

Supplement to Chapter 5

REVIEW QUESTIONS

- 5.1 Describe the content of Axioms 1, 2, and 3.
- 5.2 Give a precise statement of Axiom 4 (the Second Law).
- 5.3 Mathematically, what do we mean when we say that the entropy is extensive?
- 5.4 Show that the molar entropy function, $s(\varepsilon, v)$, is a convex function.
- 5.5 Describe the physical meaning of the three parameters $\alpha = \partial S/\partial N$, $\beta = \partial S/\partial E$, and $\gamma = \partial S/\partial V$.
- 5.6 Define an *empirical temperature*.
- 5.7 Prove that β^{-1} is an empirical temperature.
- 5.8 Prove that γ/β is the equilibrium mechanical pressure.
- 5.9 Mathematically, what do we mean when we say that α , β , and p are *intensive* variables?
- 5.10 Prove that β is an intensive variable.
- 5.11 If two phases of a simple substance are in equilibrium, how many independent variables are there in the set α , β , and p ?
- 5.12 What is a quasistatic process?
- 5.13 Prove that $dS = 0$ if a substance is slowly compressed in an insulating cylinder.
- 5.14 How many arbitrary parameters are there in the entropy function of a simple substance?
- 5.15 What is an isothermal curve in the E - V plane?
- 5.16 Describe how one can determine an isothermal curve.
- 5.17 What is an adiabatic curve in the E - V plane?
- 5.18 Describe how one can determine an adiabatic curve.
- 5.19 Using only properties derived from the axioms of thermodynamics and mechanical measurements, describe how one can determine the entropy function of a simple substance.
- 5.20 How is S related to the energy spectrum of a system (in rational units and in SI units)?
- 5.21 What happens to the derivatives of the entropy function at the boundaries of the thermodynamic state space?
- 5.22 Explain how a system can be brought to a negative temperature state.
- 5.23 What is Nernst's law?
- 5.24 Show that $S = \alpha N + \beta E + \gamma V$.
- 5.25 Derive the Gibbs-Duhem relation.
- 5.26 From $pV = NkT$ and $E = \frac{3}{2}NkT$, derive the entropy function $S(N, E, V)$ for a monatomic ideal gas.
- 5.27 Define the canonical potential ϕ , and express its partial derivatives in terms of thermodynamic variables.

5.28 Do the same for the grand potential ψ .

5.29 For a system in contact with a reservoir at coldness β , what is the condition that determines the equilibrium state?

5.30 For a system in contact with an energy reservoir at coldness β , write the probability of finding the system with energy E in terms of the entropy function of the system.

5.31 Using the fact that, for a system that can exchange particles with a reservoir, the mean square fluctuation in N is given by $(\Delta N)^2 = -\partial N/\partial\alpha$, derive the affinity of the solute for a dilute solution.

EXERCISES

Exercise 5.1 Some imaginary substance satisfies the equations of state

$$E = N(kT)^2/\hbar\omega \quad \text{and} \quad pV = NkT \quad (\text{S5.1})$$

What is the entropy function of the substance in rational units?

Solution Dividing both equations by N , we obtain formulas relating $\beta = 1/kT$ and p to the energy per particle ε and the volume per particle v .

$$\beta = \frac{1}{\sqrt{\hbar\omega\varepsilon}} \quad (\text{S5.2})$$

and

$$\beta p = \frac{1}{v} \quad (\text{S5.3})$$

But if $s^\circ(\varepsilon, v)$ is the entropy per particle in rational units, then $\beta = \partial s^\circ/\partial\varepsilon$. Integrating this differential equation with respect to ε gives

$$s^\circ = 2\sqrt{\varepsilon/\hbar\omega} + f(v) \quad (\text{S5.4})$$

where f is an unknown function. The second equation of state, combined with the fact that $\beta p = \partial s^\circ/\partial v$, can be integrated to yield the relation

$$s^\circ = \log v + g(\varepsilon) \quad (\text{S5.5})$$

where g is another unknown function. Equations (S5.4) and (S5.5), taken together, imply that

$$s^\circ = \log v + 2\sqrt{\varepsilon/\hbar\omega} + C \quad (\text{S5.6})$$

where C is an arbitrary constant. The full entropy function is then determined by the fact that the entropy is extensive.

$$S^\circ(N, E, V) = Ns^\circ(E/N, V/N) = N(\log(V/N) + 2\sqrt{E/N\hbar\omega} + C) \quad (\text{S5.7})$$

Exercise 5.2 A function of three variables $f(x, y, z)$ is *convex* if, for every pair of points $\mathbf{r}_1 = (x_1, y_1, z_1)$ and $\mathbf{r}_2 = (x_2, y_2, z_2)$, the function satisfies the inequality

$$f\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}\right) \geq \frac{f(\mathbf{r}_1) + f(\mathbf{r}_2)}{2} \quad (\text{S5.8})$$

If the relation \geq can be replaced by the stronger relation $>$, then the function is *strictly convex*. For any simple substance, show that $S(N, E, V)$ is convex but not strictly convex.

Solution Consider a uniform equilibrium state of N moles of the substance, with an energy E , in a rigid insulating container of volume V . Its entropy is $S(N, E, V)$. Because it is at equilibrium, its entropy must be larger than that of any other macroscopic state with the same total energy, particle number, and volume. Let us consider a different state, composed of two uniform phases occupying volumes V_1 and V_2 , and having energies E_1 and E_2 and molar numbers N_1 and N_2 , where $V_1 + V_2 = V$, $E_1 + E_2 = E$, and $N_1 + N_2 = N$. The entropy of that state would be $S(N_1, E_1, V_1) + S(N_2, E_2, V_2)$. At this point we must be careful—if $E_2/E_1 = N_2/N_1 = V_2/V_1$, then this “new” state is actually the original uniform macrostate, conceptually separated into two parts with volumes V_1 and V_2 , and it must therefore have the same entropy. If any of

those equalities is not satisfied, then the new state is a macroscopically distinct state and, by the second law, it must have a smaller entropy than the uniform equilibrium state. Thus

$$S(N_1 + N_2, E_1 + E_2, V_1 + V_2) \geq S(N_1, E_1, V_1) + S(N_2, E_2, V_2) \quad (\text{S5.9})$$

where the equality is satisfied if and only if $E_2/E_1 = N_2/N_1 = V_2/V_1$. The fact that the entropy is extensive implies that $S(N, E, V) = 2S(N/2, E/2, V/2)$. Using this in the left-hand side of Eq. (S5.9), and dividing the equation by 2, gives

$$S\left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}\right) \geq \frac{S(\mathbf{r}_1) + S(\mathbf{r}_2)}{2} \quad (\text{S5.10})$$

where $\mathbf{r} \equiv (N, E, V)$. Since it is possible for the equality to hold, the function is not strictly convex.

Exercise 5.3 An equation of state proposed by Berthelot in 1906 as an improvement on the ideal gas equation of state is

$$\left(p + \frac{a}{kTv^2}\right)(v - v_o) = kT \quad (\text{S5.11})$$

where a and v_o are constants (with the appropriate units) to be determined empirically for each gas and $v = V/N$. Suppose a diatomic gas satisfies Berthelot's equation and the added condition that, as $v \rightarrow \infty$, $\varepsilon \rightarrow \frac{5}{2}kT$, where v and ε are the volume and energy per particle. (a) Determine the canonical potential per particle up to an arbitrary constant. (b) Determine the constant-volume specific heat (per particle) of the gas, as a function of T and v .

Solution (a) In terms of $\beta = 1/kT$, Berthelot's equation can be written as

$$\beta p = -\frac{a\beta^2}{v^2} + \frac{1}{v - v_o} \quad (\text{S5.12})$$

But letting $\phi(\beta, v) \equiv N^{-1}\phi(N, \beta, vN)$, we know that $\beta p = \partial\phi/\partial v$. Thus Eq. (S5.12) is a differential equation for $\phi(\beta, v)$, which, when integrated with respect to v , gives

$$\phi(\beta, v) = \frac{a\beta^2}{v} + \log(v - v_o) + f(\beta) \quad (\text{S5.13})$$

where $f(\beta)$ is an unknown function. The energy per particle ε is given in terms of ϕ by

$$\varepsilon = -\frac{\partial\phi}{\partial\beta} = -\frac{2a\beta}{v} - f'(\beta) \quad (\text{S5.14})$$

The condition that $\varepsilon \rightarrow \frac{5}{2}kT$ as $v \rightarrow \infty$ implies that

$$f'(\beta) = -\frac{5}{2\beta} \quad (\text{S5.15})$$

which has the solution

$$f(\beta) = -\frac{5}{2} \log \beta + \text{const.} \quad (\text{S5.16})$$

Therefore, the canonical potential per particle is

$$\phi = \frac{a\beta^2}{v} + \log(v - v_o) - \frac{5}{2} \log \beta + \text{const.} \quad (\text{S5.17})$$

(b) The energy per particle is

$$\varepsilon = -\frac{\partial\phi}{\partial\beta} = -\frac{2a\beta}{v} + \frac{5}{2\beta} \quad (\text{S5.18})$$

Written in terms of T , this is

$$\varepsilon = -\frac{2a}{kTv} + \frac{5}{2}kT \quad (\text{S5.19})$$

The specific heat per particle at constant volume is

$$C_v = \frac{\partial \varepsilon}{\partial T} = \frac{2a}{kT^2 v} + \frac{5}{2} \quad (\text{S5.20})$$

Exercise 5.4 The almost comical limit of empirical equations of state for dense gases was reached in 1927 with the Beattie–Bridgeman equation, containing five constants, a , b , c , d , and e , whose values must be determined experimentally for each gas. The conjectured equation of state is

$$p = kT \left(1 - \frac{a}{v(kT)^3} \right) \left(\frac{1}{v} + \frac{b}{v^2} - \frac{c}{v^3} \right) - \frac{d}{v^2} + \frac{e}{v^3} \quad (\text{S5.21})$$

where $v = V/N$ is the volume per particle. (a) Make the reasonable assumption that, as $v \rightarrow \infty$, the energy per particle approaches the translational kinetic energy, $3kT/2$, plus an internal energy $\varepsilon_{\text{int}}(\beta)$ that is a known function of the inverse temperature. Let $u(\beta) = \int \varepsilon_{\text{int}} d\beta$ be the indefinite integral of ε_{int} . Determine the canonical potential per particle for the Beattie–Bridgeman equation up to an arbitrary constant. (b) Determine the energy per particle as a function of β and v .

Solution (a) Equation (S5.21) states that

$$\frac{\partial(\phi/N)}{\partial v} = \beta p = (1 - a\beta^3 v^{-1})(v^{-1} + bv^{-2} - cv^{-3}) - d\beta v^{-2} + e\beta v^{-3} \quad (\text{S5.22})$$

which, when integrated with respect to v , gives

$$\frac{\phi}{N} = \log v + (a\beta^2 - b + d\beta)v^{-1} + \frac{1}{2}(c + ab\beta^3 - e\beta)v^{-2} - \frac{1}{3}ac\beta^3 v^{-3} + f(\beta) \quad (\text{S5.23})$$

where $f(\beta)$ is an arbitrary function. The fact that, as $v \rightarrow \infty$,

$$\frac{\partial(\phi/N)}{\partial \beta} = -\frac{E}{N} \rightarrow -\frac{3}{2}\beta^{-1} - \varepsilon_{\text{int}}(\beta) \quad (\text{S5.24})$$

implies that, for very large v ,

$$\frac{\phi}{N} \sim -\frac{3}{2} \log \beta - u(\beta) + g(v) \quad (\text{S5.25})$$

where g is another arbitrary function. But Eq. (S5.23) says that, as $v \rightarrow \infty$,

$$\frac{\phi}{N} - \log v \rightarrow f(\beta) \quad (\text{S5.26})$$

These equations can be consistent only if

$$f(\beta) = -\frac{3}{2} \log \beta - u(\beta) + \text{const.} \quad (\text{S5.27})$$

Thus

$$\begin{aligned} \frac{\phi}{N} &= \log v + (a\beta^3 - b + d\beta)v^{-1} + \frac{1}{2}(c + ab\beta^3 - e\beta)v^{-2} \\ &\quad - \frac{1}{3}ac\beta^3 v^{-3} - \frac{3}{2} \log \beta - u(\beta) + C \end{aligned} \quad (\text{S5.28})$$

(b) The energy per particle is given by the thermodynamic relation

$$\begin{aligned} \frac{E}{N} &= -\frac{\partial(\phi/N)}{\partial \beta} \\ &= -(3a\beta^2 + d)v^{-1} - \left(\frac{3}{2}ab\beta^2 - e\right)v^{-2} + ac\beta^2 v^{-3} + \frac{3}{2\beta} + \varepsilon_{\text{int}}(\beta) \end{aligned} \quad (\text{S5.29})$$

Exercise 5.5 Some substance has the entropy function

$$S = \lambda V^{1/2} (NE)^{1/4} \quad (\text{S5.30})$$

where N is in moles and λ is a constant with the appropriate units. A cylinder is separated by a fixed partition into two halves, each of volume 1 m^3 . One mole of the substance with an energy of 200 J is placed in the left half, while two moles of the substance with an energy of 400 J is placed in the right half. (a) Assuming that the partition conducts heat, what will be the distribution of energy between left and right at equilibrium. (b) Assuming the the partition moves freely and also conducts heat, what will be the volumes and energies of the samples in both sides at equilibrium?

Solution (a) Let S_L and S_R be the entropies of the left and right substances. The equilibrium condition for energy transfer is that $\beta_L = \beta_R$. This says that

$$\frac{\lambda V_L^{1/2} N_L^{1/4}}{4E_L^{3/4}} = \frac{\lambda V_R^{1/2} N_R^{1/4}}{4E_R^{3/4}} \quad (\text{S5.31})$$

or

$$\left(\frac{E_R}{E_L}\right)^{3/4} = \left(\frac{V_R}{V_L}\right)^{1/2} \left(\frac{N_R}{N_L}\right)^{1/4} = 2^{1/4} \quad (\text{S5.32})$$

Therefore

$$E_R = 2^{1/3} E_L \quad (\text{S5.33})$$

By energy conservation, we know that $E_L + E_R = 600 \text{ J}$. These two equations can easily be solved to give

$$E_L = 265.5 \text{ J} \quad \text{and} \quad E_R = 334.5 \text{ J} \quad (\text{S5.34})$$

(b) If the partition is free to move, we have the additional equilibrium condition that $\partial S_L / \partial V_L = \partial S_R / \partial V_R$, which gives

$$\frac{\lambda (N_L E_L)^{1/4}}{2V_L^{1/2}} = \frac{\lambda (N_R E_R)^{1/4}}{2V_R^{1/2}} \quad (\text{S5.35})$$

The two equilibrium conditions are

$$\frac{N_L^{1/4} E_L^{1/4}}{V_L^{1/2}} = \frac{N_R^{1/4} E_R^{1/4}}{V_R^{1/2}} \quad (\text{S5.36})$$

and

$$\frac{V_L^{1/2} N_L^{1/4}}{E_L^{3/4}} = \frac{V_R^{1/2} N_R^{1/4}}{E_R^{3/4}} \quad (\text{S5.37})$$

Multiplying corresponding sides of the two equations gives an equation that does not involve V_L or V_R .

$$\frac{N_L^{1/2}}{E_L^{1/2}} = \frac{N_R^{1/2}}{E_R^{1/2}} \quad (\text{S5.38})$$

This states that

$$\frac{E_R}{E_L} = \frac{N_R}{N_L} = 2 \quad (\text{S5.39})$$

which implies that

$$E_R = 400 \text{ J} \quad \text{and} \quad E_L = 200 \text{ J}. \quad (\text{S5.40})$$

Using this in Eq. (S5.37) shows that $V_R = 2V_L$, which, combined with the fact that $V_L + V_R = 2 \text{ m}^3$, determines the equilibrium volumes.

$$V_L = \frac{2}{3} \text{ m}^3 \quad \text{and} \quad V_R = \frac{4}{3} \text{ m}^3 \quad (\text{S5.41})$$

This simply says that, at equilibrium, the gases on both sides have the same energy per particle and volume per particle — a fairly trivial result.

Exercise 5.6 A *negative definite* $N \times N$ real symmetric matrix can be defined in two equivalent ways. We say that the matrix A is negative definite if all of its eigenvalues are negative numbers or if the expectation value of A , namely $\langle v|A|v \rangle = \sum v_i A_{ij} v_j$, is negative for every nonzero vector (v_1, v_2, \dots, v_N) . Show that the convexity property of the molar entropy function $s(\varepsilon, v)$ [see Eq. (5.5)] implies that the matrix of its second derivatives

$$M = \begin{bmatrix} s_{\varepsilon\varepsilon} & s_{\varepsilon v} \\ s_{\varepsilon v} & s_{vv} \end{bmatrix} \quad (\text{S5.42})$$

is negative definite.

Solution If we choose $\varepsilon_1 = \varepsilon + \delta\varepsilon$, $v_1 = v + \delta v$, $\varepsilon_2 = \varepsilon - \delta\varepsilon$, and $v_2 = v - \delta v$, where $\delta\varepsilon$ and δv are arbitrary but very small numbers, then Eq. (5.5) can be written as

$$s(\varepsilon + \delta\varepsilon, v + \delta v) + s(\varepsilon - \delta\varepsilon, v - \delta v) - 2s(\varepsilon, v) < 0 \quad (\text{S5.43})$$

Expanding this to second order in $\delta\varepsilon$ and δv , we notice that the zero order and first order terms cancel exactly, leaving

$$s_{\varepsilon\varepsilon} \delta\varepsilon^2 + 2s_{\varepsilon v} \delta\varepsilon \delta v + s_{vv} \delta v^2 < 0 \quad (\text{S5.44})$$

The quantity in this inequality can be expressed in matrix form as

$$\begin{bmatrix} \delta\varepsilon & \delta v \end{bmatrix} \begin{bmatrix} s_{\varepsilon\varepsilon} & s_{\varepsilon v} \\ s_{\varepsilon v} & s_{vv} \end{bmatrix} \begin{bmatrix} \delta\varepsilon \\ \delta v \end{bmatrix} < 0 \quad (\text{S5.45})$$

Since the inequality must hold for all values of $(\delta\varepsilon, \delta v)$ except $(0,0)$, the matrix must be negative definite.

Exercise 5.7 Suppose the matrix

$$A = \begin{bmatrix} a & c \\ c & b \end{bmatrix} \quad (\text{S5.46})$$

is negative definite. Then it is easy to prove that $a < 0$ and $b < 0$. But one can also get another inequality, involving the off-diagonal element c , by using the fact that the determinant of A is equal to the product of its two eigenvalues, which must be positive. That is,

$$ab - c^2 > 0 \quad (\text{S5.47})$$

Use these inequalities to show that the convexity of $s(\varepsilon, v)$ is equivalent to the two fairly obvious conditions that

$$\left(\frac{\partial T}{\partial \varepsilon} \right)_v > 0 \quad \text{and} \quad \left(\frac{\partial p}{\partial v} \right)_T < 0 \quad (\text{S5.48})$$

That is, the temperature increases if we add energy to a substance at fixed volume and the pressure decreases if we expand a substance at fixed temperature. These are both examples of a general principle, called *Le Châtelier's principle*, which states that, for a system in a stable equilibrium state, a change in any quantity must create a force that brings that quantity back to its equilibrium value.

Solution First we notice that the combination of the two inequalities $a < 0$ and $ab > c^2$ implies the third inequality $b < 0$. Thus the third inequality can be ignored. Applied to the matrix of the second derivatives of $s(\varepsilon, v)$, the first inequality is

$$\left(\frac{\partial^2 s}{\partial \varepsilon^2} \right) < 0 \quad (\text{S5.49})$$

But $\partial s / \partial \varepsilon = \beta = 1/T$. Thus this can be written as

$$\left(\frac{\partial(1/T)}{\partial \varepsilon} \right)_v = -\frac{1}{T^2} \left(\frac{\partial T}{\partial \varepsilon} \right)_v < 0 \quad (\text{S5.50})$$

or $(\partial T/\partial \varepsilon)_v > 0$. The determinantal inequality is

$$s_{\varepsilon\varepsilon}s_{vv} - s_{\varepsilon v}^2 > 0 \tag{S5.51}$$

The difficulty in deriving the second inequality is that it involves a derivative with the temperature held constant. This is equivalent to a derivative with β held constant. To get the required identity we have to consider the free expansion coefficient as a function of β and v . Using the fact that

$$\gamma(\beta, v) = \gamma(\varepsilon(\beta, v), v) \tag{S5.52}$$

we can see that

$$\left(\frac{\partial \gamma}{\partial v}\right)_\beta = \left(\frac{\partial \gamma}{\partial \varepsilon}\right)_v \left(\frac{\partial \varepsilon}{\partial v}\right)_\beta + \left(\frac{\partial \gamma}{\partial v}\right)_\varepsilon \tag{S5.53}$$

First we note that

$$\left(\frac{\partial \gamma}{\partial \varepsilon}\right)_v = s_{\varepsilon v} \quad \text{and} \quad \left(\frac{\partial \gamma}{\partial v}\right)_\varepsilon = s_{vv} \tag{S5.54}$$

which gives us two of the terms in Eq. (S5.51). To handle $(\partial \varepsilon/\partial v)_\beta$ we need a partial derivative identity whose proof will be given in Chapter 6. For any function of two variables $z = z(x, y)$, it is always true that, when y is expressed as a function of x and z ,

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{(\partial z/\partial x)_y}{(\partial z/\partial y)_x} \tag{S5.55}$$

This says that

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_\beta = -\frac{(\partial \beta/\partial v)_\varepsilon}{(\partial \beta/\partial \varepsilon)_v} = -\frac{s_{\varepsilon v}}{s_{\varepsilon\varepsilon}} \tag{S5.56}$$

Therefore, using Eqs. (S5.54) and (S5.56), we see that

$$s_{\varepsilon\varepsilon} \left(\frac{\partial \gamma}{\partial v}\right)_\beta = s_{\varepsilon\varepsilon}s_{vv} - s_{\varepsilon v}^2 > 0 \tag{S5.57}$$

But we know that $s_{\varepsilon\varepsilon} < 0$. Thus we can write this inequality as

$$\left(\frac{\partial \gamma}{\partial v}\right)_\beta = \beta \left(\frac{\partial p}{\partial v}\right)_\beta = \frac{1}{T} \left(\frac{\partial p}{\partial v}\right)_T < 0 \tag{S5.58}$$

Since the temperature is always a positive number this is equivalent to the relation $(\partial p/\partial v)_T < 0$.

Exercise 5.8 All of the equilibrium states that we have considered have been stable equilibrium states. As an example of an unstable equilibrium state, consider the system shown in Fig. S5.1, consisting of a soda straw with equal soap bubbles on the ends. (a) Using Laplace’s law, which states that, for a bubble of radius R , $p(\text{inside}) - p(\text{outside}) = 4\sigma/R$, where σ is the surface tension of the soap solution, show that the situation shown in the figure will not persist indefinitely. (b) Describe the final, stable, equilibrium state.

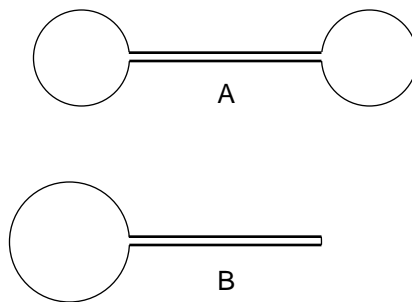


Fig. S5.1 (A) An unstable equilibrium state of two soap bubbles. (B) One of the two possible stable equilibrium states.

Solution (a) Suppose there is a small spontaneous fluctuation in which the radius of the left bubble increases by an amount δR . The increase in the volume of the left bubble would be $\delta V = 4\pi R^2 \delta R$. But the extra gas must come from the right bubble, which would then decrease in radius by an amount δR . The pressure difference in the two ends would become (these pressures are inside pressures)

$$p_L - p_R = \frac{4\sigma}{R + \delta R} - \frac{4\sigma}{R - \delta R} \approx -\frac{8\sigma}{R^2} \delta R \quad (\text{S5.59})$$

This pressure difference is in a direction that increases the size of the already larger left bubble, which would then expand even more.

(b) Assuming that the initial fluctuation was in the direction described, the final state would be one in which almost all of the gas was in the left bubble, which would have a radius $R_o \approx 2^{1/3}R$. The right end of the soda straw would be capped by a meniscus of radius R_o [see Fig. S5.1(B)]. It is now easy to see that this equilibrium state is stable. A small transfer of gas from right to left causes a small drop in pressure in the left bubble but a much larger drop in pressure in the meniscus. Thus the relative pressure is such as to force gas from left to right, in accord with Le Châtelier's principle. This is a simple mechanical example of spontaneous symmetry breakdown. Although the system has obvious left-right symmetry, the stable equilibrium states do not. As always, there is more than one stable equilibrium state, and the set of them does exhibit the system symmetry.

Exercise 5.9 One mole of a substance satisfies the equations $s^3/v = aT$ and $\varepsilon = pv$, where a is a constant. Determine the molar entropy function.

Solution The relation $\partial s/\partial \varepsilon = 1/T$, combined with the first equation, gives the differential equation

$$\frac{\partial s}{\partial \varepsilon} = \frac{av}{s^3} \quad (\text{S5.60})$$

or

$$s^3 \frac{\partial s}{\partial \varepsilon} = av \quad (\text{S5.61})$$

This can be integrated with respect to ε to give

$$s^4/4 = av\varepsilon + f(v) \quad (\text{S5.62})$$

Multiplying the second equation of state by β and using the fact that $\beta p = \partial s/\partial v$, we get another differential equation for s .

$$\varepsilon \frac{\partial s}{\partial \varepsilon} = v \frac{\partial s}{\partial v} \quad (\text{S5.63})$$

Multiplying this by s^3 gives

$$\varepsilon s^3 \frac{\partial s}{\partial \varepsilon} = v s^3 \frac{\partial s}{\partial v} \quad (\text{S5.64})$$

But $s^3 \partial s/\partial \varepsilon$ can be evaluated using Eq. (S5.61).

$$a\varepsilon v = v s^3 \frac{\partial s}{\partial v} \quad (\text{S5.65})$$

Cancelling the factors of v and integrating with respect to v gives

$$s^4/4 = a\varepsilon v + g(\varepsilon) \quad (\text{S5.66})$$

This equation is consistent with Eq. (S5.62) only if

$$s^4/4 = a\varepsilon v + \text{const.} \quad (\text{S5.67})$$

which gives

$$s = (4a\varepsilon v + C)^{1/4} \quad (\text{S5.68})$$

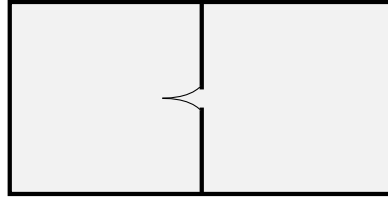


Fig. S5.2 A device, using a one-way valve, intended to defeat the Second Law.

Exercise 5.10 Shown in Fig. S5.2 is a device for defeating the Second Law. Two compartments, initially containing ideal gases at the same temperature and density, are connected by a passage that is closed by rubber flaps. No particles can pass from left to right because the flaps act as a one-way valve. Most particles cannot pass from right to left either, but every now and then a particle will have enough energy to push through the flaps. Since only high-energy particles get through and they only pass through in one direction, if we wait long enough, the gas on the left will become more dense and hotter than the gas on the right. But the uniform state is the state of maximum entropy, and thus the system will have gone from a higher to a lower entropy state. What’s wrong with this?

Solution We will do this analysis in two parts. First we will show, in a rough, pictorial way, that the statements made in the exercise are wrong and there are, at least approximately, as many particles that go from left to right as from right to left. But this rough argument cannot show that the valve has no effect at all on the particle densities in the right and left chambers. In order to show that, we will have to construct a much more precise argument that actually relies on some of the detailed properties of Hamiltonian dynamics.

Suppose that the amount of energy necessary to open the flaps wide enough to let a particle through is E and that the rate at which particles hit the space between the two flaps is R . If the system is at temperature T , then the probability that a particle coming from the right will have enough energy to open the flaps is roughly $e^{-E/kT}$. Thus a rough estimate of the rate at which particles pass from right to left is $Re^{-E/kT}$. Now, the valve is itself a mechanical system that can have both kinetic and potential energy. If the flaps are open then they have potential energy E . The probability of finding them in an open, rather than a closed state, is, again very roughly, $e^{-E/kT}$. But then the rate at which particles are let in from left to right by the spontaneous opening of the flaps is approximately $Re^{-E/kT}$. We can see that the argument made in the statement of this problem, that indicated that *no* particles moved from left to right, is seriously wrong. However, even this improved description of the operation of the system leaves one with the suspicion that *more* particles will go from right to left than vice versa. Let us now clearly eliminate that possibility.

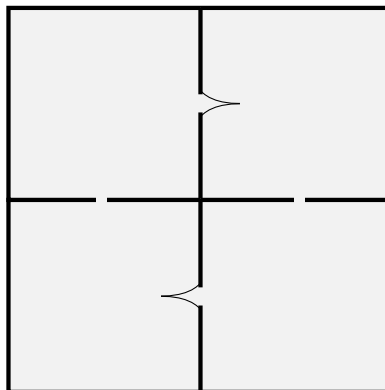


Fig. S5.3 If the one-way valve really works, then one should expect a steady clockwise circulation of particles through the valves.

We connect the system, via two holes, to an identical system that has a valve in the reverse direction. It is clear that, because of symmetry, in this new system no density differential will develop between the two sides. However, if in the original system the valve had any effect at all, then in this new system there would

be a definite tendency for particles to circulate in a clockwise sense, going from right to left through the bottom valve and from left to right through the top one. We will now rigorously prove that there is no such tendency. We will describe the system by classical mechanics. This means that, for a detailed description, we would have to model the valve by some classical mechanism with a finite number of coordinates and corresponding canonical momenta. Our argument will not rely on any detailed model of the valve. We assume that the double system is completely isolated and has an energy E . Therefore all of its possible microstates are points on some huge energy surface $\omega(E)$ in the phase space of the system. We choose some fixed, long, time interval, $0 < t < T$. We choose some particular particle, which we call the marker particle. To every possible state on the energy surface we assign an integer, called the circulation number for that state. It is calculated by taking that state as an initial state for the system at time 0, letting the system progress according to Hamilton's equations during the time interval $(0, T)$, and adding +1 each time the marker particle passes through one of the valves in the normal direction and -1 each time it passes through one of the valves in the wrong direction. Now, if there is any tendency at all for particles to pass through the valves in the normal direction, then the average circulation number (averaged over all states on the energy surface) will be positive. Consider the set of states with circulation number 5. Call that set of states I_5 , where the I indicates that, in computing the circulation number, we are considering these as initial states. Define as F_5 (F for final) the set of states that I_5 goes into at time T . Now, take any microstate in F_5 and reverse the velocities of every particle ($p_1 \rightarrow -p_1, p_2 \rightarrow -p_2$, etc.). The set of states we get this way we call F_5^* . Because Hamiltonian mechanics is exactly symmetrical with respect to time reversal (that is, a motion picture of a system moving according to Hamilton's equations is, if run backwards, still a system moving according to Hamilton's equations), each state in F_5^* will in the time interval $0 < t < T$ run exactly backwards and have a circulation number -5 . In fact, it is easy to see that F_5^* is identical with I_{-5} . Let $P(I_5)$ be the probability that a state, picked at random on the energy surface (that is, with the microcanonical probability), will be in I_5 . Then, by Liouville's theorem, $P(I_5) = P(F_5)$. But reversing the velocities does not change the probability of a state in the microcanonical ensemble. Therefore $P(F_5) = P(F_5^*) = P(I_{-5})$. This shows that averaging the circulation number over the microcanonical ensemble gives zero because the sets I_K and I_{-K} cancel in pairs for each K . There is no statistical tendency for particles to go through a valve in the "right" as opposed to the "wrong" direction.

Exercise 5.11 A container of volume V is partitioned into two subvolumes, V_A and V_B , that contain different ideal gases at the same temperature and pressure. A valve is opened in the wall separating the subvolumes so that the gases can mix. Obviously the system will now go to a new, uniformly mixed, equilibrium state, which must therefore have a larger entropy than the initial state. What is the change in entropy? This extra entropy is called the *entropy of mixing*.

Solution The solution of this problem will illustrate a general method that is useful in many thermodynamics problems. The initial state of the system is composed of two substances at equilibrium for which we can calculate the entropy. The final state is a uniform equilibrium state whose entropy we would like to calculate. But the intermediate states, during the mixing process, will be complicated nonuniform states that cannot really be analyzed at all by equilibrium thermodynamics. What we will have to do is to find a different, quasistatic process that goes from the same initial to the same final state. It will have to be chosen so that we can calculate the entropy changes in the quasistatic process. The reason why this method is legitimate, even though the intermediate states are very different, is that the entropy of the system depends on its macrostate and not on how the system got to that macrostate.

The quasistatic process that we will use is one that utilizes *semipermeable membranes*. A semipermeable membrane is a membrane that allows one type of molecule to pass through it freely but not molecules of the other type. A semipermeable membrane must be clearly distinguished from a *one-way membrane* that allows particles to pass through in one direction but not in the other. By considering the last exercise it is clear that a one-way membrane would violate the Second Law of thermodynamics and is therefore impossible. Semipermeable membranes, in contrast, work differently for different molecules, but they work the same way in both directions. Semipermeable membranes that pass water molecules but not salt are widely used in saltwater purification plants. Although it is often technically impossible to design a semipermeable membrane for two arbitrarily chosen molecules, the difficulty does not arise because they involve any violation of

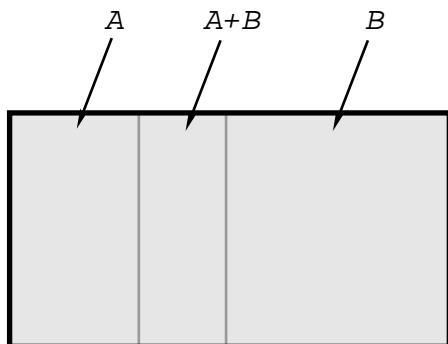


Fig. S5.4 The left membrane passes A molecules, but not B molecules. The right membrane passes B s but not A s. Both membranes are slowly moved to the left and right limits of the container.

thermodynamics. It is purely an engineering problem. We begin with a pair of semipermeable membranes, positioned together between volumes V_A and V_B , as shown in Fig. S5.4. The left membrane can pass A particles but not B particles. The right one does the reverse. The two of them together act as a completely impermeable barrier. We surround the cylinder by a large reservoir at temperature T . We first gradually move the left membrane to the far left end of the cylinder. At any intermediate stage the density of A molecules on both sides of the membrane will be equal since the membrane freely passes A molecules and the density of B molecules to the right of the membrane will be N_B/V_R , where V_R is the temporary volume to the right of the left membrane. By the law of partial pressures, the excess force on the membrane, directed toward the left, will be $F_L = AN_BkT/V_R$. The amount of work done by this excess force on the external agent that is keeping the membrane in position is $dW = F dx = N_BkT dV_R/V_R$. The total work done on the outside agent is

$$W_L = N_BkT \int_{V_B}^V \frac{dV_R}{V_R} = N_BkT \log(V/V_B)$$

In exactly the same way, the mechanical energy absorbed from the system in quasistatically moving the right membrane from its initial position to a position at the far right is

$$W_R = N_AkT \log(V/V_A) \quad (\text{S5.69})$$

The system within the cylinder began with $N_A + N_B$ particles at temperature T and therefore with an energy of $(N_A + N_B)kT$. This is also the energy of the gas within the cylinder in its final state. Thus all the work done on the external agents (that is, $W_L + W_R$) must have been compensated by thermal energy being conducted to the gas in the cylinder by the reservoir. But, when a substance at temperature T absorbs an amount of heat dQ , its entropy changes by $dS = dQ/T$. Since T is constant throughout the procedure, the total entropy change of the gas within the cylinder is

$$\Delta S = (W_L + W_R)/T = kN_A \log(V/V_A) + kN_B \log(V/V_B) \quad (\text{S5.70})$$

Because the initial pressures were equal,

$$\frac{N_A}{V_A} = \frac{N_B}{V_B} = \frac{N_A + N_B}{V}$$

which allows us to write ΔS in terms of N_A and N_B alone.

$$\Delta S = kN_A \log\left(\frac{N_A + N_B}{N_A}\right) + kN_B \log\left(\frac{N_A + N_B}{N_B}\right) \quad (\text{S5.71})$$

The most revealing way to write this is to use Stirling's approximation and rational units to cast it into the form ($N_{AB} = N_A + N_B$)

$$\Delta S^\circ = \log(N_{AB}!) - \log(N_A!) - \log(N_B!) \quad (\text{S5.72})$$

Thus we see that, by purely thermodynamic methods, we can rediscover the N factorials that were found to be necessary in Eq. (3.83), based on the microscopic probabilistic interpretation of entropy.

Exercise 5.12 An air conditioner is a device that absorbs heat energy from a cooler reservoir (our room) and dumps it into a hotter reservoir (the outside). A refrigerator does the same thing between its cooler inside volume and our warmer room. Now everyone knows that air conditioners and refrigerators always come with electrical plugs—they never operate without electrical energy input. This may seem like a simple consequence of the law of conservation of energy. With regard to energy, one never gets something for nothing. But a more careful analysis shows that this is not true. If we absorb one joule of energy from inside our room and dump it into the hot air outside, we have completely satisfied the law of energy conservation. Why is it necessary to also take another joule of expensive electrical energy, convert it into useless heat, and dump that outside into the hot air? If it is only due to things like friction in the air conditioner machinery, then one might hope by careful engineering to make an air conditioner that will reduce our electrical bills to something much lower than the very high values that air conditioners currently cause. This exercise will show that it is the Second Law of thermodynamics, rather than energy conservation, that guarantees to the electric company a substantial summer income.

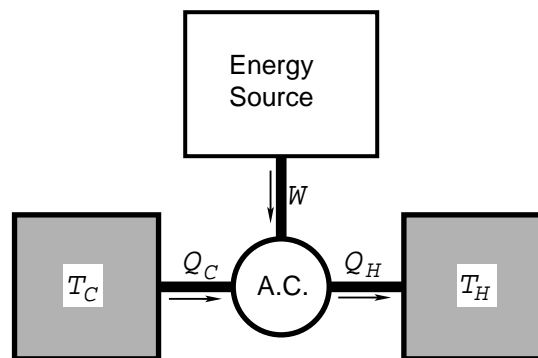


Fig. S5.5 An air conditioner is a device that uses energy in order to pass heat from a lower-temperature reservoir to a higher temperature one.

We model an air conditioner (or a refrigerator) as a device that absorbs heat energy from a cool reservoir at temperature T_C and also absorbs a certain amount of electrical or mechanical work and dumps the energy into a hot reservoir at temperature T_H . We will assume that the whole system, composed of the two reservoirs and the device, is isolated. The device absorbs an amount of heat Q_C from the cool reservoir and an amount of energy W in mechanical or electrical form and transfers an amount of heat Q_H to the hot reservoir. We define the *efficiency* of the device as the ratio

$$E = \frac{Q_C}{W} \quad (\text{S5.73})$$

Clearly, it behooves us, if we do not own the electric company, to make the efficiency as large as possible. Show that, unfortunately, there is a fundamental limit, given by

$$E \leq \frac{T_C}{T_H - T_C} \quad (\text{S5.74})$$

Solution We will make the reasonable assumption that, after running for a certain time interval, the device itself is in the same state that it was initially. We will also assume that the reservoirs are large enough that their temperature changes are negligible. This assumption simplifies the analysis, but it is not really essential. The entropy change of the whole system is therefore

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} \geq 0 \quad (\text{S5.75})$$

where the final inequality reflects the fact that isolated systems only increase their total entropy. This inequality can be expressed as

$$\frac{Q_H}{Q_C} \geq \frac{T_H}{T_C} \quad (\text{S5.76})$$

By energy conservation, $Q_H = Q_C + W$. Therefore

$$\begin{aligned} E &= \frac{Q_C}{W} \\ &= \frac{Q_C}{Q_H - Q_C} \\ &= \frac{1}{Q_H/Q_C - 1} \\ &\leq \frac{1}{T_H/T_C - 1} = \frac{T_C}{T_H - T_C} \end{aligned} \quad (\text{S5.77})$$

Exercise 5.13 A *heat pump* is essentially an air conditioner turned around and used to pump heat into the house when the temperature outside is colder than that inside. A *radiant heater* is simply a device inside the house that converts electrical energy completely into heat energy. A typical situation is an inside temperature of 21°C ($\sim 70^\circ\text{F}$) and an outside temperature of 4°C ($\sim 39^\circ\text{F}$). Defining the efficiency of an electrical heater as the ratio of the heat added to the warm reservoir to the electrical power used, compare the best possible efficiencies of a heat pump and a radiant heater in the situation described.

Solution For a heat pump we have defined the efficiency as

$$E = \frac{Q_H}{W} \quad (\text{S5.78})$$

But $Q_H = W + Q_C$ and, according to the Second Law, $Q_H/T_H \geq Q_C/T_C$. Thus

$$\begin{aligned} E &= \frac{Q_H}{Q_H - Q_C} \\ &= \frac{1}{1 - Q_C/Q_H} \\ &< \frac{1}{1 - T_C/T_H} = \frac{T_H}{T_H - T_C} \end{aligned} \quad (\text{S5.79})$$

In this case $T_H = 21 + 273 = 294\text{K}$ and $T_C = 4 + 273 = 277\text{K}$. Using Eq. (S5.79), we see that the maximum efficiency of the heat pump is 17.3. The efficiency of radiant heater is exactly 1, since $Q_H = W$. Thus, it is theoretically possible for a heat pump to be enormously more efficient than the most common style of electrical heater.

Exercise 5.14 The last two exercises involved devices in which mechanical (or electrical) energy is supplied to move heat between reservoirs in the direction opposite to that in which it would spontaneously flow. A *heat engine* does just the opposite. By allowing heat to move from a hotter to a cooler reservoir, it extracts a fraction of the heat energy and converts it into mechanical work, such as lifting a weight or compressing a spring. A nuclear power plant is an excellent example of a heat engine. The energy of nuclear fission reactions is used to create a high-temperature thermal reservoir within the core of the reactor. A water-driven steam turbine absorbs energy from the high-temperature reservoir, uses some of the energy to drive an electrical generator, and dumps the excess energy as heat into a cool reservoir, called a cooling pond. Again, the most desirable thing would be to convert 100% of the heat energy to electrical energy, but we will see that, on top of the necessary imperfections in steam turbines and electrical generators, there is a fundamental limitation, due to the Second Law, on the fraction of nuclear energy that can be converted to electrical power.

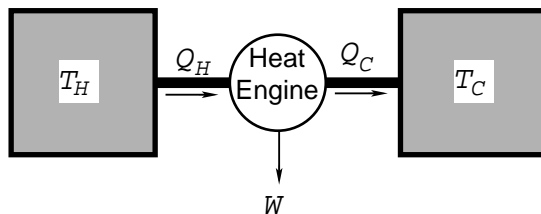


Fig. S5.6 A heat engine absorbs an amount of energy Q_H from a high-temperature reservoir, converts an amount W of it into mechanical energy, and dumps the rest into a low-temperature reservoir.

For a heat engine, the natural definition of efficiency is the ratio of mechanical or electrical work extracted to the thermal energy absorbed from the high-temperature source.

$$E = \frac{W}{Q_H} \quad (\text{S5.80})$$

The aim of this exercise is to show that

$$E \leq 1 - \frac{T_C}{T_H} \quad (\text{S5.81})$$

Solution In this case, after the device has run for a period of time, an amount of thermal energy Q_H has been extracted from the high-temperature reservoir, part of it W has been converted to mechanical energy, and the excess, $Q_C = Q_H - W$, has been transferred to the low-temperature reservoir. The change in entropy of the system, which must be nonnegative, is

$$\Delta S = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} \geq 0 \quad (\text{S5.82})$$

This means that

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H} \quad (\text{S5.83})$$

and

$$E = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H} \quad (\text{S5.84})$$

Exercise 5.15 Assuming that one could produce a cylinder with a frictionless piston, describe a heat engine that would actually achieve the theoretically maximum efficiency, that is, one that would satisfy Eq. (S5.84) as an equality. Such an engine is called a *Carnot engine*, after Sadi Carnot, the originator of thermodynamics.

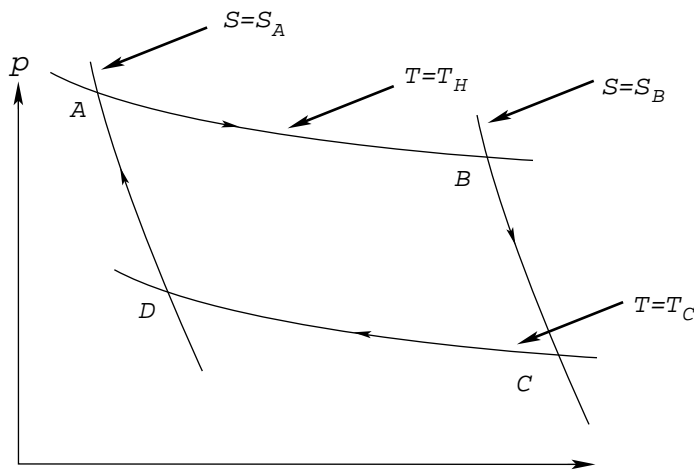


Fig. S5.7 The path of the substance within the cylinder, on the p - V plane, as it is taken through the cyclic process described in the exercise, is composed of two adiabats and two isotherms.

Solution Our system consists of two large thermal reservoirs at temperature T_H and T_C plus a cylinder filled with a gas (not necessarily ideal), closed by a frictionless piston and with a heat-conducting upper end. We assume that, in its initial state, the gas has volume V_o and temperature T_H . We must assume that we have investigated the properties of the gas previously so that we can draw curves of constant temperature (isotherms) and curves of constant entropy (adiabats), for the sample of gas in the cylinder, on the p - V plane. We first draw the T_C and T_H isotherms (see Fig. S5.7). Since the initial state of the gas has temperature T_H , it is some point A on the high-temperature isotherm. We draw the adiabat through A and call the point at which it intersects the low-temperature isotherm D . We now put the cylinder in contact with the T_H reservoir and allow the gas to expand extremely slowly so that it will remain, during its expansion, at temperature T_H . Its thermodynamic state will therefore move down the T_H isotherm. We stop the expansion at some arbitrary point B . We now disconnect the cylinder from the reservoir, so that it is thermally isolated, and again allow it to expand very slowly. As we saw in Section 5.11, it will now move along an adiabat. We stop the expansion when the temperature reaches T_C . We place the cylinder in contact with the low-temperature reservoir and very gradually compress the gas, moving along the T_C isotherm. We stop when we have arrived at the previously determined point D . We again isolate the cylinder and gradually compress the gas, moving along the adiabat to our initial state A .

Let us now see how much work has been done on the external agent that is controlling the piston. Each time the piston moves a small amount, the work done on the external agent is $F dx = p dV$. Thus, in moving along the isotherm from A to B , the total work done is

$$W_{AB} = \int_A^B p(v) dV \quad (\text{S5.85})$$

But this is exactly the area under the isothermal curve in the p - V plane. The same thing is true for the curve from B to C . In going from C to D and from D to A , it is the external agent that must do work in order to compress the gas. It is easy to see that the net work done on the external agent (that is, the net work that has been extracted from the system) is just the area in the p - V plane bounded by the four curves.

In going from A to B , the heat energy absorbed from the hot reservoir is

$$Q_{AB} = T_H(S_B - S_A) \quad (\text{S5.86})$$

But, by energy conservation, the difference in the energy states of the gas at A and B must be

$$E_B - E_A = Q_{AB} - W_{AB} \quad (\text{S5.87})$$

In going from B to C , the work done by the gas must equal its loss in internal energy.

$$E_B - E_C = W_{BC} \quad (\text{S5.88})$$

Using similar arguments (W_{CD} is the work done *by* the external agent and Q_{CD} is the heat energy given *to* the cold reservoir),

$$\begin{aligned} Q_{CD} &= T_C(S_B - S_A) \\ E_D - E_C &= W_{CD} - Q_{CD} \\ \text{and } E_A - E_D &= W_{DA} \end{aligned} \quad (\text{S5.89})$$

The net work over the cycle is given by

$$\begin{aligned} W &= W_{AB} + W_{BC} - W_{CD} - W_{DA} \\ &= Q_{AB} - Q_{CD} \end{aligned} \quad (\text{S5.90})$$

The efficiency is defined as

$$\frac{W}{Q_{AB}} = 1 - \frac{Q_{CD}}{Q_{AB}} = 1 - \frac{T_C}{T_H} \quad (\text{S5.91})$$

Two things should be noted about this Carnot engine. First, because all the processes must be carried out extremely slowly, it is not, in spite of its maximal efficiency, a practical design for an industrial engine. The more important point is that every step in the cycle is completely reversible. If we traverse the path in the p - V plane in the opposite sense, namely $ADCBA$, then the Carnot engine acts as a refrigerator, absorbing an amount of work W and transferring an amount of heat Q_{AB} to the hotter reservoir. It is easy to verify that, as a refrigerator, it also has the maximum possible efficiency. That it is reversible is a direct consequence of the fact that the complete cycle does not change the sum of the entropies of the two reservoirs.

Exercise 5.16 The Berthelot equation of state, mentioned in Exercise 5.3, can be expressed in the form

$$p = \frac{kT}{v - v_o} - \frac{a}{kTv^2} \quad (\text{S5.92})$$

The fact that it contains two constants, v_o and a , that are different for different gases, is inconvenient for drawing general conclusions about systems that satisfy the equation. This contrasts with the ideal gas equation, which has the same form, free of arbitrary constants, for all substances that are adequately described by it. Show that, by measuring volumes, pressures, temperatures, and energies in appropriate units, the equations of state of all substances that satisfy the conditions described in Exercise 5.3 can be brought into the simplified universal forms

$$\tilde{p} = \frac{1}{\tilde{v} - 1} - \frac{\tilde{\beta}^2}{\tilde{v}^2} \quad (\text{S5.93})$$

and

$$\tilde{E} = \frac{5}{2\tilde{\beta}} - \frac{2\tilde{\beta}}{\tilde{v}} \quad (\text{S5.94})$$

Collections of substances whose equations of state can all be brought into a unified form by such rescaling procedures are said to satisfy a *law of corresponding states*.

Solution It is best to make the necessary transformations on the canonical potential, from which both equations of state immediately follow. It has been shown that the canonical potential per particle is

$$\phi = \frac{a\beta^2}{v} + \log(v - v_o) - \frac{5}{2} \log \beta + \text{const.} \quad (\text{S5.95})$$

By extracting $-\log v_o$ from the constant term, which would have no effect on the equations of state, we can rewrite this as

$$\phi = \frac{a}{v_o} \frac{\beta^2}{\tilde{v}} + \log(\tilde{v} - 1) - \frac{5}{2} \log \beta + \text{const.} \quad (\text{S5.96})$$

where $\tilde{v} = v/v_o$. By extracting $-\frac{5}{2} \log(\sqrt{a/v_o})$ from the constant term and defining a scaled inverse temperature $\tilde{\beta} = \sqrt{a/v_o} \beta$, we can eliminate all the arbitrary constants in ϕ .

$$\phi = \frac{\tilde{\beta}^2}{\tilde{v}} + \log(\tilde{v} - 1) - \frac{5}{2} \log \tilde{\beta} + \text{const.} \quad (\text{S5.97})$$

The equations of state are

$$E = -\frac{\partial \phi}{\partial \beta} = \left(\frac{v_o}{a}\right)^{1/2} \frac{\partial \phi}{\partial \tilde{\beta}} = \left(\frac{v_o}{a}\right)^{1/2} \left(\frac{5}{2\tilde{\beta}} - \frac{2\tilde{\beta}}{\tilde{v}}\right) \quad (\text{S5.98})$$

and

$$\beta p = \frac{\partial \phi}{\partial v} = v_o \frac{\partial \phi}{\partial \tilde{v}} = v_o \left(\frac{1}{v_o - 1} - \frac{\tilde{\beta}^2}{\tilde{v}^2}\right) \quad (\text{S5.99})$$

Further defining the dimensionless energies and pressures by

$$\tilde{E} = \frac{E}{\sqrt{v_o/a}} \quad \text{and} \quad \tilde{p} = \frac{p}{\sqrt{v_o a}} \quad (\text{S5.100})$$

we obtain dimensionless equations of state valid for all diatomic Berthelot gases.

$$\tilde{E} = \frac{5}{2\tilde{\beta}} - \frac{2\tilde{\beta}}{\tilde{v}} \quad (\text{S5.101})$$

and

$$\tilde{p} = \frac{1}{\tilde{\beta}(\tilde{v} - 1)} - \frac{\tilde{\beta}}{\tilde{v}^2} \quad (\text{S5.102})$$

Letting $\tilde{\beta} = 1/\tilde{\tau}$, where $\tilde{\tau}$ is related to the Kelvin temperature by $\tilde{\tau} = \sqrt{v_o/a} kT$, we can write these equations in terms of the dimensionless temperature variable $\tilde{\tau}$ as

$$\tilde{E} = \frac{5}{2}\tilde{\tau} - \frac{2}{\tilde{\tau}\tilde{v}} \quad (\text{S5.103})$$

and

$$\tilde{p} = \frac{\tilde{\tau}}{\tilde{v} - 1} - \frac{1}{\tilde{\tau}\tilde{v}^2} \quad (\text{S5.104})$$

Exercise 5.17 If, for notational simplicity, the tildes are dropped in the dimensionless Berthelot pressure equation, then it reads

$$p = \frac{\tau}{v - 1} - \frac{1}{\tau v^2} \quad (\text{S5.105})$$

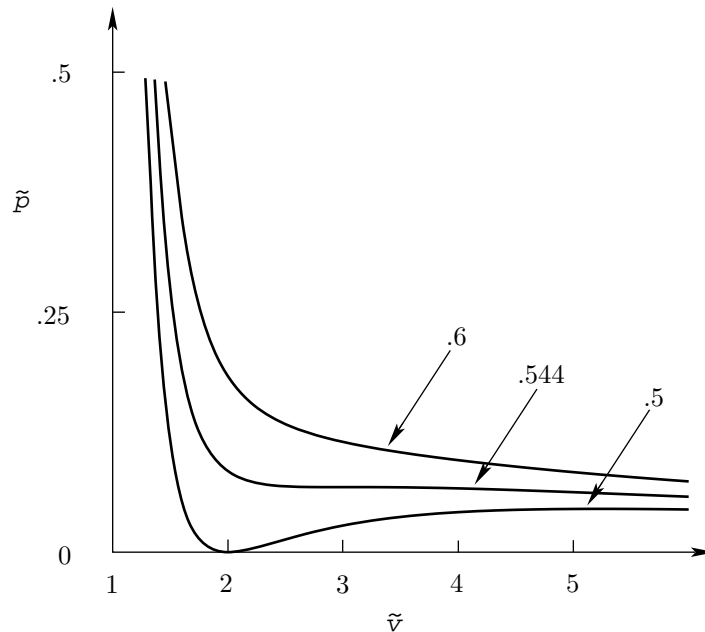


Fig. S5.8 Isotherms of the dimensionless Berthelot equation. The values of the dimensionless temperature τ are shown.

Shown in Fig. S5.8 are the isotherms corresponding to the dimensionless temperatures, $\tau = 0.5, 0.544$, and 0.6 . Show that, for $\tau < 0.544$, there is a region in which the equation describes a substance that is unstable with respect to separation into two uniform phases of different densities.

Solution In Exercise 5.7 it was shown that the conditions of stability with respect to phase separation were that $(\partial T/\partial \varepsilon)_v > 0$ and $(\partial p/\partial v)_T < 0$. Since the isotherms shown in the figure are plots of p at constant T , the fact that, below the *critical temperature* $\tau = 0.544$ (which will be calculated in a later exercise) they have sections of positive slope, indicates that the Berthelot equation of state cannot be taken as a valid description of any uniform phase for those values of T and v .

Exercise 5.18 In Fig. S5.9 are plotted the p - v isotherms for a typical simple substance such as neon or oxygen. The states within the region outlined by the dashed curve are two-phase states in which the substance is part liquid and part gas. A sample that begins in a liquid state at point A and is maintained at constant temperature by being kept in thermal contact with a reservoir while its volume is gradually increased will smoothly expand as a pure liquid until it reaches point B . Any further expansion will cause the liquid to evaporate (or boil, depending on the rate and details of the process), forming a state composed of two phases, liquid and gas, in equilibrium. As we saw in Section 5.10, a two-phase state of a simple substance has a pressure that is a unique function of its temperature. Therefore, the portion of the isotherm that connects the pure liquid state on the left segment of the dashed line with the pure gas phase on the right segment is perfectly horizontal, as it has been drawn. Once the substance has completely vaporized, reaching point C on the isotherm, any further expansion of the purely gaseous sample will cause a steady reduction in pressure. It often happens that one has reasonably accurate simple analytic expressions for the thermodynamic functions of the liquid phase and different analytic expressions for the thermodynamic functions of the gas phase. Choosing a temperature, let us say $T = T_o$, one could separately use these expressions to draw a liquid isotherm and a gas isotherm. One is then faced with the problem of where to draw the horizontal portion, connecting the two isotherms and representing the two-phase states. The question to be answered here is: What is the additional condition that determines the location of the two-phase instability and thus the locus of the dashed line in the figure?

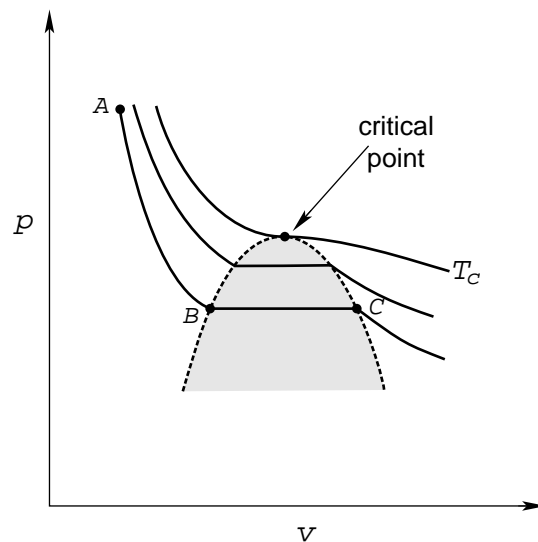


Fig. S5.9 The p - V isotherms of a simple substance. Within the shaded region, the states of the substance are composed of a mixture of liquid and gas. The isotherms for T greater or equal to the *critical temperature* T_c do not have a two-phase section. The critical isotherm touches the two-phase region at the *critical point*.

Note: Statistical mechanical arguments indicate that the *exact* thermodynamic functions have very subtle nonanalyticities at the location of the two-phase boundary that could, if one had an exact representation of the thermodynamic functions, be used to locate those boundaries. However, the deviations from analytic behavior as one approaches the two-phase boundary are so subtle that, to the knowledge of the author, they have never been experimentally detected. That is, when a pure gas sample in a very clean container, free of dust specks or other potential condensation sites, is slowly compressed at constant temperature beyond the dashed stability line, it does not immediately undergo a phase transition but instead moves along an

apparently smooth extension of the gas-phase isotherm into a uniform undercooled state. It is undercooled in the sense that at that pressure the only stable gas phases are at higher temperatures. If the substance is maintained in that unstable uniform state, eventually something, such as a cosmic-ray ionization track or a spontaneous density fluctuation, will trigger the transition to the stable two-phase state. In careful experiments, however, “eventually” can be a very long time. The same phenomenon occurs on the other side of the two-phase region when a uniform liquid is carefully expanded beyond its point of stability.

Solution As was pointed out in Section 5.10, the equilibrium between two simple phases requires that three conditions be fulfilled. The two phases must have equal pressures, temperatures, and affinities. Since we are discussing gas and liquid isotherms at the same temperature T_0 , the temperature equality condition is satisfied trivially. The pressure equality condition simply means that the two-phase line must be drawn horizontally, which we have already noted. It does not tell us where it must be drawn. It is the condition that $\alpha_L = \alpha_G$ that determines the exact position of the phase transition. As we move down the liquid isotherm toward lower-density states, the affinity for particles steadily increases. Conversely, as we move up the gas isotherm toward higher-density states the affinity falls. At some pressure the affinities of the gas and liquid phases are equal. That is the location of the horizontal phase transition line.

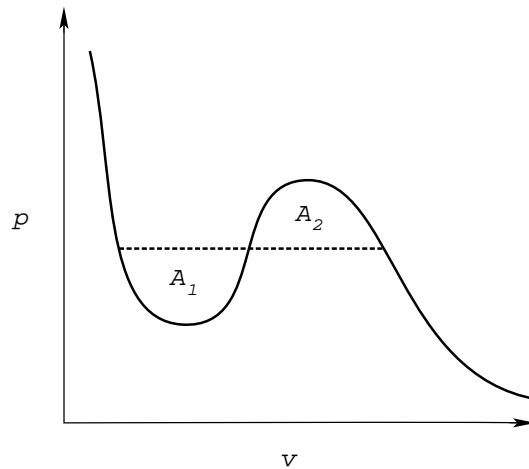


Fig. S5.10 Maxwell’s rule is that the horizontal portion of the isotherm should be drawn so that $A_1 = A_2$.

Exercise 5.19 Because it exhibits isotherms with positive slope in the p - v plane, the Berthelot equation, discussed in Exercise 5.17, cannot possibly describe the equilibrium states of a substance for all values of p and v . Maxwell devised an argument that allows one to analyze liquid–gas phase transitions using empirical equations of state such as the Berthelot equation. It must be emphasized that Maxwell’s scheme is an approximate method, not a true fundamental theory of phase transitions. Maxwell assumed that there is a two-phase region in which the isotherms are horizontal and that within that region the empirical equation of state is not valid. This assumption is certainly true. The essential approximation of Maxwell’s method is the assumption that the single empirical equation of state *is* valid everywhere outside the two-phase region. Show that Maxwell’s assumption implies that the horizontal portion of the isotherm satisfies the geometrical condition $A_1 = A_2$, where the areas A_1 and A_2 are shown in Fig. S5.10. Hint: Assume that the entropy function associated with the empirical equation of state, although it does not have the proper convexity properties, is at least an extensive function. (Certainly, no empirical equation that led to a nonextensive entropy function would ever be taken seriously.)

Solution In the last exercise we noted that the condition determining the location of the two-phase line is that $\alpha_L = \alpha_G$. But, by Eq. (5.46), along an isotherm

$$d\alpha = -\beta v dp \quad (\text{S5.106})$$

Also, this formula was derived using only the fact that the entropy was extensive. The derivation did not rely on any convexity properties of the entropy. Therefore we can expect this relation to be satisfied by

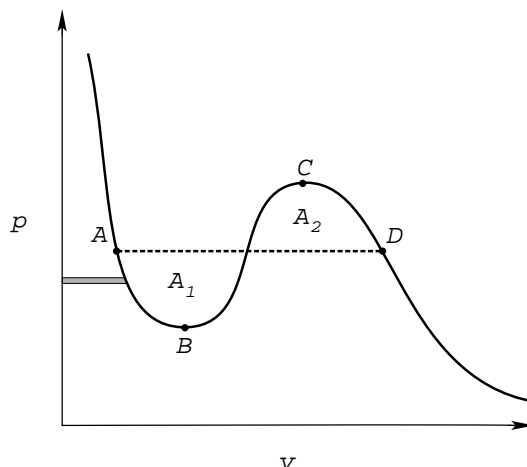


Fig. S5.11 The shaded area is equal to $-v dp$.

the empirical equation, even in the region where that equation does not represent the true properties of the substance. Since β is a constant on the isotherm and $\alpha_L = \alpha_G$ at the limits of the two-phase region, Eq. (S5.106) implies that

$$\beta^{-1} \int_A^D d\alpha = - \int_A^D v dp = 0 \quad (\text{S5.107})$$

(See Fig. S5.11.) But, from A to B , $-v dp$ is a positive number equal to the area element shown in the figure. From B to C , $-v dp$ is negative, and, from C to D , $-v dp$ is again positive. It is easy to see that the full integral is given by

$$- \int_A^D v dp = A_2 - A_1 \quad (\text{S5.108})$$

which gives Maxwell's geometrical construction.

Exercise 5.20 The highest point of the two-phase region in the p - v plane is the liquid-gas critical point. The temperature of the isotherm passing through that point is the critical temperature T_c . The isotherms at higher temperature do not pass through the two-phase region. Therefore, there is no liquid-gas phase transition at temperatures higher than T_c . For a substance describable by the dimensionless Bertholet equation (with the Maxwell construction), determine τ_c .

Solution At the critical point on the critical isotherm both $\partial p / \partial v$ and $\partial^2 p / \partial v^2$ are zero. This gives the following two simultaneous equations for v_c and τ_c .

$$\frac{\partial p}{\partial v} = -\frac{\tau_c}{(v_c - 1)^2} + \frac{2}{\tau_c v_c^3} = 0 \quad (\text{S5.109})$$

and

$$\frac{\partial^2 p}{\partial v^2} = \frac{2\tau_c}{(v_c - 1)^3} - \frac{6}{\tau_c v_c^4} = 0 \quad (\text{S5.110})$$

These can be rewritten as

$$\frac{\tau_c}{(v_c - 1)^2} = \frac{2}{\tau_c v_c^3} \quad (\text{S5.111})$$

and

$$\frac{\tau_c}{(v_c - 1)^3} = \frac{3}{\tau_c v_c^4} \quad (\text{S5.112})$$

Dividing the two sides of the first equation by the corresponding sides of the second gives a linear equation for v_c .

$$v_c - 1 = \frac{2}{3} v_c \quad (\text{S5.113})$$

or $v_c = 3$. Putting this value into Eq. (S5.111) gives

$$\tau_c = \sqrt{8/27} = 0.544 \quad (\text{S5.114})$$

Classical Thermodynamics

Our presentation of thermodynamics has deviated greatly from the traditional one. Its aim has been to bring together, under the title of thermodynamics, all those macroscopic features of systems that appear in the thermodynamic limit and that are not obvious consequences of the laws of mechanics or quantum mechanics. For the benefit of the reader who has not been exposed to a more standard treatment of thermodynamics, the next few exercises will be devoted to a very brief version of the concepts and methods of classical thermodynamics.

In the usual treatment of the subject, the first law of thermodynamics is the statement that heat is a form of energy, or, put differently, that the sum of the heat extracted from a body plus the mechanical work done by the body on any outside systems is equal to the decrease in the body's internal energy. During the period of time when thermodynamics was being developed, the proposition that the well-established but limited law of the conservation of mechanical energy, which was valid only in the absence of friction or other dissipative influences, could be extended into an absolute and universally applicable conservation principle was a daring and far from generally accepted idea. The fact that radiant energy could propagate through space devoid of matter meant that this universal "energy" could not include only the well-understood kinetic and potential energies of mechanics but must contain a radiant energy term. One must remember that, at the time, no electromagnetic theory encompassing radiant energy existed. In fact, the particulate nature of matter was still in serious dispute. However, in this day, when every student has seen photographs of individual atoms, when the general conservation of energy is an established theorem of mechanics, electromagnetics, and quantum theory, to include energy conservation as a physical postulate of thermodynamics, rather than treating it as a theorem of the logically prior subjects of mechanics and quantum mechanics, gives to the subject a peculiarly antique character. It seems, to most students, like a study of the astrolabe or Ptolemaic astronomy. Certainly the Pythagorean theorem is essential to almost any calculation in Newtonian mechanics. But, for good reasons, it is not considered to be a law of mechanics. That theorem, along with all of Euclidean geometry, is assumed as prior knowledge at the very start of an introduction to mechanics. In the same way, even in this "traditional" presentation of thermodynamics, which will be based on the postulates of Clausius and Kelvin, energy conservation will simply be taken as prior assumed knowledge.

We begin by postulating the existence of a large collection of substances, each separately isolated and in internal equilibrium. Our aim is to study what happens when these substances are brought into interaction with one another. The substances will be referred to as objects. It must be kept in mind that, at the start, no temperature scale of any kind has been defined.

Given two objects A and B , we define a *cyclic process* for transferring thermal energy from A to B as any means of doing so that, when it is completed, leaves everything else in the world (except A and B) in its original state. The phrase suggests some sort of cyclic machine that keeps coming back to the same state, and many particular examples are of that form. However, a much more trivial example of a cyclic process is the process of simply putting the objects into contact for a while and then separating them. Using the notion of a cyclic process, we now make an important definition. For any two objects, we say that " A is hotter than B " if any cyclic process exists that can transfer heat energy from A to B .

The central law of classical thermodynamics, in a form due to Rudolf Clausius, can now be given as the seemingly trivial statement: "If A is hotter than B , then B is not hotter than A ." The appearance of triviality is entirely misleading. It might be compared with the apparent triviality of the axioms of Euclid that were carefully constructed so that, by stepwise logical deduction, an edifice of astonishing sophistication could be built upon them. First, let us convince ourselves that Clausius' statement of the second law is actually a strong statement with nonobvious consequences. It says, for instance, that if, when we place objects A and B in contact, heat spontaneously flows from A to B , then it is impossible to construct any device, no matter how ingenious and complicated, that will have the sole effect of transferring energy in the reverse direction (from B to A). The important restriction is expressed by the phrase "sole effect," which means that the device will leave everything else in the world, including itself, unchanged. That the second law is not trivial is well illustrated by a recent personal experience of the author. A few years ago I was shown

a paper that a colleague had been asked to review for a prestigious physics journal. The paper had been submitted to the journal by a professor of physics at a respected American university. It described a device that purported to defeat the second law of thermodynamics by using magnetic fields. The reviewer revealed the flaws in the paper's reasoning and it was finally rejected for publication. But, although a century and a half has passed since the wide dissemination of the second law of thermodynamics, a steady stream of papers, mostly by clearly incompetent authors, that describe devices or processes in violation of the second law, are still submitted to scientific journals. Einstein expressed a widely held view of the second law of thermodynamics when he said that, of all the fundamental laws of physics, it is probably the one that has the most secure foundation. The reasoning behind this view is that, since it is really an expression of the law of large numbers, it has the character of a mathematical theorem rather than an empirically derived physical law that might have to be modified in the light of more careful experiments in the future.*

The basic arguments, beginning from the second law and leading to the definition of temperature and entropy, will be given as a series of exercises.

Exercise 5.21 Prove that, for any three objects, the statements “ A is hotter than B ” and “ B is hotter than C ” imply that A is hotter than C .

Solution The proof is relatively trivial. If A is hotter than B , then a quantity of heat ΔQ can be transferred by a cyclic process from A to B . But, because B is hotter than C , that same quantity of heat could then be transferred from B to C . Since B is left in its initial state, the net effect is a cyclic process that has transferred heat from A to C .

Given two objects, A hotter than B , a *heat engine* operating between A and B is any device that absorbs an amount of heat energy ΔQ_A from A , uses some of the energy to do mechanical work ΔW , and dumps the remaining energy, $\Delta Q_B = \Delta Q_A - \Delta W$, into object B . It is convenient to picture the mechanical work as simply the lifting of a weight in a gravitational field. The fact that we have assumed that $\Delta Q_A = \Delta Q_B + \Delta W$ means that we have neglected friction or other dissipative processes within the heat engine. Therefore, it is somewhat of an idealized device. However, there is no fundamental limit to how close we can come to an ideal heat engine and it is such a useful concept that we will simply ignore all the technical complications that would occur if we restricted ourselves to truly realizable processes. A special category of heat engines are *reversible engines*. These are heat engines that can be operated in both directions. That is, by absorbing the heat energy ΔQ_B from the colder object and adding to it the mechanical work ΔW , it can transmit the heat energy $Q_A = Q_B + \Delta W$ to the hotter object. In this analysis we will just postulate the existence of these idealized reversible engines. In previous exercises we have shown that, ignoring internal friction, and using slow quasistatic processes, it is possible to construct such reversible engines.

Exercise 5.22 Given any heat engine operating between two objects, A hotter than B , we define the *efficiency ratio* of the heat engine as $R(A, B) = \Delta Q_A / Q_B$. (Note that this is not the definition of the *efficiency* used in Exercise 5.14.) A heat engine that could convert all the heat energy Q_A into work would have an efficiency ratio of infinity, something that we will show is impossible. Using the second law, prove that all reversible engines operating between the same two objects have the same efficiency ratio.

Solution Suppose that two reversible heat engines, operating between objects A and B , have efficiency ratios $R(A, B)$ and $R'(A, B)$ with $R' < R$ (Fig. S5.12). We run the first one in the forward direction, extracting heat energy Q_A from A , storing mechanical energy ΔW , and dumping heat energy Q_B into B . We now use the stored energy ΔW to run the second heat engine in reverse, absorbing heat energy Q'_B from

* However, no law devised by man is ever completely secure. One of the predictions of Einstein's own theory of general relativity is the existence of black holes. When a chunk of matter falls into a black hole, the matter, along with all its degrees of freedom and possible quantum states, effectively disappears from the universe, taking some entropy with it. There is a corresponding increase in the radius of the black hole. In the presence of black holes, the law of increase of entropy must be modified so that it is the thermodynamic entropy plus some constant times the sum of the radii of all the black holes that must increase. Without a foundation in general relativity, we will have to ignore such, somewhat speculative, modern developments in thermodynamics.

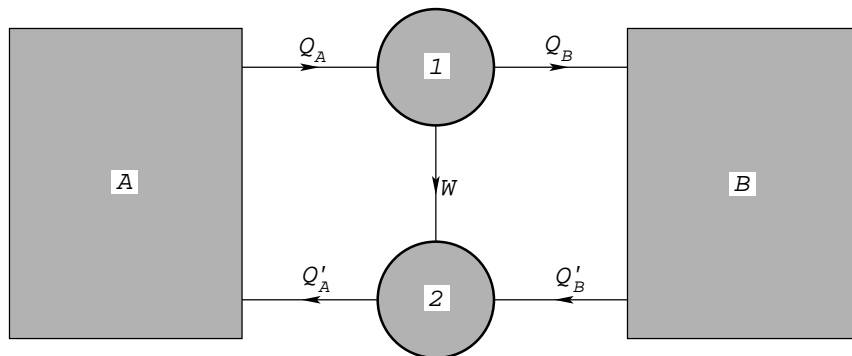


Fig. S5.12 If the efficiency ratios of the two reversible heat engines are not equal, then it is possible to use the pair of engines to transfer heat from a cooler to a hotter body.

B and transmitting heat energy Q'_A into A . By conservation of energy,

$$\Delta W = Q_A - Q_B = Q'_A - Q'_B \quad (\text{S5.115})$$

But $Q_A = RQ_B$ and $Q'_A = R'Q'_B$, which says that

$$(R - 1)Q_B = (R' - 1)Q'_B \quad (\text{S5.116})$$

or

$$Q'_B = \frac{R - 1}{R' - 1} Q_B > Q_B \quad (\text{S5.117})$$

Thus the net effect has been to extract heat energy $Q'_B - Q_B$ from the colder object. Since no net work has been done, that heat energy must have been transferred to the hotter object, in violation of the second law. Therefore, all reversible heat engines operating between two given bodies have the same value of Q_A/Q_B .

Exercise 5.23 Given any three objects, with A hotter than B hotter than C , prove that

$$R(A, B)R(B, C) = R(A, C) \quad (\text{S5.118})$$

Solution The argument needed is very similar to the one used in Exercise 5.20. We run a reversible engine between A and B in the forward direction, extracting heat Q_A from A and dumping heat Q_B into B . We then run a reversible engine between B and C , extracting the heat Q_B from B (which leaves B in its original state) and dumping heat Q_C into C . But the combination of the two processes constitutes a reversible heat engine between A and C with an efficiency ratio

$$\frac{Q_A}{Q_C} = \frac{Q_A}{Q_B} \frac{Q_B}{Q_C} \quad (\text{S5.119})$$

Exercise 5.24 The notion of “hotter” has been defined, but we still have no numerical scale of hotness. However, the result of the previous exercise provides a simple method of defining a convenient temperature scale that does not depend on the properties of any particular substance. A temperature scale is a set of numbers, assigned, one to each object, so that $T_A > T_B$ means that A is hotter than B . The thermodynamic temperature scale is defined in two steps. (a) We first declare that, given any two objects A and B , the ratio of their temperatures is just their efficiency ratio. That is

$$\frac{T_A}{T_B} = R(A, B) = \frac{Q_A}{Q_B} \quad (\text{S5.120})$$

This allows the temperature ratio of any two objects to be measured by running any reversible engine between them. The result of the previous exercise guarantees that the ratios so obtained are mathematically consistent. That is, that

$$\frac{T_A}{T_B} \frac{T_B}{T_C} = \frac{T_A}{T_C} \quad (\text{S5.121})$$

(b) The second step is completely trivial. We simply choose some convenient object, say O , and assign to it an arbitrary positive number T_o as its temperature.

Knowing one temperature and all ratios is obviously enough to assign temperatures to every object. Because a reversible engine always extracts more heat from the hotter reservoir than it delivers to the colder (or else the second law could easily be violated), we are assured that $T_A > T_B$ implies that A is hotter than B .

Exercise 5.25 There is another formulation of the second law, due to Kelvin. It postulates that it is impossible to construct any device whose sole effect would be to absorb heat energy from an object and convert it completely into mechanical work, such as lifting a weight. It is always possible to convert stored mechanical energy into the internal thermal energy of any chosen object. For example, one can use the mechanical energy to generate an electrical current through the object that will increase the object's thermal energy no matter how hot it was initially. Use this fact to show that the Kelvin and Clausius statements of the second law are logically equivalent.

Solution Assume that Kelvin's law is false. Then we can construct an engine that will absorb an amount of heat Q from an object and use it to lift a weight, increasing its potential energy by an amount $\Delta W = Q$. But then we can take that mechanical energy and use it to heat up an object that is hotter than the original one. Thus the falsity of Kelvin's law implies the falsity of Clausius' law.

Now assume that Clausius' law is false. Then we can transfer heat Q from a colder to a hotter object. But, by running a reversible engine in the forward direction between the two objects, we could store up mechanical energy while removing from the hotter object the heat Q that had been transferred to it. The net result of the process would be to absorb heat from the colder body and convert it entirely into mechanical work. Thus the falsity of Clausius' law implies the falsity of Kelvin's law. Either both are true or both are false. That is the definition of logical equivalence.

The most remarkable discovery of Clausius was that *reversible* processes conserve a completely new physical property that he called the *entropy*. Since, at the time, there was not the slightest hint of the role played by probability and statistics in macroscopic phenomena, the discovery and precise definition of entropy by purely macroscopic, mechanical arguments was a work of tremendous genius. It was only many years later that Ludwig Boltzmann discovered the probabilistic meaning of the thermodynamic entropy.

Exercise 5.26 We now want to define the entropy and to show that it is conserved by reversible processes and increased by irreversible ones. Like the potential energy, the entropy of any object is only defined within an arbitrary additive constant. Therefore, beginning with all our objects in some particular equilibrium states, we assign to each an arbitrary entropy, S_{oA}, S_{oB}, \dots , for that particular state. Now, if the object has a temperature T and it absorbs an amount of heat Q , then, by definition, its entropy changes by an amount $\Delta S = Q/T$. (a) Show that reversible processes conserve the total entropy of the system. (b) Show that the total entropy is not a conserved quantity by showing that it can be increased by cyclic but irreversible processes. (c) Show that no cyclic process can lower the total entropy.

Solution (a) Let us run a reversible engine in the forward direction (the same result can be obtained by running it in the reverse direction) between two arbitrary objects, A and B , at temperatures T_A and T_B , with $T_A > T_B$. Then the heat extracted from A , namely Q_A , is related to the heat transmitted to B by

$$\frac{Q_A}{Q_B} = \frac{T_A}{T_B} \quad (\text{S5.122})$$

or

$$\frac{Q_A}{T_A} = \frac{Q_B}{T_B} \quad (\text{S5.123})$$

Since heat is extracted from A and added to B , $\Delta S_A = -\Delta Q_A/T_A$ and $\Delta S_B = Q_B/T_B$. Thus

$$\Delta S_A + \Delta S_B = 0 \quad (\text{S5.124})$$

(b) Transferring heat by means of a reversible engine is not a cyclic process because the engine stores mechanical energy and therefore does not come back to its initial state. Suppose we transfer heat by a cyclic

process from A to B (recall that the simplest cyclic process is just putting A and B in thermal contact for a while). In a cyclic process the heat lost by A must all be gained by B . Thus $Q_A = Q_B$. Then

$$\Delta S_A + \Delta S_B = Q_A \left(\frac{1}{T_B} - \frac{1}{T_A} \right) > 0 \quad (\text{S5.125})$$

(c) We will consider a cyclic process involving three objects, A , B , and C , but it should be clear that the same analysis could be extended to any number of objects. Let Q_A be the heat energy added to or extracted from object A . If Q_A is positive, then heat has been added to A . If it is negative, then heat has been extracted. Since the process is cyclic,

$$Q_A + Q_B + Q_C = 0 \quad (\text{S5.126})$$

Now we assume that the process has lowered the total entropy. Then

$$\frac{Q_A}{T_A} + \frac{Q_B}{T_B} + \frac{Q_C}{T_C} < 0 \quad (\text{S5.127})$$

We now run a reversible engine between B and C that makes a change $-Q_C$ in the energy of C and a change Q'_B in B . Because it is reversible

$$\frac{Q'_B}{T_B} - \frac{Q_C}{T_C} = 0 \quad (\text{S5.128})$$

This reversible process has either stored or used up some mechanical work. The net effect has been to leave C in its original state. Since the reversible process makes no change in the entropy, the net process gives an entropy change

$$\frac{Q_A}{T_A} + \frac{Q_B + Q'_B}{T_B} < 0 \quad (\text{S5.129})$$

We now run a reversible engine between A and B that absorbs an amount of heat $Q_B + Q'_B$ from B and transmits an amount of heat $\Delta Q'_A$ to A . Again

$$\frac{Q'_A}{T_A} - \frac{Q_B + Q'_B}{T_B} = 0 \quad (\text{S5.130})$$

Now B and C are in their original states. The total entropy change of the system is

$$\frac{Q_A + Q'_A}{T_A} < 0 \quad (\text{S5.131})$$

But T_A is a positive number. Thus the total change in the thermal energy of A is

$$Q_A + Q'_A < 0 \quad (\text{S5.132})$$

Thermal energy has been extracted from A and must therefore be stored as mechanical work in the reversible engines used in the last two stages. This violates Kelvin's law.

Certainly this set of exercises does not constitute a complete and adequate treatment of classical thermodynamics. They have been intended only to show the style of the subject and to demonstrate the ingenious arguments constructed by the early thermodynamicists in bridging the gap between the impossibility postulates, expressed in words, and a detailed mathematical structure that could be used to analyze and predict the properties of real substances and devices.