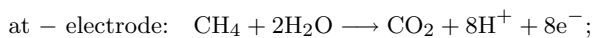
Calculate the voltage of the cell. What is the minimum voltage required for electrolysis of water? Explain briefly.

Problem 5.5. Consider a fuel cell that uses methane (“natural gas”) as fuel. The reaction is



- (a) Use the data at the back of this book to determine the values of ΔH and ΔG for this reaction, for one mole of methane. Assume that the reaction takes place at room temperature and atmospheric pressure, and that the water comes out in liquid form.

- (b) Assuming ideal performance, how much electrical work can you get out of the cell, for each mole of methane fuel?
- (c) How much waste heat is produced, for each mole of methane fuel?
- (d) The steps of this reaction are



What is the voltage of the cell?

Problem 5.6. A muscle can be thought of as a fuel cell, producing work from the metabolism of glucose:



- (a) Use the data at the back of this book to determine the values of ΔH and ΔG for this reaction, for one mole of glucose. Assume that the reaction takes place at room temperature and atmospheric pressure.
- (b) What is the maximum amount of work that a muscle can perform, for each mole of glucose consumed, assuming ideal operation?
- (c) Still assuming ideal operation, how much heat is absorbed or expelled by the chemicals during the metabolism of a mole of glucose? (Be sure to say which direction the heat flows.)
- (d) Use the concept of entropy to explain why the heat flows in the direction it does.
- (e) How would your answers to parts (b) and (c) change, if the operation of the muscle is not ideal?

Problem 5.7. The metabolism of a glucose molecule (see previous problem) occurs in many steps, resulting in the synthesis of 38 molecules of ATP (adenosine triphosphate) out of ADP (adenosine diphosphate) and phosphate ions. When the ATP splits back into ADP and phosphate, it liberates energy that is used in a host of important processes including protein synthesis, active transport of molecules across cell membranes, and muscle contraction. In a muscle, the reaction $\text{ATP} \rightarrow \text{ADP} + \text{phosphate}$ is catalyzed by an enzyme called myosin that is attached to a muscle filament. As the reaction takes place, the myosin molecule pulls on an adjacent filament, causing the muscle to contract. The force it exerts averages about 4 piconewtons and acts over a distance of about 11 nm. From this data and the results of the previous problem, compute the “efficiency” of a muscle, that is, the ratio of the actual work done to the maximum work that the laws of thermodynamics would allow.

Thermodynamic Identities

If you’re given the enthalpy or free energy of a substance under one set of conditions, but need to know its value under some other conditions, there are some handy formulas that are often useful. These formulas resemble the thermodynamic identity,

$$dU = T dS - P dV + \mu dN, \quad (5.16)$$

but are written for H or F or G instead of U .

I’ll start by deriving the formula for the change in H . If we imagine changing

H , U , P , and V by infinitesimal amounts, then the definition $H = U + PV$ tells us that

$$dH = dU + P dV + V dP. \quad (5.17)$$

The last two terms give the change in the product PV , according to the product rule for derivatives. Now use the thermodynamic identity 5.16 to eliminate dU , and cancel the $P dV$ terms to obtain

$$dH = T dS + V dP + \mu dN. \quad (5.18)$$

This “thermodynamic identity for H ” tells you how H changes as you change the entropy, pressure, and/or number of particles.*

Similar logic can be applied to F or G . From the definition of the Helmholtz free energy ($F = U - TS$), we have

$$dF = dU - T dS - S dT. \quad (5.19)$$

Plugging in equation 5.16 for dU and canceling the $T dS$ terms gives

$$dF = -S dT - P dV + \mu dN. \quad (5.20)$$

I’ll call this result the “thermodynamic identity for F .” From it one can derive a variety of formulas for partial derivatives. For instance, holding V and N fixed yields the identity

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}. \quad (5.21)$$

Similarly, holding T and either N or V fixed gives

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}. \quad (5.22)$$

Finally, you can derive the thermodynamic identity for G ,

$$dG = -S dT + V dP + \mu dN, \quad (5.23)$$

and from it the following partial derivative formulas:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}. \quad (5.24)$$

These formulas are especially useful for computing Gibbs free energies at nonstandard temperatures and pressures. For example, since the volume of a mole of

*Because of the thermodynamic identity for U , it is most natural to think of U as a function of the variables S , V , and N . Similarly, it is most natural to think of H as a function of S , P , and N . Adding the PV term to U is therefore a kind of change of variables, from V to P . Similarly, subtracting TS changes variables from S to T . The technical name for such a change is **Legendre transformation**.

graphite is $5.3 \times 10^{-6} \text{ m}^3$, its Gibbs free energy increases by $5.3 \times 10^{-6} \text{ J}$ for each pascal (N/m^2) of additional pressure.

In all of these formulas I have implicitly assumed that the system contains only one type of particles. If it is a mixture of several types, then you need to replace μdN with $\sum \mu_i dN_i$ in every thermodynamic identity. In the partial-derivative formulas with N fixed, *all* the N 's must be held fixed. And each formula with $\partial/\partial N$ becomes several formulas; so for a mixture of two types of particles,

$$\mu_1 = \left(\frac{\partial G}{\partial N_1} \right)_{T,P,N_2} \quad \text{and} \quad \mu_2 = \left(\frac{\partial G}{\partial N_2} \right)_{T,P,N_1}. \quad (5.25)$$

Problem 5.8. Derive the thermodynamic identity for G (equation 5.23), and from it the three partial derivative relations 5.24.

Problem 5.9. Sketch a qualitatively accurate graph of G vs. T for a pure substance as it changes from solid to liquid to gas at fixed pressure. Think carefully about the slope of the graph. Mark the points of the phase transformations and discuss the features of the graph briefly.

Problem 5.10. Suppose you have a mole of water at 25°C and atmospheric pressure. Use the data at the back of this book to determine what happens to its Gibbs free energy if you raise the temperature to 30°C . To compensate for this change, you could increase the pressure on the water. How much pressure would be required?

Problem 5.11. Suppose that a hydrogen fuel cell, as described in the text, is to be operated at 75°C and atmospheric pressure. We wish to estimate the maximum electrical work done by the cell, using only the room-temperature data at the back of this book. It is convenient to first establish a zero-point for each of the three substances, H_2 , O_2 , and H_2O . Let us take G for both H_2 and O_2 to be zero at 25°C , so that G for a mole of H_2O is -237 kJ at 25°C .

- (a) Using these conventions, estimate the Gibbs free energy of a mole of H_2 at 75°C . Repeat for O_2 and H_2O .
- (b) Using the results of part (a), calculate the maximum electrical work done by the cell at 75°C , for one mole of hydrogen fuel. Compare to the ideal performance of the cell at 25°C .

Problem 5.12. Functions encountered in physics are generally well enough behaved that their mixed partial derivatives do not depend on which derivative is taken first. Therefore, for instance,

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

where each $\partial/\partial V$ is taken with S fixed, each $\partial/\partial S$ is taken with V fixed, and N is always held fixed. From the thermodynamic identity (for U) you can evaluate the partial derivatives in parentheses to obtain

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

a nontrivial identity called a **Maxwell relation**. Go through the derivation of this relation step by step. Then derive an analogous Maxwell relation from each of

the other three thermodynamic identities discussed in the text (for H , F , and G). Hold N fixed in all the partial derivatives; other Maxwell relations *can* be derived by considering partial derivatives with respect to N , but after you've done four of them the novelty begins to wear off. For applications of these Maxwell relations, see the next four problems.

Problem 5.13. Use a Maxwell relation from the previous problem and the third law of thermodynamics to prove that the thermal expansion coefficient β (defined in Problem 1.7) must be zero at $T = 0$.

Problem 5.14. The partial-derivative relations derived in Problems 1.46, 3.33, and 5.12, plus a bit more partial-derivative trickery, can be used to derive a completely general relation between C_P and C_V .

- (a) With the heat capacity expressions from Problem 3.33 in mind, first consider S to be a function of T and V . Expand dS in terms of the partial derivatives $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$. Note that one of these derivatives is related to C_V .
- (b) To bring in C_P , consider V to be a function of T and P and expand dV in terms of partial derivatives in a similar way. Plug this expression for dV into the result of part (a), then set $dP = 0$ and note that you have derived a nontrivial expression for $(\partial S/\partial T)_P$. This derivative is related to C_P , so you now have a formula for the difference $C_P - C_V$.
- (c) Write the remaining partial derivatives in terms of measurable quantities using a Maxwell relation and the result of Problem 1.46. Your final result should be

$$C_P = C_V + \frac{TV\beta^2}{\kappa_T}.$$

- (d) Check that this formula gives the correct value of $C_P - C_V$ for an ideal gas.
- (e) Use this formula to argue that C_P cannot be less than C_V .
- (f) Use the data in Problem 1.46 to evaluate $C_P - C_V$ for water and for mercury at room temperature. By what percentage do the two heat capacities differ?
- (g) Figure 1.14 shows measured values of C_P for three elemental solids, compared to predicted values of C_V . It turns out that a graph of β vs. T for a solid has same general appearance as a graph of heat capacity. Use this fact to explain why C_P and C_V agree at low temperatures but diverge in the way they do at higher temperatures.

Problem 5.15. The formula for $C_P - C_V$ derived in the previous problem can also be derived starting with the definitions of these quantities in terms of U and H . Do so. Most of the derivation is very similar, but at one point you need to use the relation $P = -(\partial F/\partial V)_T$.

Problem 5.16. A formula analogous to that for $C_P - C_V$ relates the isothermal and isentropic compressibilities of a material:

$$\kappa_T = \kappa_S + \frac{TV\beta^2}{C_P}.$$

(Here $\kappa_S = -(1/V)(\partial V/\partial P)_S$ is the reciprocal of the adiabatic bulk modulus considered in Problem 1.39.) Derive this formula. Also check that it is true for an ideal gas.

Problem 5.17. The enthalpy and Gibbs free energy, as defined in this section, give special treatment to mechanical (compression-expansion) work, $-P dV$. Analogous quantities can be defined for other kinds of work, for instance, magnetic work.* Consider the situation shown in Figure 5.7, where a long solenoid (N turns, total length L) surrounds a magnetic specimen (perhaps a paramagnetic solid). If the magnetic field inside the specimen is \vec{B} and its total magnetic moment is \vec{M} , then we define an auxiliary field $\vec{\mathcal{H}}$ (often called simply the magnetic field) by the relation

$$\vec{\mathcal{H}} \equiv \frac{1}{\mu_0} \vec{B} - \frac{\vec{M}}{V},$$

where μ_0 is the “permeability of free space,” $4\pi \times 10^{-7} \text{ N/A}^2$. Assuming cylindrical symmetry, all vectors must point either left or right, so we can drop the $\vec{}$ symbols and agree that rightward is positive, leftward negative. From Ampere’s law, one can also show that when the current in the wire is I , the \mathcal{H} field inside the solenoid is NI/L , whether or not the specimen is present.

- Imagine making an infinitesimal change in the current in the wire, resulting in infinitesimal changes in B , M , and \mathcal{H} . Use Faraday’s law to show that the work required (from the power supply) to accomplish this change is $W_{\text{total}} = V\mathcal{H} dB$. (Neglect the resistance of the wire.)
- Rewrite the result of part (a) in terms of \mathcal{H} and M , then subtract off the work that would be required even if the specimen were not present. If we define W , the work done on the *system*,[†] to be what’s left, show that $W = \mu_0 \mathcal{H} dM$.
- What is the thermodynamic identity for this system? (Include magnetic work but not mechanical work or particle flow.)
- How would you define analogues of the enthalpy and Gibbs free energy for a magnetic system? (The Helmholtz free energy is defined in the same way as for a mechanical system.) Derive the thermodynamic identities for each of these quantities, and discuss their interpretations.

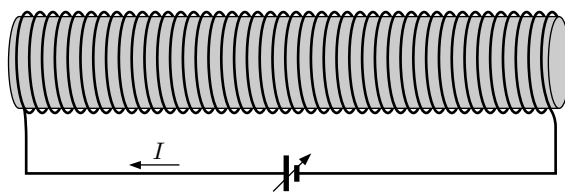


Figure 5.7. A long solenoid, surrounding a magnetic specimen, connected to a power supply that can change the current, performing magnetic work.

*This problem requires some familiarity with the theory of magnetism in matter. See, for instance, David J. Griffiths, *Introduction to Electrodynamics*, third edition (Prentice-Hall, Englewood Cliffs, NJ, 1999), Chapter 6.

[†]This is not the only possible definition of the “system.” Different definitions are suitable for different physical situations, unfortunately leading to much confusion in terminology. For a more complete discussion of the thermodynamics of magnetism see Mandl (1988), Carrington (1994), and/or Pippard (1957).

5.2 Free Energy as a Force toward Equilibrium

For an *isolated* system, the *entropy* tends to increase; the system's entropy is what governs the direction of spontaneous change. But what if a system is *not* isolated? Suppose, instead, that our system is in good thermal contact with its environment (see Figure 5.8). Now energy can pass between the system and the environment, and the thing that tends to increase is not the *system's* entropy but rather the *total* entropy of system plus environment. In this section I'd like to restate this rule in a more useful form.

I'll assume that the environment acts as a “reservoir” of energy, large enough that it can absorb or release unlimited amounts of energy without changing its temperature. The total entropy of the universe can be written as $S + S_R$, where a subscript R indicates a property of the reservoir, while a quantity without a subscript refers to the system alone. The fundamental rule is that the total entropy of the universe tends to increase, so let's consider a small change in the total entropy:

$$dS_{\text{total}} = dS + dS_R. \quad (5.26)$$

I would like to write this quantity entirely in terms of system variables. To do so, I'll apply the thermodynamic identity, in the form

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN, \quad (5.27)$$

to the reservoir. First I'll assume that V and N for the reservoir are fixed—only energy travels in and out of the system. Then $dS_R = dU_R/T_R$, so equation 5.26 can be written

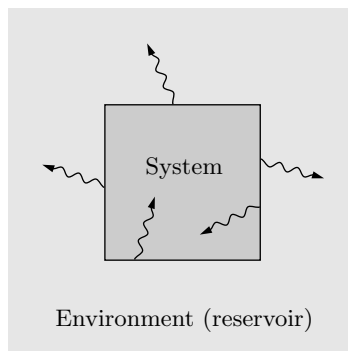
$$dS_{\text{total}} = dS + \frac{1}{T_R} dU_R. \quad (5.28)$$

But the temperature of the reservoir is the same as the temperature of the system, while the change dU_R in the reservoir's energy is minus the change dU in the system's energy. Therefore,

$$dS_{\text{total}} = dS - \frac{1}{T} dU = -\frac{1}{T} (dU - T dS) = -\frac{1}{T} dF. \quad (5.29)$$

Aha! Under these conditions (fixed T , V , and N), an increase in the total entropy of the universe is the same thing as a *decrease* in the Helmholtz free energy of the

Figure 5.8. For a system that can exchange energy with its environment, the total entropy of both tends to increase.



system. So we can forget about the reservoir, and just remember that the system will do whatever it can to *minimize* its Helmholtz free energy. By the way, we could have guessed this result from equation 5.5, $\Delta F \leq W$. If *no* work is done on the system, F can only decrease.

If instead we let the volume of the system change but keep it at the same constant *pressure* as the reservoir, then the same line of reasoning gives

$$dS_{\text{total}} = dS - \frac{1}{T} dU - \frac{P}{T} dV = -\frac{1}{T}(dU - T dS + P dV) = -\frac{1}{T} dG, \quad (5.30)$$

so it is the *Gibbs* free energy that tends to decrease. Again, we could have guessed this from equation 5.8, $\Delta G \leq W_{\text{other}}$.

Let me summarize these points, just for emphasis:

- At constant energy and volume, S tends to increase.
- At constant temperature and volume, F tends to decrease.
- At constant temperature and pressure, G tends to decrease.

All three statements assume that no particles are allowed to enter or leave the system (but see Problem 5.23).

We can understand these tendencies intuitively by looking again at the definitions of the Helmholtz and Gibbs free energies. Recall that

$$F \equiv U - TS. \quad (5.31)$$

So in a constant-temperature environment, saying that F tends to decrease is the same as saying that U tends to decrease while S tends to increase. Well, we already know that S tends to increase. But does a system's energy tend to spontaneously decrease? Your intuition probably says yes, and this is correct, but *only* because when the system loses energy, its environment gains that energy, and therefore the *entropy* of the environment increases. At low temperature, this effect tends to be more important, since the entropy transferred to the environment for a given energy transfer is large, proportional to $1/T$. But at high temperature, the environment doesn't gain as much entropy, so the entropy of the system becomes more important in determining the behavior of F .

Similar considerations apply to the Gibbs free energy,

$$G \equiv U + PV - TS. \quad (5.32)$$

Now, however, the entropy of the environment can increase in two ways: It can acquire energy from the system, or it can acquire volume from the system. So the system's U and V “want” to decrease, while S “wants” to increase, all in the interest of maximizing the total entropy of the universe.

Problem 5.18. Imagine that you drop a brick on the ground and it lands with a thud. Apparently the energy of this system tends to spontaneously decrease. Explain why.

Problem 5.19. In the previous section I derived the formula $(\partial F/\partial V)_T = -P$. Explain why this formula makes intuitive sense, by discussing graphs of F vs. V with different slopes.

Problem 5.20. The first excited energy level of a hydrogen atom has an energy of 10.2 eV, if we take the ground-state energy to be zero. However, the first excited level is really four independent states, all with the same energy. We can therefore assign it an entropy of $S = k \ln 4$, since for this given value of the energy, the multiplicity is 4. Question: For what temperatures is the Helmholtz free energy of a hydrogen atom in the first excited level positive, and for what temperatures is it negative? (Comment: When F for the level is negative, the atom will spontaneously go from the ground state into that level, since $F = 0$ for the ground state and F always tends to decrease. However, for a system this small, the conclusion is only a probabilistic statement; random fluctuations will be very significant.)

Extensive and Intensive Quantities

The number of potentially interesting thermodynamic variables has been growing lately. We now have U , V , N , S , T , P , μ , H , F , and G , among others. One way to organize all these quantities is to pick out the ones that double if you simply double the amount of stuff, adding the new alongside what you had originally (see Figure 5.9). Under this hypothetical operation, you end up with twice the energy and twice the volume, but *not* twice the temperature. Those quantities that *do* double are called **extensive quantities**. Those quantities that are *unchanged* when the amount of stuff doubles are called **intensive quantities**. Here's a list, divided according to this classification:

Extensive: V , N , S , U , H , F , G , mass

Intensive: T , P , μ , density

If you multiply an extensive quantity by an intensive quantity, you end up with an extensive quantity; for example, volume \times density = mass. By the same token, if you divide one extensive quantity by another, you get an intensive quantity. If you multiply two extensive quantities together, you get something that is *neither*; if you're confronted with such a product in one of your calculations, there's a good chance you did something wrong. Adding two quantities of the same type

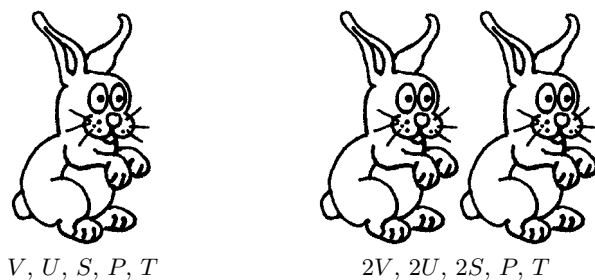


Figure 5.9. Two rabbits have twice as much volume, energy, and entropy as one rabbit, but not twice as much pressure or temperature.

yields another quantity of that type; for instance, $H = U + PV$. Adding an extensive quantity to an intensive one isn't allowed at all, so (for instance) you'll never encounter the sum $G + \mu$, even though G and μ have the same units. There's nothing wrong with exponentiating an extensive quantity, however; then you get a quantity that is *multiplicative*, like $\Omega = e^{S/k}$.

It's a good exercise to go back over the various equations involving F and G and show that they make sense in terms of extensiveness and intensiveness. For instance, in the thermodynamic identity for G ,

$$dG = -S dT + V dP + \sum_i \mu_i dN_i, \quad (5.33)$$

each term is extensive, because each product involves one extensive and one intensive quantity.

Problem 5.21. Is heat capacity (C) extensive or intensive? What about specific heat (c)? Explain briefly.

Gibbs Free Energy and Chemical Potential

Using the idea of extensive and intensive quantities, we can now derive another useful relation involving the Gibbs free energy. First recall the partial-derivative relation

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}. \quad (5.34)$$

This equation says that if you add one particle to a system, holding the temperature and pressure fixed, the Gibbs free energy of the system increases by μ (see Figure 5.10). If you keep adding more particles, each one again adds μ to the Gibbs free energy. Now you might think that during this procedure the value of μ could gradually change, so that by the time you've doubled the number of particles, μ has a very different value from when you started. But in fact, if T and P are held fixed, this can't happen: Each additional particle must add exactly the *same* amount to G , because G is an extensive quantity that must simply grow in proportion to the number of particles. The constant of proportionality, according to equation 5.34, is simply μ :

$$G = N\mu. \quad (5.35)$$

This amazingly simple equation gives us a new interpretation of the chemical potential, at least for a pure system with only one type of particle: μ is just the Gibbs free energy per particle.

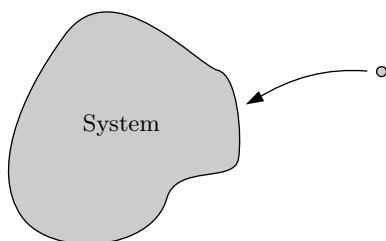


Figure 5.10. When you add a particle to a system, holding the temperature and pressure fixed, the system's Gibbs free energy increases by μ .

The preceding argument is subtle, so please think it through carefully. Perhaps the best way to understand it is to think about why the same logic can't be applied to the Helmholtz free energy, starting with the true relation

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}. \quad (5.36)$$

The problem here is that to increase F by an amount μ , you have to add a particle while holding the temperature and *volume* fixed. Now, as you add more and more particles, μ *does* gradually change, because the system is becoming more dense. It's true that F is an extensive quantity, but this does *not* imply that F doubles when you double the density of the system, holding its volume fixed. In the previous paragraph it was crucial that the two variables being held fixed in equation 5.34, T and P , were both intensive, so that all extensive quantities could grow in proportion to N .

For a system containing more than one type of particle, equation 5.35 generalizes in a natural way:

$$G = N_1\mu_1 + N_2\mu_2 + \cdots = \sum_i N_i\mu_i. \quad (5.37)$$

The proof is the same as before, except that we imagine building up the system in infinitesimal increments keeping the proportions of the various species fixed throughout the process. This result does *not* imply, however, that G for a mixture is simply equal to the sum of the G 's for the pure components. The μ 's in equation 5.37 are generally *different* from their values for the corresponding pure substances.

As a first application of equation 5.35, let me now derive a very general formula for the chemical potential of an ideal gas. Consider a fixed amount of gas at a fixed temperature, as we vary the pressure. By equations 5.35 and 5.24,

$$\frac{\partial \mu}{\partial P} = \frac{1}{N} \frac{\partial G}{\partial P} = \frac{V}{N}. \quad (5.38)$$

But by the ideal gas law this quantity is just kT/P . Integrating both sides from P° up to P therefore gives

$$\mu(T, P) - \mu(T, P^\circ) = kT \ln(P/P^\circ). \quad (5.39)$$

Here P° can be any convenient reference pressure. Usually we take P° to be atmospheric pressure (1 bar, to be precise). The standard symbol for μ for a gas at atmospheric pressure is μ° , so we can write

$$\mu(T, P) = \mu^\circ(T) + kT \ln(P/P^\circ). \quad (5.40)$$

Values of μ° (at least at room temperature) can be gotten from tables of Gibbs free energies ($\mu = G/N$). Equation 5.40 then tells you how μ varies as the pressure (or equivalently, the density) changes. And in a *mixture* of ideal gases, equation 5.40 applies to each species separately, if you take P to be the *partial* pressure of that species. This works because ideal gases are mostly empty space: How an ideal gas exchanges particles with its environment isn't going to be affected by the presence of another ideal gas.

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**),

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

- Derive the thermodynamic identity for Φ , and the related formulas for the partial derivatives of Φ with respect to T , V , and μ .
- Prove that, for a system in thermal and diffusive equilibrium (with a reservoir that can supply both energy and particles), Φ tends to decrease.
- Prove that $\Phi = -PV$.
- 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

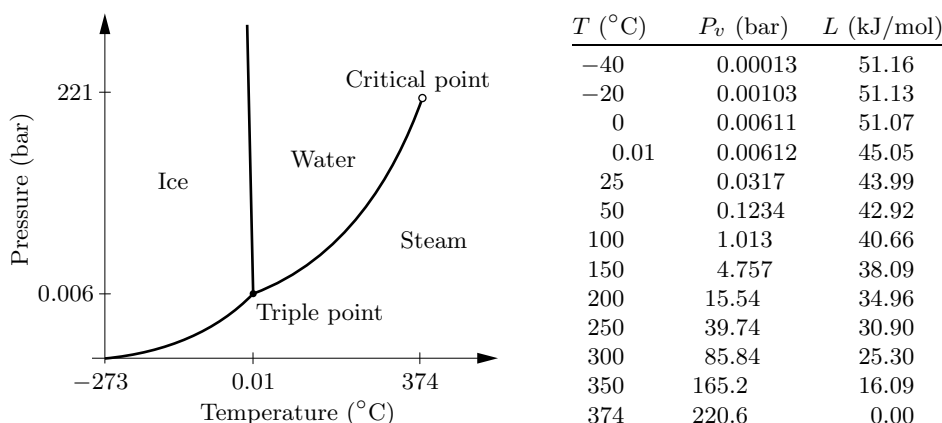


Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).

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 $T = 0.01^{\circ}\text{C}$ 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

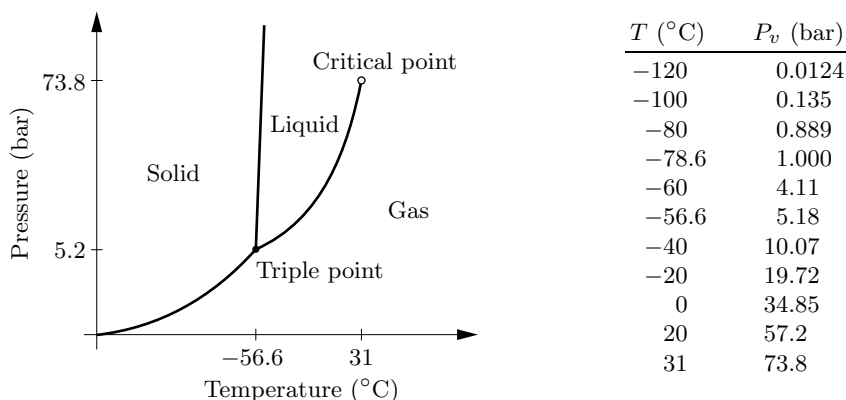


Figure 5.12. Phase diagram for carbon dioxide (not to scale). The table gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Data from Lide (1994) and Reynolds (1979).

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 H₂O. 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 ⁴He and the rare isotope ³He. The boiling point of ⁴He 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 ³He 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 ⁴He and 30 bars for ³He. The solid-liquid phase boundary for ⁴He is almost horizontal below 1 K, while for ³He this boundary has a *negative* slope below 0.3 K. Even more interesting, ⁴He has two distinct liquid phases: a “normal” phase called helium I, and a **superfluid**

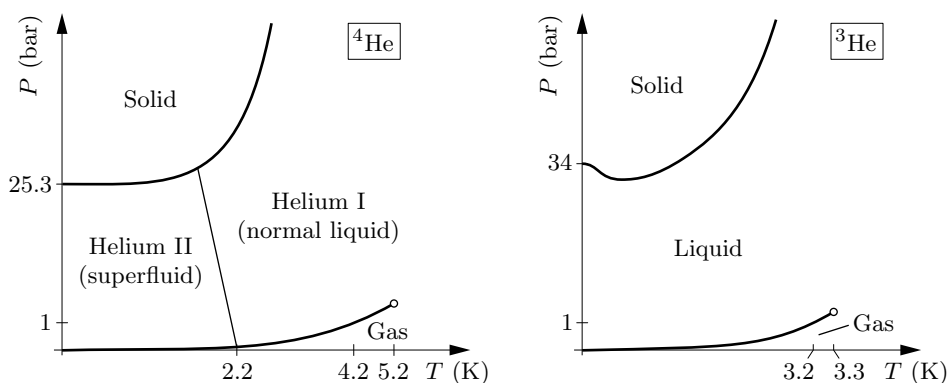


Figure 5.13. Phase diagrams of ⁴He (left) and ³He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ³He below 3 mK.

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.*

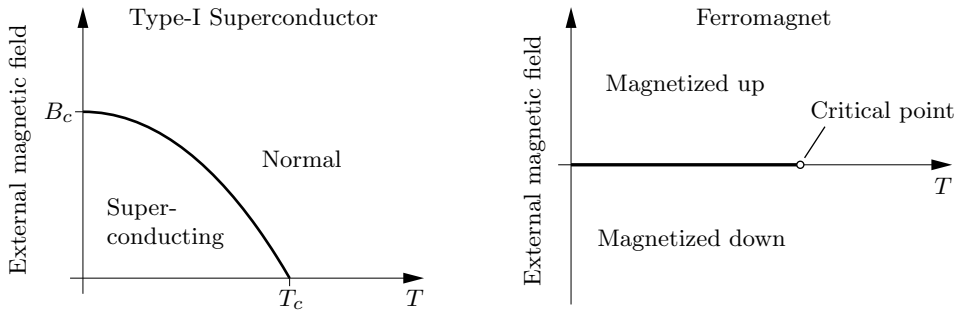


Figure 5.14. Left: Phase diagram for a typical type-I superconductor. For lead, $T_c = 7.2$ K and $B_c = 0.08$ T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis.

*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,

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

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 $V = 5.31 \times 10^{-6} \text{ m}^3$ for graphite and $V = 3.42 \times 10^{-6} \text{ m}^3$ 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,

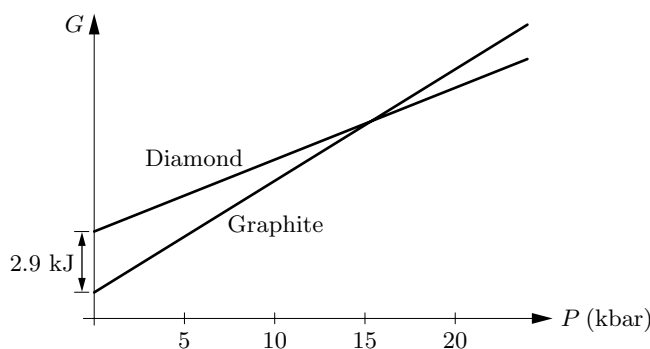


Figure 5.15. Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases.

*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

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

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 $3 \times 10^{-6} \text{ bar}^{-1}$, 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.

- 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.
- 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.

- Taking ΔS to be independent of T , find the range of temperatures over which kyanite, andalusite, and sillimanite should be stable (at 1 bar).
- Referring to the room-temperature heat capacities of the three forms of Al_2SiO_5 , discuss the accuracy the approximation $\Delta S = \text{constant}$.

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

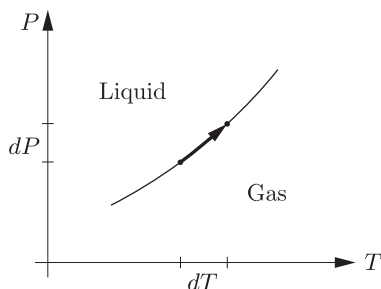
Since entropy determines the temperature dependence of the Gibbs free energy, while volume determines its pressure dependence, the shape of any phase boundary line on a PT diagram is related in a very simple way to the entropies and volumes of the two phases. Let me now derive this relation.

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:

$$G_l = G_g \quad \text{at phase boundary.} \quad (5.43)$$

(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

$$dG_l = dG_g \quad \text{to remain on phase boundary.} \quad (5.44)$$

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

$$-S_l dT + V_l dP = -S_g dT + V_g dP. \quad (5.45)$$

(I've omitted the μdN 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 :

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}. \quad (5.46)$$

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

$$\frac{dP}{dT} = \frac{L}{T \Delta V}, \quad (5.47)$$

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 $1.9 \times 10^{-6} \text{ m}^3$. (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

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{3.4 \text{ J/K}}{1.9 \times 10^{-6} \text{ m}^3} = 1.8 \times 10^6 \text{ Pa/K} = 18 \text{ bar/K}. \quad (5.48)$$

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.*

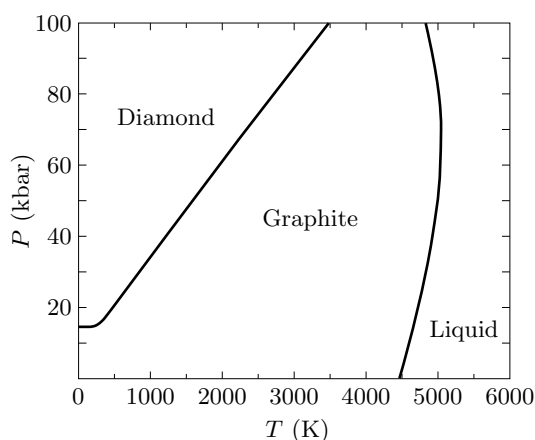


Figure 5.17. The experimental phase diagram of carbon. The stability region of the gas phase is not visible on this scale; the graphite-liquid-gas triple point is at the bottom of the graphite-liquid phase boundary, at 110 bars pressure. From David A. Young, *Phase Diagrams of the Elements* (University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

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

- Use the Clausius-Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.
- How much pressure would you have to put on an ice cube to make it melt at -1°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.)
- 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?

*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 ^3He solid-liquid phase boundary is negative (see Figure 5.13).

- Which phase, solid or liquid, is more dense? Which phase has more entropy (per mole)? Explain your reasoning carefully.
- 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 ^4He solid-liquid phase boundary is essentially horizontal below 1 K.)
- Suppose that you compress liquid ^3He 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.

- 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?
- 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.
- 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:



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 H₂O 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

*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.



Figure 5.18. Cumulus clouds form when rising air expands adiabatically and cools to the dew point (Problem 5.44); the onset of condensation slows the cooling, increasing the tendency of the air to rise further (Problem 5.45). These clouds began to form in late morning, in a sky that was clear only an hour before the photo was taken. By mid-afternoon they had developed into thunderstorms.

the latter using the “barometric equation” from Problem 1.16. You should finally obtain

$$\frac{dT}{dz} = -\left(\frac{2Mg}{7R}\right) \frac{1 + \frac{P_v}{P} \frac{L}{RT}}{1 + \frac{2}{7} \frac{P_v}{P} \left(\frac{L}{RT}\right)^2},$$

where M is the mass of a mole of air. The prefactor is just the dry adiabatic lapse rate calculated in Problem 1.40, while the rest of the expression gives the correction due to heating from the condensing water vapor. The whole result is called the **wet adiabatic lapse rate**; it is the critical temperature gradient above which saturated air will spontaneously convect.

- (d) Calculate the wet adiabatic lapse rate at atmospheric pressure (1 bar) and 25°C, then at atmospheric pressure and 0°C. Explain why the results are different, and discuss their implications. What happens at higher altitudes, where the pressure is lower?

Problem 5.46. Everything in this section so far has ignored the *boundary* between two phases, as if each molecule were unequivocally part of one phase or the other. In fact, the boundary is a kind of transition zone where molecules are in an environment that differs from both phases. Since the boundary zone is only a few molecules thick, its contribution to the total free energy of a system is very often negligible. One important exception, however, is the first tiny droplets or bubbles or grains that form as a material begins to undergo a phase transformation. The formation of these initial specks of a new phase is called **nucleation**. In this problem we will consider the nucleation of water droplets in a cloud.

The surface forming the boundary between any two given phases generally has a fixed thickness, regardless of its area. The additional Gibbs free energy of this surface is therefore directly proportional to its area; the constant of proportionality is called the **surface tension**, σ :

$$\sigma \equiv \frac{G_{\text{boundary}}}{A}.$$

If you have a blob of liquid in equilibrium with its vapor and you wish to stretch it into a shape that has the same volume but more surface area, then σ is the minimum work that you must perform, per unit of additional area, at fixed temperature and pressure. For water at 20°C, $\sigma = 0.073 \text{ J/m}^2$.

- (a) Consider a spherical droplet of water containing N_l molecules, surrounded by $N - N_l$ molecules of water vapor. Neglecting surface tension for the moment, write down a formula for the total Gibbs free energy of this system in terms of N , N_l , and the chemical potentials of the liquid and vapor. Rewrite N_l in terms of v_l , the volume per molecule in the liquid, and r , the radius of the droplet.
- (b) Now add to your expression for G a term to represent the effect of surface tension, written in terms of r and σ .
- (c) Sketch a qualitative graph of G vs. r for both signs of $\mu_g - \mu_l$, and discuss the implications. For which sign of $\mu_g - \mu_l$ does there exist a nonzero equilibrium radius? Is this equilibrium stable?
- (d) Let r_c represent the critical equilibrium radius that you discussed qualitatively in part (c). Find an expression for r_c in terms of $\mu_g - \mu_l$. Then rewrite the difference of chemical potentials in terms of the relative humidity (see Problem 5.42), assuming that the vapor behaves as an ideal gas. (The relative humidity is defined in terms of equilibrium of a vapor with a flat surface, or with an infinitely large droplet.) Sketch a graph of the critical radius as a function of the relative humidity, including numbers. Discuss the implications. In particular, explain why it is unlikely that the clouds in our atmosphere would form by spontaneous aggregation of water molecules into droplets. (In fact, cloud droplets form around nuclei of dust particles and other foreign material, when the relative humidity is close to 100%.)

Problem 5.47. For a *magnetic* system held at constant T and \mathcal{H} (see Problem 5.17), the quantity that is minimized is the magnetic analogue of the Gibbs free energy, which obeys the thermodynamic identity

$$dG_m = -S dT - \mu_0 M d\mathcal{H}.$$

Phase diagrams for two magnetic systems are shown in Figure 5.14; the vertical axis on each of these figures is $\mu_0 \mathcal{H}$.

- (a) Derive an analogue of the Clausius-Clapeyron relation for the slope of a phase boundary in the \mathcal{H} - T plane. Write your equation in terms of the difference in entropy between the two phases.
- (b) Discuss the application of your equation to the ferromagnet phase diagram in Figure 5.14.
- (c) In a type-I superconductor, surface currents flow in such a way as to completely cancel the magnetic field (B , not \mathcal{H}) inside. Assuming that M is negligible when the material is in its normal (non-superconducting) state, discuss the application of your equation to the superconductor phase diagram in Figure 5.14. Which phase has the greater entropy? What happens to the difference in entropy between the phases at each end of the phase boundary?

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**,

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

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:

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

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, $dU = -PdV$ or $P = -(\partial U/\partial V)_S$. The contribution to the pressure from just the potential energy is therefore

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

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

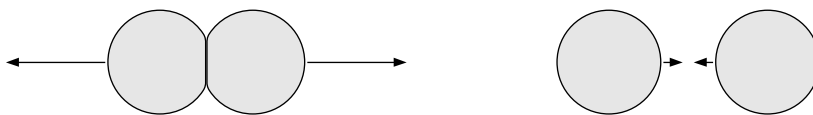


Figure 5.19. When two molecules come very close together they repel each other strongly. When they are a short distance apart they attract each other.

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

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

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 $6 \times 10^{-29} \text{ m}^3 \approx (4 \text{ \AA})^3$, 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 $2.5 \text{ eV}\cdot\text{\AA}^3$. 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 ångströms. 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

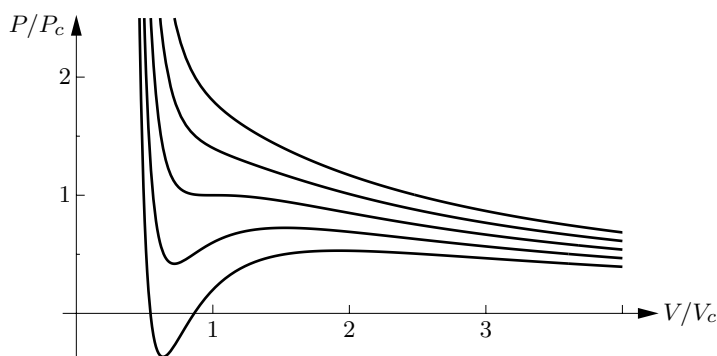


Figure 5.20. Isotherms (lines of constant temperature) for a van der Waals fluid. From bottom to top, the lines are for 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c , the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point; in these units the minimum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

$$dG = -S dT + V dP + \mu dN. \quad (5.53)$$

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

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

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

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

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

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

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

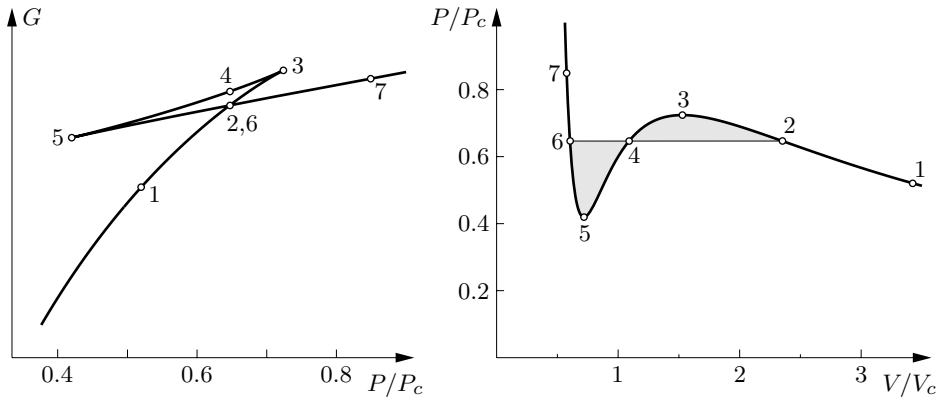


Figure 5.21. Gibbs free energy as a function of pressure for a van der Waals fluid at $T = 0.9T_c$. The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable.

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:

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

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

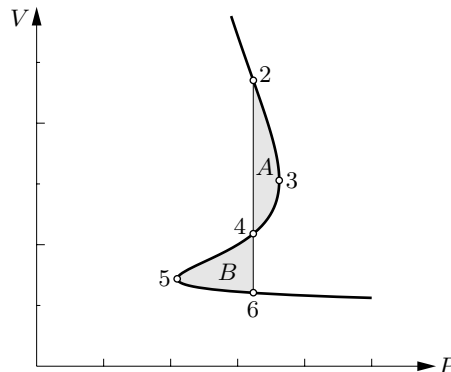


Figure 5.22. The same isotherm as in Figure 5.21, plotted sideways. Regions A and B have equal areas.

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 in Figure 5.23; at $T/T_c = 0.8$, the measured vapor pressure is only about $0.2P_c$, instead of $0.4P_c$ as predicted.

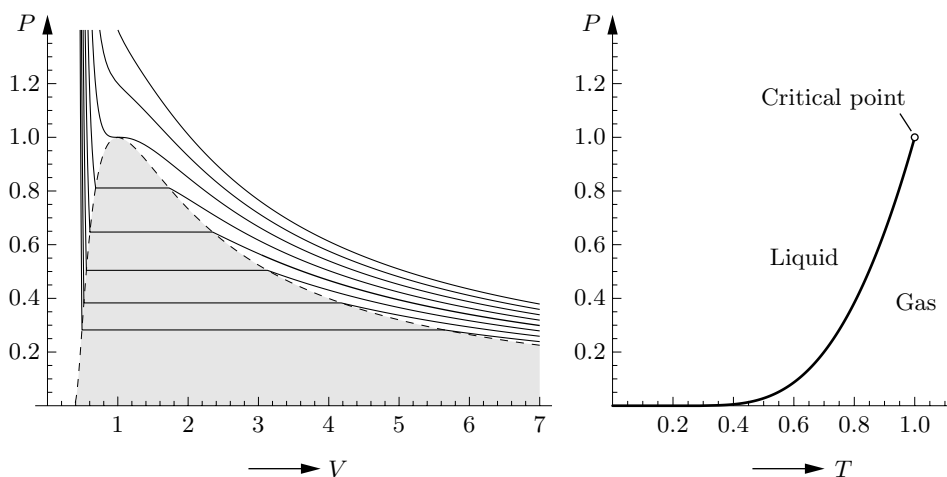


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are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

More accurate models of the behavior of dense fluids are beyond the scope of this book,* but at least we've taken a first step toward understanding the liquid-gas phase transformation.

Problem 5.48. As you can see from Figure 5.20, the critical point is the unique point on the original van der Waals isotherms (before the Maxwell construction) where both the first and second derivatives of P with respect to V (at fixed T) are zero. Use this fact to show that

$$V_c = 3Nb, \quad P_c = \frac{1}{27} \frac{a}{b^2}, \quad \text{and} \quad kT_c = \frac{8}{27} \frac{a}{b}.$$

Problem 5.49. Use the result of the previous problem and the approximate values of a and b given in the text to estimate T_c , P_c , and V_c/N for N_2 , H_2O , and He . (Tabulated values of a and b are often determined by working backward from the measured critical temperature and pressure.)

Problem 5.50. The **compression factor** of a fluid is defined as the ratio PV/NkT ; the deviation of this quantity from 1 is a measure of how much the fluid differs from an ideal gas. Calculate the compression factor of a van der Waals fluid at the critical point, and note that the value is independent of a and b . (Experimental values of compression factors at the critical point are generally lower than the van der Waals prediction, for instance, 0.227 for H_2O , 0.274 for CO_2 , 0.305 for He .)

Problem 5.51. When plotting graphs and performing numerical calculations, it is convenient to work in terms of **reduced variables**,

$$t \equiv T/T_c, \quad p \equiv P/P_c, \quad v \equiv V/V_c.$$

Rewrite the van der Waals equation in terms of these variables, and notice that the constants a and b disappear.

Problem 5.52. Plot the van der Waals isotherm for $T/T_c = 0.95$, working in terms of reduced variables. Perform the Maxwell construction (either graphically or numerically) to obtain the vapor pressure. Then plot the Gibbs free energy (in units of NkT_c) as a function of pressure for this same temperature and check that this graph predicts the same value for the vapor pressure.

Problem 5.53. Repeat the preceding problem for $T/T_c = 0.8$.

Problem 5.54. Calculate the *Helmholtz* free energy of a van der Waals fluid, up to an undetermined function of temperature as in equation 5.56. Using reduced variables, carefully plot the Helmholtz free energy (in units of NkT_c) as a function of volume for $T/T_c = 0.8$. Identify the two points on the graph corresponding to the liquid and gas at the vapor pressure. (If you haven't worked the preceding problem, just read the appropriate values off Figure 5.23.) Then prove that the Helmholtz free energy of a *combination* of these two states (part liquid, part gas) can be represented by a straight line connecting these two points on the graph. Explain why the combination is more stable, at a given volume, than the homogeneous state represented by the original curve, and describe how you could have determined the two transition volumes directly from the graph of F .

*Chapter 8 introduces an accurate approximation for treating *weakly* interacting gases, as well as the more general technique of Monte Carlo simulation, which can be applied to dense fluids.

Problem 5.55. In this problem you will investigate the behavior of a van der Waals fluid near the critical point. It is easiest to work in terms of reduced variables throughout.

- (a) Expand the van der Waals equation in a Taylor series in $(V - V_c)$, keeping terms through order $(V - V_c)^3$. Argue that, for T sufficiently close to T_c , the term quadratic in $(V - V_c)$ becomes negligible compared to the others and may be dropped.
- (b) The resulting expression for $P(V)$ is antisymmetric about the point $V = V_c$. Use this fact to find an approximate formula for the vapor pressure as a function of temperature. (You may find it helpful to plot the isotherm.) Evaluate the slope of the phase boundary, dP/dT , at the critical point.
- (c) Still working in the same limit, find an expression for the difference in volume between the gas and liquid phases at the vapor pressure. You should find $(V_g - V_l) \propto (T_c - T)^\beta$, where β is known as a **critical exponent**. Experiments show that β has a universal value of about $1/3$, but the van der Waals model predicts a larger value.
- (d) Use the previous result to calculate the predicted latent heat of the transformation as a function of temperature, and sketch this function.
- (e) The shape of the $T = T_c$ isotherm defines another critical exponent, called δ : $(P - P_c) \propto (V - V_c)^\delta$. Calculate δ in the van der Waals model. (Experimental values of δ are typically around 4 or 5.)
- (f) A third critical exponent describes the temperature dependence of the isothermal compressibility,

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.$$

This quantity diverges at the critical point, in proportion to a power of $(T - T_c)$ that in principle could differ depending on whether one approaches the critical point from above or below. Therefore the critical exponents γ and γ' are defined by the relations

$$\kappa \propto \begin{cases} (T - T_c)^{-\gamma} & \text{as } T \rightarrow T_c \text{ from above,} \\ (T_c - T)^{-\gamma'} & \text{as } T \rightarrow T_c \text{ from below.} \end{cases}$$

Calculate κ on both sides of the critical point in the van der Waals model, and show that $\gamma = \gamma'$ in this model.

5.4 Phase Transformations of Mixtures

Phase transformations become a lot more complicated when a system contains two or more types of particles. Consider air, for example, a mixture of approximately 79% nitrogen and 21% oxygen (neglecting various minor components for simplicity). What happens when you lower the temperature of this mixture, at atmospheric pressure? You might expect that all the oxygen would liquefy at 90.2 K (the boiling point of pure oxygen), leaving a gas of pure nitrogen which would then liquefy at 77.4 K (the boiling point of pure nitrogen). In fact, however, no liquid at all forms until the temperature drops to 81.6 K, when a liquid consisting of 48% oxygen begins to condense. Similar behavior occurs in liquid-solid transitions, such as the crystallization of alloys and igneous rocks. How can we understand this behavior?

Free Energy of a Mixture

As usual, the key is to look at the (Gibbs) free energy,

$$G = U + PV - TS. \quad (5.58)$$

Let's consider a system of two types of molecules, A and B , and suppose that they are initially separated, sitting side by side at the same temperature and pressure (see Figure 5.24). Imagine varying the proportions of A and B while holding the total number of molecules fixed, say at one mole. Let G_A° be the free energy of a mole of pure A , and G_B° the free energy of a mole of pure B . For an unmixed combination of part A and part B , the total free energy is just the sum of the separate free energies of the two subsystems:

$$G = (1-x)G_A^\circ + xG_B^\circ \quad (\text{unmixed}), \quad (5.59)$$

where x is the fraction of B molecules, so that $x = 0$ for pure A and $x = 1$ for pure B . A graph of G vs. x for this unmixed system is a straight line, as shown in Figure 5.25.

Now suppose that we remove the partition between the two sides and stir the A and B molecules together to form a homogeneous mixture. (I'll use the term **mixture** only when the substances are mixed at the molecular level. A "mixture" of salt and pepper does not qualify.) What happens to the free energy? From the definition $G = U + PV - TS$, we see that G can change because of changes in U , V , and/or S . The energy, U , might increase or decrease, depending on how the forces between dissimilar molecules compare to the forces between identical molecules. The volume, as well, may increase or decrease depending on these forces and on the shapes of the molecules. The entropy, however, will most certainly *increase*, because there are now many more possible ways to arrange the molecules.

As a first approximation, therefore, let us neglect any changes in U and V and assume that the entire change in G comes from the entropy of mixing. As a further simplification, let's also assume that the entropy of mixing can be calculated as in Problem 2.38, so that for one mole,

$$\Delta S_{\text{mixing}} = -R[x \ln x + (1-x) \ln(1-x)]. \quad (5.60)$$

A graph of this expression is shown in Figure 5.25. This expression is correct for ideal gases, and also for liquids and solids when the two types of molecules are the same size and have no "preference" for having like or unlike neighbors. When this

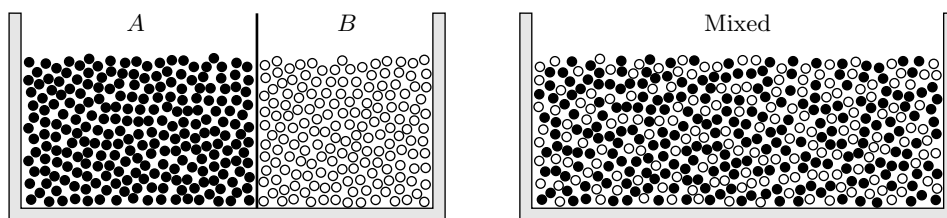


Figure 5.24. A collection of two types of molecules, before and after mixing.

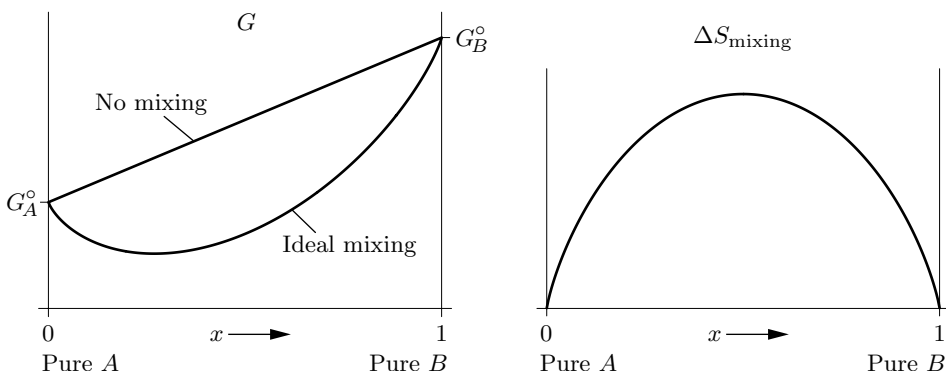


Figure 5.25. Before mixing, the free energy of a collection of A and B molecules is a linear function of $x = N_B/(N_A + N_B)$. After mixing it is a more complicated function; shown here is the case of an “ideal” mixture, whose entropy of mixing is shown at right. Although it isn’t obvious on this scale, the graphs of both ΔS_{mixing} and G (after mixing) have vertical slopes at the endpoints.

expression for the mixing entropy holds and when U and V do not change upon mixing, the free energy of the mixture is

$$G = (1-x)G_A^o + xG_B^o + RT[x \ln x + (1-x) \ln(1-x)] \quad (\text{ideal mixture}). \quad (5.61)$$

This function is plotted in Figure 5.25. A mixture having this simple free energy function is called an **ideal mixture**. Liquid and solid mixtures rarely come close to being ideal, but the ideal case still makes a good starting point for arriving at some qualitative understanding.

One important property of expression 5.60 for the entropy of mixing is that its derivative with respect to x goes to infinity at $x = 0$ and to minus infinity at $x = 1$. The graph of this expression therefore has a vertical slope at each endpoint. Similarly, expression 5.61 for the Gibbs free energy has an infinite derivative at each endpoint: Adding a tiny amount of impurity to either pure substance lowers the free energy significantly, except when $T = 0$.^{*} Although the precise formulas written above hold only for ideal solutions, the infinite slope at the endpoints is a general property of the free energy of any mixture. Because a system will spontaneously seek out the state of lowest free energy, this property tells us that equilibrium phases almost always contain impurities.

Nonideal mixtures often have the same qualitative properties as ideal mixtures, but not always. The most important exception is when mixing the two substances increases the total energy. This happens in liquids when unlike molecules are less attracted to each other than are like molecules, as with oil and water. The energy change upon mixing is then a concave-down function of x , as shown in Figure 5.26. At $T = 0$ the free energy ($G = U + PV - TS$) is also a concave-down function

^{*}Hiding one needle in a stack of pure hay increases the entropy a lot more than does adding a needle to a haystack already containing thousands of needles.

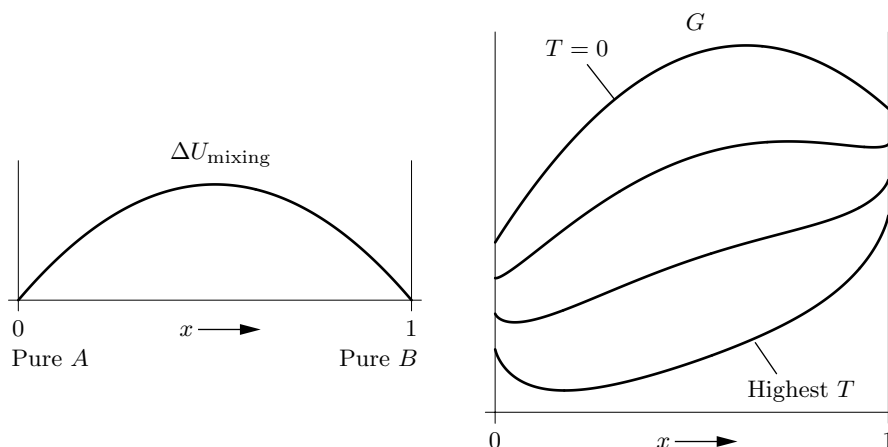


Figure 5.26. Mixing A and B can often increase the energy of the system; shown at left is the simple case where the mixing energy is a quadratic function (see Problem 5.58). Shown at right is the free energy in this case, at four different temperatures.

(if we neglect any change in V upon mixing). At nonzero T , however, there is a competition in G between the concave-down contribution from the mixing energy and the concave-up contribution from $-T$ times the mixing entropy. At sufficiently high T the entropy contribution always wins and G is everywhere concave-up. But even at very low nonzero T , the entropy contribution *still* dominates the shape of G near the endpoints $x = 0$ and $x = 1$. This is because the entropy of mixing has an infinite derivative at the endpoints, while the energy of mixing has only a finite derivative at the endpoints: When there is very little impurity, the mixing energy is simply proportional to the number of impurity molecules. Thus, at small nonzero T , the free energy function is concave-up near the endpoints and concave-down near the middle, as shown in Figure 5.26.

But a concave-down free energy function indicates an unstable mixture. Pick any two points on the graph of G and connect them with a straight line. This line denotes the free energy of an *unmixed* combination of the two phases represented by the endpoints (just as the straight line in Figure 5.25 denotes the free energy of the unmixed pure phases). Whenever the graph of G is concave-down, you can draw a straight connecting line that lies *below* the curve, and therefore the unmixed combination has a lower free energy than the homogeneous mixture. The lowest possible connecting line intersects the curve as a tangent at each end (see Figure 5.27). The tangent points indicate the compositions of the two separated phases, denoted x_a and x_b in the figure. Thus, if the composition of the system lies between x_a and x_b , it will spontaneously separate into an A -rich phase of composition x_a and a B -rich phase of composition x_b . We say that the system has a **solubility gap**, or that the two phases are **immiscible**. Decreasing the temperature of this system widens the solubility gap (see Figure 5.26), while increasing the temperature narrows the gap until it disappears when G is everywhere concave-up.

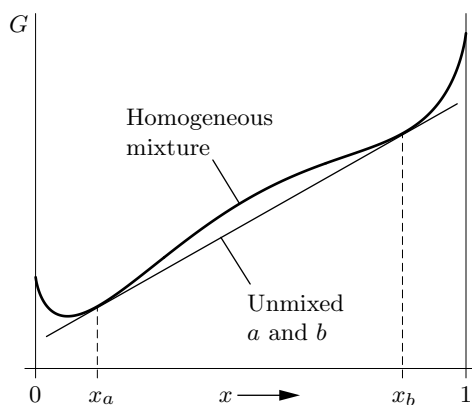


Figure 5.27. To construct the equilibrium free energy curve, draw the lowest possible straight line across the concave-down section, tangent to the curve at both ends. At compositions between the tangent points the mixture will spontaneously separate into phases whose compositions are x_a and x_b , in order to lower its free energy.

If we plot the compositions x_a and x_b at each temperature, we obtain a T vs. x phase diagram like those shown in Figure 5.28. Above the curve the equilibrium state is a single homogeneous mixture, while below the curve the system separates into two phases whose compositions lie on the curve. For the familiar case of oil and water at atmospheric pressure, the critical temperature where complete mixing would occur is far above the boiling point of water. The figure shows a less familiar mixture, water and phenol ($\text{C}_6\text{H}_5\text{OH}$), whose critical mixing temperature is 67°C .

Solubility gaps occur in solid as well as liquid mixtures. For solids, however, there is often the further complication that the pure- A and pure- B solids have qualitatively different crystal structures. Let us call these structures α and β , respectively. Adding a few B molecules to the α phase, or a few A molecules

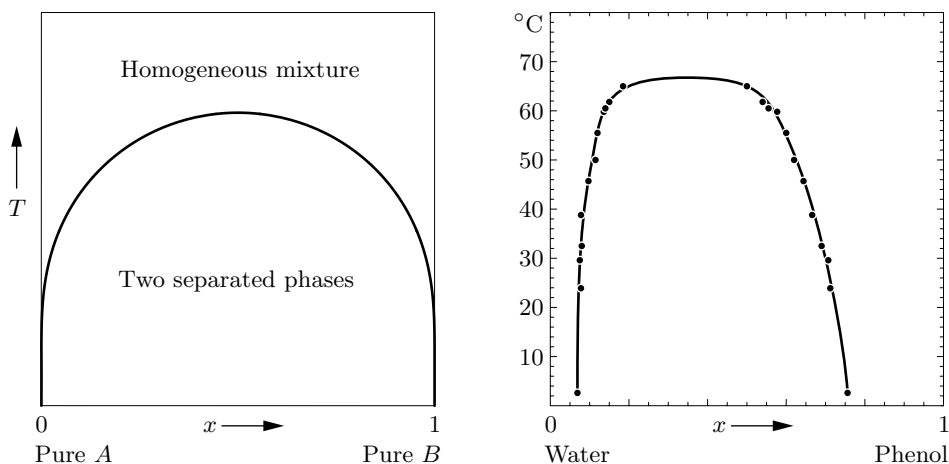
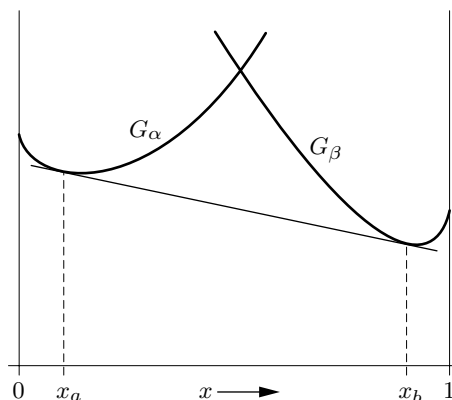


Figure 5.28. Left: Phase diagram for the simple model system whose mixing energy is plotted in Figure 5.26. Right: Experimental data for a real system, water + phenol, that shows qualitatively similar behavior. Adapted with permission from Alan N. Campbell and A. Jean R. Campbell, *Journal of the American Chemical Society* **59**, 2481 (1937). Copyright 1937 American Chemical Society.

to the β phase, is always possible, again because of the infinite slope of the entropy of mixing function. But a large amount of impurity will usually stress the crystal lattice significantly, greatly raising its energy. A free energy diagram for such a system therefore looks like Figure 5.29. Again we can draw a straight line tangent to the two concave-up sections, so there is a solubility gap: The stable configuration at intermediate compositions is an unmixed combination of the two phases indicated by the tangent points. For some solids the situation is even more complicated because other crystal structures are stable at intermediate compositions. For example, brass, an alloy of copper and zinc, has five possible crystal structures, each stable within a certain composition range.

Figure 5.29. Free energy graphs for a mixture of two solids with different crystal structures, α and β . Again, the lowest possible straight connecting line indicates the range of compositions where an unmixed combination of α and β phases is more stable than a homogeneous mixture.



Problem 5.56. Prove that the entropy of mixing of an ideal mixture has an infinite slope, when plotted vs. x , at $x = 0$ and $x = 1$.

Problem 5.57. Consider an ideal mixture of just 100 molecules, varying in composition from pure A to pure B . Use a computer to calculate the mixing entropy as a function of N_A , and plot this function (in units of k). Suppose you start with all A and then convert one molecule to type B ; by how much does the entropy increase? By how much does the entropy increase when you convert a second molecule, and then a third, from A to B ? Discuss.

Problem 5.58. In this problem you will model the mixing energy of a mixture in a relatively simple way, in order to relate the existence of a solubility gap to molecular behavior. Consider a mixture of A and B molecules that is ideal in every way but one: The potential energy due to the interaction of neighboring molecules depends upon whether the molecules are like or unlike. Let n be the average number of nearest neighbors of any given molecule (perhaps 6 or 8 or 10). Let u_0 be the average potential energy associated with the interaction between neighboring molecules that are the same (A - A or B - B), and let u_{AB} be the potential energy associated with the interaction of a neighboring unlike pair (A - B). There are no interactions beyond the range of the nearest neighbors; the values of u_0 and u_{AB} are independent of the amounts of A and B ; and the entropy of mixing is the same as for an ideal solution.

- (a) Show that when the system is unmixed, the total potential energy due to all neighbor-neighbor interactions is $\frac{1}{2}Nnu_0$. (Hint: Be sure to count each

neighboring pair only once.)

- (b) Find a formula for the total potential energy when the system is mixed, in terms of x , the fraction of B . (Assume that the mixing is totally random.)
- (c) Subtract the results of parts (a) and (b) to obtain the change in energy upon mixing. Simplify the result as much as possible; you should obtain an expression proportional to $x(1-x)$. Sketch this function vs. x , for both possible signs of $u_{AB} - u_0$.
- (d) Show that the slope of the mixing energy function is finite at both endpoints, unlike the slope of the mixing *entropy* function.
- (e) For the case $u_{AB} > u_0$, plot a graph of the Gibbs free energy of this system vs. x at several temperatures. Discuss the implications.
- (f) Find an expression for the maximum temperature at which this system has a solubility gap.
- (g) Make a very rough estimate of $u_{AB} - u_0$ for a liquid mixture that has a solubility gap below 100°C .
- (h) Plot the phase diagram (T vs. x) for this system.

Phase Changes of a Miscible Mixture

Now let us return to the process described at the beginning of this section, the liquefaction of a mixture of nitrogen and oxygen. Liquid nitrogen and oxygen are completely miscible, so the free energy function of the liquid mixture is everywhere concave-up. The free energy of the gaseous mixture is also everywhere concave-up. By considering the relation between these two functions at various temperatures, we can understand the behavior of this system and sketch its phase diagram.

Figure 5.30 shows the free energy functions of a model system that behaves as an ideal mixture in both the gaseous and liquid phases. Think of the components A and B as nitrogen and oxygen, whose behavior should be qualitatively similar. The boiling points of pure A and pure B are denoted T_A and T_B , respectively. At temperatures greater than T_B the stable phase is a gas regardless of composition, so the free energy curve of the gas lies entirely below that of the liquid. As the temperature drops, both free energy functions increase ($\partial G/\partial T = -S$), but that of the gas increases more because the gas has more entropy. At $T = T_B$ the curves intersect at $x = 1$, where the liquid and gas phases of pure B are in equilibrium. As T decreases further the intersection point moves to the left, until at $T = T_A$ the curves intersect at $x = 0$. At still lower temperatures the free energy of the liquid is less than that of the gas at all compositions.

At intermediate temperatures, between T_A and T_B , either the liquid or the gas phase may be more stable, depending on composition. But notice, from the shape of the curves, that you can draw a straight line, tangent to both curves, that lies below both curves. Between the two tangent points, therefore, the stable configuration is an *unmixed* combination of a gas whose composition is indicated by the left tangent point and a liquid whose composition is indicated by the right tangent point. The straight line denotes the free energy of this unmixed combination. By drawing such a straight line for every temperature between T_A and T_B , we can construct the T vs. x phase diagram for this system. The mixture is entirely gas in the upper region

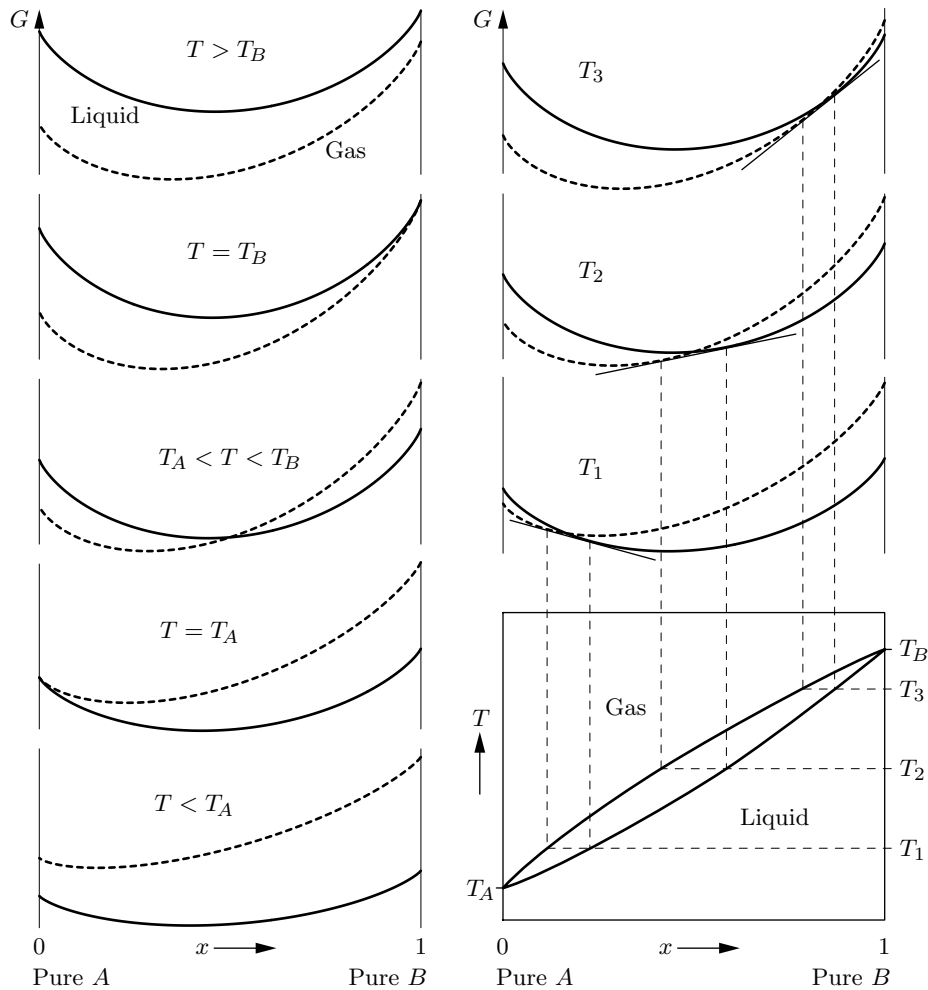


Figure 5.30. The five graphs at left show the liquid and gas free energies of an ideal mixture at temperatures above, below, at, and between the boiling points T_A and T_B . Three graphs at intermediate temperatures are shown at right, along with the construction of the phase diagram.

of the diagram, entirely liquid in the lower region, and an unmixed combination in the region between the two curves.

Figure 5.31 shows the *experimental* phase diagram for the nitrogen-oxygen system. Although this diagram isn't exactly the same as that of the ideal A - B model system, it has all the same qualitative features. From the diagram you can see that if you start with an air-like mixture of 79% nitrogen and 21% oxygen and lower the temperature, it remains a gas until the temperature reaches 81.6 K. At this point a liquid begins to condense. A horizontal line at this temperature intersects the lower curve at $x = 0.48$, so the liquid is initially 48% oxygen. Because oxygen condenses more easily than nitrogen, the liquid is enriched in oxygen compared to

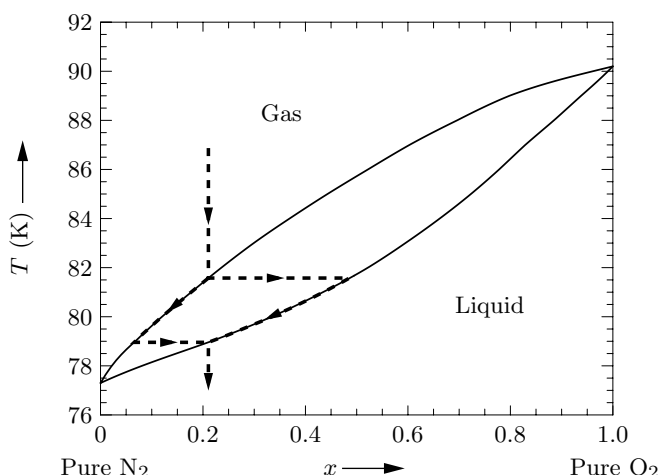


Figure 5.31. Experimental phase diagram for nitrogen and oxygen at atmospheric pressure. Data from *International Critical Tables* (volume 3), with endpoints adjusted to values in Lide (1994).

the gas. But it is not pure oxygen, because the entropy of mixing gives too much of a thermodynamic advantage to impure phases. As the temperature decreases further, the gas becomes depleted of oxygen and its composition follows the upper curve, down and to the left. Meanwhile the composition of the liquid follows the lower curve, also increasing its nitrogen/oxygen ratio. At 79.0 K the liquid composition reaches the overall composition of 21% oxygen, so there can't be any gas left; the last bit of gas to condense contains about 7% oxygen.

The liquid-gas transitions of many other mixtures behave similarly. Furthermore, for some mixtures the solid-liquid transition behaves in this way. Examples of such mixtures include copper-nickel, silicon-germanium, and the common minerals olivene (varying from Fe_2SiO_4 to Mg_2SiO_4) and plagioclase feldspar (see Problem 5.64). In all of these systems, the crystal structure of the solid is essentially the same throughout the entire range of composition, so the two pure solids can form approximately ideal mixtures in all proportions. Such a mixture is called a **solid solution**.

Problem 5.59. Suppose you cool a mixture of 50% nitrogen and 50% oxygen until it liquefies. Describe the cooling sequence in detail, including the temperatures and compositions at which liquefaction begins and ends.

Problem 5.60. Suppose you start with a liquid mixture of 60% nitrogen and 40% oxygen. Describe what happens as the temperature of this mixture increases. Be sure to give the temperatures and compositions at which boiling begins and ends.

Problem 5.61. Suppose you need a tank of oxygen that is 95% pure. Describe a process by which you could obtain such a gas, starting with air.

Problem 5.62. Consider a completely miscible two-component system whose overall composition is x , at a temperature where liquid and gas phases coexist. The composition of the gas phase at this temperature is x_a and the composition

of the liquid phase is x_b . Prove the **lever rule**, which says that the proportion of liquid to gas is $(x - x_a)/(x_b - x)$. Interpret this rule graphically on a phase diagram.

Problem 5.63. Everything in this section assumes that the total pressure of the system is fixed. How would you expect the nitrogen-oxygen phase diagram to change if you increase or decrease the pressure? Justify your answer.

Problem 5.64. Figure 5.32 shows the phase diagram of plagioclase feldspar, which can be considered a mixture of albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$).

- Suppose you discover a rock in which each plagioclase crystal varies in composition from center to edge, with the centers of the largest crystals composed of 70% anorthite and the outermost parts of all crystals made of essentially pure albite. Explain in some detail how this variation might arise. What was the composition of the liquid magma from which the rock formed?
- Suppose you discover another rock body in which the crystals near the top are albite-rich while the crystals near the bottom are anorthite-rich. Explain how this variation might arise.

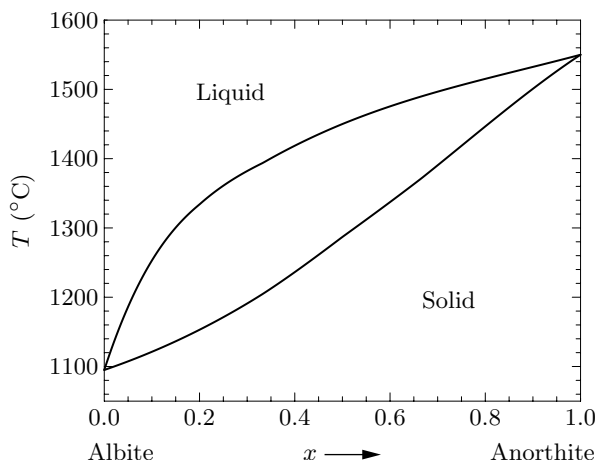


Figure 5.32. The phase diagram of plagioclase feldspar (at atmospheric pressure). From N. L. Bowen, “The Melting Phenomena of the Plagioclase Feldspars,” *American Journal of Science* **35**, 577–599 (1913).

Problem 5.65. In constructing the phase diagram from the free energy graphs in Figure 5.30, I assumed that both the liquid and the gas are ideal mixtures. Suppose instead that the liquid has a substantial positive mixing energy, so that its free energy curve, while still concave-up, is much flatter. In this case a portion of the curve may still lie *above* the gas’s free energy curve at T_A . Draw a qualitatively accurate phase diagram for such a system, showing how you obtained the phase diagram from the free energy graphs. Show that there is a particular composition at which this gas mixture will condense with no change in composition. This special composition is called an **azeotrope**.

Problem 5.66. Repeat the previous problem for the opposite case where the liquid has a substantial *negative* mixing energy, so that its free energy curve dips below the gas's free energy curve at a temperature higher than T_B . Construct the phase diagram and show that this system also has an azeotrope.

Problem 5.67. In this problem you will derive approximate formulas for the shapes of the phase boundary curves in diagrams such as Figures 5.31 and 5.32, assuming that both phases behave as ideal mixtures. For definiteness, suppose that the phases are liquid and gas.

- (a) Show that in an ideal mixture of A and B , the chemical potential of species A can be written

$$\mu_A = \mu_A^\circ + kT \ln(1 - x),$$

where μ_A° is the chemical potential of *pure* A (at the same temperature and pressure) and $x = N_B/(N_A + N_B)$. Derive a similar formula for the chemical potential of species B . Note that both formulas can be written for either the liquid phase or the gas phase.

- (b) At any given temperature T , let x_l and x_g be the compositions of the liquid and gas phases that are in equilibrium with each other. By setting the appropriate chemical potentials equal to each other, show that x_l and x_g obey the equations

$$\frac{1 - x_l}{1 - x_g} = e^{\Delta G_A^\circ / RT} \quad \text{and} \quad \frac{x_l}{x_g} = e^{\Delta G_B^\circ / RT},$$

where ΔG° represents the change in G for the pure substance undergoing the phase change at temperature T .

- (c) Over a limited range of temperatures, we can often assume that the main temperature dependence of $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ comes from the explicit T ; both ΔH° and ΔS° are approximately constant. With this simplification, rewrite the results of part (b) entirely in terms of ΔH_A° , ΔH_B° , T_A , and T_B (eliminating ΔG and ΔS). Solve for x_l and x_g as functions of T .
- (d) Plot your results for the nitrogen-oxygen system. The latent heats of the pure substances are $\Delta H_{\text{N}_2}^\circ = 5570 \text{ J/mol}$ and $\Delta H_{\text{O}_2}^\circ = 6820 \text{ J/mol}$. Compare to the experimental diagram, Figure 5.31.
- (e) Show that you can account for the shape of Figure 5.32 with suitably chosen ΔH° values. What are those values?

Phase Changes of a Eutectic System

Most two-component solid mixtures do not maintain the same crystal structure over the entire range of composition. The situation shown in Figure 5.29 is more common: two different crystal structures, α and β , at compositions close to pure A and pure B , with an unmixed combination of α and β being stable at intermediate compositions. Let us now consider the solid-liquid transitions of such a system, assuming that A and B are completely miscible in the liquid phase. Again the idea is to look at the free energy functions at various temperatures (see Figure 5.33). For definiteness, suppose that T_B , the melting temperature of pure B , is higher than T_A , the melting temperature of pure A .

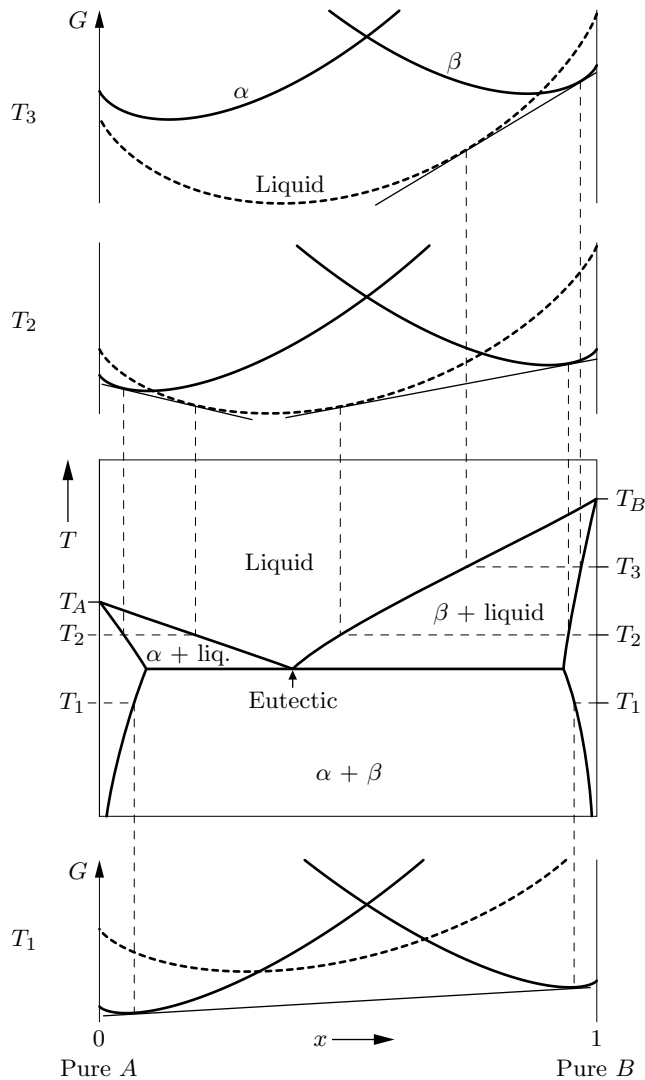


Figure 5.33. Construction of the phase diagram of a eutectic system from free energy graphs.

At high temperatures the free energy of the liquid will be below that of either solid phase. Then, as the temperature decreases, all three free-energy functions will increase ($\partial G/\partial T = -S$), but the free energy of the liquid will increase fastest because it has the most entropy. Below T_B the liquid's free energy curve intersects that of the β phase, so there is a range of compositions for which the stable configuration is an unmixed combination of liquid and β . As the temperature decreases this range widens and reaches further toward the A side of the diagram. Eventually the liquid curve intersects the α curve as well and there is an A-rich range of compositions for which the stable phase is an unmixed combination of liquid

and α . As T decreases further this range reaches toward the B side of the diagram until finally it intersects the liquid + β range at the **eutectic point**. At still lower temperatures the stable configuration is an unmixed combination of the α and β solids; the free energy of the liquid is higher than that of this combination.

The eutectic point defines a special composition at which the melting temperature is as low as possible, lower than that of either pure substance. A liquid near the eutectic composition remains stable at low temperatures because it has more mixing entropy than the unmixed combination of solids would have. (A solid mixture would have about as much mixing entropy, but is forbidden by the large positive mixing *energy* that results from stressing the crystal lattice.)

A good example of a eutectic mixture is the tin-lead solder used in electrical circuits. Figure 5.34 shows the phase diagram of the tin-lead system. Common electrical solder is very close to the eutectic composition of 38% lead by weight (or 26% by number of atoms). Using this composition has several advantages: the melting temperature is as low as possible (183°C); the solder freezes suddenly rather than gradually; and the cooled metal is relatively strong, with small crystals of the two phases uniformly alternating at the microscopic scale.

Many other mixtures behave in a similar way. Most pure liquid crystals freeze at inconveniently high temperatures, so eutectic mixtures are often used to obtain liquid crystals for use at room temperature. A less exotic mixture is water + table salt (NaCl), which can remain a liquid at temperatures as low as -21°C , at the eutectic composition of 23% NaCl by weight.* Another familiar example is the coolant used in automobile engines, a mixture of water and ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$). Pure water freezes at 0°C , and pure ethylene glycol at -13°C ,

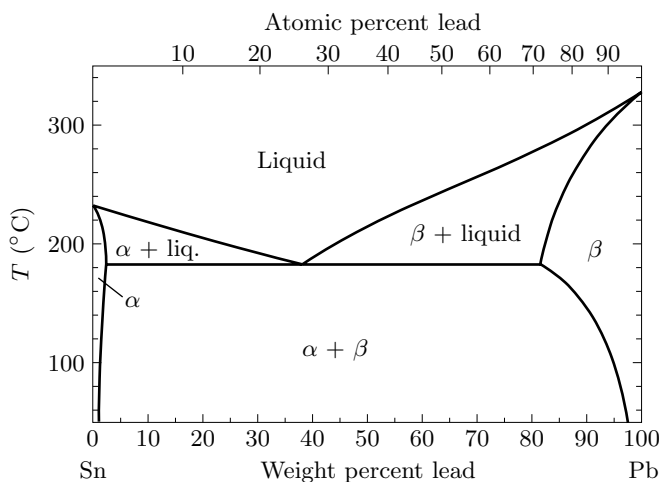


Figure 5.34. Phase diagram for mixtures of tin and lead. From Thaddeus B. Massalski, ed., *Binary Alloy Phase Diagrams*, second edition (ASM International, Materials Park, OH, 1990).

*The water + NaCl phase diagram is shown in Zemansky and Dittman (1997).

so neither would remain a liquid on winter nights in a cold climate. Fortunately, a 50-50 mixture (by volume) of these two liquids does not begin to freeze until the temperature reaches -31°C . The eutectic point is lower still, at -49°C and a composition of 56% ethylene glycol by volume.*

Although the phase diagram of a eutectic system may seem complicated enough, many two-component systems are further complicated by the existence of other crystal structures of intermediate compositions; Problems 5.71 and 5.72 explore some of the possibilities. Then there are *three*-component systems, for which the composition axis of the phase diagram is actually a plane (usually represented by a triangle). You can find hundreds of intricate phase diagrams in books on metallurgy, ceramics, and petrology. All can be understood qualitatively in terms of free energy graphs as we have done here. Because this is an introductory text, though, let us move on and explore the properties of some simple mixtures more quantitatively.

Problem 5.68. Plumber's solder is composed of 67% lead and 33% tin by weight. Describe what happens to this mixture as it cools, and explain why this composition might be more suitable than the eutectic composition for joining pipes.

Problem 5.69. What happens when you spread salt crystals over an icy sidewalk? Why is this procedure rarely used in *very* cold climates?

Problem 5.70. What happens when you add salt to the ice bath in an ice cream maker? How is it possible for the temperature to *spontaneously* drop below 0°C ? Explain in as much detail as you can.

Problem 5.71. Figure 5.35 (left) shows the free energy curves at one particular temperature for a two-component system that has three possible solid phases (crystal structures), one of essentially pure *A*, one of essentially pure *B*, and one of intermediate composition. Draw tangent lines to determine which phases are present at which values of *x*. To determine qualitatively what happens at other temperatures, you can simply shift the liquid free energy curve up or down (since the entropy of the liquid is larger than that of any solid). Do so, and construct

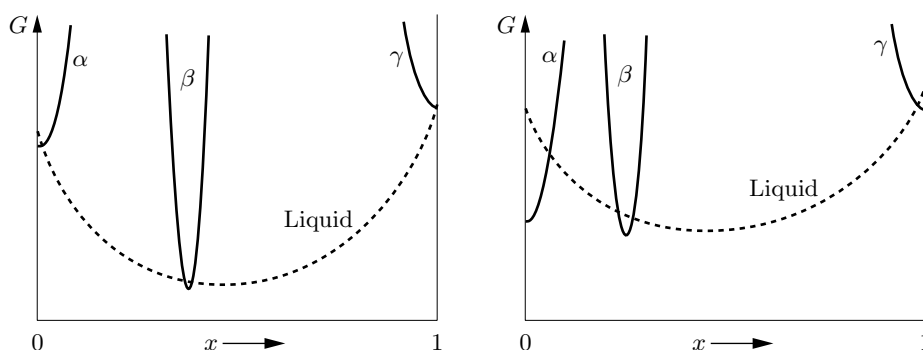


Figure 5.35. Free energy diagrams for Problems 5.71 and 5.72.

*For the full phase diagram see J. Bevan Ott, J. Rex Goates, and John D. Lamb, *Journal of Chemical Thermodynamics* **4**, 123–126 (1972).

a qualitative phase diagram for this system. You should find two eutectic points. Examples of systems with this behavior include water + ethylene glycol and tin + magnesium.

Problem 5.72. Repeat the previous problem for the diagram in Figure 5.35 (right), which has an important qualitative difference. In this phase diagram, you should find that β and liquid are in equilibrium only at temperatures *below* the point where the liquid is in equilibrium with infinitesimal amounts of α and β . This point is called a **peritectic point**. Examples of systems with this behavior include water + NaCl and leucite + quartz.

5.5 Dilute Solutions

A **solution** is the same thing as a mixture, except that we think of one component (the **solvent**) as being primary and the other components (the **solutes**) as being secondary. A solution is called **dilute** if the solute molecules are much less abundant than the solvent molecules (see Figure 5.36), so that each solute molecule is “always” surrounded by solvent molecules and “never” interacts directly with other solute molecules. In many ways the solute in a dilute solution behaves like an ideal gas. We can therefore predict many of the properties of a dilute solution (including its boiling and freezing points) quantitatively.

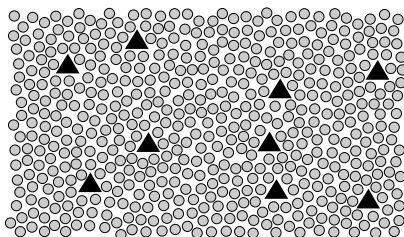


Figure 5.36. A dilute solution, in which the solute is much less abundant than the solvent.

Solvent and Solute Chemical Potentials

To predict the properties of a dilute solution interacting with its environment, we'll need to know something about the chemical potentials of the solvent and solutes. The chemical potential, μ_A , of species A is related to the Gibbs free energy by $\mu_A = \partial G / \partial N_A$, so what we need is a formula for the Gibbs free energy of a dilute solution in terms of the numbers of solvent and solute molecules. Coming up with the correct formula for G is a bit tricky but very worthwhile: Once we have this formula, a host of applications become possible.

Suppose we start with a *pure* solvent of A molecules. Then the Gibbs free energy is just N_A times the chemical potential:

$$G = N_A \mu_0(T, P) \quad (\text{pure solvent}), \quad (5.62)$$

where μ_0 is the chemical potential of the pure solvent, a function of temperature and pressure.

Now imagine that we add a single B molecule, holding the temperature and pressure fixed. Under this operation the (Gibbs) free energy changes by

$$dG = dU + P dV - T dS. \quad (5.63)$$

The important thing about dU and $P dV$ is that neither depends on N_A : Both depend only on how the B molecule interacts with its immediate neighbors, regardless of how many other A molecules are present. For the $T dS$ term, however, the situation is more complicated. Part of dS is independent of N_A , but another part comes from our freedom in choosing *where* to put the B molecule. The number of choices is proportional to N_A , so this operation increases the multiplicity by a factor proportional to N_A , and therefore dS , the increase in entropy, includes a term $k \ln N_A$:

$$dS = k \ln N_A + (\text{terms independent of } N_A). \quad (5.64)$$

The change in the free energy can therefore be written

$$dG = f(T, P) - kT \ln N_A \quad (\text{adding one } B \text{ molecule}), \quad (5.65)$$

where $f(T, P)$ is a function of temperature and pressure but not of N_A .

Next imagine that we add *two* B molecules to the pure solvent. For this operation we can almost apply the preceding argument twice and conclude that

$$dG = 2f(T, P) - 2kT \ln N_A \quad (\text{wrong}). \quad (5.66)$$

The problem is that there is a further change in entropy resulting from the fact that the two B molecules are identical. Interchanging these two molecules does not result in a distinct state, so we need to divide the multiplicity by 2, or subtract $k \ln 2$ from the entropy. With this modification,

$$dG = 2f(T, P) - 2kT \ln N_A + kT \ln 2 \quad (\text{adding two } B \text{ molecules}). \quad (5.67)$$

The generalization to many B molecules is now straightforward. In the free energy we get N_B times $f(T, P)$ and N_B times $-kT \ln N_A$. To account for the interchangeability of the B molecules, we also get a term $kT \ln N_B! \approx kT N_B (\ln N_B - 1)$. Adding all these terms to the free energy of the pure solvent, we finally obtain

$$G = N_A \mu_0(T, P) + N_B f(T, P) - N_B kT \ln N_A + N_B kT \ln N_B - N_B kT. \quad (5.68)$$

This expression is valid in the limit $N_B \ll N_A$, that is, when the solution is dilute. For a nondilute solution the situation would be much more complicated because the B molecules would also interact with each other. If a solution contains more than one solute, all the terms in equation 5.68 except the first get repeated, with N_B replaced by N_C , N_D , and so on.

The solvent and solute chemical potentials follow immediately from equation 5.68:

$$\mu_A = \left(\frac{\partial G}{\partial N_A} \right)_{T, P, N_B} = \mu_0(T, P) - \frac{N_B kT}{N_A}; \quad (5.69)$$

$$\mu_B = \left(\frac{\partial G}{\partial N_B} \right)_{T, P, N_A} = f(T, P) + kT \ln(N_B/N_A). \quad (5.70)$$

As we would expect, adding more solute reduces the chemical potential of A and increases the chemical potential of B . Note also that both of these quantities, being intensive, depend only on the ratio N_B/N_A , not on the absolute number of solvent or solute molecules.

It is conventional to rewrite equation 5.70 in terms of the **molality*** of the solution, which is defined as the number of moles of solute per kilogram of solvent:

$$\text{molality} = m = \frac{\text{moles of solute}}{\text{kilograms of solvent}}. \quad (5.71)$$

The molality is a constant times the ratio N_B/N_A , and the constant can be absorbed into the function $f(T, P)$ to give a new function called $\mu^\circ(T, P)$. The solute chemical potential can then be written

$$\mu_B = \mu^\circ(T, P) + kT \ln m_B, \quad (5.72)$$

where m_B is the molality of the solute (in moles per kilogram) and μ° is the chemical potential under the “standard” condition $m_B = 1$. Values of μ° can be obtained from tables of Gibbs free energies, so equation 5.72 relates the tabulated value to the value at any other molality (so long as the solution is dilute).

Problem 5.73. If expression 5.68 is correct, it must be extensive: Increasing both N_A and N_B by a common factor while holding all intensive variables fixed should increase G by the same factor. Show that expression 5.68 has this property. Show that it would *not* have this property had we not added the term proportional to $\ln N_B!$.

Problem 5.74. Check that equations 5.69 and 5.70 satisfy the identity $G = N_A\mu_A + N_B\mu_B$ (equation 5.37).

Problem 5.75. Compare expression 5.68 for the Gibbs free energy of a dilute solution to expression 5.61 for the Gibbs free energy of an ideal mixture. Under what circumstances should these two expressions agree? Show that they do agree under these circumstances, and identify the function $f(T, P)$ in this case.

Osmotic Pressure

As a first application of equation 5.69, consider a solution that is separated from some pure solvent by a membrane that allows only solvent molecules, not solute molecules, to pass through (see Figure 5.37). One example of such a semipermeable membrane is the membrane surrounding any plant or animal cell, which is permeable to water and other very small molecules but not to larger molecules or charged ions. Other semipermeable membranes are used in industry, for instance, in the desalination of seawater.

According to equation 5.69, the chemical potential of the solvent in the solution is less than that of the pure solvent, at a given temperature and pressure. Particles

*Molality is not the same as **molarity**, the number of moles of solute per liter of solution. For dilute solutions in water, however, the two are almost identical.

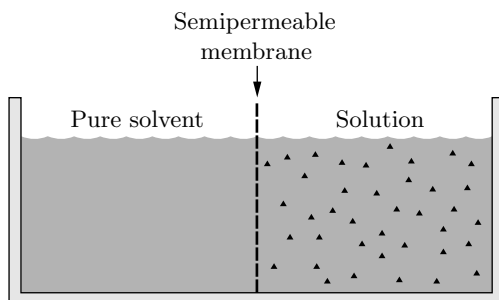


Figure 5.37. When a solution is separated by a semipermeable membrane from pure solvent at the same temperature and pressure, solvent will spontaneously flow into the solution.

tend to flow toward lower chemical potential, so in this situation the solvent molecules will spontaneously flow from the pure solvent into the solution. This flow of molecules is called **osmosis**. That osmosis should happen is hardly surprising: Solvent molecules are constantly bombarding the membrane on both sides, but more frequently on the side where the solvent is more concentrated, so naturally they hit the holes and pass through from that side more often.

If you want to *prevent* osmosis from happening, you can do so by applying some additional pressure to the solution (see Figure 5.38). How much pressure is required? Well, when the pressure is just right to stop the osmotic flow, the chemical potential of the solvent must be the same on both sides of the membrane. Using equation 5.69, this condition is

$$\mu_0(T, P_1) = \mu_0(T, P_2) - \frac{N_B k T}{N_A}, \quad (5.73)$$

where P_1 is the pressure on the side with pure solvent and P_2 is the pressure on the side of the solution. Assuming that these two pressures are not *too* different, we can approximate

$$\mu_0(T, P_2) \approx \mu_0(T, P_1) + (P_2 - P_1) \frac{\partial \mu_0}{\partial P}, \quad (5.74)$$

and plug this expression into equation 5.73 to obtain

$$(P_2 - P_1) \frac{\partial \mu_0}{\partial P} = \frac{N_B k T}{N_A}. \quad (5.75)$$

To evaluate the derivative $\partial \mu_0 / \partial P$, recall that the chemical potential of a pure substance is just the Gibbs free energy per particle, G/N . Since $\partial G / \partial P = V$ (at

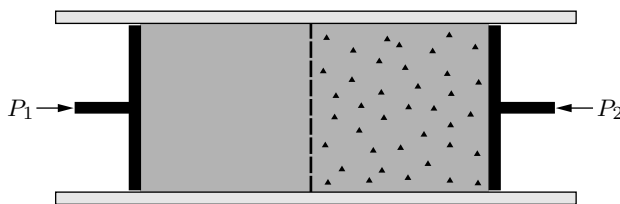


Figure 5.38. To prevent osmosis, P_2 must exceed P_1 by an amount called the osmotic pressure.

fixed T and N), our derivative is

$$\frac{\partial \mu_0}{\partial P} = \frac{V}{N}, \quad (5.76)$$

the volume per molecule of the pure solvent. But since the solution is dilute, *its* volume per solvent molecule is essentially the same. Let's therefore take V in equation 5.76 to be the volume of the solution, and N to be the number of solvent molecules in the solution, that is, N_A . Then equation 5.75 becomes

$$(P_2 - P_1) \frac{V}{N_A} = \frac{N_B kT}{N_A}, \quad (5.77)$$

or simply

$$(P_2 - P_1) = \frac{N_B kT}{V} = \frac{n_B RT}{V} \quad (5.78)$$

(where n_B/V is the number of *moles* of solute per unit volume). This pressure difference is called the **osmotic pressure**. It is the excess pressure required on the side of the solution to prevent osmosis.

Equation 5.78 for the osmotic pressure of a dilute solution is called **van't Hoff's formula**, after Jacobus Hendricus van't Hoff. It says that the osmotic pressure is exactly the same as the pressure of an ideal gas of the same concentration as the solute. In fact, it's tempting to think of the osmotic pressure as being exerted entirely *by* the solute, once we have balanced the pressure of the solvent on both sides. This interpretation is bad physics, but I still use it as a mnemonic aid to remember the formula.

As an example, consider the solution of ions, sugars, amino acids, and other molecules inside a biological cell. In a typical cell there are about 200 water molecules for each molecule of something else, so this solution is reasonably dilute. Since a mole of water has a mass of 18 g and a volume of 18 cm³, the number of moles of solute per unit volume is

$$\frac{n_B}{V} = \left(\frac{1}{200} \right) \left(\frac{1 \text{ mol}}{18 \text{ cm}^3} \right) \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 278 \text{ mol/m}^3. \quad (5.79)$$

If you put a cell into pure water, it will absorb water by osmosis until the pressure inside exceeds the pressure outside by the osmotic pressure, which at room temperature is

$$(278 \text{ mol/m}^3)(8.3 \text{ J/mol}\cdot\text{K})(300 \text{ K}) = 6.9 \times 10^5 \text{ N/m}^2, \quad (5.80)$$

or about 7 atm. An animal cell membrane subjected to this much pressure will burst, but plant cells have rigid walls that can withstand such a pressure.

Problem 5.76. Seawater has a salinity of 3.5%, meaning that if you boil away a kilogram of seawater, when you're finished you'll have 35 g of solids (mostly NaCl) left in the pot. When dissolved, sodium chloride dissociates into separate Na^+ and Cl^- ions.

- Calculate the osmotic pressure difference between seawater and fresh water. Assume for simplicity that all the dissolved salts in seawater are NaCl.
- If you apply a pressure difference *greater* than the osmotic pressure to a solution separated from pure solvent by a semipermeable membrane, you get **reverse osmosis**: a flow of solvent *out* of the solution. This process can be used to desalinate seawater. Calculate the minimum work required to desalinate one liter of seawater. Discuss some reasons why the actual work required would be greater than the minimum.

Problem 5.77. Osmotic pressure measurements can be used to determine the molecular weights of large molecules such as proteins. For a solution of large molecules to qualify as “dilute,” its molar concentration must be very low and hence the osmotic pressure can be too small to measure accurately. For this reason, the usual procedure is to measure the osmotic pressure at a variety of concentrations, then extrapolate the results to the limit of zero concentration. Here are some data* for the protein hemoglobin dissolved in water at 3°C:

Concentration (grams/liter)	Δh (cm)
5.6	2.0
16.6	6.5
32.5	12.8
43.4	17.6
54.0	22.6

The quantity Δh is the equilibrium difference in fluid level between the solution and the pure solvent, as shown in Figure 5.39. From these measurements, determine the approximate molecular weight of hemoglobin (in grams per mole).

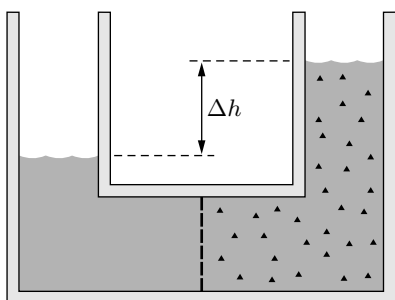


Figure 5.39. An experimental arrangement for measuring osmotic pressure. Solvent flows across the membrane from left to right until the difference in fluid level, Δh , is just enough to supply the osmotic pressure.

*From H. B. Bull, *An Introduction to Physical Biochemistry*, second edition (F. A. Davis, Philadelphia, 1971), p. 182. The measurements were made by H. Gutfreund.

Problem 5.78. Because osmotic pressures can be quite large, you may wonder whether the approximation made in equation 5.74 is valid in practice: Is μ_0 really a linear function of P to the required accuracy? Answer this question by discussing whether the derivative of this function changes significantly, over the relevant pressure range, in realistic examples.

Boiling and Freezing Points

In Section 5.4 we saw how impurities can shift the boiling and freezing points of a substance. For dilute solutions, we are now in a position to compute this shift quantitatively.

Consider first the case of a dilute solution at its boiling point, when it is in equilibrium with its gas phase (see Figure 5.40). Assume for simplicity that the solute does not evaporate at all—this is an excellent approximation for salt in water, for instance. Then the gas contains no solute, so we need only consider the equilibrium condition for the solvent:

$$\mu_{A,\text{liq}}(T, P) = \mu_{A,\text{gas}}(T, P). \quad (5.81)$$

Using equation 5.69 to rewrite the left-hand side, this condition becomes

$$\mu_0(T, P) - \frac{N_B kT}{N_A} = \mu_{\text{gas}}(T, P), \quad (5.82)$$

where μ_0 is the chemical potential of the pure solvent.

Now, as in the osmotic pressure derivation above, the procedure is to expand each μ function about the nearby point where the pure solvent would be in equilibrium. Because μ depends on both temperature and pressure, we can hold either fixed while allowing the other to vary. Let us first vary the pressure. Let P_0 be the vapor pressure of the pure solvent at temperature T , so that

$$\mu_0(T, P_0) = \mu_{\text{gas}}(T, P_0). \quad (5.83)$$

In terms of the chemical potentials at P_0 , equation 5.82 becomes

$$\mu_0(T, P_0) + (P - P_0) \frac{\partial \mu_0}{\partial P} - \frac{N_B kT}{N_A} = \mu_{\text{gas}}(T, P_0) + (P - P_0) \frac{\partial \mu_{\text{gas}}}{\partial P}. \quad (5.84)$$

The first term on each side cancels by equation 5.83, and each $\partial \mu / \partial P$ is the volume

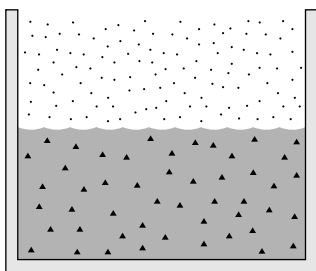


Figure 5.40. The presence of a solute reduces the tendency of a solvent to evaporate.

per particle for that phase, so

$$(P - P_0) \left(\frac{V}{N} \right)_{\text{liq}} - \frac{N_B kT}{N_A} = (P - P_0) \left(\frac{V}{N} \right)_{\text{gas}}. \quad (5.85)$$

The volume per particle in the gas phase is just kT/P_0 , while the volume per particle in the liquid is negligible in comparison. This equation therefore reduces to

$$P - P_0 = \frac{-N_B}{N_A} P_0 \quad \text{or} \quad \frac{P}{P_0} = 1 - \frac{N_B}{N_A}. \quad (5.86)$$

The vapor pressure is reduced by a fraction equal to the ratio of the numbers of solute and solvent molecules. This result is known as **Raoult's law**. At the molecular level, the reduction in vapor pressure happens because the addition of solute reduces the number of solvent molecules at the surface of the liquid—hence they escape into the vapor less frequently.

Alternatively, we could hold the pressure fixed and solve for the shift in temperature needed to maintain equilibrium in the presence of the solute. Let T_0 be the boiling point of the pure solvent at pressure P , so that

$$\mu_0(T_0, P) = \mu_{\text{gas}}(T_0, P). \quad (5.87)$$

In terms of the chemical potentials at T_0 , equation 5.82 becomes

$$\mu_0(T_0, P) + (T - T_0) \frac{\partial \mu_0}{\partial T} - \frac{N_B kT}{N_A} = \mu_{\text{gas}}(T_0, P) + (T - T_0) \frac{\partial \mu_{\text{gas}}}{\partial T}. \quad (5.88)$$

Again the first term on each side cancels. Each $\partial \mu / \partial T$ is just minus the entropy per particle for that phase (because $\partial G / \partial T = -S$), so

$$-(T - T_0) \left(\frac{S}{N} \right)_{\text{liq}} - \frac{N_B kT}{N_A} = -(T - T_0) \left(\frac{S}{N} \right)_{\text{gas}}. \quad (5.89)$$

It's simplest to set the N under each S equal to N_A , remembering that each S now refers to N_A molecules of solvent. The *difference* in entropy between the gas and the liquid is L/T_0 , where L is the latent heat of vaporization. Therefore the temperature shift is

$$T - T_0 = \frac{N_B k T_0^2}{L} = \frac{n_B R T_0^2}{L}, \quad (5.90)$$

where I've approximated $T \approx T_0$ on the right-hand side.

As an example let's compute the boiling temperature of seawater. A convenient quantity to consider is one kilogram; then L is 2260 kJ. A kilogram of seawater contains 35 g of dissolved salts, mostly NaCl. The average atomic mass of Na and Cl is about 29, so 35 g of salt dissolves into $35/29 = 1.2$ moles of ions. Therefore the boiling temperature is shifted (relative to fresh water) by

$$T - T_0 = \frac{(1.2 \text{ mol})(8.3 \text{ J/mol}\cdot\text{K})(373 \text{ K})^2}{2260 \text{ kJ}} = 0.6 \text{ K}. \quad (5.91)$$

To compute the shift in the vapor pressure at a given temperature, we need to know that a kilogram of water contains $1000/18 = 56$ moles of water molecules. Hence, by Raoult's law,

$$\frac{\Delta P}{P_0} = -\frac{1.2 \text{ mol}}{56 \text{ mol}} = -0.022. \quad (5.92)$$

Both of these effects are quite small: Seawater evaporates almost as easily as fresh water. Ironically, the shift in boiling temperature becomes large only for a nondilute solution, when the formulas of this section become inaccurate (though they can still give a rough estimate).

A formula essentially identical to equation 5.90 gives the shift in the *freezing* temperature of a dilute solution. Because the proof is so similar, I'll let you do it (see Problem 5.81). I'll also let you think about why the freezing temperature is *reduced* rather than increased. For water and most other solvents the shift in freezing temperature is somewhat larger than the shift in boiling temperature, due to the smaller value of L .

Together with osmotic pressure, the shifts in the vapor pressure, boiling temperature, and freezing temperature are all known as **colligative properties** of dilute solutions. All of these effects depend only on the *amount* of solute, not on *what* the solute is.

Problem 5.79. Most pasta recipes instruct you to add a teaspoon of salt to a pot of boiling water. Does this have a significant effect on the boiling temperature? Justify your answer with a rough numerical estimate.

Problem 5.80. Use the Clausius-Clapeyron relation to derive equation 5.90 directly from Raoult's law. Be sure to explain the logic carefully.

Problem 5.81. Derive a formula, similar to equation 5.90, for the shift in the freezing temperature of a dilute solution. Assume that the solid phase is pure solvent, no solute. You should find that the shift is negative: The freezing temperature of a solution is *less* than that of the pure solvent. Explain in general terms why the shift should be negative.

Problem 5.82. Use the result of the previous problem to calculate the freezing temperature of seawater.

5.6 Chemical Equilibrium

One interesting fact about chemical reactions is that they hardly ever go to completion. Consider, for example, the dissociation of water into H^+ and OH^- ions:



Under ordinary conditions, this reaction tends strongly to go to the left; an ordinary glass of water at equilibrium contains about 500 million water molecules for every pair of H^+ and OH^- ions. Naively, we tend to think of the water molecule as being “more stable” than the ions. But this can't be the whole story—otherwise there would be *no* ions in a glass full of water, when in fact there are quadrillions of them.

One way to understand why there are always some “unstable” ions even at equilibrium is to visualize the collisions at the molecular level. At room temperature, the water molecules are constantly colliding with each other at rather high speed. Every once in a while, one of these collisions is violent enough to break a molecule apart into two ions. The ions then tend to become separated, and do not recombine until they chance to meet new partners in the very dilute solution. Eventually an equilibrium is reached between the breaking apart and recombining, both of which occur rather rarely.

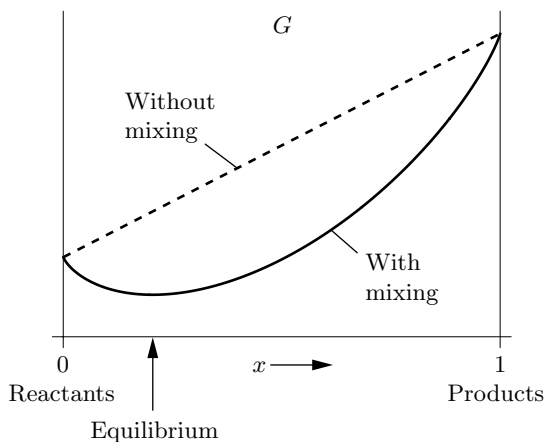
At a more abstract level, we can think about equilibrium in terms of the Gibbs free energy. At room temperature and atmospheric pressure, the concentration of each species at equilibrium is determined by the condition that the total Gibbs free energy,

$$G = U - TS + PV, \quad (5.94)$$

be minimized. We might expect that the minimum would occur when there are only water molecules, with no ions present. Indeed, it is true that a glass of water has much less Gibbs free energy than a glass full of H^+ and OH^- ions, simply because it has so much less energy. However, breaking just a *few* molecules apart into ions can lower the Gibbs free energy still further, because the *entropy* increases substantially. At higher temperature this entropy will contribute more to G , so there will be more ions.

It is instructive to plot the Gibbs free energy as a function of the **extent** of the reaction, which in this case is the fraction x of the water molecules that are split into ions. If every water molecule is intact then $x = 0$, while if every molecule were dissociated then x would equal 1. If we were to keep the dissociated ions separate from the intact water, then a graph of G vs. x would be a straight line with a large positive slope (see Figure 5.41). When we let the ions mix with the molecules, however, the entropy of mixing introduces an additional concave-upward term in G . As discussed in Section 5.4, the derivative of this term is infinite at the endpoints $x = 0$ and $x = 1$. Therefore, no matter how great the energy difference between the reactants and the products, the equilibrium point—the minimum of G —will lie

Figure 5.41. If reactants and products remained separate, the free energy would be a linear function of the extent of the reaction. With mixing, however, G has a minimum somewhere between $x = 0$ and $x = 1$.



at least a little bit inward from the lower of the two endpoints. (In practice it may be closer than one part in Avogadro's number; in such cases the reaction effectively *does* go to completion.)

We can characterize the equilibrium point by the condition that the slope of the Gibbs free energy graph is zero. This means that if one more H_2O molecule dissociates, G is unchanged:

$$0 = dG = \sum_i \mu_i dN_i. \quad (5.95)$$

In the last expression I've used the thermodynamic identity for G , plus the assumption that the temperature and pressure are fixed. The sum runs over all three species: H_2O , H^+ , and OH^- . But the changes in the three N_i 's are not independent: An increase of one H^+ is always accompanied by an increase of one OH^- and a decrease of one H_2O . One set of possible changes is

$$dN_{\text{H}_2\text{O}} = -1, \quad dN_{\text{H}^+} = 1, \quad dN_{\text{OH}^-} = 1. \quad (5.96)$$

Plugging these numbers into equation 5.95 yields

$$\mu_{\text{H}_2\text{O}} = \mu_{\text{H}^+} + \mu_{\text{OH}^-}. \quad (5.97)$$

This relation among the chemical potentials must be satisfied at equilibrium. Since each chemical potential is a function of the concentration of that species (a higher concentration implying a higher chemical potential), this condition determines the various concentrations at equilibrium.

Before generalizing this result to an arbitrary chemical reaction, let's consider another example, the combination of nitrogen and hydrogen to form ammonia:



Again, the reaction is at equilibrium when $\sum_i \mu_i dN_i = 0$. One possible set of dN 's is

$$dN_{\text{N}_2} = -1, \quad dN_{\text{H}_2} = -3, \quad dN_{\text{NH}_3} = +2, \quad (5.99)$$

resulting in the equilibrium condition

$$\mu_{\text{N}_2} + 3\mu_{\text{H}_2} = 2\mu_{\text{NH}_3}. \quad (5.100)$$

By now you can probably see the pattern: The equilibrium condition is always the same as the reaction equation itself, but with the names of the chemical species replaced by their chemical potentials and \longleftrightarrow replaced by $=$. To write this rule as a formula we need some notation. Let X_i represent the chemical name of the i th species involved in a reaction, and let ν_i represent the stoichiometric coefficient of this species in the reaction equation, that is, the number of i molecules that participate each time the reaction happens. (For instance, $\nu_{\text{H}_2} = 3$ in the previous example.) An arbitrary reaction equation then looks like this:

$$\nu_1 X_1 + \nu_2 X_2 + \cdots \longleftrightarrow \nu_3 X_3 + \nu_4 X_4 + \cdots. \quad (5.101)$$

In the corresponding equilibrium condition, we simply replace each species name with its chemical potential:

$$\nu_1\mu_1 + \nu_2\mu_2 + \cdots = \nu_3\mu_3 + \nu_4\mu_4 + \cdots \quad (5.102)$$

The next step in understanding chemical equilibrium is to write each chemical potential μ_i in terms of the concentration of that species; then one can solve for the equilibrium concentrations. I could try to explain how to do this in general, but because gases, solutes, solvents, and pure substances must all be treated differently, I think it's easier (and more interesting) to demonstrate the procedure through the four worked examples that make up the rest of this section.

Problem 5.83. Write down the equilibrium condition for each of the following reactions:

- (a) $2\text{H} \leftrightarrow \text{H}_2$
- (b) $2\text{CO} + \text{O}_2 \leftrightarrow 2\text{CO}_2$
- (c) $\text{CH}_4 + 2\text{O}_2 \leftrightarrow 2\text{H}_2\text{O} + \text{CO}_2$
- (d) $\text{H}_2\text{SO}_4 \leftrightarrow 2\text{H}^+ + \text{SO}_4^{2-}$
- (e) $2p + 2n \leftrightarrow {}^4\text{He}$

Nitrogen Fixation

First consider the gaseous reaction 5.98, in which N_2 and H_2 combine to form ammonia (NH_3). This reaction is called nitrogen “fixation” because it puts the nitrogen into a form that can be used by plants to synthesize amino acids and other important molecules.

The equilibrium condition for this reaction is written in equation 5.100. If we assume that each species is an ideal gas, we can use equation 5.40 for each chemical potential to obtain

$$\mu_{\text{N}_2}^\circ + kT \ln\left(\frac{P_{\text{N}_2}}{P^\circ}\right) + 3\mu_{\text{H}_2}^\circ + 3kT \ln\left(\frac{P_{\text{H}_2}}{P^\circ}\right) = 2\mu_{\text{NH}_3}^\circ + 2kT \ln\left(\frac{P_{\text{NH}_3}}{P^\circ}\right). \quad (5.103)$$

Here each μ° represents the chemical potential of that species in its “standard state,” when its partial pressure is P° . Normally we take P° to be 1 bar. Gathering all the μ° 's on the right and all the logarithms on the left gives

$$kT \ln\left(\frac{P_{\text{N}_2}}{P^\circ}\right) + 3kT \ln\left(\frac{P_{\text{H}_2}}{P^\circ}\right) - 2kT \ln\left(\frac{P_{\text{NH}_3}}{P^\circ}\right) = 2\mu_{\text{NH}_3}^\circ - \mu_{\text{N}_2}^\circ - 3\mu_{\text{H}_2}^\circ. \quad (5.104)$$

Now if we multiply through by Avogadro's number, what's on the right is the “standard” Gibbs free energy of the reaction, written ΔG° . This quantity is the hypothetical change in G when one mole of pure N_2 reacts with three moles of pure H_2 to form two moles of pure ammonia, all at 1 bar. The important thing about ΔG° is that you can often look it up in reference tables. Meanwhile, we can combine the logarithms on the left into one big logarithm; thus,

$$RT \ln\left(\frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2 (P^\circ)^2}\right) = \Delta G^\circ, \quad (5.105)$$

or with a bit more rearranging,

$$\frac{P_{\text{NH}_3}^2 (P^\circ)^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = e^{-\Delta G^\circ / RT}. \quad (5.106)$$

Equation 5.106 is our final result. On the left-hand side are the equilibrium partial pressures of the three gases, raised to the powers of their stoichiometric coefficients, with reactants in the denominator and products in the numerator. There are also enough powers of the reference pressure P° to make the whole expression dimensionless. The quantity on the right-hand side is called the **equilibrium constant**, K :

$$K \equiv e^{-\Delta G^\circ / RT}. \quad (5.107)$$

It is a function of temperature (both through ΔG° and through the explicit T) but not of the amounts of the gases that are present. Often we compute K once and for all (at a given T) and then simply write

$$\frac{P_{\text{NH}_3}^2 (P^\circ)^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = K. \quad (5.108)$$

This equation is called the **law of mass action** (don't ask me why).

Even if you don't know the value of K , equation 5.108 tells you quite a bit about this reaction. If the gases are initially in equilibrium and you add more nitrogen or hydrogen, some of what you add will have to react to form ammonia in order to maintain equilibrium. If you add more ammonia, some will have to convert to nitrogen and hydrogen. If you double the partial pressure of both the hydrogen and the nitrogen, the partial pressure of the ammonia must *quadruple* in order to maintain equilibrium. Increasing the *total* pressure therefore favors the production of more ammonia. One way to remember how a system in equilibrium will respond to these kinds of changes, at least qualitatively, is **Le Chatelier's principle**:

When you disturb a system in equilibrium, it will respond in a way that partially offsets the disturbance.

So for instance, when you *increase* the total pressure, more nitrogen and hydrogen will react to form ammonia, decreasing the total number of molecules and thus *reducing* the total pressure.

To be more quantitative, we need a numerical value for the equilibrium constant K . Sometimes you can find tabulated values of equilibrium constants, but more often you need to compute them from ΔG° values using equation 5.107. For the production of two moles of ammonia at 298 K, standard tables give the value $\Delta G^\circ = -32.9$ kJ. The equilibrium constant at room temperature is therefore

$$K = \exp\left(\frac{+32,900 \text{ J}}{(8.31 \text{ J/K})(298 \text{ K})}\right) = 5.9 \times 10^5, \quad (5.109)$$

so this reaction tends strongly to the right, favoring the production of ammonia from nitrogen and hydrogen.

At higher temperatures, K becomes much smaller (see Problem 5.86), so you might think that industrial production of ammonia would be carried out at relatively low temperature. However, the equilibrium condition tells us absolutely nothing about the *rate* of the reaction. It turns out that, unless a good catalyst is present, this reaction proceeds negligibly slowly at temperatures below about 700°C. Certain bacteria do contain excellent catalysts (enzymes) that can fix nitrogen at room temperature. For industrial production, though, the best known catalyst still requires a temperature of about 500°C to achieve an acceptable production rate. At this temperature the equilibrium constant is only 6.9×10^{-5} , so very high pressures are needed to produce a reasonable amount of ammonia. The industrial nitrogen-fixation process used today, employing an iron-molybdenum catalyst, temperatures around 500°C, and total pressures around 400 atm, was developed in the early 20th century by the German chemist Fritz Haber. This process has revolutionized the production of chemical fertilizers, and also, unfortunately, facilitated the manufacture of explosives.

Problem 5.84. A mixture of one part nitrogen and three parts hydrogen is heated, in the presence of a suitable catalyst, to a temperature of 500°C. What fraction of the nitrogen (atom for atom) is converted to ammonia, if the final total pressure is 400 atm? Pretend for simplicity that the gases behave ideally despite the very high pressure. The equilibrium constant at 500°C is 6.9×10^{-5} . (Hint: You'll have to solve a quadratic equation.)

Problem 5.85. Derive the **van't Hoff equation**,

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2},$$

which gives the dependence of the equilibrium constant on temperature.* Here ΔH° is the enthalpy change of the reaction, for pure substances in their standard states (1 bar pressure for gases). Notice that if ΔH° is positive (loosely speaking, if the reaction requires the absorption of heat), then higher temperature makes the reaction tend more to the right, as you might expect. Often you can neglect the temperature dependence of ΔH° ; solve the equation in this case to obtain

$$\ln K(T_2) - \ln K(T_1) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Problem 5.86. Use the result of the previous problem to estimate the equilibrium constant of the reaction $\text{N}_2 + 3\text{H}_2 \leftrightarrow 2\text{NH}_3$ at 500°C, using only the room-temperature data at the back of this book. Compare your result to the actual value of K at 500°C quoted in the text.

*Van't Hoff's *equation* is not to be confused with van't Hoff's *formula* for osmotic pressure. Same person, different physical principle.

Dissociation of Water

As a second example of chemical equilibrium, consider again the dissociation of water into H^+ and OH^- ions, discussed briefly at the beginning of this section:



At equilibrium the chemical potentials of the three species satisfy

$$\mu_{\text{H}_2\text{O}} = \mu_{\text{H}^+} + \mu_{\text{OH}^-}. \quad (5.111)$$

Assuming that the solution is dilute (a very good approximation under normal conditions), the chemical potentials are given by equations 5.69 (for H_2O) and 5.72 (for H^+ and OH^-). Furthermore, the deviation of $\mu_{\text{H}_2\text{O}}$ from its value for pure water is negligible. The equilibrium condition is therefore

$$\mu_{\text{H}_2\text{O}}^\circ = \mu_{\text{H}^+}^\circ + kT \ln m_{\text{H}^+} + \mu_{\text{OH}^-}^\circ + kT \ln m_{\text{OH}^-}, \quad (5.112)$$

where each μ° represents the chemical potential of the substance in its “standard state”—pure liquid for H_2O and a concentration of one mole per kilogram solvent for the ions. The m ’s are molalities, understood to be measured in units of one mole solute per kilogram of solvent.

As in the previous example, the next step is to gather the μ° ’s on the right, the logarithms on the left, and multiply through by Avogadro’s number:

$$RT \ln(m_{\text{H}^+} m_{\text{OH}^-}) = -N_A(\mu_{\text{H}^+}^\circ + \mu_{\text{OH}^-}^\circ - \mu_{\text{H}_2\text{O}}^\circ) = -\Delta G^\circ, \quad (5.113)$$

where ΔG° is the standard change in G for the reaction, again a value that can be looked up in tables. A bit of rearrangement gives

$$m_{\text{H}^+} m_{\text{OH}^-} = e^{-\Delta G^\circ / RT}, \quad (5.114)$$

the equilibrium condition for the ion molalities.

Before plugging in numbers, it’s worthwhile to pause and compare this result to the equilibrium condition in the previous example, equation 5.106. In both cases the right-hand side is called the equilibrium constant,

$$K = e^{-\Delta G^\circ / RT}, \quad (5.115)$$

and is given by the same exponential function of the standard change in the Gibbs free energy. But the “standard” states are now completely different: pure liquid for the solvent and 1 molal for the solutes instead of 1 bar partial pressure for the gases of the previous example. Correspondingly, the left-hand side of equation 5.114 involves molalities instead of partial pressures (but still raised to the powers of their stoichiometric coefficients, in this case both equal to 1). Most significantly, the amount or concentration of water does not appear at all on the left-hand side of equation 5.114. This is because in a dilute solution there is always plenty of

solvent available for the reaction, no matter how much has already reacted. (The same would be true of a pure liquid or solid that reacts only at its surface.)

A final difference between ideal gas reactions and reactions in solution is that in the latter case, the equilibrium constant can in principle depend on the total pressure. In practice, however, this dependence is usually negligible except at very high (e.g., geological) pressures (see Problem 5.88).

The value of ΔG° for the dissociation of one mole of water at room temperature and atmospheric pressure is 79.9 kJ, so the equilibrium constant for this reaction is

$$K = \exp\left(-\frac{79,900 \text{ J}}{(8.31 \text{ J/K})(298 \text{ K})}\right) = 1.0 \times 10^{-14}. \quad (5.116)$$

If all the H^+ and OH^- ions come from dissociation of water molecules, then they must be equally abundant, so in this case

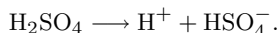
$$m_{\text{H}^+} = m_{\text{OH}^-} = 1.0 \times 10^{-7}. \quad (5.117)$$

The 7 in this result is called the **pH** of pure water. More generally, the pH is defined as minus the base-10 logarithm of the molality of H^+ ions:

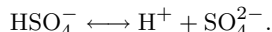
$$\text{pH} \equiv -\log_{10} m_{\text{H}^+}. \quad (5.118)$$

If other substances are dissolved in water, the pH can shift significantly. When the pH is less than 7 (indicating a higher H^+ concentration) we say the solution is **acidic**, while when the pH is greater than 7 (indicating a lower H^+ concentration) we say the solution is **basic**.

Problem 5.87. Sulfuric acid, H_2SO_4 , readily dissociates into H^+ and HSO_4^- ions:



The hydrogen sulfate ion, in turn, can dissociate again:



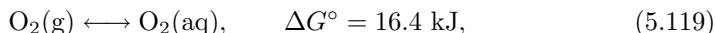
The equilibrium constants for these reactions, in aqueous solutions at 298 K, are approximately 10^2 and $10^{-1.9}$, respectively. (For dissociation of acids it is usually more convenient to look up K than ΔG° . By the way, the negative base-10 logarithm of K for such a reaction is called **pK**, in analogy to pH. So for the first reaction $\text{pK} = -2$, while for the second reaction $\text{pK} = 1.9$.)

- (a) Argue that the first reaction tends so strongly to the right that we might as well consider it to have gone to completion, in any solution that could possibly be considered dilute. At what pH values would a significant fraction of the sulfuric acid *not* be dissociated?
- (b) In industrialized regions where lots of coal is burned, the concentration of sulfate in rainwater is typically 5×10^{-5} mol/kg. The sulfate can take any of the chemical forms mentioned above. Show that, at this concentration, the second reaction will also have gone essentially to completion, so all the sulfate is in the form of SO_4^{2-} . What is the pH of this rainwater?
- (c) Explain why you can neglect dissociation of water into H^+ and OH^- in answering the previous question.
- (d) At what pH would dissolved sulfate be equally distributed between HSO_4^- and SO_4^{2-} ?

Problem 5.88. Express $\partial(\Delta G^\circ)/\partial P$ in terms of the volumes of solutions of reactants and products, for a chemical reaction of dilute solutes. Plug in some reasonable numbers, to show that a pressure increase of 1 atm has only a negligible effect on the equilibrium constant.

Oxygen Dissolving in Water

When oxygen (O_2) gas dissolves in water (see Figure 5.42), there is no chemical reaction per se, but we can still apply the techniques of this section to find out how much O_2 will dissolve. The “reaction” equation and tabulated ΔG° value are



where g is for “gas” and aq is for “aqueous” (i.e., dissolved in water). The ΔG° value is for one mole of oxygen at 1 bar pressure dissolving in 1 kg of water (to give a solution with molality 1), all at 298 K.

When the dissolved oxygen is in equilibrium with the oxygen in the adjacent gas, their chemical potentials must be equal:

$$\mu_{\text{gas}} = \mu_{\text{solute}}. \quad (5.120)$$

Using equation 5.40 for μ_{gas} and equation 5.72 for μ_{solute} , we can write both chemical potentials in terms of standard-state values and the respective concentrations:

$$\mu_{\text{gas}}^\circ + kT \ln(P/P^\circ) = \mu_{\text{solute}}^\circ + kT \ln m. \quad (5.121)$$

Here P is the partial pressure of O_2 in the gas, P° is the standard pressure of 1 bar, and m is the molality of the dissolved oxygen in moles per kilogram of water. Once again, the procedure is to gather the μ° 's on the right and the logarithms on the left, then multiply through by Avogadro's number:

$$RT \ln \left(\frac{P/P^\circ}{m} \right) = N_A (\mu_{\text{solute}}^\circ - \mu_{\text{gas}}^\circ) = \Delta G^\circ; \quad (5.122)$$

or equivalently,

$$\frac{m}{P/P^\circ} = e^{-\Delta G^\circ/RT}. \quad (5.123)$$

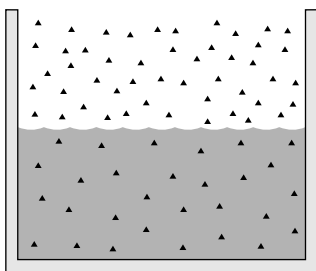


Figure 5.42. The dissolution of a gas in a liquid, such as oxygen in water, can be treated as a chemical reaction with its own equilibrium constant.

Equation 5.123 says that the ratio of the amount of dissolved oxygen to the amount in the adjacent gas is a constant, at any given temperature and total pressure. This result is known as **Henry's law**. As in the previous example, the dependence of ΔG° on the total pressure is usually negligible unless the pressure is very large. The constant on the right-hand side of the equation is sometimes called a "Henry's law constant," but one often finds these constants tabulated in very different ways—as reciprocals and/or in terms of mole fraction rather than molality.

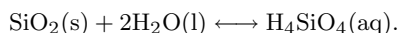
For oxygen in water at room temperature the right-hand side of equation 5.123 is

$$\exp\left(-\frac{16,400 \text{ J}}{(8.31 \text{ J/K})(298 \text{ K})}\right) = 0.00133 = \frac{1}{750}, \quad (5.124)$$

meaning that if the partial pressure of oxygen is 1 bar, about 1/750 of a mole of oxygen will dissolve in each kilogram of water. In our atmosphere at sea level the partial pressure of oxygen is only about 1/5 as much, and the amount of dissolved oxygen in water is proportionally less. Still, each liter of water contains the equivalent of about 7 cm³ of pure oxygen (if it were a gas at atmospheric pressure), enough for fish to breathe.

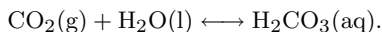
Problem 5.89. The standard enthalpy change upon dissolving one mole of oxygen at 25°C is −11.7 kJ. Use this number and the van't Hoff equation (Problem 5.85) to calculate the equilibrium (Henry's law) constant for oxygen in water at 0°C and at 100°C. Discuss the results briefly.

Problem 5.90. When solid quartz "dissolves" in water, it combines with water molecules in the reaction

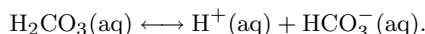


- (a) Use this data in the back of this book to compute the amount of silica dissolved in water in equilibrium with solid quartz, at 25°C.
- (b) Use the van't Hoff equation (Problem 5.85) to compute the amount of silica dissolved in water in equilibrium with solid quartz at 100°C.

Problem 5.91. When carbon dioxide "dissolves" in water, essentially all of it reacts to form carbonic acid, H₂CO₃:



The carbonic acid can then dissociate into H⁺ and bicarbonate ions,



(The table at the back of this book gives thermodynamic data for both of these reactions.) Consider a body of otherwise pure water (or perhaps a raindrop) that is in equilibrium with the atmosphere near sea level, where the partial pressure of carbon dioxide is 3.4×10^{-4} bar (or 340 parts per million). Calculate the molality of carbonic acid and of bicarbonate ions in the water, and determine the pH of the solution. Note that even "natural" precipitation is somewhat acidic.

Ionization of Hydrogen

As a final example of chemical equilibrium, let's consider the ionization of atomic hydrogen into a proton and an electron,



an important reaction in stars such as our sun. This reaction is so simple that we can compute the equilibrium constant from first principles, without looking up anything in a table.

Following the same steps as in the previous examples, we can write the equilibrium condition for the partial pressures as

$$kT \ln \left(\frac{P_{\text{H}} P^{\circ}}{P_p P_e} \right) = \mu_p^{\circ} + \mu_e^{\circ} - \mu_{\text{H}}^{\circ}, \quad (5.126)$$

where each μ° is the chemical potential of that species at 1 bar pressure. Under most conditions we can treat all three species as structureless monatomic gases, for which we derived an explicit formula for μ in Section 3.5:

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right] = -kT \ln \left[\frac{kT}{P} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right]. \quad (5.127)$$

(Here m is the mass of the particle, not molality.) The only subtlety is that this formula includes only kinetic energy, taking the energy zero-point to be the state where all the particles are at rest. In computing the *difference* of the μ° 's we also need to include the ionization energy, $I = 13.6$ eV, that you need to put in to convert H to $p + e$ even if there is no kinetic energy. I'll put this in by subtracting I from μ_{H} :

$$\mu_{\text{H}}^{\circ} = -kT \ln \left[\frac{kT}{P^{\circ}} \left(\frac{2\pi m_{\text{H}} kT}{h^2} \right)^{3/2} \right] - I. \quad (5.128)$$

For p and e , the formulas for μ° are identical but with different masses and without the final $-I$.

Plugging all three μ° 's into equation 5.126 gives a big mess, but since $m_p \approx m_{\text{H}}$, everything except the $-I$ in the chemical potentials of these two species cancels. Dividing through by $-kT$, we're left with

$$-\ln \left(\frac{P_{\text{H}} P^{\circ}}{P_p P_e} \right) = \ln \left[\frac{kT}{P^{\circ}} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \right] - \frac{I}{kT}. \quad (5.129)$$

A bit of algebra then yields the following result:

$$\frac{P_p}{P_{\text{H}}} = \frac{kT}{P_e} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-I/kT}. \quad (5.130)$$

This formula is called the **Saha equation**. It gives the ratio of the amount of ionized hydrogen (that is, protons) to the amount of un-ionized hydrogen as a

function of temperature and the concentration of electrons. (Note that the combination P_e/kT is the same as N_e/V , the number of electrons per unit volume.) At the surface of the sun the temperature is about 5800 K, so the exponential factor is only $e^{-I/kT} = 1.5 \times 10^{-12}$. Meanwhile the electron concentration is roughly $2 \times 10^{19} \text{ m}^{-3}$; the Saha equation thus predicts a ratio of

$$\frac{P_p}{P_H} = \frac{(1.07 \times 10^{27} \text{ m}^{-3})(1.5 \times 10^{-12})}{2 \times 10^{19} \text{ m}^{-3}} = 8 \times 10^{-5}. \quad (5.131)$$

Even at the surface of the sun, less than one hydrogen atom in 10,000 is ionized.

Problem 5.92. Suppose you have a box of atomic hydrogen, initially at room temperature and atmospheric pressure. You then raise the temperature, keeping the volume fixed.

- (a) Find an expression for the *fraction* of the hydrogen that is ionized as a function of temperature. (You'll have to solve a quadratic equation.) Check that your expression has the expected behavior at very low and very high temperatures.
- (b) At what temperature is exactly half of the hydrogen ionized?
- (c) Would raising the initial pressure cause the temperature you found in part (b) to increase or decrease? Explain.
- (d) Plot the expression you found in part (a) as a function of the dimensionless variable $t = kT/I$. Choose the range of t values to clearly show the interesting part of the graph.

Thermodynamics has something to say about everything but does not tell us everything about anything.

—Martin Goldstein and Inge F. Goldstein,
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