

Chapter 14

Free Energy and the Direction of Change

The random dispersal of energy, basis of the second law of thermodynamics, transforms the chance encounters of individual molecules into the statistical certainty of a macroscopic chemical reaction. The end—a thoroughly predictable state of equilibrium—is predetermined from the beginning, encoded in the stoichiometry and structure of the reactants and products. And with the Gibbs free energy we have, at last, our long sought expression of chemical drive: a drive toward an ever broader spread of global energy and growth of global entropy, captured by just a few macroscopic parameters.

Chapter 14 and its accompanying exercises aim to clarify the relationship between statistical inevitability and chemical equilibrium, and to make a tool out of the abstract thermodynamic concepts of enthalpy and entropy.

1. A spontaneous process runs “downhill” along a slope of free energy, able to proceed on its own absent any external driving force. The final state of equilibrium, when attained, is both thermodynamically more stable and statistically more likely than the initial state. The result is to subdivide a fixed pool of energy among a larger number of microscopic modes, thus ensuring an increase in global entropy.

To say that a process is spontaneous is to say only that it *can* take place. Whether a spontaneous reaction *will* take place is a kinetic question, whereas thermodynamic spontaneity merely addresses the fixed relationship between two potential states of equilibrium. The issue of spontaneity focuses solely on the beginning and end of a process, with no consideration of the path in between. Thermodynamics predicts whether a transformation from one state to another might be possible, but it provides no insight into how such a transformation might actually be brought about.

A spontaneous reaction may be fast or slow, irrespective of its potential—large or small—to release free energy and thereby disorder the universe. A large drop in free energy does not guarantee a rapid outcome, nor does a small drop in free energy necessarily demand a slow course of reaction. The rate depends on the mechanism by

which the molecules interact microscopically, and the rate can be changed by a catalyst or inhibitor without altering the proportions of the final mixture. The composition at equilibrium is fixed for all time by the intrinsic difference in free energy between reactants and products.

To fall spontaneously off a tall building, for example, is to follow a particularly direct and rapid route downward in a field of gravitational potential energy. Yet if one were to walk down the staircase of the same building, step by step, one would realize an identical change in potential energy (a thermodynamically fixed quantity) but at a much slower rate (a kinetic variable).

See Chapter 18 for a full treatment of chemical kinetics.

2. A process is spontaneous because it adds to the entropy of the universe; it produces a global macrostate that offers access to more microstates than previously available.

We use the Gibbs free energy

$$\Delta G = \Delta H - T \Delta S$$

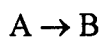
to address global entropy in compact fashion, focusing our attention on changes local to the system alone: a change in enthalpy (ΔH) and a change in entropy (ΔS). Implicit in these local changes, however, is also the total change in entropy for the universe (system and surroundings combined):

$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T}$$

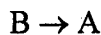
Whenever ΔG is negative, owing to some favorable combination of ΔH , ΔS , and T , the entropy of the universe grows as a result. The process is spontaneous.

Exothermic reactions ($\Delta H < 0$) therefore contribute favorably to ΔG , as do reactions in which the entropy of the system increases ($\Delta S > 0$). Processes that either absorb heat from the surroundings ($\Delta H > 0$) or decrease the entropy of the system ($\Delta S < 0$) can be either spontaneous or nonspontaneous, depending on the temperature. A process handicapped both by $\Delta H > 0$ and by $\Delta S < 0$ is nonspontaneous at all temperatures.

To be nonspontaneous, though, is not to be strictly forbidden, but rather to be “less likely” while still possible. Consider that for every spontaneous reaction



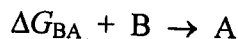
there is also a nonspontaneous reverse reaction



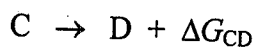
that can and does take place. Despite the unfavorable statistics, molecules of B sometimes do transform into molecules of A—and they do so during the beginning, middle, and end of the reaction. Nevertheless, more molecules of A eventually turn into

molecules of B, and consequently the thermodynamically favored product (B) is present in greater numbers at equilibrium.

If, in seeming defiance, we wish to force the nonspontaneous reaction



uphill to completion, then we must draw the energy from some other *spontaneous* process



in which the free energy released (ΔG_{CD}) exceeds the free energy ΔG_{BA} needed to produce B. If so, then the universe will enjoy greater entropy as a result of the coupled reactions. (See, for example, the description of an electrolytic cell given in Section 17-9.)

3. We consider commonplace examples of thermodynamic spontaneity and nonspontaneity.

(a) An apple falls spontaneously downward in the earth's gravitational field, from high potential to low. We never see an apple, by itself, jump *up* from ground to branch.

(b) Energy must be supplied externally to push a ball uphill, from low gravitational energy to high. The process is not spontaneous.

(c) Complete segregation of N_2 and O_2 molecules into separate halves of a room is statistically unlikely to the point of impossibility. The process of segregation is nonspontaneous, whereas the process of intermingling is spontaneous. See Example 14-4 in *PoC*.

(d) The intermingling of the different molecules is statistically more probable (enormously so). Mixing occurs spontaneously here, but see also Exercise 46.

(e) A battery discharges spontaneously, converting chemical energy (the free energy of reaction) into electrical energy. See Chapter 17 for an extended analysis of electrochemical processes, in particular the relationship between free energy and electrical potential.

(f) Heat flows spontaneously only from a body at higher temperature to a body at lower temperature. The passage of heat from a hand at 300 K to a hand at 301 K is therefore nonspontaneous. Such a process would create net order in the universe.

4. Each die, thrown separately, may turn up one of six faces. When two dice are thrown, the total number of outcomes is the product of two independent sets of events:

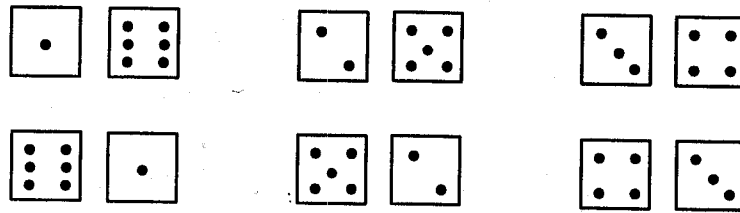
$$6 \times 6 = 36$$

(a) The possible outcomes are all shown in Figure 14.1 (overleaf).

No.	Dice	Sum	No.	Dice	Sum	No.	Dice	Sum
1		2	7		3	13		4
2		3	8		4	14		5
3		4	9		5	15		6
4		5	10		6	16		7
5		6	11		7	17		8
6		7	12		8	18		9
19		5	25		6	31		7
20		6	26		7	32		8
21		7	27		8	33		9
22		8	28		9	34		10
23		9	29		10	35		11
24		10	30		11	36		12

FIGURE 14.1 The 36 outcomes possible when two dice are thrown.

(b) See Figure 14.2 for the distribution of microstates. The most probable macrostate, represented by six microstates out of 36, has a sum equal to 7:



The least probable macrostates, with sums of 2 and 12, are each represented by only one microstate:



See Examples 14-1 and 14-2, as well as Exercise 45, for variations on the theme of throwing dice.

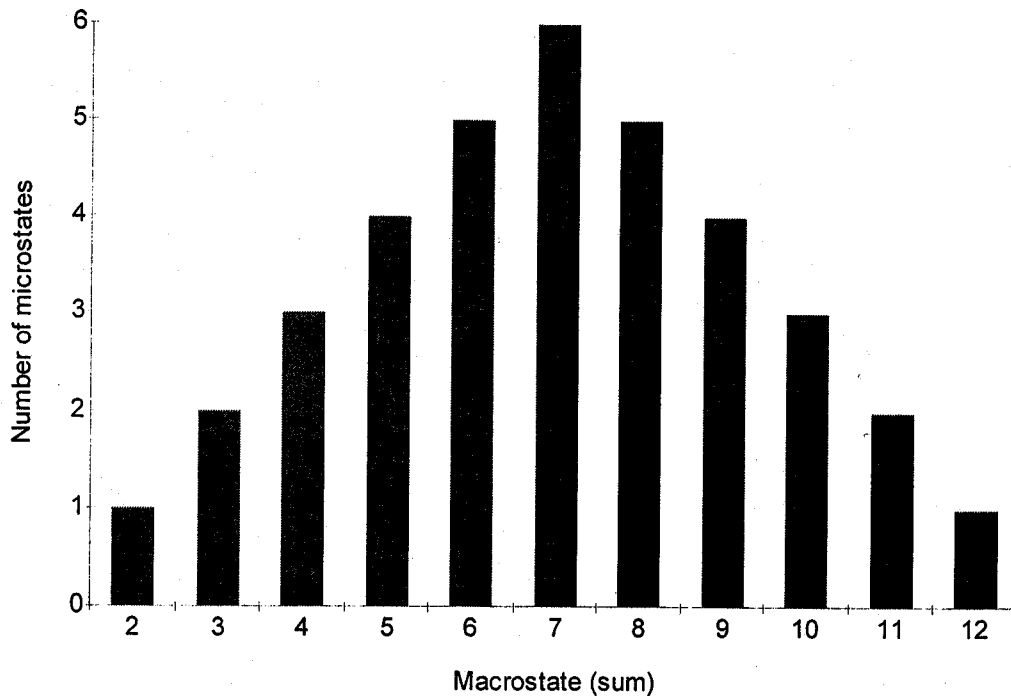


FIGURE 14.2 Distribution of microstates corresponding to the sum of two dice. The height of each bar represents the number of possible outcomes that yield the designated sum.

5. Again, each individual die may produce six independent outcomes.

(a) Infer from the results for two dice (Exercise 4) that four dice will yield a total of 6^4 microstates:

One die:	6
Two dice:	$6 \times 6 = 36$
Three dice:	$6 \times 6 \times 6 = 216$
Four dice:	$6 \times 6 \times 6 \times 6 = 1296$

For N dice, the general result is 6^N :

$$6 \times 6 \times \overset{N \text{ times}}{\dots} \times 6 = 6^N$$

(b) With $N = 4$, the totals range from 4 through 24. Least likely are the two extremes, 4 and 24, which are represented by only one microstate apiece:



Most likely is the macrostate at the center of the distribution, with a sum equal to 14.

6. Macroscopic chemical processes are dominated by the near-certain statistics of large systems.

(a) There are 6^N possible outcomes when N dice are thrown, as explained in the previous two exercises. If $N = 10^{13}$ (ten trillion), the resulting number

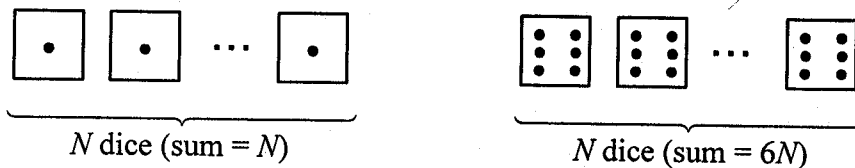
$$6^N = 6^{10,000,000,000,000}$$

is incomprehensibly large. Even the logarithm is huge:

$$\ln(6^N) = N \ln 6 = 1.8 \times 10^{13}$$

(b) The distribution sharpens to the point where the most probable macrostate becomes overwhelmingly likely. Outcomes narrowly clustered around this optimum sum, midway between the extremes, have a combined probability nearly equal to 1. Every possible face (1, 2, 3, 4, 5, 6) appears $\frac{1}{6} \times 10^{13}$ times, in random order.

Least likely are uniform outcomes in which each die shows either 1 (macrostate = N) or 6 (macrostate = $6N$), represented by only one microstate apiece:



The probability for such states is infinitesimally small:

$$\frac{1}{6^N} = \frac{1}{6^{10,000,000,000,000}} \approx 0$$

(c) The random apportionment of energy in chemical systems is similarly governed by the statistics of large numbers. Effectively, only combinations very close to the most probable distribution have nonzero probability.

7. Statistical entropy, defined as

$$S = k_B \ln W,$$

is a measure of microscopic disorder. It reflects the number of microstates (W) consistent with a given set of macroscopic variables. The more ways a system can disperse its energy into internal modes, the greater is the entropy. An ordered crystal, for example, is allowed just a relatively small number of microstates. Its entropy is low.

A spontaneous process occurs only in the direction of greater global disorder, toward a broader dispersal of energy. Although random and undirected, the drive toward higher entropy—given expression in the second law of thermodynamics—is statistically dominant in macroscopic systems. See Sections 14-2 and 14-3, as well as Examples 14-1, 14-2, and 14-4.

Exercises 8 through 16, touching qualitatively on the macroscopic interpretation of heat, entropy, and the second law, are meant to complement the statistical viewpoint taken in the text.

8. Work, taken as a macroscopic phenomenon, is coordinated and *organized*. The parts are large, simple, and few; and they all move in the same direction. Heat, by contrast, arises from the unchoreographed motion of countless particles. Heat represents the random investment of energy into thoroughly disorganized microscopic work, and therein lies a distinction that we shall explore in the next several questions.

9. Like marchers in a parade, organized motion (work) is likely to degenerate into disorganized motion, if only because there are so many possible ways to degrade an ordered state. Nobody should be surprised, after all, to see one, or two, or three marchers

or more fall spontaneously out of step. Watch them long enough, surely, and accidents will continue to happen until the once orderly process turns into a disorderly rabble.

But to go the other way—to transform a randomly milling crowd spontaneously into a parade—is statistically a far more difficult feat. Analogously, to transform heat into work is to trade microscopic disorder for macroscopic order. We can do it, but only at the cost of creating disorder elsewhere in the form of new heat.

10. The issues raised briefly in the two preceding questions suggest at least a plausible relationship between the macroscopic and microscopic formulations of the second law: Converting heat into work is tantamount to transforming random microscopic motion into directed macroscopic motion. The macroscopic impossibility of achieving an absolutely loss-free conversion is a reflection of the underlying microscopic statistics.

We know from experience, for example, that if we extract heat from a reservoir to do work elsewhere, then the temperature and thermal energy of the original heat source must decrease. This whole process, which creates order in the first reservoir, would be impossible were we not to transfer at least a portion of the heat to a second, *colder* reservoir where it can stir up thermal motion and thereby increase the entropy:

$$\Delta S > \frac{q_{\text{rev}}}{T}$$

The lower the temperature of the second reservoir, the less heat must be squandered to achieve the requisite increase in entropy—but, again, experience teaches us that no machine is 100% efficient. We can do no better than convert *some* of the heat into work, using the rest to increase disorder in some colder portion of the universe. In practice, the loss-free limit of $T = 0$ K is unattainable.

11. The first law of thermodynamics says that the very best one can do is not to lose. Nobody can destroy any old energy, but nobody can make any new energy either. So if we are prudent and clever, we should at least be able to husband our resources and keep all the energy already on hand. Such is our hope.

Unfortunately, the second law says that indeed we *always* lose. In the course of any real-life spontaneous process (an internal combustion engine, for example), some of the energy is inevitably “lost” through dissipative channels such as friction. A random flow of heat dribbles its way into the infinitely many microscopic modes of the universe, rendered inaccessible for useful work by the sheer power of statistical probability. Global disorder grows inexorably.

See also the preceding exercise.

12. The second law of thermodynamics remains intact, Billy’s newly ordered space notwithstanding. To generate the necessary energy, his body must convert carbohydrates into carbon dioxide and water—and, in so doing, he releases heat as a product of the exothermic combustion reactions. This heat, taken up by the surroundings, brings about a broader spread of energy overall. Entropy goes up, and Billy leaves the wider world a more disordered place.

13. Local order can always be purchased in return for an increase in disorder somewhere else, provided that a spontaneous process is available to finance the nonspontaneous activity. And so it is with our horses and men: Huffing and puffing and sweating, they expend energy to recreate an ordered Humpty-Dumpty from a disordered heap of broken eggshell. Some of this energy, however, is unavoidably diverted into wasted heat, which stirs up molecules in the surroundings and brings about a net increase in global entropy.

Humpty-Dumpty enjoys newfound order, but the universe as a whole suffers an irreversible increase in disorder.

14. System and surroundings are artificial distinctions we make solely for our analytical convenience. Spontaneity is determined not by what happens to an arbitrarily defined "system" but rather by what happens to the universe overall.

Local order indeed appears all around us, beginning with our own highly organized bodies. Liquids freeze, gases condense, crowds settle down—clearly there is no law against spontaneous organization. If, however, some particular portion of the universe manages to become more ordered, then another portion must become even more *disordered* for the process to go forward spontaneously.

Nature demands only that global entropy increase. What we choose to call system or surroundings is up to us.

15. Refrigeration requires work: electrical and mechanical. The refrigerator cannot extract heat from its cold contents to run the compressor. Energy must be provided instead from an external source, and the conversion of energy into work is inevitably less than 100% efficient. Waste heat is always produced.

Experience (codified in the second law) shows that more heat is released to the surroundings outside the refrigerator than is removed from the system inside the refrigerator. Since the temperature outside is higher than the temperature inside, an increase in global entropy such that

$$\Delta S_{\text{surr}} > \Delta S_{\text{sys}}$$

can be sustained only if q_{surr} (the waste heat) is greater than q_{sys} (the extracted heat):

$$\frac{q_{\text{surr}}}{T_{\text{surr}}} > \frac{q_{\text{sys}}}{T_{\text{sys}}} \quad \left(q_{\text{surr}} > q_{\text{sys}}, T_{\text{surr}} > T_{\text{sys}} \right)$$

16. Biff heats up the surrounding space, as we deduce from the preceding exercise. Consider: Heat passes spontaneously only from a body at high temperature to a body at low temperature, and thus no device can transfer heat from a cool environment to a warm environment without doing work. To operate a mechanical compressor, a refrigerator must draw energy from an electrical outlet—not from the refrigerated contents themselves. And since the process is less than 100% efficient, more heat will be released than removed.

Exercises 17 through 19 demonstrate qualitatively how enthalpy, entropy, temperature, and free energy are interconnected in chemical processes. Quantitative calculations involving these thermodynamic functions appear later in the set.

17. The criterion for spontaneity,

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ < 0$$

is defined so that the *system* undergoes the changes in enthalpy (ΔH°) and entropy (ΔS°). When ΔG° for the system is negative, the change in global entropy (system plus surroundings) is guaranteed to be positive. See Section 14-5.

(a) If ΔS° for a spontaneous reaction is negative, as it is when CaO(s) and $\text{CO}_2(\text{g})$ combine to produce $\text{CaCO}_3(\text{s})$, then ΔH° must also be negative. Such a process is exothermic, and ΔG° becomes negative at all temperatures below a threshold value T_0 :

$$T_0 = \frac{\Delta H^\circ}{\Delta S^\circ}$$

See pages 512–513 in *PoC*.

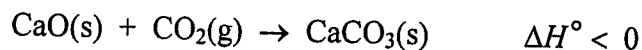
(b) An exothermic reaction produces a flow of heat from system to surroundings, thereby creating more disorder outside. If entropy decreases inside the system, as here, then the disordering flow of heat to the surroundings (where entropy increases) must outweigh the ordering that takes place inside (where entropy decreases):

$$\Delta S_{\text{surr}} > 0 > \Delta S_{\text{sys}}$$

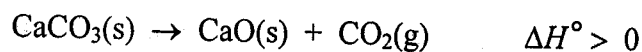
(c) The combined entropy of system plus surroundings (the universe) always increases upon completion of a spontaneous reaction.

18. When the sense of a reaction is reversed, the values of all state functions change sign.

(a) If the reaction



is exothermic (as deduced in the preceding exercise), then the reverse process is endothermic:



(b) Similarly, the change in entropy for a reverse reaction is equal in magnitude but opposite in sign to its value for the corresponding forward reaction. If ΔS° for the

forward reaction is negative (see Exercise 17), then it must be positive for the reverse reaction. Entropy increases upon production of a gas from the solid reactant.

(c) Here, with $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$, the expression

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

turns negative at temperatures sufficiently high for the favorable entropic term ($T \Delta S^\circ$) to dominate the unfavorable enthalpic term (ΔH°). The process is spontaneous at any temperature greater than T_0 :

$$T_0 = \frac{\Delta H^\circ}{\Delta S^\circ}$$

See *PoC*, pages 512–513.

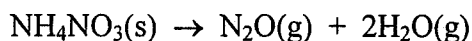
19. If the change in standard free energy is negative at all temperatures,

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ < 0$$

then we must have

$$\Delta H^\circ < 0 \quad \text{and} \quad \Delta S^\circ > 0$$

for the reaction as written:



Enthalpy in the system goes down. Entropy in the system goes up. Entropy in the universe goes up. See *PoC*, pages 512–513.

(a) The reaction is exothermic: $\Delta H^\circ < 0$.

(b) The products (three moles of gas) have higher entropy than the reactant (one mole of solid), as concluded above: $\Delta S^\circ > 0$.

(c) The reverse reaction, although not spontaneous, indeed does occur, but it occurs with lower probability than the spontaneous forward reaction. The proportions of reactants and products at equilibrium are determined by the change in free energy under standard conditions.

The following two problems, reminiscent of Exercises 7 through 9 and 18 through 23 in Chapter 13, use the ideal gas to explore heat, disorder, and equilibrium in a simple system.

20. See Section 14-9, as well as pages 384–391 and 466 in *PoC*, for material related to thermal equilibrium and the Boltzmann distribution.

(a) Thermal equilibrium is not established instantaneously. It takes time for energy to be redistributed among the particles and for a Boltzmann distribution to be attained.

(b) The gas particles exchange energy while colliding with themselves and with the walls of the container. Eventually they come to thermal equilibrium, establishing a temperature consistent with a Boltzmann distribution.

(c) The final temperature will conform to the ideal gas law:

$$PV = nRT$$

$$T = \frac{PV}{nR} = \frac{(1.00 \text{ atm})(1.00 \text{ L})}{(1.00 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})} = 12.2 \text{ K}$$

21. The equilibrated system from the preceding exercise is suddenly put into thermal contact with its surroundings.

(a) We calculated in Exercise 20 that the isolated gas comes to internal equilibrium at a temperature of 12.2 K. When exposed to the surroundings at 273 K (a different temperature), the gas finds itself out of equilibrium with the external world. Heat will flow until a common temperature is established.

(b) Heat passes from the hot surroundings (the world at 273 K) to the cold system (the gas at 12.2 K).

The exchange of energy occurs at the boundary between system and surroundings, mediated by collisions of the microscopic particles. Molecules in the boundary walls are bombarded by molecules from the system on one side and the surroundings on the other. Collision by collision, energy is reapportioned within and without.

(c) Away from thermal equilibrium, with heat flowing in from the surroundings, the gas cannot be characterized by a single temperature. Only when a new Boltzmann distribution is established does the system have a proper thermodynamic temperature once again.

(d) The final temperature of the gas is 273 K, provided that the change in energy of the surroundings is negligibly small (as we assume).

Exercises 22 and 23 deal with qualitative aspects of entropy and disorder. For related material, see pages 514–516 and also Examples 14-3 and 14-5 in PoC.

22. Here we consider the *total* entropy of a system, to be followed in Exercise 23 by the molar entropy (an intensive property).

(a) There are twice as many molecules of H_2O in 200 mL as in 100 mL. The larger amount supports more microscopic arrangements and hence has the greater entropy (a measure of disorder). Entropy is an extensive property, scaling with the size of the system.

(b) Mole for mole, a gas is more disordered than a liquid at the same temperature. Note, however, that 100 milliliters of vapor contain only 0.004 mol H_2O at 1 atm and 298 K, whereas 100 milliliters of liquid contain over 5.5 mol under the same conditions. Since entropy is an extensive property, increasing in proportion to the number of moles, the liquid in this example has more *total* entropy than an equal volume of gas.

(c) The entropy of a gas increases with volume, as shown on pages 504–505 of *PoC*. There are more ways to arrange the particles in a larger space:

$$\Delta S = nR \ln\left(\frac{W_2}{W_1}\right) = nR \ln\left(\frac{V_2}{V_1}\right) \quad (\text{fixed } T)$$

Recognize, next, that for equal amounts of an ideal gas at the same temperature, volume is inversely proportional to pressure:

$$V = \frac{nRT}{P}$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \quad (\text{fixed } n, T)$$

The system at the lower pressure (1 atm) thus has the larger volume and the larger entropy.

(d) For gases with the same volume and temperature, the number of moles is directly proportional to the pressure:

$$n = \left(\frac{V}{RT}\right)P$$

One liter of CH_4 at 2 atm and 298 K therefore contains twice as many moles as one liter of CH_4 at 1 atm and 298 K. Entropy, an extensive property, is double for the system at 2 atm.

23. Molar entropy, in contrast to total entropy, is an intensive property: a quantity stated *per unit amount*.

(a) Octane, a molecule larger and more complex than butane, has more internal modes into which energy can be redistributed—more atoms, more electrons, more bonds, more vibrations, more rotations. Liquid C_8H_{18} has a higher molar entropy than liquid C_4H_{10} at the same temperature.

(b) Entropy increases with temperature, because the system acquires more thermal energy to redistribute among the particles. Methane at 300 K has a higher molar entropy than methane at 250 K.

(c) The ice cube and the drink are in thermal equilibrium. The liquid, more disordered than the solid, has the higher molar entropy.

(d) The third law of thermodynamics stipulates that the entropy of a perfect crystal in equilibrium at 0 K is exactly zero. With that provision, we say that elemental oxygen and elemental titanium have the same entropy at absolute zero: 0.

24. See page 514 in *PoC* for a statement of the third law.

(a) Entropy, unlike enthalpy, can indeed be referred to a specific point of origin: a hypothetical system of perfect order ($W = 1$), realized when a crystalline substance in its equilibrium state approaches 0 K. The third law postulates that the entropy of such a state goes to zero at absolute zero.

(b) Different substances show different amounts of disorder when compared with their hypothetical states of perfect order at 0 K. Accordingly, we assign to each substance an absolute entropy that reflects the changes undergone between 0 K and the standard temperature.

QUESTION: An absolute entropy, referred to a state of perfect order ($W = 1$), can never be less than zero. Why, then, does Table C-16 show negative standard entropies for certain solvated ions?

ANSWER: Because those particular values are *not* absolute entropies. By convention, solution-phase entropies are measured relative to an arbitrary standard:

$$S^\circ[H^+(aq)] = 0$$

Calculations of standard reaction entropy and free energy are described in Sections 14-6 and 14-7 of PoC and illustrated in Example 14-6. Table C-16 in Appendix C (pages A85–A92) contains all the necessary thermodynamic data.

25. The standard entropy of reaction, a function of state, is obtained by summation over all the products and all the reactants:

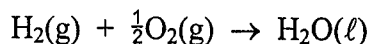


$$\Delta S^\circ = cS^\circ(C) + dS^\circ(D) - aS^\circ(A) - bS^\circ(B)$$

The procedure is no different from the one we use to compute the standard enthalpy and free energy of reaction.

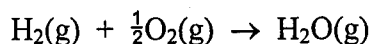
For the summation method in general, see Section 13-4 and Examples 13-9 through 13-11. For specific applications to entropy, see Example 14-6 (beginning on page R14.12 of *PoC*).

(a) Entropy decreases when gaseous reactants are transformed into a liquid product:



$$\begin{aligned} \Delta S^\circ &= S^\circ[\text{H}_2\text{O}(\ell)] - S^\circ[\text{H}_2(\text{g})] - \frac{1}{2}S^\circ[\text{O}_2(\text{g})] \\ &= \left(\frac{70.0 \text{ J}}{\text{mol K}} \times 1 \text{ mol} \right) - \left(\frac{130.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol} \right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times \frac{1}{2} \text{ mol} \right) \\ &= -163.1 \text{ J K}^{-1} \end{aligned}$$

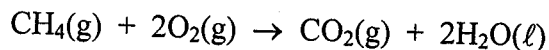
(b) Compare the formation of liquid water (part a) with the formation of water *vapor* in the reaction below:



$$\begin{aligned} \Delta S^\circ &= S^\circ[\text{H}_2\text{O}(\text{g})] - S^\circ[\text{H}_2(\text{g})] - \frac{1}{2}S^\circ[\text{O}_2(\text{g})] \\ &= \left(\frac{188.7 \text{ J}}{\text{mol K}} \times 1 \text{ mol} \right) - \left(\frac{130.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol} \right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times \frac{1}{2} \text{ mol} \right) \\ &= -44.4 \text{ J K}^{-1} \end{aligned}$$

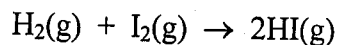
The change in entropy is more modest, since all participants exist in the gas phase.

(c) Three moles of gas become one mole of gas and two moles of liquid in the combustion reaction as written:



$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{CO}_2(\text{g})] + 2S^\circ[\text{H}_2\text{O}(\ell)] - S^\circ[\text{CH}_4(\text{g})] - 2S^\circ[\text{O}_2(\text{g})] \\ &= \left(\frac{213.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) + \left(\frac{70.0 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{186.2 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) \\ &= -242.6 \text{ J K}^{-1}\end{aligned}$$

(d) Two moles of reactants are converted into two moles of product, all in the gas phase:

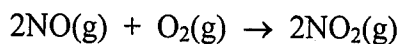


$$\begin{aligned}\Delta S^\circ &= 2S^\circ[\text{HI}(\text{g})] - S^\circ[\text{H}_2(\text{g})] - S^\circ[\text{I}_2(\text{g})] \\ &= \left(\frac{206.6 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{130.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{260.7 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) \\ &= 21.9 \text{ J K}^{-1}\end{aligned}$$

The net change in entropy is comparatively low.

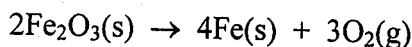
26. Use the same method as in the preceding exercise. All pertinent data may be found in Table C-16 (pages A85–A92 of *PoC*).

(a) Three moles of gaseous reactants are transformed into two moles of gaseous product, with an attendant drop in entropy:



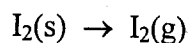
$$\begin{aligned}\Delta S^\circ &= 2S^\circ[\text{NO}_2(\text{g})] - 2S^\circ[\text{NO}(\text{g})] - S^\circ[\text{O}_2(\text{g})] \\ &= \left(\frac{240.0 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{210.7 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) \\ &= -146.4 \text{ J K}^{-1}\end{aligned}$$

(b) Entropy goes up when a solid is transformed into a gas:



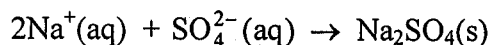
$$\begin{aligned}\Delta S^\circ &= 4S^\circ[\text{Fe}(\text{s})] + 3S^\circ[\text{O}_2(\text{g})] - 2S^\circ[\text{Fe}_2\text{O}_3(\text{s})] \\ &= \left(\frac{27.3 \text{ J}}{\text{mol K}} \times 4 \text{ mol}\right) + \left(\frac{205.0 \text{ J}}{\text{mol K}} \times 3 \text{ mol}\right) - \left(\frac{87.4 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) \\ &= 549.4 \text{ J K}^{-1}\end{aligned}$$

(c) Similar. The entropy of sublimation (a solid-to-gas transformation) is positive:



$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{I}_2(\text{g})] - S^\circ[\text{I}_2(\text{s})] \\ &= \left(\frac{260.7 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{116.1 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) \\ &= 144.6 \text{ J K}^{-1}\end{aligned}$$

(d) Remember that entropies in aqueous solution are referred arbitrarily to $S^\circ[\text{H}^+(\text{aq})] = 0$, not to absolute zero:



$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{Na}_2\text{SO}_4(\text{s})] - 2S^\circ[\text{Na}^+(\text{aq})] - S^\circ[\text{SO}_4^{2-}(\text{aq})] \\ &= \left(\frac{149.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{59.0 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{20.1 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) \\ &= 11.5 \text{ J K}^{-1}\end{aligned}$$

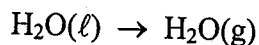
27. Both the enthalpy and entropy of a system increase during vaporization and decrease during condensation:

	ΔH°	ΔS°	ΔG°
vaporization	+	+	depends on T
condensation	-	-	depends on T

The resulting change in free energy, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, depends on the temperature. A process will be spontaneous if ΔG° is negative.

At 25°C, we obtain the free energy of reaction by summing the formation data given in Table C-16 of *PoC* (pages A85–A92).

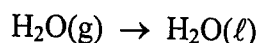
(a) For H₂O, the transformation from liquid to gas is not spontaneous at 25°C and 1 atm. Water normally exists as a liquid under these conditions:



$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{H}_2\text{O}(\text{g})] - \Delta G_f^\circ[\text{H}_2\text{O}(\ell)] \\ &= (-228.6 \text{ kJ mol}^{-1}) - (-237.2 \text{ kJ mol}^{-1}) \\ &= 8.6 \text{ kJ mol}^{-1}\end{aligned}$$

Note, specifically, that the equilibrium vapor pressure of water is only 23.8 torr at 25°C, substantially less than 1 atm. See Figure 11-12 and pages 516–517 in *PoC*, as well as Table C-15 (page A84).

(b) The condensation reaction is the reverse of the process considered in (a). The sign of ΔG° is opposite (negative), and the transformation is spontaneous:



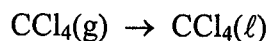
$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta G_f^\circ[\text{H}_2\text{O}(\text{g})] \\ &= (-237.2 \text{ kJ mol}^{-1}) - (-228.6 \text{ kJ mol}^{-1}) \\ &= -8.6 \text{ kJ mol}^{-1}\end{aligned}$$

(c) Carbon tetrachloride normally exists as a liquid at 25°C, with a vapor pressure less than 1 atm. Vaporization is not spontaneous at this temperature:



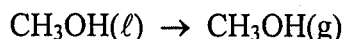
$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{CCl}_4(\text{g})] - \Delta G_f^\circ[\text{CCl}_4(\ell)] \\ &= (-60.6 \text{ kJ mol}^{-1}) - (-65.3 \text{ kJ mol}^{-1}) \\ &= 4.7 \text{ kJ mol}^{-1}\end{aligned}$$

(d) The condensation reaction, opposite to vaporization, is spontaneous at 25°C:



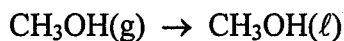
$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{CCl}_4(\ell)] - \Delta G_f^\circ[\text{CCl}_4(\text{g})] \\ &= (-65.3 \text{ kJ mol}^{-1}) - (-60.6 \text{ kJ mol}^{-1}) \\ &= -4.7 \text{ kJ mol}^{-1}\end{aligned}$$

(e) Methanol, too, is normally a liquid at 25°C and 1 atm. The free energy of vaporization is positive, and consequently the conversion of liquid into gas is nonspontaneous:



$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{CH}_3\text{OH}(\text{g})] - \Delta G_f^\circ[\text{CH}_3\text{OH}(\ell)] \\ &= (-162.0 \text{ kJ mol}^{-1}) - (-166.4 \text{ kJ mol}^{-1}) \\ &= 4.4 \text{ kJ mol}^{-1}\end{aligned}$$

(f) Methanol condenses spontaneously under the same conditions:

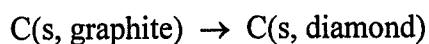


$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{CH}_3\text{OH}(\ell)] - \Delta G_f^\circ[\text{CH}_3\text{OH}(\text{g})] \\ &= (-166.4 \text{ kJ mol}^{-1}) - (-162.0 \text{ kJ mol}^{-1}) \\ &= -4.4 \text{ kJ mol}^{-1}\end{aligned}$$

The change in free energy is negative.

28. Similar to the preceding exercise.

(a) The transformation from graphite to diamond,

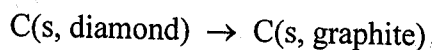


is not spontaneous at 25°C and 1 atm:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{C(s, diamond)}] - \Delta G_f^\circ[\text{C(s, graphite)}] \\ &= 2.9 \text{ kJ mol}^{-1} - 0 \text{ kJ mol}^{-1} \\ &= 2.9 \text{ kJ mol}^{-1}\end{aligned}$$

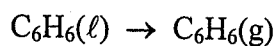
The normal state of carbon is graphite, as evidenced by its free energy of formation: 0.

(b) Diamond at 25°C and 1 atm is transformed spontaneously (but not quickly) into graphite:



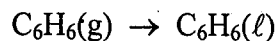
$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{C(s, graphite)}] - \Delta G_f^\circ[\text{C(s, diamond)}] \\ &= 0 \text{ kJ mol}^{-1} - 2.9 \text{ kJ mol}^{-1} \\ &= -2.9 \text{ kJ mol}^{-1}\end{aligned}$$

(c) Benzene, with a positive free energy of vaporization, is normally a liquid at 25°C and 1 atm:



$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{C}_6\text{H}_6(\text{g})] - \Delta G_f^\circ[\text{C}_6\text{H}_6(\ell)] \\ &= (129.7 \text{ kJ mol}^{-1}) - (124.5 \text{ kJ mol}^{-1}) \\ &= 5.2 \text{ kJ mol}^{-1}\end{aligned}$$

(d) The reverse reaction, condensation, is spontaneous:



$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{C}_6\text{H}_6(\ell)] - \Delta G_f^\circ[\text{C}_6\text{H}_6(\text{g})] \\ &= (124.5 \text{ kJ mol}^{-1}) - (129.7 \text{ kJ mol}^{-1}) \\ &= -5.2 \text{ kJ mol}^{-1}\end{aligned}$$

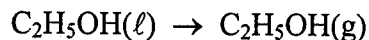
(e) Butane, which boils at -0.5°C , is a gas at 25°C and 1 atm. The free energy of vaporization is slightly negative:

$$\begin{aligned}\text{C}_4\text{H}_{10}(\ell) &\rightarrow \text{C}_4\text{H}_{10}(\text{g}) \\ \Delta G^{\circ} &= \Delta G_f^{\circ}[\text{C}_4\text{H}_{10}(\text{g})] - \Delta G_f^{\circ}[\text{C}_4\text{H}_{10}(\ell)] \\ &= (-15.7 \text{ kJ mol}^{-1}) - (-15.0 \text{ kJ mol}^{-1}) \\ &= -0.7 \text{ kJ mol}^{-1}\end{aligned}$$

(f) The free energy of condensation, opposite in sign to the free energy of vaporization, is positive. Butane does not condense spontaneously at 25°C and 1 atm:

$$\begin{aligned}\text{C}_4\text{H}_{10}(\text{g}) &\rightarrow \text{C}_4\text{H}_{10}(\ell) \\ \Delta G^{\circ} &= \Delta G_f^{\circ}[\text{C}_4\text{H}_{10}(\ell)] - \Delta G_f^{\circ}[\text{C}_4\text{H}_{10}(\text{g})] \\ &= (-15.0 \text{ kJ mol}^{-1}) - (-15.7 \text{ kJ mol}^{-1}) \\ &= 0.7 \text{ kJ mol}^{-1}\end{aligned}$$

29. Similar to Example 14-7. We consider the temperature dependence of ΔG° , taking the vaporization of ethanol as a specific case:



(a) Use the tabulated values of ΔG_f° to calculate ΔG° at 25°C and 1 atm:

$$\begin{aligned}\Delta G^{\circ} &= \Delta G_f^{\circ}[\text{C}_2\text{H}_5\text{OH}(\text{g})] - \Delta G_f^{\circ}[\text{C}_2\text{H}_5\text{OH}(\ell)] \\ &= (-168.6 \text{ kJ mol}^{-1}) - (-174.9 \text{ kJ mol}^{-1}) \\ &= 6.3 \text{ kJ mol}^{-1}\end{aligned}$$

(b) At temperatures other than 25°C , first calculate ΔH° and ΔS° separately:

$$\begin{aligned}\Delta H^{\circ} &= \Delta H_f^{\circ}[\text{C}_2\text{H}_5\text{OH}(\text{g})] - \Delta H_f^{\circ}[\text{C}_2\text{H}_5\text{OH}(\ell)] \\ &= (-235.1 \text{ kJ mol}^{-1}) - (-277.7 \text{ kJ mol}^{-1}) \\ &= 42.6 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{C}_2\text{H}_5\text{OH}(\text{g})] - S^\circ[\text{C}_2\text{H}_5\text{OH}(\ell)] \\ &= (282.6 \text{ J mol}^{-1} \text{ K}^{-1}) - (160.7 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 121.9 \text{ J mol}^{-1} \text{ K}^{-1} = 0.1219 \text{ kJ mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Next, assume that ΔH° and ΔS° at 78.2°C have approximately the same values they do at 25°C :

$$T = (78.2 + 273.15) \text{ K} = 351.4 \text{ K}$$

$$\begin{aligned}\Delta G^\circ(T) &= \Delta H^\circ - T\Delta S^\circ \\ &\approx (42.6 \text{ kJ mol}^{-1}) - (351.4 \text{ K})(0.1219 \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ &\approx -0.2 \text{ kJ mol}^{-1}\end{aligned}$$

Note that there should be no difference in free energy between liquid and gas at the boiling point. The small value we compute arises from our approximate treatment of ΔH° and ΔS° and also from uncertainty in the experimental data.

See Example 14-10 for the estimation of ΔS_{vap} from ΔH_{vap} .

30. With liquid and vapor in equilibrium at the boiling temperature, the difference in free energy is zero,

$$\Delta G = 0 = \Delta H_{\text{vap}} - T_b \Delta S_{\text{vap}}$$

and hence

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{\Delta H_f(\text{g}) - \Delta H_f(\ell)}{T_b}$$

Into this expression we substitute standard formation data, and we assume that ΔH_f° remains roughly constant between 25°C and 80.1°C (the boiling temperature):

$$\Delta H_f^\circ[\text{C}_6\text{H}_6(\text{g})] = 82.9 \text{ kJ mol}^{-1} = 82,900 \text{ J mol}^{-1} \quad (\text{at } 25^\circ\text{C})$$

$$\Delta H_f^\circ[\text{C}_6\text{H}_6(\ell)] = 49.0 \text{ kJ mol}^{-1} = 49,000 \text{ J mol}^{-1} \quad (\text{at } 25^\circ\text{C})$$

$$T_b = 80.1^\circ\text{C} = 353.3 \text{ K}$$

Making this approximation, we obtain

$$\Delta S_{\text{vap}} \approx \frac{(82,900 - 49,000) \text{ J mol}^{-1}}{353.3 \text{ K}} \approx 96 \text{ J mol}^{-1} \text{ K}^{-1}$$

for the entropy of vaporization.

31. There is no difference in free energy between liquid and vapor at the boiling temperature. The two phases are in equilibrium:

$$\begin{aligned} \Delta G &= 0 = \Delta H_{\text{vap}} - T_b \Delta S_{\text{vap}} \\ \Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_b} = \frac{\Delta H_f(\text{g}) - \Delta H_f(\ell)}{T_b} \end{aligned}$$

For Br_2 , the data are

$$\Delta H_f^\circ(\text{g}) = 30.9 \text{ kJ mol}^{-1} = 30,900 \text{ J mol}^{-1} \quad (\text{at } 25^\circ\text{C})$$

$$\Delta H_f^\circ(\ell) = 0 \text{ J mol}^{-1} \quad (\text{standard state at } 25^\circ\text{C})$$

$$T_b = 58.78^\circ\text{C} = 331.93 \text{ K}$$

and the entropy of vaporization is approximately $93 \text{ J mol}^{-1} \text{ K}^{-1}$:

$$\Delta S_{\text{vap}} \approx \frac{(30,900 - 0) \text{ J mol}^{-1}}{331.93 \text{ K}} \approx 93 \text{ J mol}^{-1} \text{ K}^{-1}$$

Our simplifying assumption is to use formation data at 25°C to calculate ΔH_{vap} at the boiling temperature.

32. The method is the same as in the preceding exercise:

$$\Delta H_f^\circ[\text{Hg}(\text{g})] = 61,400 \text{ J mol}^{-1} \quad (\text{at } 25^\circ\text{C})$$

$$\Delta H_f^\circ[\text{Hg}(\ell)] = 0 \text{ J mol}^{-1} \quad (\text{standard state at } 25^\circ\text{C})$$

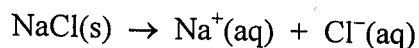
$$T_b = 356.6^\circ\text{C} = 629.8 \text{ K}$$

$$\Delta S_{\text{vap}} \approx \frac{61,400 \text{ J mol}^{-1}}{629.8 \text{ K}} = 97 \text{ J mol}^{-1} \text{ K}^{-1}$$

33. Each of the following reactions involves the dissolution of an inorganic solute in water. See Chapter 15 for an extended treatment of dissolution–precipitation equilibria.

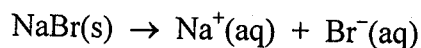
As usual, we obtain the free energy of reaction at 25°C by summing the formation data provided in Table C-16 (pages A85–A92).

(a) Sodium chloride, a soluble salt, has a negative free energy of solution:



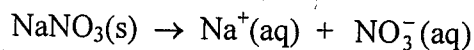
$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{Na}^+(\text{aq})] + \Delta G_f^\circ[\text{Cl}^-(\text{aq})] - \Delta G_f^\circ[\text{NaCl(s)}] \\ &= (-261.9 \text{ kJ mol}^{-1}) + (-131.2 \text{ kJ mol}^{-1}) - (-384.2 \text{ kJ mol}^{-1}) \\ &= -8.9 \text{ kJ mol}^{-1}\end{aligned}$$

(b) Similar, for sodium bromide:



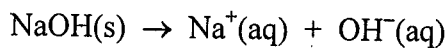
$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{Na}^+(\text{aq})] + \Delta G_f^\circ[\text{Br}^-(\text{aq})] - \Delta G_f^\circ[\text{NaBr(s)}] \\ &= (-261.9 \text{ kJ mol}^{-1}) + (-104.0 \text{ kJ mol}^{-1}) - (-349.0 \text{ kJ mol}^{-1}) \\ &= -16.9 \text{ kJ mol}^{-1}\end{aligned}$$

(c) Sodium nitrate has a small, but negative, free energy of solution at 25°C. The dissolution process is spontaneous:



$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{Na}^+(\text{aq})] + \Delta G_f^\circ[\text{NO}_3^-(\text{aq})] - \Delta G_f^\circ[\text{NaNO}_3(\text{s})] \\ &= (-261.9 \text{ kJ mol}^{-1}) + (-108.7 \text{ kJ mol}^{-1}) - (-367.0 \text{ kJ mol}^{-1}) \\ &= -3.6 \text{ kJ mol}^{-1}\end{aligned}$$

(d) Dissolution of NaOH in water,



is also spontaneous at 25°C. The change in standard free energy is negative:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{Na}^+(\text{aq})] + \Delta G_f^\circ[\text{OH}^-(\text{aq})] - \Delta G_f^\circ[\text{NaOH}(\text{s})] \\ &= (-261.9 \text{ kJ mol}^{-1}) + (-157.2 \text{ kJ mol}^{-1}) - (-379.5 \text{ kJ mol}^{-1}) \\ &= -39.6 \text{ kJ mol}^{-1}\end{aligned}$$

(e) The dissolution of AgCl is nonspontaneous at 25°C. ΔG° is positive (in contrast to the other four examples), and the equilibrium constant is substantially less than 1. Silver chloride is the least soluble of the five compounds considered:

$$\begin{aligned}\text{AgCl}(\text{s}) &\rightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \\ \Delta G^\circ &= \Delta G_f^\circ[\text{Ag}^+(\text{aq})] + \Delta G_f^\circ[\text{Cl}^-(\text{aq})] - \Delta G_f^\circ[\text{AgCl}(\text{s})] \\ &= (77.1 \text{ kJ mol}^{-1}) + (-131.2 \text{ kJ mol}^{-1}) - (-109.8 \text{ kJ mol}^{-1}) \\ &= 55.7 \text{ kJ mol}^{-1}\end{aligned}$$

34. As a first approximation, we apply Le Châtelier's principle to predict the following rough relationship between ΔH° and solubility:

1. If ΔH° is positive, the dissolution is endothermic and the equilibrium constant increases with temperature. More material will dissolve at a higher temperature.
2. If ΔH° is negative, the dissolution is exothermic and the equilibrium constant decreases with temperature. Less material will dissolve at a higher temperature.

These expectations are borne out in many cases, but there are significant irregularities. For example, the enthalpy of solution often varies with concentration. An exothermic dissolution at low concentration may turn endothermic at high concentration, rendering the standard value (applicable at 1 M) largely irrelevant. As a result, the effect of temperature on the solubility of a particular substance usually must be determined experimentally. See the concluding remarks in Example 15-9 (on page R15.15 of *PoC*).

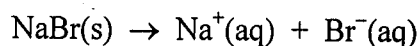
(a) Local enthalpy and entropy both increase during the dissolution of sodium chloride:

$$\begin{aligned}\text{NaCl}(\text{s}) &\rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \\ \Delta H^\circ &= \Delta H_f^\circ[\text{Na}^+(\text{aq})] + \Delta H_f^\circ[\text{Cl}^-(\text{aq})] - \Delta H_f^\circ[\text{NaCl}(\text{s})] \\ &= (-240.1 \text{ kJ mol}^{-1}) + (-167.2 \text{ kJ mol}^{-1}) - (-411.2 \text{ kJ mol}^{-1}) \\ &= 3.9 \text{ kJ mol}^{-1} \quad (\text{endothermic})\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{Na}^+(\text{aq})] + S^\circ[\text{Cl}^-(\text{aq})] - S^\circ[\text{NaCl}(\text{s})] \\ &= (59.0 \text{ J mol}^{-1} \text{ K}^{-1}) + (56.5 \text{ J mol}^{-1} \text{ K}^{-1}) - (72.1 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 43.4 \text{ J mol}^{-1} \text{ K}^{-1} \quad (\text{entropy increases})\end{aligned}$$

The change in entropy is favorable for dissolution; the change in enthalpy is not.

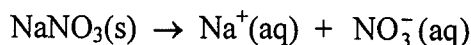
(b) The dissolution of sodium bromide is slightly exothermic:



$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{Na}^+(\text{aq})] + \Delta H_f^\circ[\text{Br}^-(\text{aq})] - \Delta H_f^\circ[\text{NaBr}(\text{s})] \\ &= (-240.1 \text{ kJ mol}^{-1}) + (-121.6 \text{ kJ mol}^{-1}) - (-361.1 \text{ kJ mol}^{-1}) \\ &= -0.6 \text{ kJ mol}^{-1} \quad (\text{borderline exothermic})\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{Na}^+(\text{aq})] + S^\circ[\text{Br}^-(\text{aq})] - S^\circ[\text{NaBr}(\text{s})] \\ &= (59.0 \text{ J mol}^{-1} \text{ K}^{-1}) + (82.4 \text{ J mol}^{-1} \text{ K}^{-1}) - (86.8 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 54.6 \text{ J mol}^{-1} \text{ K}^{-1} \quad (\text{entropy increases})\end{aligned}$$

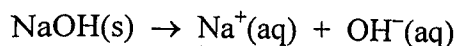
(c) The dissolution of sodium nitrate is endothermic (which works against spontaneity), but the products have greater entropy than the reactants (which works in favor of spontaneity):



$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{Na}^+(\text{aq})] + \Delta H_f^\circ[\text{NO}_3^-(\text{aq})] - \Delta H_f^\circ[\text{NaNO}_3(\text{s})] \\ &= (-240.1 \text{ kJ mol}^{-1}) + (-205.0 \text{ kJ mol}^{-1}) - (-467.9 \text{ kJ mol}^{-1}) \\ &= 22.8 \text{ kJ mol}^{-1} \quad (\text{endothermic})\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{Na}^+(\text{aq})] + S^\circ[\text{NO}_3^-(\text{aq})] - S^\circ[\text{NaNO}_3(\text{s})] \\ &= (59.0 \text{ J mol}^{-1} \text{ K}^{-1}) + (146.4 \text{ J mol}^{-1} \text{ K}^{-1}) - (116.5 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 88.9 \text{ J mol}^{-1} \text{ K}^{-1} \quad (\text{entropy increases})\end{aligned}$$

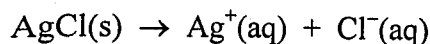
(d) For sodium hydroxide, the change in enthalpy is favorable but the change in entropy is not:



$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{Na}^+(\text{aq})] + \Delta H_f^\circ[\text{OH}^-(\text{aq})] - \Delta H_f^\circ[\text{NaOH(s)}] \\ &= (-240.1 \text{ kJ mol}^{-1}) + (-230.0 \text{ kJ mol}^{-1}) - (-425.6 \text{ kJ mol}^{-1}) \\ &= -44.5 \text{ kJ mol}^{-1} \quad (\text{exothermic})\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{Na}^+(\text{aq})] + S^\circ[\text{OH}^-(\text{aq})] - S^\circ[\text{NaOH(s)}] \\ &= (59.0 \text{ J mol}^{-1} \text{ K}^{-1}) + (-10.8 \text{ J mol}^{-1} \text{ K}^{-1}) - (64.5 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= -16.3 \text{ J mol}^{-1} \text{ K}^{-1} \quad (\text{entropy decreases})\end{aligned}$$

(e) Although entropy increases when silver chloride is dissolved, the process is strongly endothermic:

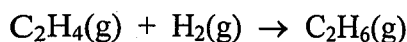


$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{Ag}^+(\text{aq})] + \Delta H_f^\circ[\text{Cl}^-(\text{aq})] - \Delta H_f^\circ[\text{AgCl(s)}] \\ &= (105.6 \text{ kJ mol}^{-1}) + (-167.2 \text{ kJ mol}^{-1}) - (-127.1 \text{ kJ mol}^{-1}) \\ &= 65.5 \text{ kJ mol}^{-1} \quad (\text{endothermic})\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{Ag}^+(\text{aq})] + S^\circ[\text{Cl}^-(\text{aq})] - S^\circ[\text{AgCl(s)}] \\ &= (72.7 \text{ J mol}^{-1} \text{ K}^{-1}) + (56.5 \text{ J mol}^{-1} \text{ K}^{-1}) - (96.2 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 33.0 \text{ J mol}^{-1} \text{ K}^{-1} \quad (\text{entropy increases})\end{aligned}$$

35. Here we calculate changes in standard enthalpy, entropy, and free energy for a series of reactions involving simple organic molecules.

(a) Addition of hydrogen to ethylene ($\text{H}_2\text{C}=\text{CH}_2$, an unsaturated hydrocarbon) produces ethane ($\text{H}_3\text{C}-\text{CH}_3$, a saturated hydrocarbon):



The reaction is exothermic (new bonds are formed) and spontaneous, even though the change in entropy is negative (two moles of gas become one):

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{C}_2\text{H}_6(\text{g})] - \Delta H_f^\circ[\text{C}_2\text{H}_4(\text{g})] - \Delta H_f^\circ[\text{H}_2(\text{g})] \\ &= \left(-\frac{84.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{52.3 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) \\ &= -137.0 \text{ kJ} \quad [\text{per mole C}_2\text{H}_4(\text{g})]\end{aligned}$$

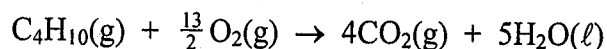
$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{C}_2\text{H}_6(\text{g})] - S^\circ[\text{C}_2\text{H}_4(\text{g})] - S^\circ[\text{H}_2(\text{g})] \\ &= \left(\frac{229.5 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{219.5 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{130.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) \\ &= -120.6 \text{ J K}^{-1} \quad [\text{per mole C}_2\text{H}_4(\text{g})]\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{C}_2\text{H}_6(\text{g})] - \Delta G_f^\circ[\text{C}_2\text{H}_4(\text{g})] - \Delta G_f^\circ[\text{H}_2(\text{g})] \\ &= \left(-\frac{32.9 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{68.1 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) \\ &= -101.0 \text{ kJ} \quad [\text{per mole C}_2\text{H}_4(\text{g})]\end{aligned}$$

Note that the separate values of ΔG° , ΔH° , and ΔS° are consistent with the Gibbs relationship at 25°C:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -137.0 \text{ kJ mol}^{-1} - (298.15 \text{ K})(-0.1206 \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ &= -101.0 \text{ kJ mol}^{-1}\end{aligned}$$

(b) The combustion of gaseous butane to carbon dioxide and liquid water,



is exothermic. Enthalpy decreases by 2878.3 kJ per mole of $\text{C}_4\text{H}_{10}(\text{g})$:

$$\begin{aligned}
 \Delta H^\circ &= 4 \Delta H_f^\circ[\text{CO}_2(\text{g})] + 5 \Delta H_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta H_f^\circ[\text{C}_4\text{H}_{10}(\text{g})] - \frac{13}{2} \Delta H_f^\circ[\text{O}_2(\text{g})] \\
 &= \left(-\frac{393.5 \text{ kJ}}{\text{mol}} \times 4 \text{ mol} \right) + \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 5 \text{ mol} \right) \\
 &\quad - \left(-\frac{124.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times \frac{13}{2} \text{ mol} \right) \\
 &= -2878.3 \text{ kJ} \quad [\text{per mole C}_4\text{H}_{10}(\text{g})]
 \end{aligned}$$

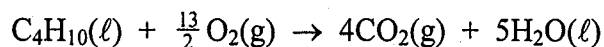
At the same time, however, there is a decrease in entropy. Gaseous reactants outnumber gaseous products:

$$\begin{aligned}
 \Delta S^\circ &= 4 S^\circ[\text{CO}_2(\text{g})] + 5 S^\circ[\text{H}_2\text{O}(\ell)] - S^\circ[\text{C}_4\text{H}_{10}(\text{g})] - \frac{13}{2} S^\circ[\text{O}_2(\text{g})] \\
 &= \left(\frac{213.6 \text{ J}}{\text{mol K}} \times 4 \text{ mol} \right) + \left(\frac{70.0 \text{ J}}{\text{mol K}} \times 5 \text{ mol} \right) - \left(\frac{310.0 \text{ J}}{\text{mol K}} \times 1 \text{ mol} \right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times \frac{13}{2} \text{ mol} \right) \\
 &= -438.1 \text{ J K}^{-1} \quad [\text{per mole C}_4\text{H}_{10}(\text{g})]
 \end{aligned}$$

This combination of favorable enthalpy and unfavorable entropy, in sum, makes the reaction spontaneous at 25°C:

$$\begin{aligned}
 \Delta G^\circ &= 4 \Delta G_f^\circ[\text{CO}_2(\text{g})] + 5 \Delta G_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta G_f^\circ[\text{C}_4\text{H}_{10}(\text{g})] - \frac{13}{2} \Delta G_f^\circ[\text{O}_2(\text{g})] \\
 &= \left(-\frac{394.4 \text{ kJ}}{\text{mol}} \times 4 \text{ mol} \right) + \left(-\frac{237.2 \text{ kJ}}{\text{mol}} \times 5 \text{ mol} \right) \\
 &\quad - \left(-\frac{15.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times \frac{13}{2} \text{ mol} \right) \\
 &= -2747.9 \text{ kJ} \quad [\text{per mole C}_4\text{H}_{10}(\text{g})]
 \end{aligned}$$

(c) Enthalpy and entropy both decrease when liquid butane undergoes combustion:



Values for ΔH° and ΔS° are calculated on the next page:

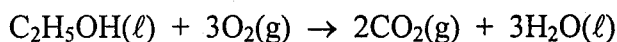
$$\begin{aligned}
 \Delta H^\circ &= 4\Delta H_f^\circ[\text{CO}_2(\text{g})] + 5\Delta H_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta H_f^\circ[\text{C}_4\text{H}_{10}(\ell)] - \frac{13}{2}\Delta H_f^\circ[\text{O}_2(\text{g})] \\
 &= \left(-\frac{393.5 \text{ kJ}}{\text{mol}} \times 4 \text{ mol}\right) + \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 5 \text{ mol}\right) \\
 &\quad - \left(-\frac{147.6 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times \frac{13}{2} \text{ mol}\right) \\
 &= -2855.4 \text{ kJ} \quad [\text{per mole C}_4\text{H}_{10}(\ell)]
 \end{aligned}$$

$$\begin{aligned}
 \Delta S^\circ &= 4S^\circ[\text{CO}_2(\text{g})] + 5S^\circ[\text{H}_2\text{O}(\ell)] - S^\circ[\text{C}_4\text{H}_{10}(\ell)] - \frac{13}{2}S^\circ[\text{O}_2(\text{g})] \\
 &= \left(\frac{213.6 \text{ J}}{\text{mol K}} \times 4 \text{ mol}\right) + \left(\frac{70.0 \text{ J}}{\text{mol K}} \times 5 \text{ mol}\right) \\
 &\quad - \left(\frac{231.0 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times \frac{13}{2} \text{ mol}\right) \\
 &= -359.1 \text{ J K}^{-1} \quad [\text{per mole C}_4\text{H}_{10}(\ell)]
 \end{aligned}$$

Note that the number of molecules in the gas phase decreases upon going from reactants to products, leading to a decrease in entropy for the system. The change in free energy, arising from a favorable ΔH° and an unfavorable ΔS° , is nevertheless strongly negative at 25°C:

$$\begin{aligned}
 \Delta G^\circ &= 4\Delta G_f^\circ[\text{CO}_2(\text{g})] + 5\Delta G_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta G_f^\circ[\text{C}_4\text{H}_{10}(\ell)] - \frac{13}{2}\Delta G_f^\circ[\text{O}_2(\text{g})] \\
 &= \left(-\frac{394.4 \text{ kJ}}{\text{mol}} \times 4 \text{ mol}\right) + \left(-\frac{237.2 \text{ kJ}}{\text{mol}} \times 5 \text{ mol}\right) \\
 &\quad - \left(-\frac{15.0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times \frac{13}{2} \text{ mol}\right) \\
 &= -2748.6 \text{ kJ} \quad [\text{per mole C}_4\text{H}_{10}(\ell)]
 \end{aligned}$$

(d) Similar. The combustion of liquid ethanol to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$,



brings about a decrease in both enthalpy and entropy for the system:

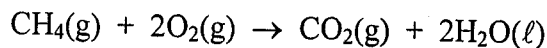
$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ[\text{CO}_2(\text{g})] + 3\Delta H_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta H_f^\circ[\text{C}_2\text{H}_5\text{OH}(\ell)] - 3\Delta H_f^\circ[\text{O}_2(\text{g})] \\ &= \left(-\frac{393.5 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) + \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) \\ &\quad - \left(-\frac{277.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) \\ &= -1366.7 \text{ kJ} \quad [\text{per mole C}_2\text{H}_5\text{OH}(\ell)]\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 2S^\circ[\text{CO}_2(\text{g})] + 3S^\circ[\text{H}_2\text{O}(\ell)] - S^\circ[\text{C}_2\text{H}_5\text{OH}(\ell)] - 3S^\circ[\text{O}_2(\text{g})] \\ &= \left(\frac{213.6 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) + \left(\frac{70.0 \text{ J}}{\text{mol K}} \times 3 \text{ mol}\right) \\ &\quad - \left(\frac{160.7 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times 3 \text{ mol}\right) \\ &= -138.5 \text{ J K}^{-1} \quad [\text{per mole C}_2\text{H}_5\text{OH}(\ell)]\end{aligned}$$

The reaction as a whole is spontaneous, releasing 1325.5 kilojoules of free energy per mole of ethanol burned:

$$\begin{aligned}\Delta G^\circ &= 2\Delta G_f^\circ[\text{CO}_2(\text{g})] + 3\Delta G_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta G_f^\circ[\text{C}_2\text{H}_5\text{OH}(\ell)] - 3\Delta G_f^\circ[\text{O}_2(\text{g})] \\ &= \left(-\frac{394.4 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) + \left(-\frac{237.2 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) \\ &\quad - \left(-\frac{174.9 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) \\ &= -1325.5 \text{ kJ} \quad [\text{per mole C}_2\text{H}_5\text{OH}(\ell)]\end{aligned}$$

(e) Similar to (b). The combustion of methane (a gaseous hydrocarbon) to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ is strongly exothermic, but entropy decreases when three moles of gas are transformed into one:



Enthalpy goes down:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{CO}_2(\text{g})] + 2\Delta H_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta H_f^\circ[\text{CH}_4(\text{g})] - 2\Delta H_f^\circ[\text{O}_2(\text{g})] \\ &= \left(-\frac{393.5 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(-\frac{285.8 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) \\ &\quad - \left(-\frac{74.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) \\ &= -890.3 \text{ kJ} \quad [\text{per mole CH}_4(\text{g})]\end{aligned}$$

Entropy goes down as well:

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{CO}_2(\text{g})] + 2S^\circ[\text{H}_2\text{O}(\ell)] - S^\circ[\text{CH}_4(\text{g})] - 2S^\circ[\text{O}_2(\text{g})] \\ &= \left(\frac{213.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) + \left(\frac{70.0 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) \\ &\quad - \left(\frac{186.2 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{205.0 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) \\ &= -242.6 \text{ J K}^{-1} \quad [\text{per mole CH}_4(\text{g})]\end{aligned}$$

The change in free energy at 25°C , dominated by the enthalpy term, is large and negative:

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{CO}_2(\text{g})] + 2\Delta G_f^\circ[\text{H}_2\text{O}(\ell)] - \Delta G_f^\circ[\text{CH}_4(\text{g})] - 2\Delta G_f^\circ[\text{O}_2(\text{g})] \\ &= \left(-\frac{394.4 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) + \left(-\frac{237.2 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) \\ &\quad - \left(-\frac{50.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) \\ &= -818.0 \text{ kJ} \quad [\text{per mole CH}_4(\text{g})]\end{aligned}$$

The effect of temperature on spontaneity is treated in Section 14-5 (pages 512–513) and Example 14-7.

36. First, we calculate ΔH° and ΔS° using the standard summation methods. If ΔH° is negative and ΔS° is positive, then the reaction is spontaneous at all temperatures. And if ΔH° is positive and ΔS° is negative, then the reaction is *nonspontaneous* at all temperatures. Either way, the direction of spontaneous change is independent of T .

If, however, both quantities are either positive or negative,

$$\Delta H^\circ > 0, \quad \Delta S^\circ > 0 \quad \text{or} \quad \Delta H^\circ < 0, \quad \Delta S^\circ < 0$$

then we determine the temperature T_0 at which the change in free energy first becomes equal to zero:

$$\Delta G^\circ = \Delta H^\circ - T_0 \Delta S^\circ = 0$$

$$T_0 = \frac{\Delta H^\circ}{\Delta S^\circ}$$

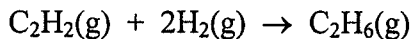
An exothermic process hampered by a negative change in entropy will be spontaneous at temperatures below T_0 :

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ < 0 \quad (\Delta H^\circ < 0, \quad \Delta S^\circ < 0, \quad T < T_0)$$

An endothermic process aided by a positive change in entropy will be spontaneous at temperatures above T_0 :

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ < 0 \quad (\Delta H^\circ > 0, \quad \Delta S^\circ > 0, \quad T > T_0)$$

(a) The 2:1 addition of molecular hydrogen to acetylene ($\text{HC}\equiv\text{CH}$) yields the molecule ethane ($\text{H}_3\text{C}-\text{CH}_3$), a saturated hydrocarbon:



A net decrease in enthalpy, favorable for reaction, accompanies the breaking and making of bonds in this system:

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ[\text{C}_2\text{H}_6(\text{g})] - \Delta H_f^\circ[\text{C}_2\text{H}_2(\text{g})] - 2\Delta H_f^\circ[\text{H}_2(\text{g})] \\ &= \left(-\frac{84.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) - \left(\frac{226.7 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 2 \text{ mol} \right) \\ &= -311.4 \text{ kJ} \quad (\text{exothermic}) \end{aligned}$$

The substitution of one mole of gas for three, however, also brings about a decrease in entropy—an unfavorable tendency:

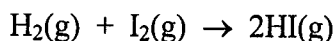
$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{C}_2\text{H}_6(\text{g})] - S^\circ[\text{C}_2\text{H}_2(\text{g})] - 2S^\circ[\text{H}_2(\text{g})] \\ &= \left(\frac{229.5 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{200.8 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{130.6 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) \\ &= -232.5 \text{ J K}^{-1} = -0.2325 \text{ kJ K}^{-1} \quad (\text{entropy decreases})\end{aligned}$$

The opposing tendencies are balanced at $T_0 = 1339 \text{ K}$,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T_0 \Delta S^\circ = 0 \\ T_0 &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-311.4 \text{ kJ}}{-0.2325 \text{ kJ K}^{-1}} = 1339 \text{ K}\end{aligned}$$

and the reaction is spontaneous at all temperatures below. A large, exothermic change in enthalpy counteracts the unfavorable decrease in entropy until the temperature finally becomes too high.

(b) The formation of gaseous hydrogen iodide,



is spontaneous at all temperatures:

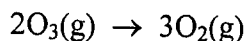
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0 \quad (\Delta H^\circ < 0, \Delta S^\circ > 0)$$

Enthalpy decreases and entropy increases:

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ[\text{HI}(\text{g})] - \Delta H_f^\circ[\text{H}_2(\text{g})] - \Delta H_f^\circ[\text{I}_2(\text{g})] \\ &= \left(\frac{26.5 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{62.4 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) \\ &= -9.4 \text{ kJ} \quad (\text{exothermic})\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 2S^\circ[\text{HI}(\text{g})] - S^\circ[\text{H}_2(\text{g})] - S^\circ[\text{I}_2(\text{g})] \\ &= \left(\frac{206.6 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{130.6 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{260.7 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) \\ &= 21.9 \text{ J K}^{-1} \quad (\text{entropy increases})\end{aligned}$$

(c) Enthalpy decreases and entropy increases when two moles of ozone are transformed into three moles of molecular oxygen:



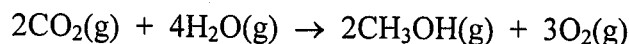
$$\begin{aligned}\Delta H^\circ &= 3\Delta H_f^\circ[\text{O}_2(\text{g})] - 2\Delta H_f^\circ[\text{O}_3(\text{g})] \\ &= \left(\frac{0 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) - \left(\frac{142.7 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) \\ &= -285.4 \text{ kJ} \quad (\text{exothermic})\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 3S^\circ[\text{O}_2(\text{g})] - 2S^\circ[\text{O}_3(\text{g})] \\ &= \left(\frac{205.0 \text{ J}}{\text{mol K}} \times 3 \text{ mol}\right) - \left(\frac{238.8 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) \\ &= 137.4 \text{ J K}^{-1} \quad (\text{entropy increases})\end{aligned}$$

Both tendencies are favorable for reaction, and the process is spontaneous at all temperatures ($T > 0 \text{ K}$):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0 \quad (\Delta H^\circ < 0, \Delta S^\circ > 0)$$

(d) The equation as written,



is the reverse of a combustion reaction. Enthalpy goes up and entropy goes down:

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ[\text{CH}_3\text{OH}(\text{g})] + 3\Delta H_f^\circ[\text{O}_2(\text{g})] - 2\Delta H_f^\circ[\text{CO}_2(\text{g})] - 4\Delta H_f^\circ[\text{H}_2\text{O}(\text{g})] \\ &= \left(-\frac{200.7 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) + \left(\frac{0 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) \\ &\quad - \left(-\frac{393.5 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(-\frac{241.8 \text{ kJ}}{\text{mol}} \times 4 \text{ mol}\right) \\ &= 1352.8 \text{ kJ} \quad (\text{endothermic})\end{aligned}$$

$$\begin{aligned}
 \Delta S^\circ &= 2S^\circ[\text{CH}_3\text{OH}(\text{g})] + 3S^\circ[\text{O}_2(\text{g})] - 2S^\circ[\text{CO}_2(\text{g})] - 4S^\circ[\text{H}_2\text{O}(\text{g})] \\
 &= \left(\frac{239.7 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) + \left(\frac{205.0 \text{ J}}{\text{mol K}} \times 3 \text{ mol}\right) \\
 &\quad - \left(\frac{213.6 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{188.7 \text{ J}}{\text{mol K}} \times 4 \text{ mol}\right) \\
 &= -87.6 \text{ J K}^{-1} \quad (\text{entropy decreases})
 \end{aligned}$$

With $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, the process is nonspontaneous at all temperatures:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ > 0 \quad (\Delta H^\circ > 0, \Delta S^\circ < 0)$$

37. The method is the same as in the preceding exercise. First, we calculate ΔH° and ΔS° using the standard summation technique. Reactions that cause enthalpy to decrease and entropy to increase are spontaneous at all temperatures:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0 \quad (\Delta H^\circ < 0, \Delta S^\circ > 0)$$

Reactions that cause enthalpy to increase and entropy to decrease are spontaneous at *no* temperature:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ > 0 \quad (\Delta H^\circ > 0, \Delta S^\circ < 0)$$

For all others, we determine the temperature T_0 at which ΔG° becomes equal to zero:

$$\Delta G^\circ = \Delta H^\circ - T_0 \Delta S^\circ = 0$$

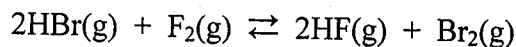
$$T_0 = \frac{\Delta H^\circ}{\Delta S^\circ}$$

A given process is spontaneous either above or below this breakpoint, in whichever range the change in free energy is negative. Results are tabulated below:

	ΔH° (kJ)	ΔS° (J K ⁻¹)	RANGE OF SPONTANEITY
(a)	-114.2	-146.4	$T < 780 \text{ K}$
(b)	77.2	121.0	$T > 638 \text{ K}$
(c)	178.5	158.8	$T > 1124 \text{ K}$
(d)	-98.0	62.9	$T > 0 \text{ K}$

See Section 14-8 and Example 14-8 for the relationship between free energy and the equilibrium constant.

38. We have a gas-phase equilibrium—an exchange reaction—involving hydrogen bromide, molecular fluorine, hydrogen fluoride, and molecular bromine:



(a) The first step is to compute ΔH° and ΔS° for the process in the forward direction:

The standard enthalpy change:

$$\begin{aligned}\Delta H^\circ &= 2 \Delta H_f^\circ[\text{HF(g)}] + \Delta H_f^\circ[\text{Br}_2(\text{g})] - 2 \Delta H_f^\circ[\text{HBr(g)}] - \Delta H_f^\circ[\text{F}_2(\text{g})] \\ &= \left(-\frac{273.3 \text{ kJ}}{\text{mol}} \times 2 \text{ mol} \right) + \left(\frac{30.9 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) \\ &\quad - \left(-\frac{36.3 \text{ kJ}}{\text{mol}} \times 2 \text{ mol} \right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) \\ &= -443.1 \text{ kJ} = -4.431 \times 10^5 \text{ J} \quad (\text{exothermic})\end{aligned}$$

And the standard entropy change:

$$\begin{aligned}\Delta S^\circ &= 2 S^\circ[\text{HF(g)}] + S^\circ[\text{Br}_2(\text{g})] - 2 S^\circ[\text{HBr(g)}] - S^\circ[\text{F}_2(\text{g})] \\ &= \left(\frac{173.8 \text{ J}}{\text{mol K}} \times 2 \text{ mol} \right) + \left(\frac{245.5 \text{ J}}{\text{mol K}} \times 1 \text{ mol} \right) - \left(\frac{198.7 \text{ J}}{\text{mol K}} \times 2 \text{ mol} \right) - \left(\frac{202.8 \text{ J}}{\text{mol K}} \times 1 \text{ mol} \right) \\ &= -7.1 \text{ J K}^{-1} \quad (\text{entropy decreases})\end{aligned}$$

Next, we calculate ΔG° and K at each of the specified temperatures:

At $T = 300 \text{ K}$:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -4.431 \times 10^5 \text{ J} - (300 \text{ K})(-7.1 \text{ J K}^{-1}) \\ &= -440,970 \text{ J} = -4.410 \times 10^5 \text{ J}\end{aligned}$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{-440,970 \text{ J}}{(8.3145 \text{ J K}^{-1})(300 \text{ K})}\right] = 6.0 \times 10^{76}$$

At $T = 600$ K:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -4.431 \times 10^5 \text{ J} - (600 \text{ K})(-7.1 \text{ J K}^{-1}) \\ &= -4.388 \times 10^5 \text{ J}\end{aligned}$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{-4.388 \times 10^5 \text{ J}}{(8.3145 \text{ J K}^{-1})(600 \text{ K})}\right] = 1.6 \times 10^{38}$$

At $T = 900$ K:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ &= -4.431 \times 10^5 \text{ J} - (900 \text{ K})(-7.1 \text{ J K}^{-1}) \\ &= -4.367 \times 10^5 \text{ J}\end{aligned}$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{-4.367 \times 10^5 \text{ J}}{(8.3145 \text{ J K}^{-1})(900 \text{ K})}\right] = 2.2 \times 10^{25}$$

Results are summarized below:

T (K)	ΔH° (kJ)	ΔS° (J K ⁻¹)	ΔG° (kJ)	K
300	-443.1	-7.1	-441.0	6.0×10^{76}
600	-443.1	-7.1	-438.8	1.6×10^{38}
900	-443.1	-7.1	-436.7	2.2×10^{25}

(b) The reaction is strongly exothermic but brings about a slight decrease in entropy. In turn, the equilibrium constant also decreases over the range of temperatures considered (by as much as 50 orders of magnitude). However, since K is effectively infinite even at 900 kelvins, changes of this sort are unlikely to produce a noticeable difference in yield. The reaction goes to completion.

(c) A change in pressure has no effect on the yield at equilibrium, for the reasons described in Section 12-6 of *PoC*. Equal numbers of gaseous particles are present on both sides of the equation.

(d) A catalyst has no effect on the equilibrium yield, which is fixed by the preexisting difference in standard free energy. A catalyst only alters the rate at which equilibrium is approached. See Sections 3-6 and 18-5.

39. We use the relationship

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$$

to calculate the temperature corresponding to a given value of K :

$$T = \frac{\Delta H^\circ}{\Delta S^\circ - R \ln K}$$

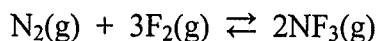
See Section 14-8 in *PoC* and also Example 14-8.

When K is equal to a power of 10 (as in this exercise), we shall find it convenient to convert the natural logarithm into its equivalent base-10 form:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ - 2.3026R \log K}$$

For help with logarithms, see Appendix B in *PoC* (pages A42–A47).

(a) Start by computing ΔH° and ΔS° for the reaction as written:



$$\begin{aligned} \Delta H^\circ &= 2\Delta H_f^\circ[\text{NF}_3(\text{g})] - \Delta H_f^\circ[\text{N}_2(\text{g})] - 3\Delta H_f^\circ[\text{F}_2(\text{g})] \\ &= \left(-\frac{132.1 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 3 \text{ mol}\right) \\ &= -264.2 \text{ kJ} = -2.642 \times 10^5 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= 2S^\circ[\text{NF}_3(\text{g})] - S^\circ[\text{N}_2(\text{g})] - 3S^\circ[\text{F}_2(\text{g})] \\ &= \left(\frac{260.8 \text{ J}}{\text{mol K}} \times 2 \text{ mol}\right) - \left(\frac{191.5 \text{ J}}{\text{mol K}} \times 1 \text{ mol}\right) - \left(\frac{202.8 \text{ J}}{\text{mol K}} \times 3 \text{ mol}\right) \\ &= -278.3 \text{ J K}^{-1} \end{aligned}$$

Then calculate T when $K = 1$ (and hence $\log K = 0$):

$$\begin{aligned}
 T &= \frac{\Delta H^\circ}{\Delta S^\circ - 2.3026R \log K} \\
 &= \frac{-2.642 \times 10^5 \text{ J}}{-278.3 \text{ J K}^{-1} - (2.3026)(8.3145 \text{ J K}^{-1})(\log 1)} \\
 &= \frac{-2.642 \times 10^5 \text{ J}}{-278.3 \text{ J K}^{-1} - (2.3026)(8.3145 \text{ J K}^{-1})(0)} \\
 &= 949 \text{ K}
 \end{aligned}$$

(b) Substitute $\log K = 1$ when $K = 10$:

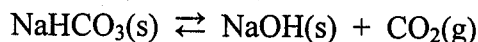
$$\begin{aligned}
 T &= \frac{\Delta H^\circ}{\Delta S^\circ - 2.3026R \log K} \\
 &= \frac{-2.642 \times 10^5 \text{ J}}{-278.3 \text{ J K}^{-1} - (2.3026)(8.3145 \text{ J K}^{-1})(\log 10)} \\
 &= \frac{-2.642 \times 10^5 \text{ J}}{-278.3 \text{ J K}^{-1} - (2.3026)(8.3145 \text{ J K}^{-1})(1)} \\
 &= 888 \text{ K}
 \end{aligned}$$

(c) Substitute $\log K = -1$ when $K = 0.1$:

$$\begin{aligned}
 T &= \frac{\Delta H^\circ}{\Delta S^\circ - 2.3026R \log K} \\
 &= \frac{-2.642 \times 10^5 \text{ J}}{-278.3 \text{ J K}^{-1} - (2.3026)(8.3145 \text{ J K}^{-1})(\log 0.1)} \\
 &= \frac{-2.642 \times 10^5 \text{ J}}{-278.3 \text{ J K}^{-1} - (2.3026)(8.3145 \text{ J K}^{-1})(-1)} \\
 &= 1019 \text{ K}
 \end{aligned}$$

40. For additional material dealing with the temperature dependence of K , see pages 450–452, 456–457, and R15.14–R15.15 in *PoC*.

(a) Since ΔG° is positive (see below), the reaction



is nonspontaneous at 298 K (the temperature at which the formation data are applicable):

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{NaOH}(\text{s})] + \Delta G_f^\circ[\text{CO}_2(\text{g})] - \Delta G_f^\circ[\text{NaHCO}_3(\text{s})] \\ &= (-379.5 \text{ kJ mol}^{-1}) + (-394.4 \text{ kJ mol}^{-1}) - (-851.0 \text{ kJ mol}^{-1}) \\ &= 77.1 \text{ kJ mol}^{-1}\end{aligned}$$

(b) The question asks whether the equilibrium constant

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{\Delta H^\circ}{RT}\right) \exp\left(\frac{\Delta S^\circ}{R}\right) = P_{\text{CO}_2}$$

increases with temperature. It will do so (and the equilibrium pressure of CO_2 will increase as well) if the reaction is endothermic. To find out, we calculate ΔH° in the usual way:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{NaOH}(\text{s})] + \Delta H_f^\circ[\text{CO}_2(\text{g})] - \Delta H_f^\circ[\text{NaHCO}_3(\text{s})] \\ &= (-425.6 \text{ kJ mol}^{-1}) + (-393.5 \text{ kJ mol}^{-1}) - (-950.8 \text{ kJ mol}^{-1}) \\ &= 131.7 \text{ kJ mol}^{-1}\end{aligned}$$

The reaction is indeed endothermic, and therefore $K(T)$ increases with T . The equilibrium pressure P_{CO_2} is higher at 700 K than at 298 K.

41. We have another exercise dealing with temperature, free energy, and equilibrium, this time applied to the decomposition of calcium carbonate:



(a) First, we sum the standard free energies of formation to calculate ΔG° at 25°C :

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ[\text{CaO(s)}] + \Delta G_f^\circ[\text{CO}_2(\text{g})] - \Delta G_f^\circ[\text{CaCO}_3(\text{s})] \\ &= (-603.3 \text{ kJ mol}^{-1}) + (-394.4 \text{ kJ mol}^{-1}) - (-1128.8 \text{ kJ mol}^{-1}) \\ &= 131.1 \text{ kJ mol}^{-1} = 1.311 \times 10^5 \text{ J mol}^{-1}\end{aligned}$$

Doing so, we automatically obtain the equilibrium constant, $K(T)$, at the standard temperature of 298.15 K:

$$K(T) = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{1.311 \times 10^5 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] \approx 1 \times 10^{-23}$$

Since this value is much less than the instantaneous reaction quotient,

$$Q = P_{\text{CO}_2} = 1 \quad (\text{given})$$

our room-temperature system is far from equilibrium when the partial pressure of CO_2 is 1 atm:

$$Q \gg K$$

There are too many products and too few reactants.

(b) Recalling the general result of Exercise 39,

$$T = \frac{\Delta H^\circ}{\Delta S^\circ - R \ln K}$$

we calculate ΔH° and ΔS° in anticipation of using these values later on:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ[\text{CaO(s)}] + \Delta H_f^\circ[\text{CO}_2(\text{g})] - \Delta H_f^\circ[\text{CaCO}_3(\text{s})] \\ &= (-634.9 \text{ kJ mol}^{-1}) + (-393.5 \text{ kJ mol}^{-1}) - (-1206.9 \text{ kJ mol}^{-1}) \\ &= 178.5 \text{ kJ mol}^{-1} = 1.785 \times 10^5 \text{ J mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ[\text{CaO(s)}] + S^\circ[\text{CO}_2(\text{g})] - S^\circ[\text{CaCO}_3(\text{s})] \\ &= (38.1 \text{ J mol}^{-1} \text{ K}^{-1}) + (213.6 \text{ J mol}^{-1} \text{ K}^{-1}) - (92.9 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 158.8 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Now realize that an equilibrium pressure of 1 atm would mean that the equilibrium constant, $K(T) = P_{\text{CO}_2}$, is equal to 1. From the associated *zero* value of ΔG° ,

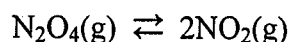
$$\Delta G^\circ = -RT \ln K = -RT \ln 1 = 0$$

we can then determine the corresponding temperature:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 0$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{1.785 \times 10^5 \text{ J mol}^{-1}}{158.8 \text{ J mol}^{-1} \text{ K}^{-1}} = 1124 \text{ K}$$

42. We return to the dissociation-dimerization equilibrium first considered in Sections 12-6 and 12-7:



Note that the difference in standard free energy is 4.8 kJ per mole of N_2O_4 dissociated:

$$\begin{aligned} \Delta G^\circ &= 2 \Delta G_f^\circ[\text{NO}_2(\text{g})] - \Delta G_f^\circ[\text{N}_2\text{O}_4(\text{g})] \\ &= \left(\frac{51.3 \text{ kJ}}{\text{mol}} \times 2 \text{ mol} \right) - \left(\frac{97.8 \text{ kJ}}{\text{mol}} \times 1 \text{ mol} \right) \\ &= 4.8 \text{ kJ} \end{aligned}$$

(a) Given initial concentrations for both N_2O_4 and NO_2 (each 1.00 mol L^{-1}), we calculate the corresponding ideal pressures

$$P_{\text{N}_2\text{O}_4} = P_{\text{NO}_2} = \frac{nRT}{V} = \frac{(1.00 \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.00 \text{ L}} = 24.5 \text{ atm}$$

and thence the reaction quotient:

$$Q = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(24.5)^2}{24.5} = 24.5$$

The equilibrium constant at 298 K follows from the value of ΔG° , calculated previously:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left[-\frac{4.8 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}\right] = 0.14$$

With Q unequal to K , the process is not yet in equilibrium.

(b) Since Q is greater than K , the system contains too much product and too little reactant. The process shifts to the left, converting NO_2 into N_2O_4 until equilibrium is finally attained.

Along the way, a total of 12.7 kilojoules' worth of residual free energy is released:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= 4.8 \text{ kJ mol}^{-1} + (0.0083145 \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K})(\ln 24.5) \\ &= 12.7 \text{ kJ mol}^{-1}\end{aligned}$$

See Section 14-8 and Example 14-9 in *PoC*.

43. Given just the value of the equilibrium constant at some temperature T , we have sufficient information to estimate the standard change in free energy:

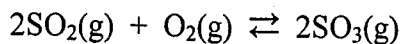
$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ &= -(0.0083145 \text{ kJ mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \ln(1.8 \times 10^{-5}) \\ &= 27 \text{ kJ mol}^{-1}\end{aligned}$$

Note the relationship between natural and base-10 logarithms, explained in Appendix B (pages A42–A47 of *PoC*):

$$\ln K = \ln 10 \times \log K = 2.3026 \log K$$

For more (much more) on acid–base equilibria, see Chapter 16.

44. We consider the production of sulfur trioxide from sulfur dioxide and oxygen:



(a) The residual, *instantaneous* difference in free energy, ΔG , is zero for any system at equilibrium. The *standard* difference, ΔG° , is fixed by the stoichiometry and structure of the reacting species:

$$\begin{aligned}\Delta G^\circ &= 2 \Delta G_f^\circ[\text{SO}_3(\text{g})] - 2 \Delta G_f^\circ[\text{SO}_2(\text{g})] - \Delta G_f^\circ[\text{O}_2(\text{g})] \\ &= \left(-\frac{371.1 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(\frac{-300.1 \text{ kJ}}{\text{mol}} \times 2 \text{ mol}\right) - \left(\frac{0 \text{ kJ}}{\text{mol}} \times 1 \text{ mol}\right) \\ &= -142.0 \text{ kJ}\end{aligned}$$

(b) Any increase in the pressure of oxygen will decrease the value of the reaction quotient, Q , and thus decrease the value of $\ln Q$. Since ΔG varies with $\ln Q$, the residual difference in free energy decreases as well:

$$Q = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}}$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

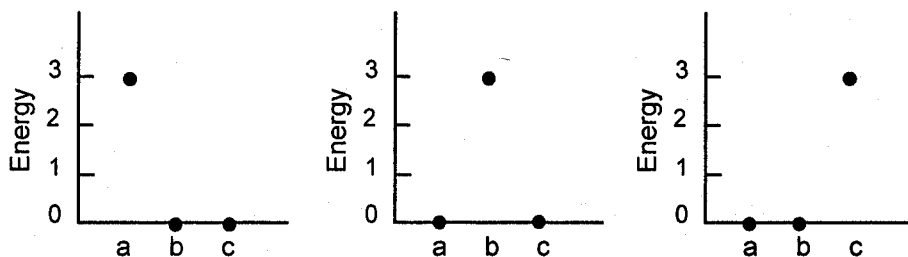
(c) The standard free energy difference, ΔG° , is a property of the molecules themselves. It is unaffected by any changes in the partial pressures.

We conclude with a reprise of the statistical concepts stressed earlier in the chapter.

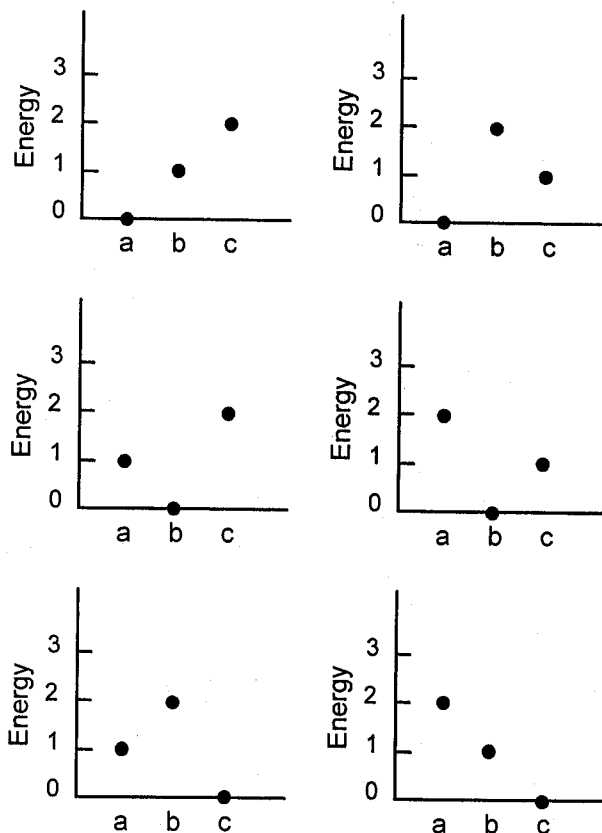
45. See Examples 14-1 and 14-2 in *PoC*, as well as Exercises 4 through 6, for similar problems of this sort.

(a) Three quantized units of energy (with possible values 0, 1, 2, 3) are apportioned among three particles. There are three distributions.

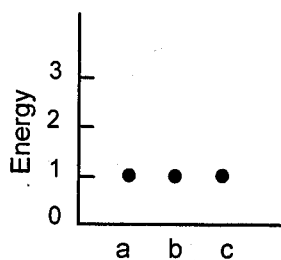
Distribution 1. One particle has all three units of energy; each of the other two particles has zero. There are three ways to realize this configuration (three microstates):



Distribution 2. One particle has two units of energy; another particle has one; the third has zero. There are six possible microstates:



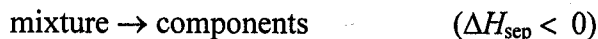
Distribution 3. Each particle has one unit of energy. Only one microstate is possible:



(b) Distribution 2 contains the most microstates: six out of a possible 10.

(c) The number of combinations in a real chemical system is effectively infinite, and the most likely macrostate is overwhelmingly probable.

46. The enthalpy of the separated liquids is presumably lower than the enthalpy of the mixed liquids. If so, then the *separation* process



will be spontaneous below a certain threshold temperature T_0 (equal to $\Delta H_{\text{sep}}/\Delta S_{\text{sep}}$):

$$\Delta G_{\text{sep}} = \Delta H_{\text{sep}} - T \Delta S_{\text{sep}} < 0 \quad (\Delta H_{\text{sep}} < 0, \Delta S_{\text{sep}} < 0, T < T_0)$$

Given such conditions, a decrease in entropy for the system (the immiscible liquids) is overcome by an increase in entropy for the surroundings (everything else). Separation, not mixing, then becomes the statistically favored outcome, offering more microstates and consequently a net increase in entropy for the universe.

QUESTION: What is the enthalpy of mixing for an ideal solution?

ANSWER: The enthalpy of mixing for any ideal system, gas or solution, will always be zero. Since the particles all interact in the same way, neither the total energy nor the total volume nor the total enthalpy is altered upon mixing:

$$\Delta E_{\text{mix}} = E_{\text{mixture}} - E_{\text{components}} = (E_1 + E_2 + \dots) - (E_1 + E_2 + \dots) = 0$$

$$\Delta V_{\text{mix}} = V_{\text{mixture}} - V_{\text{components}} = (V_1 + V_2 + \dots) - (V_1 + V_2 + \dots) = 0$$

$$\Delta H_{\text{mix}} = H_{\text{mixture}} - H_{\text{components}} = \Delta E + P\Delta V = 0 \quad (\text{at constant pressure})$$

Each quantity adds without change, and entropy alone acts as the driving force.