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:

$$H \equiv U + PV. \tag{5.1}$$

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**,

$$F \equiv U - TS. \tag{5.2}$$

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 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**,

$$G \equiv U - TS + PV. \tag{5.3}$$

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.

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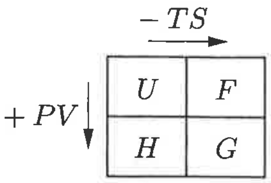
*In the context of creating a system, the term *free* energy is a misnomer. The energy that comes for free is TS, the term we *subtracted* to get F. In this context, F should be called the *costly* energy. The people who named F were instead thinking of the reverse process, where you annihilate the system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

$$\Delta F = \Delta U - T\,\Delta S = Q + W - T\,\Delta S, \tag{5.4}$$

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,

$$\Delta F \le W \qquad \text{at constant } T. \tag{5.5}$$

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

$$\Delta G = \Delta U - T\,\Delta S + P\,\Delta V = Q + W - T\,\Delta S + P\,\Delta V. \tag{5.6}$$

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:

$$W = -P\,\Delta V + W_{\text{other}}. \tag{5.7}$$

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

$$\Delta G \le W_{\text{other}} \qquad \text{at constant } T,\ P. \tag{5.8}$$

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

$$\Delta G = \Delta H - T\,\Delta S. \tag{5.9}$$

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,

$$N_2 + 3H_2 \longrightarrow 2NH_3,$$

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

$$H_2O \longrightarrow H_2 + \tfrac{1}{2}O_2, \tag{5.10}$$

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

$$S_{H_2O} = 70\text{ J/K}; \qquad S_{H_2} = 131\text{ J/K}; \qquad S_{O_2} = 205\text{ J/K}. \tag{5.11}$$

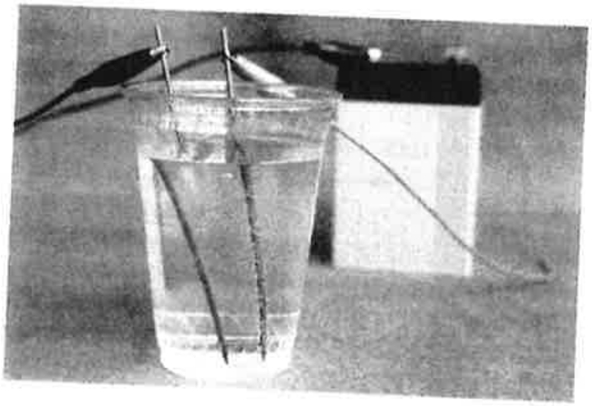


Figure 5.3. To separate water into hydrogen and oxygen, just run an electric current through it. In this home experiment the electrodes are mechanical pencil leads (graphite). Bubbles of hydrogen (too small to see) form at the negative electrode (left) while bubbles of oxygen form at the positive electrode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

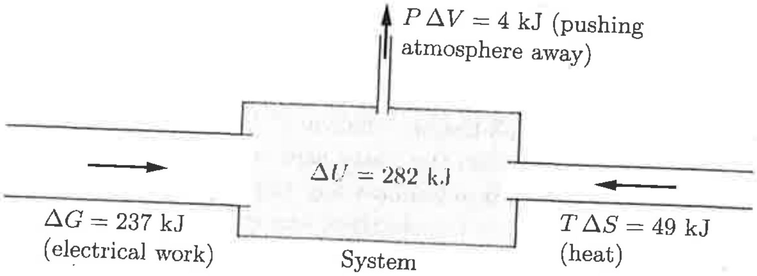


Figure 5.4. Energy-flow diagram for electrolysis of one mole of water. Under ideal conditions, 49 kJ of energy enter as heat ($T\Delta S$), so the electrical work required is only 237 kJ: $\Delta G = \Delta H - T\Delta S$. The difference between ΔH and ΔU is $P\Delta V =$ 4 kJ, the work done to make 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 $T\Delta S = (298\text{ K})(163\text{ J/K}) = 49$ 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,

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

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

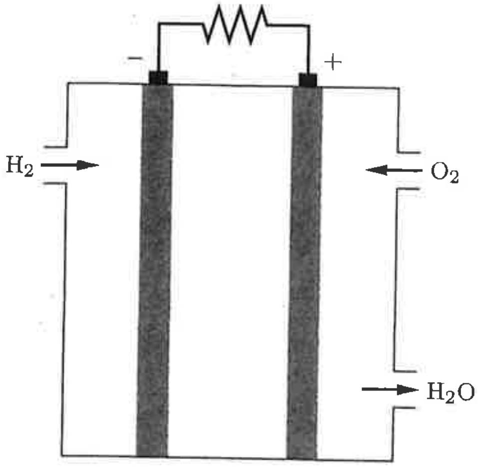


Figure 5.5. In a hydrogen fuel cell, hydrogen and oxygen gas pass through porous electrodes and react to form water, removing electrons from one electrode and depositing electrons on the other.

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

$$\mathrm{Pb} + \mathrm{PbO_2} + 4\mathrm{H^+} + 2\mathrm{SO_4^{2-}} \longrightarrow 2\mathrm{PbSO_4} + 2\mathrm{H_2O}. \tag{5.13}$$

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 kJ)/(298 K) = 260 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

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

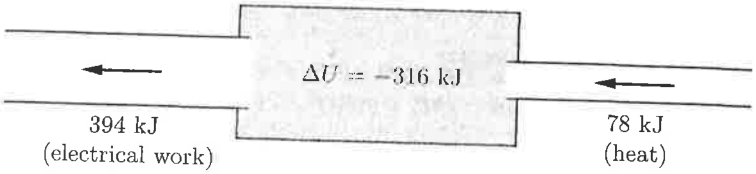

Figure 5.6. Energy-flow diagram for a lead-acid cell operating ideally. For each mole that reacts, the system's energy decreases by 316 kJ and its entropy increases by 260 J/K. Because of the entropy increase, the system can absorb 78 kJ of heat from the environment; the maximum work performed is therefore 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:

$$\begin{aligned} \text{in solution:}\quad & 2\mathrm{SO_4^{2-}} + 2\mathrm{H^+} \longrightarrow 2\mathrm{HSO_4^-}; \\ \text{at } - \text{ electrode:}\quad & \mathrm{Pb} + \mathrm{HSO_4^-} \longrightarrow \mathrm{PbSO_4} + \mathrm{H^+} + 2\mathrm{e^-}; \\ \text{at } + \text{ electrode:}\quad & \mathrm{PbO_2} + \mathrm{HSO_4^-} + 3\mathrm{H^+} + 2\mathrm{e^-} \longrightarrow \mathrm{PbSO_4} + 2\mathrm{H_2O}. \end{aligned} \tag{5.14}$$

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

$$\begin{aligned} \text{at } - \text{ electrode:}\quad & \mathrm{H_2} + 2\mathrm{OH^-} \longrightarrow 2\mathrm{H_2O} + 2\mathrm{e^-}; \\ \text{at } + \text{ electrode:}\quad & \tfrac{1}{2}\mathrm{O_2} + \mathrm{H_2O} + 2\mathrm{e^-} \longrightarrow 2\mathrm{OH^-}. \end{aligned}$$

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

$$\mathrm{CH_4} + 2\mathrm{O_2} \longrightarrow 2\mathrm{H_2O} + \mathrm{CO_2}.$$

(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.

(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

$$\begin{aligned}\text{at } - \text{ electrode:}\quad & CH_4 + 2H_2O \longrightarrow CO_2 + 8H^+ + 8e^-;\\ \text{at } + \text{ electrode:}\quad & 2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O.\end{aligned}$$

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:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O.$$

(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 ATP → ADP + 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,

$$dU = T\,dS - P\,dV + \mu\,dN, \tag{5.16}$$

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

$$dH = dU + P\,dV + V\,dP. \tag{5.17}$$

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

$$dH = T\,dS + V\,dP + \mu\,dN. \tag{5.18}$$

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

$$dF = dU - T\,dS - S\,dT. \tag{5.19}$$

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

$$dF = -S\,dT - P\,dV + \mu\,dN. \tag{5.20}$$

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

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

Similarly, holding T and either N or V fixed gives

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

Finally, you can derive the thermodynamic identity for G,

$$dG = -S\,dT + V\,dP + \mu\,dN, \tag{5.23}$$

and from it the following partial derivative formulas:

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

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

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*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 5.3×10^{-6} m^3, its Gibbs free energy increases by 5.3×10^{-6} 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 $\mu\, dN$ 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,

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

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 auxilliary 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," $4\pi\times10^{-7}$ 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.

(a) 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.)

(b) 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 $W = \mu_0\mathcal{H}\,dM$.

(c) What is the thermodynamic identity for this system? (Include magnetic work but not mechanical work or particle flow.)

(d) 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.

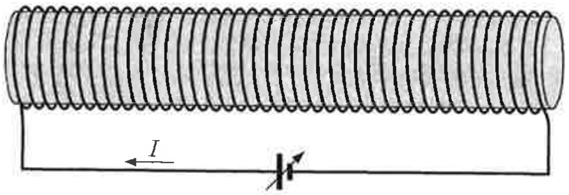

Figure 5.7. A long solenoid, surrounding a magnetic specimen, connected to a power supply that can change the current, performing magnetic work.

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*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:

$$dS_{\text{total}} = dS + dS_R. \tag{5.26}$$

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

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

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

$$dS_{\text{total}} = dS + \frac{1}{T_R}\,dU_R. \tag{5.28}$$

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,

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

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

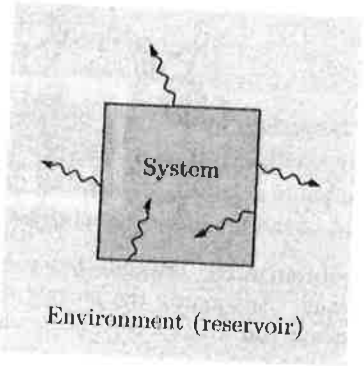

Figure 5.8. For a system that can exchange energy with its environment, the total entropy of both tends to increase.

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

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

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

$$F \equiv U - TS. \tag{5.31}$$

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,

$$G \equiv U + PV - TS. \tag{5.32}$$

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 × 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

V, U, S, P, T $\qquad$ $2V, 2U, 2S, P, T$

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,

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dN_i, \tag{5.33}$$

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

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

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:

$$G = N\mu. \tag{5.35}$$

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.

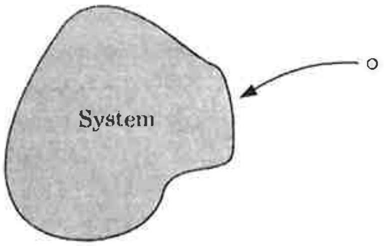

Figure 5.10. When you add a particle to a system, holding the temperature and pressure fixed, the system's Gibbs free energy increases by μ.

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

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

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:

$$G = N_1\mu_1 + N_2\mu_2 + \cdots = \sum_i N_i\mu_i. \tag{5.37}$$

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,

$$\frac{\partial \mu}{\partial P} = \frac{1}{N}\frac{\partial G}{\partial P} = \frac{V}{N}. \tag{5.38}$$

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

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

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

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

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**),

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

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

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

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

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

5.3 Phase Transformations of Pure Substances

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

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

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

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

Thermodynamic Properties of Selected Substances

All of the values in this table are for one mole of material at 298 K and 1 bar. Following the chemical formula is the form of the substance, either solid (s), liquid (l), gas (g), or aqueous solution (aq). When there is more than one common solid form, the mineral name or crystal structure is indicated. Data for aqueous solutions are at a standard concentration of 1 mole per kilogram water. The enthalpy and Gibbs free energy of formation, $\Delta_f H$ and $\Delta_f G$, represent the changes in H and G upon forming one mole of the material starting with elements in their most stable pure states (e.g., C (graphite), O_2 (g), etc.). To obtain the value of ΔH or ΔG for another reaction, subtract Δ_f of the reactants from Δ_f of the products. For ions in solution there is an ambiguity in dividing thermodynamic quantities between the positive and negative ions; by convention, H^+ is assigned the value zero and all others are chosen to be consistent with this value. Data from Atkins (1998), Lide (1994), and Anderson (1996). Please note that, while these data are sufficiently accurate and consistent for the examples and problems in this textbook, not all of the digits shown are necessarily significant; for research purposes you should always consult original literature to determine experimental uncertainties.

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
Al (s)	0	0	28.33	24.35	9.99
Al_2SiO_5 (kyanite)	−2594.29	−2443.88	83.81	121.71	44.09
Al_2SiO_5 (andalusite)	−2590.27	−2442.66	93.22	122.72	51.53
Al_2SiO_5 (sillimanite)	−2587.76	−2440.99	96.11	124.52	49.90
Ar (g)	0	0	154.84	20.79	
C (graphite)	0	0	5.74	8.53	5.30
C (diamond)	1.895	2.900	2.38	6.11	3.42
CH_4 (g)	−74.81	−50.72	186.26	35.31	
C_2H_6 (g)	−84.68	−32.82	229.60	52.63	
C_3H_8 (g)	−103.85	−23.49	269.91	73.5	
C_2H_5OH (l)	−277.69	−174.78	160.7	111.46	58.4
$C_6H_{12}O_6$ (glucose)	−1273	−910	212	115	
CO (g)	−110.53	−137.17	197.67	29.14	
CO_2 (g)	−393.51	−394.36	213.74	37.11	
H_2CO_3 (aq)	−699.65	−623.08	187.4		
HCO_3^- (aq)	−691.99	−586.77	91.2		
Ca^{2+} (aq)	−542.83	−553.58	−53.1		
$CaCO_3$ (calcite)	−1206.9	−1128.8	92.9	81.88	36.93
$CaCO_3$ (aragonite)	−1207.1	−1127.8	88.7	81.25	34.15
$CaCl_2$ (s)	−795.8	−748.1	104.6	72.59	51.6
Cl_2 (g)	0	0	223.07	33.91	
Cl^- (aq)	−167.16	−131.23	56.5	−136.4	17.3
Cu (s)	0	0	33.150	24.44	7.12
Fe (s)	0	0	27.28	25.10	7.11

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
H_2 (g)	0	0	130.68	28.82	
H (g)	217.97	203.25	114.71	20.78	
H^+ (aq)	0	0	0	0	
H_2O (l)	−285.83	−237.13	69.91	75.29	18.068
H_2O (g)	−241.82	−228.57	188.83	33.58	
He (g)	0	0	126.15	20.79	
Hg (l)	0	0	76.02	27.98	14.81
N_2 (g)	0	0	191.61	29.12	
NH_3 (g)	−46.11	−16.45	192.45	35.06	
Na^+ (aq)	−240.12	−261.91	59.0	46.4	−1.2
NaCl (s)	−411.15	−384.14	72.13	50.50	27.01
$NaAlSi_3O_8$ (albite)	−3935.1	−3711.5	207.40	205.10	100.07
$NaAlSi_2O_6$ (jadeite)	−3030.9	−2852.1	133.5	160.0	60.40
Ne (g)	0	0	146.33	20.79	
O_2 (g)	0	0	205.14	29.38	
O_2 (aq)	−11.7	16.4	110.9		
OH^- (aq)	−229.99	−157.24	−10.75	−148.5	
Pb (s)	0	0	64.81	26.44	18.3
PbO_2 (s)	−277.4	−217.33	68.6	64.64	
$PbSO_4$ (s)	−920.0	−813.0	148.5	103.2	
SO_4^{2-} (aq)	−909.27	−744.53	20.1	−293	
HSO_4^- (aq)	−887.34	−755.91	131.8	−84	
SiO_2 (α quartz)	−910.94	−856.64	41.84	44.43	22.69
H_4SiO_4 (aq)	−1449.36	−1307.67	215.13	468.98	