

Chapter 20

Entropy and the Second Law of Thermodynamics

First Edition

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Preface

The first law of thermodynamics is powerful but incomplete. It tells us how energy is conserved and transferred, yet it does not tell us which energy-conserving processes occur spontaneously, which ideal limits cannot be exceeded, or why a hot body cools beside a cold one while the formal reverse is not observed without additional intervention. This chapter introduces the second law of thermodynamics through the state function entropy and develops it as a quantitative feasibility test.

The chapter is written for calculus-based technical and engineering students. The core route begins with direction and reversibility, defines entropy through reversible comparison paths, develops entropy balances for finite systems and thermal contact, and then applies the second law to engines, refrigerators and heat pumps. A constrained statistical model connects entropy with multiplicity without treating the vague word “disorder” as a definition. The advanced pathway then asks a design-oriented question: how much work opportunity is destroyed when two finite bodies are allowed to equilibrate irreversibly rather than through an ideal reversible engine?

All numerical examples use stated idealisations. Values identified as model parameters or synthetic teaching data are not claims about a particular laboratory apparatus or commercial device. The scientific figures are original editorial diagrams or plots generated directly from the equations in this source. Standard references inform the sequence and cross-checking, but the explanations, examples, exercises and figures are prepared for this book.

The Guideline

Treat every second-law problem as a system-definition problem before treating it as an algebra problem. Identify the system, its surroundings, the boundary temperatures at which heat crosses, and whether the relevant process is cyclic, reversible, adiabatic or isolated. Then perform the energy and entropy accounts separately.

Conventions and notation

Temperatures that appear inside logarithms, reciprocal temperatures, Carnot ratios or coefficients of performance are absolute temperatures in kelvin. Heat and work are transfers, not properties stored in a system. In general equations, signed heat Q is positive when transferred into the system and work W_{by} is positive when done by the system. In the engine and refrigerator sections, however, Q_H , Q_C , W_{out} and W_{in} are explicitly defined as positive magnitudes; arrow directions carry the transfer directions.

Symbol	Meaning	SI unit
S	entropy	J K^{-1}
ΔS	entropy change between equilibrium states	J K^{-1}
S_{gen}	entropy generated by irreversibility	J K^{-1}
T	absolute thermodynamic temperature	K
Q_H, Q_C	positive heat magnitudes at hot and cold sides	J
$W_{\text{out}}, W_{\text{in}}$	positive work output/input magnitudes	J
η	thermal efficiency	1
$\text{COP}_R, \text{COP}_{HP}$	refrigerator / heat-pump coefficient of performance	1
k_B	Boltzmann constant, 1.380649×10^{-23} exactly in SI	J K^{-1}
R	molar gas constant, used here as $8.314462618 \text{ J mol}^{-1}\text{K}^{-1}$	$\text{J mol}^{-1}\text{K}^{-1}$
Ω	multiplicity of a specified macrostate	1

A reversible process is an ideal limiting process that can be undone while restoring both system and surroundings with no net change elsewhere. A quasi-static process is only one that proceeds through states arbitrarily close to equilibrium; friction, viscosity, diffusion or heat transfer through a finite temperature difference can make such a process irreversible. An adiabatic process has no heat transfer across the chosen boundary. An isolated system exchanges neither energy nor matter with its surroundings. An isentropic process has constant entropy; adiabatic and isentropic are not synonyms unless the additional reversibility conditions are satisfied.

Note

The statistical expression $S = k_B \ln \Omega$ is used only for a specified set of accessible, equiprobable microstates. The core thermodynamic definition of entropy does not require microscopic counting.

Chapter 20

Entropy and the Second Law of Thermodynamics

20.1 Direction of processes and reversibility

A rigid insulated enclosure contains two bodies, one warm and one cool. If a small amount of energy is transferred from the warm body to the cool body, the total energy of the pair is unchanged. If the same amount is transferred in the formal reverse direction, the total energy is also unchanged. Energy conservation therefore cannot, by itself, distinguish the observed spontaneous process from its unobserved reverse.

That limitation is the doorway to the second law. The second law is not a correction to energy conservation; it is an additional statement about direction, feasibility and ideal performance. It tells us why some energy-compatible transformations occur spontaneously and why others require compensating changes elsewhere.

Learning goals

After studying the core of this chapter, you should be able to:

- distinguish energy conservation from second-law feasibility;
- calculate entropy changes with a reversible comparison path even when the actual process is irreversible;
- separate entropy transfer across a boundary from entropy generation inside a process;
- apply entropy balances to isolated systems, heat engines, refrigerators and heat pumps;
- derive and use Carnot efficiency and reversible COP bounds with absolute temperatures;
- interpret $S = k_B \ln \Omega$ for a specified set of equiprobable microstates without using “disorder” as a definition;
- quantify selected finite-reservoir and lost-work limits in the advanced pathway.

20.1.1 Energy-compatible processes can have different directions

Suppose two ideal reservoirs have temperatures $T_H > T_C$. A heat amount $Q > 0$ moved from hot to cold decreases the hot reservoir energy by Q and increases the cold reservoir energy by Q . The first-law residual for the combined system is zero. Reversing the arrow gives another zero energy residual. The missing information is a directional criterion.

20.1.2 Reversible and irreversible processes

A process is *reversible* in the thermodynamic sense when both the system and its surroundings can be restored to their initial states with no net change elsewhere. This definition is stronger than “slow.” A quasi-static piston motion can still be irreversible if friction dissipates mechanical energy.

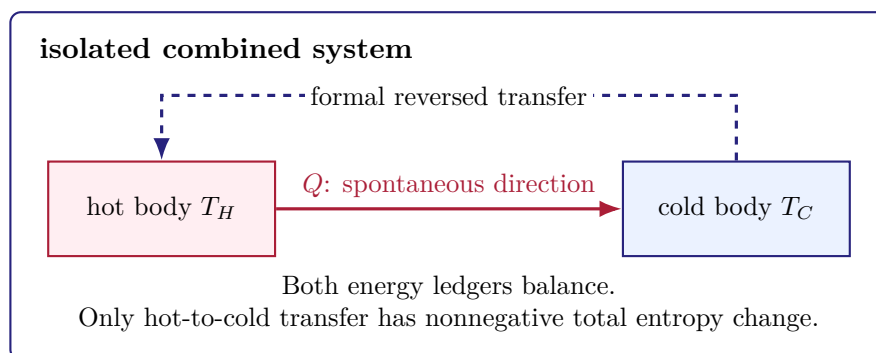


Figure 20.1: Two energy-compatible transfer directions between bodies initially at different absolute temperatures. The outer boundary excludes heat, work and mass transfer. Arrows are schematic; the reverse requires compensating changes outside this proposed isolated process.

Heat transfer across a finite temperature difference is irreversible even when it is steady. Mixing, viscous flow, electrical resistance and free expansion are further familiar sources of irreversibility.

A reversible model is an ideal limiting construction. It is valuable because it supplies a benchmark and, as we shall see, a path along which entropy changes can be calculated. Real processes may approach a reversible limit in some respects, but finite gradients and dissipation produce entropy.

Pedagogical boundary

Do not equate *reversible* with *slow*. Slowness can suppress some departures from equilibrium, but a slowly sliding piston with friction still generates entropy. Conversely, a “reversible path” in an entropy calculation is often a mathematical comparison path between the same equilibrium endpoints, not the path followed by the actual process.

20.1.3 A reversal test includes the surroundings

Restoring the system’s visible configuration is not enough to establish reversibility. A gas that expanded into a larger volume can be compressed to its original volume, but the compressor receives work and heat may have to leave the gas. If a room warms or a work-storage device loses energy during this restoration, the complete initial situation has not been recovered. The second-law restriction concerns those additional effects as well as the gas’s own endpoint.

A useful work-storage model is a weight lifted or lowered by an ideal shaft. Its height records mechanical energy, with no thermal entropy transfer attributed to this idealized work store. During a reversible piston expansion, a slightly smaller external pressure permits the gas to lift the weight. Infinitesimally increasing the external pressure can reverse the piston motion, returning the weight and gas through the same equilibrium states. This mechanical reversibility also requires thermal contacts with vanishing temperature differences and negligible friction.

By contrast, friction requires a finite pressure imbalance whose sign changes when motion reverses. Part of the work is converted into internal energy on both the forward and return strokes. Moving the piston arbitrarily slowly does not remove that finite frictional work. Returning the piston to its starting position consequently leaves changes in the thermal surroundings or the work store. This is why the qualifier “quasi-static” addresses proximity to equilibrium but does not settle the reversal test.

These models give a concrete checklist: identify the working system, the thermal contacts, the mechanical work store and any dissipative interfaces. Determine whether all of them can be restored together. The entropy balances below replace this qualitative restoration test with a quantitative account of the irreversible contribution.

Example 20.1: E20-01: Direction before calculation

A small amount of energy, 120 J, is to be transferred between reservoirs at 360 K and 300 K inside an isolated enclosure. Which direction is spontaneous?

Reasoning. The first law cannot choose the direction because either transfer can conserve the total energy of the two-reservoir system. The observed spontaneous direction is from 360 K to 300 K. Reversing the transfer requires a refrigerator supplied with external work, or another compensating change. We will quantify this direction after introducing entropy and its balance; energy conservation alone cannot select it.

Guided checks

Check 1. Does a process become reversible merely because it conserves energy? **No.** Frictional heating conserves total energy while preventing restoration of system and surroundings without compensating changes.

Check 2. Can an irreversible process connect two equilibrium endpoints? **Yes.** The intermediate states need not be equilibrium states.

Check 3. Is a quasi-static process necessarily reversible? **No.** A slowly sliding piston can remain near mechanical equilibrium while friction converts useful mechanical work into internal energy and generates entropy.

20.2 Entropy as a state function

20.2.1 Definition through a reversible comparison path

Entropy S is a state function. The entropy difference between two equilibrium states is independent of the path used to connect them. A convenient operational definition is

$$\Delta S = S_f - S_i = \int_i^f \frac{\delta Q_{\text{rev}}}{T}, \quad (20.1)$$

where the integral is evaluated along *any reversible path* connecting the same initial and final equilibrium states. The subscript “rev” belongs to the comparison path. It does not assert that the actual process was reversible.

The symbol δQ reminds us that heat is a process transfer, not a state function stored in the system. By contrast, dS is the differential of a state function. If a reversible path is isothermal at temperature T ,

$$\Delta S = \frac{Q_{\text{rev}}}{T}. \quad (20.2)$$

The temperature must be absolute.

Definition 20.1: Entropy change

For two equilibrium states i and f , the entropy change is the reversible-path integral in Eq. (20.1). Different reversible comparison paths give the same ΔS because entropy is a state function.

20.2.2 Why reversible heat divided by temperature defines a property

The distinction between δQ and dS deserves more than a notation rule. A differential of a state function has a special test: its integral around any closed path is zero. Returning to the initial equilibrium state restores the initial value of every property, including entropy. Heat need not have

this property. A cyclic engine returns to its initial state while receiving a nonzero net heat transfer and delivering the same net energy as work. Thus a heat transfer cannot be determined by the initial and final states alone.

Why, then, does division by temperature give a state-function differential for a reversible process? The physical foundation is the reversible heat-engine comparison. The absolute thermodynamic temperature scale can be defined so that a reversible engine exchanging heat magnitudes Q_H and Q_C between two reservoirs obeys $Q_H/Q_C = T_H/T_C$. This result concerns a reversible cyclic machine and its reservoirs; it does not assume an ideal-gas working substance. The Carnot section will develop its performance meaning. Here it supplies the connection between temperature and heat exchange needed to establish entropy as a property.

Imagine dividing a reversible cycle into sufficiently small heat exchanges at temperatures T_j . For each exchange, couple a reversible auxiliary machine between T_j and one common reference reservoir at T_0 . Arrange the auxiliary machine to supply exactly the heat δQ_j that the original system receives at that contact. It then receives heat $T_0\delta Q_j/T_j$ from the reference reservoir, with the same signed convention. Negative δQ_j simply reverses the relevant auxiliary operation. At the end, the original working substance and every auxiliary machine have completed cycles. All contact exchanges at T_j cancel within the combined arrangement.

Only a net heat exchange with the single reference reservoir and a net work transfer remain. The Kelvin–Planck restriction excludes positive work obtained solely by taking heat from this one reservoir. Consequently, for an arbitrary cyclic process with properly defined contact temperatures,

$$\oint \frac{\delta Q}{T_b} \leq 0. \quad (20.3)$$

For a reversible cycle the entire construction may also be reversed. Reversal changes the sign of the integral, so the inequality can hold in both directions only if

$$\oint \frac{\delta Q_{\text{rev}}}{T} = 0. \quad (20.4)$$

This is the Clausius cycle result. It is an operational consequence of the second law, rather than an extra claim that heat itself is a property.

Now take two reversible paths A and B from the same state i to the same state f . Traversing A forward and B backward creates a reversible closed path. Equation (20.4) gives

$$\int_A \frac{\delta Q_{\text{rev}}}{T} - \int_B \frac{\delta Q_{\text{rev}}}{T} = 0.$$

The two path integrals are therefore equal. We can assign a property difference $S_f - S_i$ to their common value. This argument also shows why a comparison path must be reversible: dividing the actual heat by a convenient temperature on an irreversible path does not generally reproduce the state-function difference. Entropy generation supplies the missing contribution.

The cycle inequality uses temperatures at the thermal contacts. During a strongly nonequilibrium process, one uniform “temperature of the system” may not exist. It would be unjustified to insert such a temperature into the integrand. The endpoint entropy difference remains meaningful when the initial and final states are equilibrium states, and it can still be calculated using an entirely separate reversible route. The route is a calculation device, while the entropy balance describes the actual process.

20.2.3 Free expansion: an irreversible process with a calculable entropy change

Consider an ideal gas initially confined to one side of a rigid, insulated container while the other side is evacuated. Removing the partition produces a free expansion. During the actual process,

$Q = 0$ because the walls are insulated, and $W_{\text{by}} = 0$ because the gas expands against vacuum. For an ideal gas, internal energy depends only on temperature, so $\Delta E_{\text{int}} = 0$ implies $T_f = T_i$. Yet the gas does not spontaneously return to its original smaller volume. The process is irreversible.

We cannot evaluate Eq. (20.1) by inserting the actual $Q = 0$ into δQ_{rev} . Instead, choose a reversible isothermal expansion between the same endpoints. For n moles of ideal gas,

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right). \quad (20.5)$$

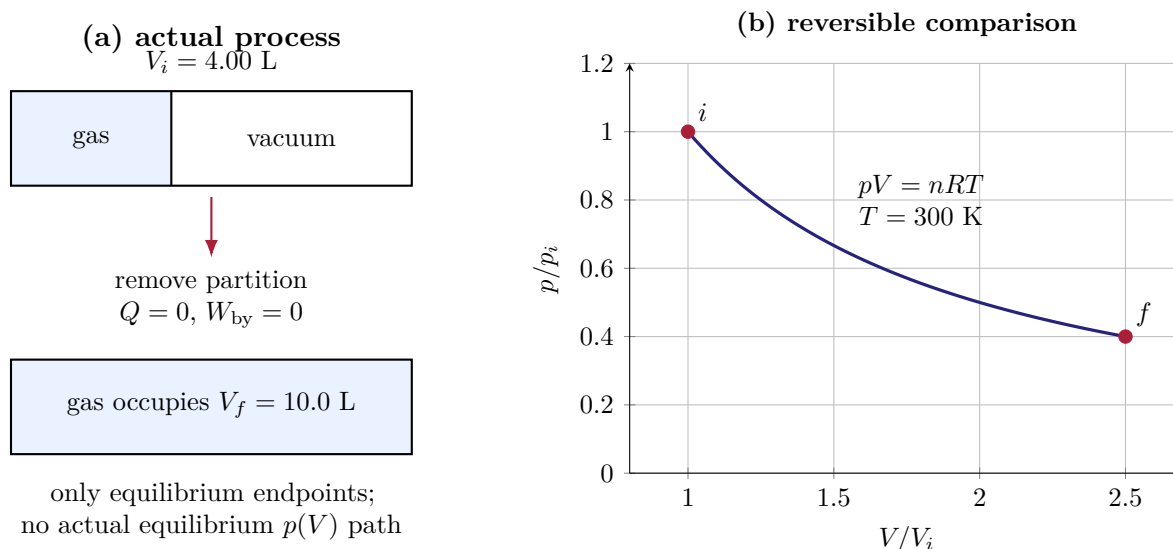


Figure 20.2: Free expansion and a separate reversible path for the same ideal-gas endpoints, $V_f/V_i = 2.5$. The initial occupied fraction in (a) is 0.40. The isotherm in (b) is a comparison used to evaluate ΔS ; its heat and work are not transfers in the actual expansion.

Example 20.2: E20-02: Free expansion and its reversible comparison

One mole of ideal gas expands freely in an insulated rigid container from 4.00 L to 10.0 L. The initial temperature is 300 K. Find the entropy change and the heat that would be absorbed along a reversible isothermal comparison path.

Actual process. $Q = 0$, $W_{\text{by}} = 0$, hence $\Delta E_{\text{int}} = 0$. For the ideal-gas model $T_f = T_i = 300 \text{ K}$.
Entropy change.

$$\Delta S = R \ln(10.0/4.00) = 7.62 \text{ J K}^{-1}.$$

Comparison-path heat.

$$Q_{\text{rev}} = T\Delta S = (300)(7.618 \dots) = 2.29 \text{ kJ}.$$

The 2.29 kJ is not heat transferred in the actual free expansion. It is the heat transfer on a reversible comparison path used to calculate the same state-function change.

20.2.4 Deriving the ideal-gas entropy change through two reversible legs

Free expansion supplies a striking special case, but a general ideal-gas change may alter both temperature and volume. Assume a fixed amount n of ideal gas, a temperature range in which its molar heat capacity $C_{V,m}$ is constant, and equilibrium endpoints (T_i, V_i) and (T_f, V_f) . The intermediate states of the actual process need not be specified. Construct a reversible route with two legs: first change temperature at fixed V_i , then change volume isothermally at T_f .

On the first leg, a rigid boundary does no expansion work. The first law and ideal-gas internal energy give $\delta Q_{\text{rev}} = dE_{\text{int}} = nC_{V,m}dT$. Reversibility requires a sequence of reservoirs whose temperatures differ infinitesimally from the gas temperature. One reservoir at the final temperature would produce a finite thermal gradient and would not be this comparison path. Integration gives

$$\Delta S_{i \rightarrow a} = nC_{V,m} \int_{T_i}^{T_f} \frac{dT}{T} = nC_{V,m} \ln \frac{T_f}{T_i}.$$

On the second leg, ideal-gas internal energy is constant because temperature is constant. A frictionless quasi-static piston allows work $\delta W_{\text{by}} = pdV$ with $p = nRT_f/V$. The heat absorbed equals that work, hence

$$\Delta S_{a \rightarrow f} = \int_{V_i}^{V_f} \frac{pdV}{T_f} = nR \int_{V_i}^{V_f} \frac{dV}{V} = nR \ln \frac{V_f}{V_i}.$$

Adding the legs yields Eq. (20.10). If either endpoint ratio is below one, its logarithmic contribution is negative. Heating tends to raise entropy at fixed volume, and expansion tends to raise it at fixed temperature; cooling or compression reverses the respective contribution. When both effects occur, their sum determines the sign.

A different route first changes volume at T_i and then changes temperature at V_f . The temperature and volume integrals have the same endpoint limits, so this route gives the same total entropy change. Its work and heat are generally different. Figure 20.3 makes that distinction visible: the area under the hot isotherm exceeds the area under the cool isotherm even though the two routes have the same initial and final states. Path independence applies to the entropy change, not to heat or work.

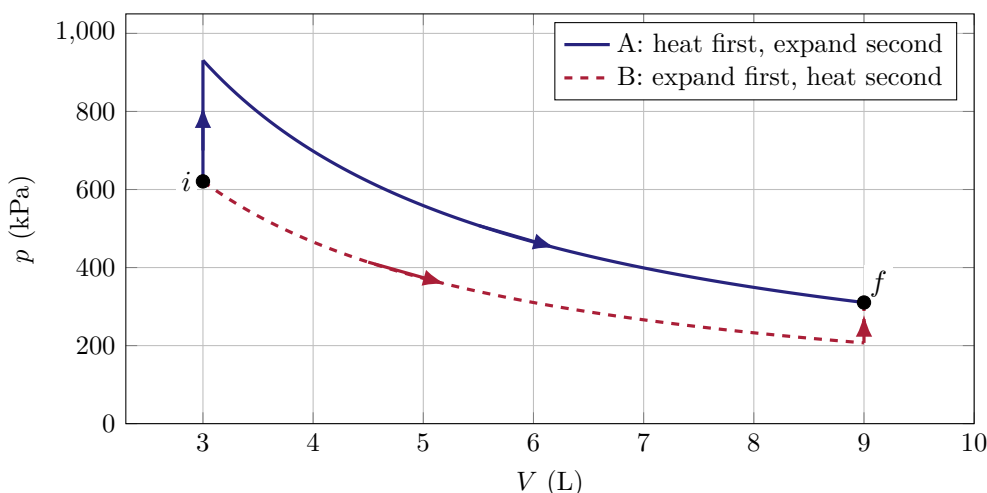


Figure 20.3: Two reversible comparison routes for Example 20.3. The vertical legs do no volume work; the curved legs have different work areas. Both routes give the same entropy difference.

Example 20.3: E20-10: Same entropy change, different heat and work

A stipulated ideal diatomic gas contains $n = 0.800$ mol with $C_{V,m} = 5R/2$ and $C_{P,m} = 7R/2$ throughout the calculation. It changes from $T_i = 280$ K, $V_i = 3.00$ L to $T_f = 420$ K, $V_f = 9.00$ L. Use the routes drawn in Figure 20.3 to calculate the entropy change, the work done by the gas and the heat absorbed on each route. Check the entropy result using pressure.

System and strategy. The gas is closed. Each comparison route consists of a reversible isochore and a reversible isotherm. The constant heat capacities are a stated teaching model, rather than a prediction for every molecular species or temperature interval. Entropy is evaluated separately on the legs; work follows from the p - V area, and heat follows from the

first law.

Endpoint pressures. With volume expressed in litres, nRT/V has the numerical unit kilopascal because $1 \text{ kPa L} = 1 \text{ J}$:

$$p_i = \frac{(0.800)R(280)}{3.00} = 620.81 \text{ kPa}, \quad p_f = \frac{(0.800)R(420)}{9.00} = 310.41 \text{ kPa}.$$

The pressure halves even though temperature rises: the threefold volume increase outweighs the factor 1.5 temperature increase.

Entropy. Both routes give

$$\begin{aligned} \Delta S &= (0.800) \frac{5R}{2} \ln(1.5) + (0.800)R \ln 3 \\ &= 6.74245 + 7.30750 = 14.04995 \text{ J K}^{-1}. \end{aligned}$$

The thermal and volume contributions are both positive. Their division between individual legs depends on which route is drawn, but their total does not.

Route A. Isochoric heating does no volume work. Expansion at 420 K gives

$$W_A = nRT_f \ln(V_f/V_i) = 3.06915 \text{ kJ}.$$

The internal-energy change is

$$\Delta E_{\text{int}} = nC_{V,m}(T_f - T_i) = 2.32805 \text{ kJ}.$$

Therefore $Q_A = \Delta E_{\text{int}} + W_A = 5.39720 \text{ kJ}$.

Route B. Expansion at 280 K gives

$$W_B = nRT_i \ln(V_f/V_i) = 2.04610 \text{ kJ}, \quad Q_B = \Delta E_{\text{int}} + W_B = 4.37415 \text{ kJ}.$$

The larger work along A is visible in the higher isotherm. The heat difference $Q_A - Q_B = 1.02305 \text{ kJ}$ equals the work difference because the internal-energy change is identical.

Independent representation check. Since $p_f/p_i = 1/2$,

$$nC_{P,m} \ln \frac{T_f}{T_i} - nR \ln \frac{p_f}{p_i} = (0.800) \frac{7R}{2} \ln 1.5 - (0.800)R \ln 0.5 = 14.04995 \text{ J K}^{-1}.$$

This reproduces the temperature–volume result. The equality checks the ideal-gas endpoint relation as well as the entropy algebra. It does not say that Q_A/T_f or Q_B/T_i equals the complete entropy change: each full route contains a heating leg with varying temperature.

20.2.5 Pressure form, exact differentials, and entropy contours

For a fixed amount of ideal gas, $V = nRT/p$ implies

$$\ln \frac{V_f}{V_i} = \ln \frac{T_f}{T_i} - \ln \frac{p_f}{p_i}.$$

Using $C_{P,m} - C_{V,m} = R$ in the temperature–volume formula therefore gives

$$\Delta S = nC_{P,m} \ln \frac{T_f}{T_i} - nR \ln \frac{p_f}{p_i}. \quad (20.6)$$

Constant-pressure heating has $\Delta S = nC_{P,m} \ln(T_f/T_i)$, whereas constant-volume heating has $\Delta S = nC_{V,m} \ln(T_f/T_i)$. These values differ for the same initial temperature and final temperature because

the final volumes and pressures differ. They are not two paths between the same complete equilibrium states. Specifying temperature alone is insufficient to specify an ideal-gas state at fixed n .

The differential derivation gives a local version of the same result. For a reversible ideal-gas change,

$$\delta Q_{\text{rev}} = nC_{V,m}dT + pdV, \quad dS = nC_{V,m}\frac{dT}{T} + nR\frac{dV}{V}.$$

Heat itself is inexact: its coefficient of dV is $p = nRT/V$, which changes with T . After division by T , the coefficient of dT depends only on T , and the coefficient of dV depends only on V . Their cross derivatives are both zero. Thus this expression is an exact differential, consistent with the cycle argument above. If $C_{V,m}$ depends on temperature, replace its logarithmic term by $n \int_{T_i}^{T_f} C_{V,m}(T)dT/T$; no constant heat capacity should be fitted outside its valid range merely to preserve a convenient logarithm.

Figure 20.4 draws constant-entropy-difference curves for the stipulated $C_{V,m}/R = 2.5$ model. Define $v = V/V_i$, $t = T/T_i$ and $\sigma = (S - S_i)/(nR)$. The state relation is $\sigma = 2.5 \ln t + \ln v$, so a contour satisfies $t = \exp(\sigma/2.5)v^{-0.4}$. Each curve is a set of equilibrium states with one entropy value. It need not be a history actually followed by the gas. In particular, an ideal reversible adiabatic path from i follows $\sigma = 0$; an irreversible adiabatic process ends on a contour with $\sigma > 0$.

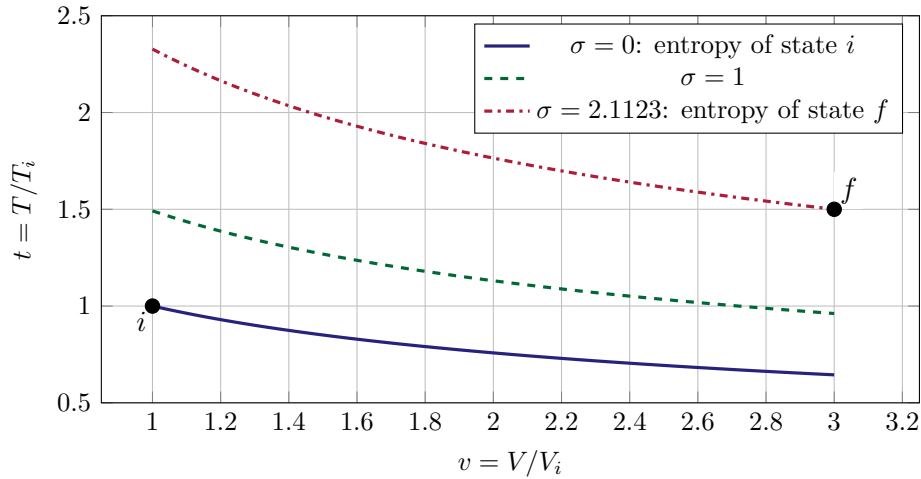


Figure 20.4: Entropy contours for the ideal-gas model in Example 20.3. Moving from the contour through i to the contour through f changes entropy by $nR(2.1123)$, regardless of the comparison route.

Setting $dS = 0$ gives $dT/T = -(R/C_{V,m})dV/V$. For constant capacities, integration recovers $TV^{\gamma-1} = \text{constant}$ with $\gamma = C_{P,m}/C_{V,m}$. This agrees with the reversible adiabatic law developed in the kinetic-theory chapter. Its entropy interpretation exposes the required qualification: an insulated boundary guarantees $Q = 0$, but it does not force $dS = 0$ when dissipation is present.

20.2.6 Useful entropy-change formulas

For a body with constant heat capacity C heated reversibly from T_i to T_f ,

$$\Delta S = C \ln\left(\frac{T_f}{T_i}\right). \quad (20.7)$$

If $C = mc$ with constant specific heat c , replace C by mc . If heat capacity depends on temperature,

$$\Delta S = \int_{T_i}^{T_f} \frac{C(T)}{T} dT. \quad (20.8)$$

For a reversible phase change at coexistence temperature T_{tr} with latent heat magnitude L per unit mass,

$$\Delta S = \frac{mL}{T_{\text{tr}}} \quad (20.9)$$

for the higher-entropy phase produced by absorbing heat; the sign reverses for the reverse transition. For an ideal gas with constant molar heat capacity $C_{V,m}$,

$$\Delta S = nC_{V,m} \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right). \quad (20.10)$$

Equivalent forms can be obtained with $C_{P,m}$ and pressure. Every logarithm contains a dimensionless ratio.

Caution

The shortcut $\Delta S = Q/T$ is valid only when the relevant reversible heat transfer occurs at a single constant temperature. It is not a general formula for an arbitrary irreversible process.

20.2.7 Finite heating and the meaning of a reversible thermal limit

For a body of constant heat capacity C , the logarithm in $\Delta S = C \ln(T_f/T_i)$ follows from adding infinitesimal entropy increments at their own temperatures. It is not an instruction to divide the actual heat by an arbitrary average temperature. With no mechanical work or phase change, the heat required to raise the body temperature is $Q = C(T_f - T_i)$. Along a reversible heating route,

$$\Delta S = \int_{T_i}^{T_f} \frac{CdT}{T}.$$

Since $1/T$ decreases with T , for $T_f > T_i > 0$ the integral obeys

$$\frac{Q}{T_f} < \Delta S < \frac{Q}{T_i}. \quad (20.11)$$

The inequalities become equalities only in the infinitesimal-temperature-change limit. Neither endpoint shortcut is exact for a finite change. One can define a logarithmic-mean temperature $T_{\log} = (T_f - T_i)/\ln(T_f/T_i)$ so that $\Delta S = Q/T_{\log}$, but this is a mathematical rewrite of the integral, not the temperature of a reservoir that makes the actual heating reversible.

Suppose instead that the same body is heated by contact with one fixed reservoir at $T_H \geq T_f$. The reservoir loses entropy Q/T_H while the body gains its state-function change. With negligible energy storage in the contact layer, the entropy generated in the combined heating arrangement is

$$S_{\text{gen}} = C \ln \frac{T_f}{T_i} - \frac{C(T_f - T_i)}{T_H}. \quad (20.12)$$

This is positive for a finite heating interval supplied by a reservoir that is never colder than the body. A higher source temperature does not change the required body energy or its endpoint entropy change, but it decreases the magnitude of the source entropy loss and increases total entropy generation.

At each instant a heat amount $\delta Q > 0$ crossing from a warmer contact at T_H to a cooler contact at T_C generates

$$\delta S_{\text{gen}} = \delta Q \left(\frac{1}{T_C} - \frac{1}{T_H} \right) = \delta Q \frac{T_H - T_C}{T_H T_C}.$$

Thus entropy generation per unit heat vanishes as the temperature difference tends to zero. If a simple thermal conductance G gives $\dot{Q} = G(T_H - T_C)$, its generation rate is $\dot{S}_{\text{gen}} = G(T_H - T_C)^2/(T_H T_C)$. Both rates tend to zero for fixed finite G . The reversible limit suppresses dissipation but also suppresses heat-transfer power in this model. It is not a promise of finite heat delivery in zero time or of a practical exchanger with unlimited area.

A useful comparison heats a body through a staircase of successively warmer reservoirs. Take N equal temperature increments, $T_j = T_i + j(T_f - T_i)/N$. At stage j , a reservoir at T_j supplies

heat $C(T_j - T_{j-1})$, while the body moves from T_{j-1} to T_j . Every finite stage remains irreversible. Nevertheless,

$$S_{\text{gen},N} = C \ln \frac{T_f}{T_i} - \sum_{j=1}^N \frac{C(T_j - T_{j-1})}{T_j} \rightarrow 0 \quad \text{as } N \rightarrow \infty. \quad (20.13)$$

The sum is a right-endpoint approximation to the entropy integral. Its limit demonstrates concretely how the reversible comparison is constructed. It also separates the body's unchanged endpoint entropy from the protocol-dependent entropy changes of its surroundings.

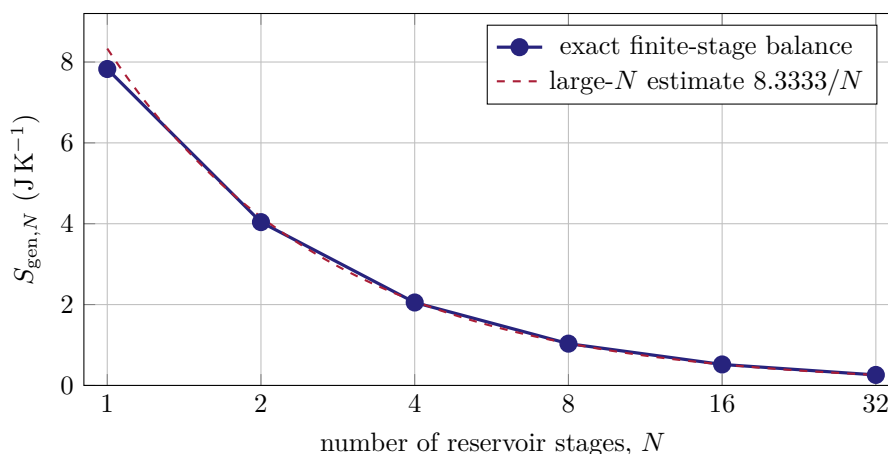


Figure 20.5: The finite-stage heating protocol in Example 20.4. The body has the same entropy gain at every N ; entropy generation falls as the heat is supplied at temperatures progressively closer to its own.

Example 20.4: E20-11: One reservoir or a temperature staircase

A model body has constant $C = 500 \text{ J K}^{-1}$ and is heated from 300 to 360 K without work. Compare heating by one reservoir at 360 K with heating by four successive reservoirs at 315, 330, 345 and 360 K. Find heat input, body entropy change and total entropy generation for each protocol. Interpret the trend in Figure 20.5.

Model. The body is treated as uniform, and the contact region stores negligible energy. Each stage ends in the limiting equilibrium state with its supplying reservoir. A real body approaches that state asymptotically, so the ideal endpoint description is not a claim of an exactly completed finite-time equilibration. Other than the specified reservoirs, the arrangement exchanges no heat or matter.

Common endpoint results. Both protocols supply

$$Q = C(360 - 300) = 30.0 \text{ kJ}, \quad \Delta S_{\text{body}} = 500 \ln(360/300) = 91.1608 \text{ J K}^{-1}.$$

Energy and body entropy depend on the prescribed endpoints under this no-work model. They do not distinguish the two protocols.

Single reservoir. The source entropy change is

$$\Delta S_H = -\frac{30000}{360} = -83.3333 \text{ J K}^{-1},$$

so $S_{\text{gen}} = 91.1608 - 83.3333 = 7.82745 \text{ J K}^{-1}$. Dividing the heat by 360 K correctly calculates the magnitude of the source entropy change, while it underestimates the body's entropy gain.

Four reservoirs. Each stage supplies $500(15) = 7500 \text{ J}$. The combined source entropy change is

$$\Delta S_{\text{sources}} = -7500 \left(\frac{1}{315} + \frac{1}{330} + \frac{1}{345} + \frac{1}{360} \right) = -89.1093 \text{ J K}^{-1}.$$

Consequently $S_{\text{gen}} = 91.1608 - 89.1093 = 2.05152 \text{ J K}^{-1}$. It is still positive: four finite temperature differences have replaced one larger difference, rather than making the heating exactly reversible.

Graph interpretation and check. The plotted generation falls toward zero, whereas the body entropy gain remains 91.1608 J K^{-1} . Each stage generates $C[\ln(T_j/T_{j-1}) - (T_j - T_{j-1})/T_j] > 0$. Expanding for a small increment and summing gives the leading large- N result

$$S_{\text{gen},N} \simeq \frac{C(T_f - T_i)}{2N} \left(\frac{1}{T_i} - \frac{1}{T_f} \right) = \frac{8.33333}{N} \text{ J K}^{-1}.$$

Its agreement with the exact points improves as N increases. The reversible limit concerns zero total generation; it does not require zero entropy change of the heated body.

20.3 Entropy changes, entropy transfer, and entropy generation

Entropy can be transported across a boundary with heat and can also be generated by irreversible processes. For a closed system interacting thermally through portions of its boundary at temperatures $T_{b,j}$,

$$\Delta S_{\text{sys}} = \sum_j \int \frac{\delta Q_j}{T_{b,j}} + S_{\text{gen}}, \quad S_{\text{gen}} \geq 0. \quad (20.14)$$

Here each Q_j is signed positive into the system. The inequality $S_{\text{gen}} \geq 0$ is the local accounting form of the second law. For a reversible process $S_{\text{gen}} = 0$. For an isolated system there is no entropy transfer across the boundary, so

$$\Delta S_{\text{isolated}} = S_{\text{gen}} \geq 0. \quad (20.15)$$

A subsystem can lose entropy and still satisfy the second law if a larger entropy increase occurs elsewhere.

Method

Entropy-balance workflow.

1. Draw the system boundary and identify every heat crossing.
2. Use the first law to establish energy consistency and any unknown final state.
3. Calculate state-function changes for the system or subsystems.
4. Evaluate entropy transfer with heat using the appropriate boundary temperatures.
5. Infer S_{gen} from the balance and check $S_{\text{gen}} \geq 0$.
6. If $S_{\text{gen}} < 0$, do not “fix” the sign. Recheck the model, temperatures, heat directions and data.

Returning to E20-01: the quantitative direction test

The entropy balance now supplies the promised test. Each reservoir remains at its specified constant temperature, so a heat transfer of 120 J from 360 to 300 K gives

$$\Delta S_{\text{pair}} = 120 \left(\frac{1}{300} - \frac{1}{360} \right) = 6.67 \times 10^{-2} \text{ J K}^{-1} > 0.$$

No entropy crosses the isolated pair’s boundary; the increase is generation. Reversing the transfer would require negative generation and cannot be an unassisted process. A refrigerator succeeds only with compensating work and surroundings changes.

20.3.1 The boundary temperature and the location of entropy generation

The temperature in an entropy-transfer term belongs to the place where heat crosses the chosen boundary. It is not automatically the temperature of a distant reservoir. This distinction matters whenever a thermal contact has a finite temperature drop. A reservoir may deliver heat at 400 K through a conductor to a system whose surface is at 300 K. The same energy crosses both ends of a steady conductor, but its associated entropy transfer is larger at the cooler end. The difference is generated within the conductor and its contact regions.

For heat magnitude Q passing through a contact from T_H to T_C , with no net entropy stored in that contact, its balance is

$$0 = \frac{Q}{T_H} - \frac{Q}{T_C} + S_{\text{gen,contact}}, \quad S_{\text{gen,contact}} = Q \left(\frac{1}{T_C} - \frac{1}{T_H} \right) > 0.$$

Moving the boundary can place this contact inside or outside the system. The assigned generation changes accordingly; the generation of the complete physical arrangement does not. This is bookkeeping about one process, rather than an ambiguity in the second law.

Figure 20.6 shows two nested choices. Boundary A encloses only a gas maintained at 300 K during a frictionless quasi-static expansion. The heat enters that boundary at the gas contact temperature. Boundary B includes the gas and the thermal contact, so heat enters B at the reservoir-side temperature. A zero-generation gas model and a positive-generation contact model can coexist. Calling the gas evolution internally reversible does not make the complete reservoir-to-gas process reversible.

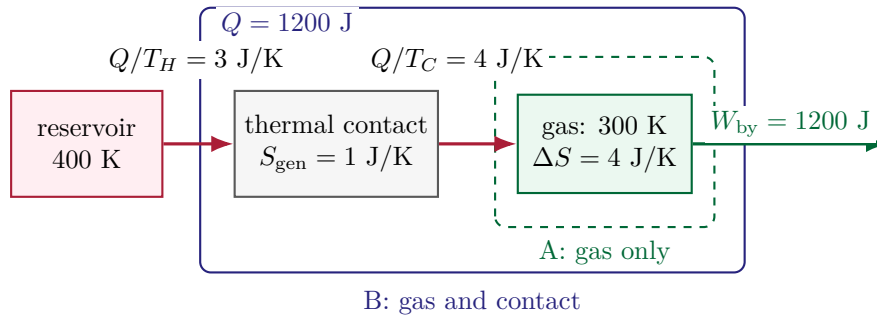


Figure 20.6: Nested entropy-accounting boundaries for Example 20.5. The heat has the same energy at both ports. Its entropy transfer increases across the finite temperature drop, with the increase generated in the contact.

Example 20.5: E20-12: One process, two system boundaries

One mole of ideal gas expands isothermally at 300 K while receiving 1200 J from a reservoir at 400 K. The piston is frictionless, its motion is quasi-static, and the gas is modelled as internally equilibrated with zero internal entropy generation. The thermal contact has a finite temperature drop but no net energy or entropy storage over the interval. Initially $V_i = 4.00 \text{ L}$. Find V_f , work output, the entropy changes of gas and reservoir, and entropy generation for boundaries A and B in Figure 20.6.

Energy and endpoints. The ideal gas has $\Delta E_{\text{int}} = 0$ at fixed temperature. Therefore $W_{\text{by}} = Q = 1200 \text{ J}$, and the frictionless expansion relation gives

$$1200 = RT \ln(V_f/V_i), \quad V_f = 4.00 \exp\left(\frac{1200}{R(300)}\right) = 6.47134 \text{ L}.$$

The gas gains entropy $\Delta S_{\text{gas}} = R \ln(V_f/V_i) = 4.00 \text{ J K}^{-1}$. The reservoir loses entropy $\Delta S_H = -1200/400 = -3.00 \text{ J K}^{-1}$.

Boundary A. Heat crosses the gas boundary at 300 K. Its entropy transfer is $1200/300 = 4.00 \text{ J K}^{-1}$. Thus

$$S_{\text{gen},A} = \Delta S_A - \frac{Q}{300} = 4.00 - 4.00 = 0.$$

This is consistent with the internally reversible gas model. Using 400 K in this boundary's transfer term would incorrectly assign contact irreversibility to the gas interior.

Boundary B. Heat enters the combined gas-plus-contact system at 400 K. The contact returns to the same stored entropy, so $\Delta S_B = 4.00 \text{ J K}^{-1}$. Therefore

$$S_{\text{gen},B} = 4.00 - \frac{1200}{400} = 1.00 \text{ J K}^{-1}.$$

The reservoir-plus-B entropy change is also $-3.00 + 4.00 = 1.00 \text{ J K}^{-1}$. This independently accounts for the complete arrangement. Work leaves with energy but contributes no entropy-transfer term in this closed-system model. The boundary choices agree once the location of the finite temperature drop is stated.

The phrase $\Delta S_{\text{sys}} \geq Q/T_{\text{reservoir}}$ can be useful when a system is extended to include its thermal contact. It becomes misleading when interpreted as the local balance of a different boundary. Always record which boundary contains a conductor, friction interface or mixer. Entropy generation is nonnegative for each appropriately defined region, and internal exchanges cancel when those regions are combined. This cancellation is the reason a subsystem's negative entropy change can coexist with positive generation in the larger arrangement.

20.3.2 Adiabatic stirring: work raises entropy without heat transfer

Free expansion is one adiabatic irreversible process, but its final ideal-gas temperature is unchanged. Mechanical stirring gives a complementary example: an insulated liquid can warm when shaft work is dissipated. Define the system to include the liquid, paddle and tank, and compare equilibrium endpoints at rest. No heat crosses the outer boundary, but work enters through the shaft. With negligible changes in macroscopic kinetic and potential energy, the first law reads $\Delta E_{\text{int}} = W_{\text{in}}$. If an effective constant heat capacity C describes the heated system, $T_f = T_i + W_{\text{in}}/C$.

The entropy difference is calculated by a reversible thermal comparison path even though the actual experiment is adiabatic. That comparison imagines heating the same system reversibly from T_i to T_f . It gives

$$S_{\text{gen}} = \Delta S = C \ln \left(1 + \frac{W_{\text{in}}}{CT_i} \right) > 0. \quad (20.16)$$

The equality of entropy change and generation follows from the actual adiabatic boundary, not from the comparison-path heat. Figure 20.7 shows the energy input and the resulting entropy increase. The curve has positive slope $dS/dW_{\text{in}} = 1/T_f$, so another joule of work produces a smaller entropy increment after the body has warmed. This does not make the later stirring reversible; its generation remains positive.

Example 20.6: E20-13: Testing an adiabatic stirrer and its proposed reverse

An insulated model liquid-and-tank system has constant $C = 1.00 \text{ kJ K}^{-1}$ and starts at 300 K. A shaft supplies 20.0 kJ, and the paddle is then stopped. Neglect changes in macroscopic kinetic and potential energy between the endpoints. Find final temperature and entropy generation. A proposal claims that reversing the paddle will restore 300 K while returning 20.0 kJ to the shaft, with no other effect. Test this proposal.

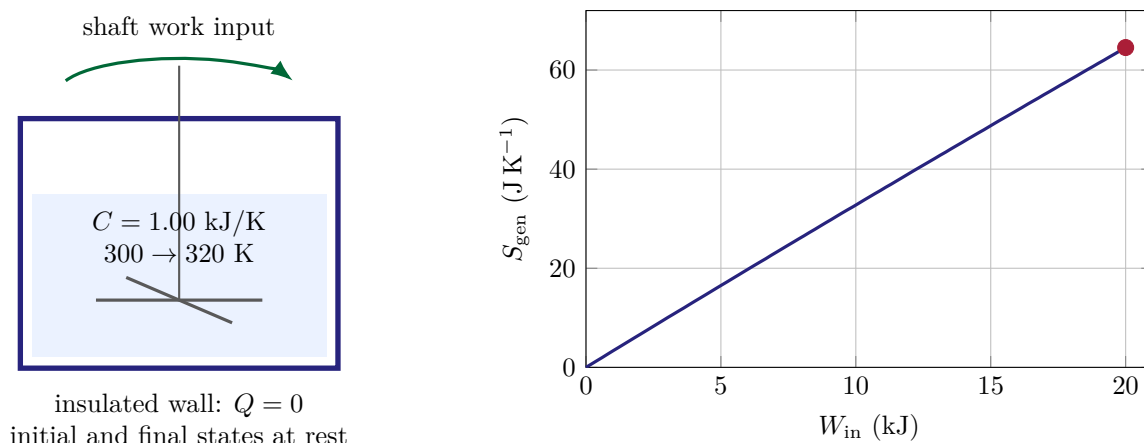


Figure 20.7: An adiabatic stirrer and its generated entropy for Example 20.6. The heat capacity is a stipulated model parameter. Work input warms the system while dissipation increases its entropy.

Forward process. The boundary is adiabatic but permits work. Under the book convention, $W_{\text{by}} = -20.0$ kJ and

$$\Delta E_{\text{int}} = Q - W_{\text{by}} = 0 - (-20.0) = 20.0 \text{ kJ}.$$

Thus $T_f = 300 + 20.0/1.00 = 320$ K. A reversible thermal comparison gives

$$\Delta S = C \ln \frac{320}{300} = 64.5385 \text{ J K}^{-1}.$$

The actual entropy transfer is zero because $Q = 0$, so $S_{\text{gen}} = 64.5385 \text{ J K}^{-1}$. The positive entropy rise is consistent with conversion of organized shaft work into internal energy through viscous dissipation.

Proposed reverse. Its energy account would be consistent: cooling by 20.0 kJ could, algebraically, accompany 20.0 kJ of work output. However, restoring the original state would require

$$\Delta S_{\text{reverse}} = C \ln(300/320) = -64.5385 \text{ J K}^{-1}.$$

With no heat or matter exchange, this would equal a negative S_{gen} , violating the second law. Reversing the rotation direction does not undo viscous dissipation; stirring in either direction supplies further positive work and generates further entropy. A permitted cooling process must export entropy, for example to a cooler surrounding body, and then has an additional external effect.

Check and interpretation. The dimensionless work ratio is $W_{\text{in}}/(CT_i) = 20/300$. For a small ratio, $C \ln[1 + W_{\text{in}}/(CT_i)] \simeq W_{\text{in}}/T_i$; the exact result is slightly smaller because the system warms during the input. Figure 20.7 accordingly bends below its initial tangent. Neither calculation uses Q/T for the actual adiabatic process.

20.3.3 Thermal contact between finite bodies

Let two bodies of constant heat capacities C_H and C_C be thermally isolated from everything except each other. If their initial temperatures are $T_H > T_C$, energy conservation gives the final equilibrium temperature

$$T_f = \frac{C_H T_H + C_C T_C}{C_H + C_C}. \quad (20.17)$$

Their entropy changes are

$$\Delta S_H = C_H \ln\left(\frac{T_f}{T_H}\right), \quad \Delta S_C = C_C \ln\left(\frac{T_f}{T_C}\right). \quad (20.18)$$

The warm body has $\Delta S_H < 0$, the cool body has $\Delta S_C > 0$, and the isolated pair satisfies $\Delta S_H + \Delta S_C = S_{\text{gen}} > 0$ unless the initial temperatures were equal.

Example 20.7: E20-03: Unequal heat capacities in direct thermal contact

A body with $C_H = 500 \text{ J K}^{-1}$ at 360 K is placed in thermal contact with a body with $C_C = 800 \text{ J K}^{-1}$ at 290 K. The pair is otherwise isolated. Treat both heat capacities as constant. Find the final temperature and the entropy generation.

Energy balance.

$$T_f = \frac{(500)(360) + (800)(290)}{1300} = 316.923 \text{ K}.$$

Individual entropy changes.

$$\Delta S_H = 500 \ln\left(\frac{316.923}{360}\right) = -63.72 \text{ J K}^{-1},$$

$$\Delta S_C = 800 \ln\left(\frac{316.923}{290}\right) = +71.02 \text{ J K}^{-1}.$$

Therefore

$$S_{\text{gen}} = \Delta S_H + \Delta S_C = 7.30 \text{ J K}^{-1} > 0.$$

The entropy decrease of the warm body is not a violation; the entropy increase of the cool body is larger.

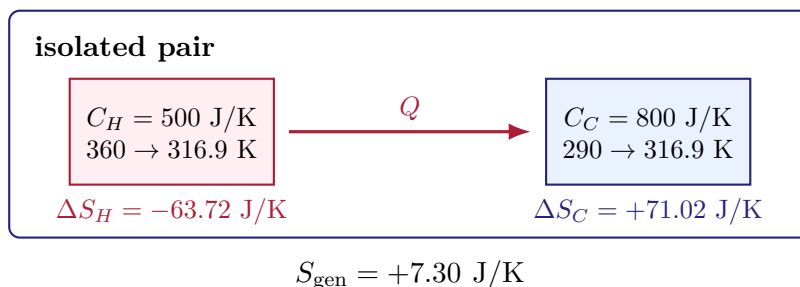


Figure 20.8: F20-03 — Entropy bookkeeping for Example 20.7. The entropy loss of the warm subsystem and the larger gain of the cool subsystem are shown separately; their sum is the entropy generated in the isolated direct-contact process.

20.3.4 A phase transition supplied by a finite thermal source

The phase-change formula $\Delta S = mL/T_{\text{tr}}$ concerns an equilibrium transition at its coexistence temperature and stated pressure. It gives the sample's entropy difference even when the actual heat arrives irreversibly from something warmer. It does not, by itself, establish that enough energy is available to transform the entire sample. With a finite thermal source, the source cools as it supplies heat. The first task is therefore to decide which final phase branch is physically accessible.

Consider ice initially at its stipulated melting temperature T_m , in contact with a warmer body having constant heat capacity C_H and initial temperature T_H . Enclose the pair adiabatically, neglect the container's heat capacity and all expansion work, and take the latent heat L to be constant in this teaching model. Before the warm body reaches T_m , it can release

$$Q_{\text{available}} = C_H(T_H - T_m).$$

Complete melting requires $Q_{\text{fusion}} = mL$. If $Q_{\text{available}} < mL$, the warm body cools to T_m while only part of the ice melts. The final state is an ice–liquid mixture at T_m , and the mass melted is $m_{\text{melt}} = C_H(T_H - T_m)/L$. Liquid warming cannot be included on this branch because ice remains in coexistence with it.

If $Q_{\text{available}} > mL$, all the ice can melt and there is energy left for liquid warming. With a stipulated constant liquid specific heat c_ℓ , the final temperature instead solves

$$C_H(T_H - T_f) = mL + mc_\ell(T_f - T_m), \quad T_f > T_m.$$

The sample entropy change then has two contributions, $mL/T_m + mc_\ell \ln(T_f/T_m)$. At the threshold $Q_{\text{available}} = mL$, these branches meet at complete melting with $T_f = T_m$. This energy-first branch selection prevents an otherwise plausible entropy calculation from assigning a nonexistent final state.

Figure 20.9 uses the partial-melting parameters of the next example. The warm-body line ends when its temperature meets the phase plateau. The plateau continues to the energy required for full melting, to show the demand that the finite source cannot satisfy. This continuation represents possible phase states under further supplied heat, rather than further states of this isolated contact process.

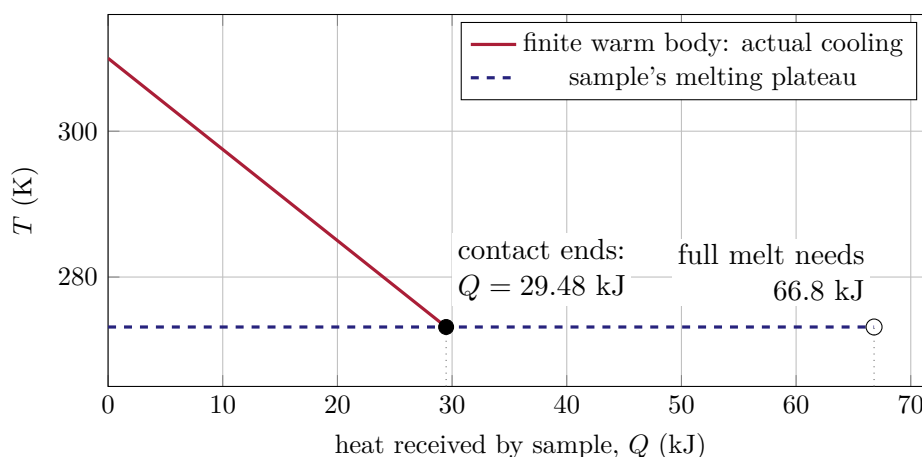


Figure 20.9: Energy selects the partial-melting branch in Example 20.8. The finite source reaches the melting temperature after delivering 29.48 kJ; the open marker shows the larger full-fusion demand.

Example 20.8: E20-14: Partial melting and a complete entropy ledger

A model warm body has $C_H = 800 \text{ J K}^{-1}$ and starts at 310 K. It contacts 0.200 kg of ice initially at $T_m = 273.15 \text{ K}$ inside an otherwise adiabatic enclosure. Use stipulated $L = 334 \text{ kJ kg}^{-1}$, and neglect container heat capacity and expansion work. Determine the final temperature, melted mass and fraction, the entropy change of each subsystem, and total entropy generation. Determine the threshold initial warm-body temperature for complete melting without liquid warming.

Choose the branch from energy. Cooling the source to the melting temperature releases

$$Q = 800(310 - 273.15) = 29480 \text{ J},$$

whereas complete fusion requires $mL = (0.200)(334000) = 66800 \text{ J}$. Figure 20.9 shows the same shortfall. Thus ice remains and the final temperature is 273.15 K. The melted mass and fraction are

$$m_{\text{melt}} = \frac{29480}{334000} = 0.0882635 \text{ kg}, \quad f = \frac{m_{\text{melt}}}{0.200} = 0.441317.$$

About 44.1% melts under this model. The total heat delivered is not large enough to justify a liquid-warming term.

Subsystem entropy changes. The ice-to-liquid transition occurs at the coexistence temperature, giving

$$\Delta S_{\text{sample}} = \frac{m_{\text{melt}} L}{T_m} = \frac{29480}{273.15} = 107.926 \text{ J K}^{-1}.$$

The source cools over a finite range, so its change requires a logarithm:

$$\Delta S_H = C_H \ln \frac{T_m}{T_H} = 800 \ln \frac{273.15}{310} = -101.241 \text{ J K}^{-1}.$$

The outer boundary transfers no entropy. Therefore

$$S_{\text{gen}} = 107.926 - 101.241 = 6.68509 \text{ J K}^{-1} > 0.$$

The sample transition has a reversible comparison path, while the source-to-sample heat transfer generates entropy through its finite temperature difference.

Threshold and check. Complete melting with no subsequent warming requires $C_H(T_H^* - T_m) = mL$, hence

$$T_H^* = T_m + \frac{mL}{C_H} = 273.15 + \frac{66800}{800} = 356.65 \text{ K}.$$

The initial 310 K lies below this threshold, confirming the chosen branch. Independently, adding the contact generation during cooling gives

$$\int_0^Q \left[\frac{1}{T_m} - \frac{1}{T_H - q/C_H} \right] dq = \frac{Q}{T_m} + C_H \ln \frac{T_m}{T_H},$$

which equals the subsystem sum. The integrand stays nonnegative and reaches zero at final equilibrium, providing a local check on the positive total.

When using measured latent heats, specify the pressure and the intended transition, and distinguish fusion from vaporization. For a high-pressure or large-volume-change process, expansion work may be consequential and the energy ledger needs the appropriate internal-energy or enthalpy treatment. The low-pressure negligible-work model used here keeps the energy and entropy accounts consistent without claiming that all phase transitions obey the same mechanical constraints.

The separate entropy changes are more revealing when they are drawn on one signed scale. Figure 20.10 shows that “entropy produced” is not the cold body’s entire entropy gain. Most of that gain compensates entropy lost by the hot body; only the remainder belongs to the isolated pair’s generation ledger. Unlike energy, this remainder is not a transfer from a third body.

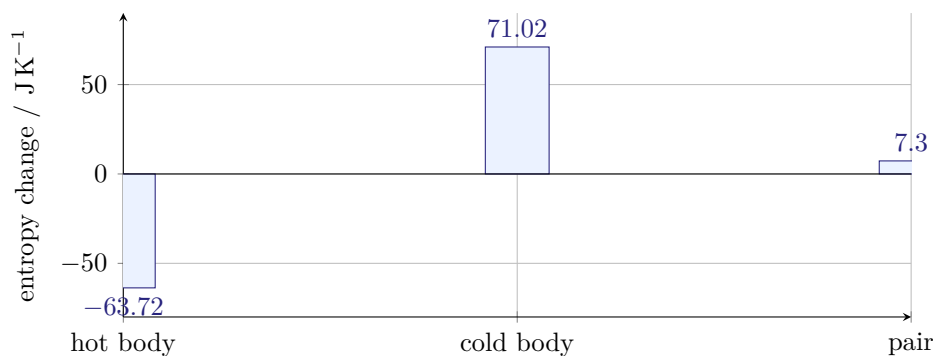


Figure 20.10: The entropy ledger for the same isolated pair as Figure 20.8. Signed bar heights represent state changes; the sum, 7.30 J K^{-1} , is entropy generation. Heat capacities are constant; no mass, heat or work crosses the outer boundary.

20.3.5 A measurement connection: warm-water mixing

A simple calorimetry activity can estimate an entropy change, but it must be described honestly. Suppose measured masses m_1, m_2 and initial temperatures T_1, T_2 are recorded, the samples are mixed in an insulated calorimeter, and a final temperature T_f is observed. If liquid water is approximated by a constant specific heat c and the calorimeter heat capacity is neglected, the model predicts

$$T_{f,\text{model}} = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2},$$

then

$$\Delta S_{\text{pair}} = m_1 c \ln \frac{T_f}{T_1} + m_2 c \ln \frac{T_f}{T_2}.$$

A difference between measured and modelled T_f may reflect heat exchange with the calorimeter, evaporation, temperature gradients, sensor response or imperfect insulation. Repeating the experiment estimates repeatability; it does not automatically remove those model biases.

20.3.6 Calorimeter capacity, residuals and uncertainty

An observed final temperature alone does not tell us whether a mixing experiment was isolated. A useful improvement is to measure the initially cold calorimeter temperature and account for its heat capacity. With hot water mass m_H , cold water mass m_C , common stipulated specific heat c , and a calorimeter initially at T_C , the no-leak model is

$$m_H c (T_H - T_f) = (m_C c + C_{\text{cal}}) (T_f - T_C).$$

Thus

$$T_f = \frac{m_H c T_H + (m_C c + C_{\text{cal}}) T_C}{(m_H + m_C) c + C_{\text{cal}}}, \quad C_{\text{cal}} = m_H c \frac{T_H - T_f}{T_f - T_C} - m_C c. \quad (20.19)$$

This inverse equation becomes very sensitive when T_f is near T_C : the denominator is a small measured temperature rise. A more precise digital display does not necessarily remove calibration bias, response lag or incomplete mixing. Before combining uncertainties, state whether they are independent standard uncertainties or conservative bounds.

The following synthetic teaching dataset was constructed with $m_H = 0.200$ kg, $m_C = 0.300$ kg, $c = 4180$ J kg⁻¹ K⁻¹, $T_C = 290.00$ K and $C_{\text{cal}} = 200$ J K⁻¹, with small explicitly synthetic temperature perturbations. No experiment is claimed.

T_H/K	T_f synthetic/K	no-calorimeter prediction/K	residual/K
310.00	297.35	298.00	-0.65
320.00	300.92	302.00	-1.08
330.00	304.66	306.00	-1.34
340.00	308.21	310.00	-1.79

Figure 20.11 shows a structured residual, not random scatter about zero. The neglected cold calorimeter absorbs energy and makes the final temperature lower than the simplified prediction. A different systematic mechanism, such as heat leakage during mixing, could also lower the temperature; the trend alone does not uniquely identify the cause.

Example 20.9: E20-22: Inferring an effective calorimeter capacity

For the masses and specific heat above, suppose an independent idealized run has $T_H = 330.00$ K, $T_C = 290.00$ K and $T_f = 304.60$ K. Infer C_{cal} under the no-leak model. Estimate its standard uncertainty if each of the three temperatures has independent standard uncertainty 0.10 K, treating masses and c as exact stipulated inputs for this calculation.

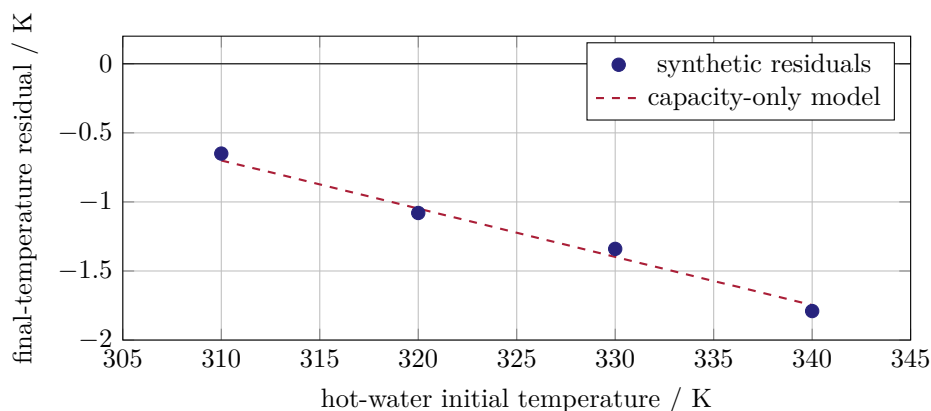


Figure 20.11: Synthetic final temperatures minus predictions that neglect the calorimeter. The dashed line uses $C_{\text{cal}} = 200 \text{ J K}^{-1}$; small deviations were added to produce the listed teaching data. A trend in residuals motivates a model revision, while independent observations are needed to discriminate heat capacity from heat leakage.

Inverse calculation. Equation (20.19) gives $C_{\text{cal}} = 200.41 \text{ J K}^{-1}$. With $A = m_H c = 836 \text{ J K}^{-1}$, the temperature sensitivities are

$$\frac{\partial C_{\text{cal}}}{\partial T_f} = -A \frac{T_H - T_C}{(T_f - T_C)^2}, \quad \frac{\partial C_{\text{cal}}}{\partial T_H} = \frac{A}{T_f - T_C}, \quad \frac{\partial C_{\text{cal}}}{\partial T_C} = A \frac{T_H - T_f}{(T_f - T_C)^2}.$$

They are -156.88 , 57.26 , and 99.62 in J K^{-2} . First-order independent propagation therefore gives $u(C_{\text{cal}}) = 0.10\sqrt{156.88^2 + 57.26^2 + 99.62^2} = 19.45 \text{ J K}^{-1}$. Report approximately $(200 \pm 19) \text{ J K}^{-1}$ with the uncertainty identified as a standard uncertainty under this model.

Interpretation. The largest sensitivity is to the final temperature. Calibrating that measurement and waiting for complete mixing can improve inference more than merely repeating a biased procedure. Correlated thermometer offsets require covariance terms; leakage requires a revised energy model. This calculation estimates an effective capacity conditional on those assumptions, not a certified material constant.

A defensible laboratory plan first calibrates the sensor near the relevant temperature range, weighs both samples, records the empty calorimeter's initial temperature, and tracks temperature during and after mixing. A time history is particularly useful for distinguishing delayed mixing from continued room heat loss. Repeat measurements estimate repeatability; changing the hot sample's temperature tests model structure. To estimate entropy, include the calorimeter term $C_{\text{cal}} \ln(T_f/T_{\text{cal,i}})$ as well as both water terms and any reservoir heat exchange. A total entropy estimate that neglects a major subsystem is an incomplete account even when the energy fit looks good.

20.4 Heat engines and cycle balances

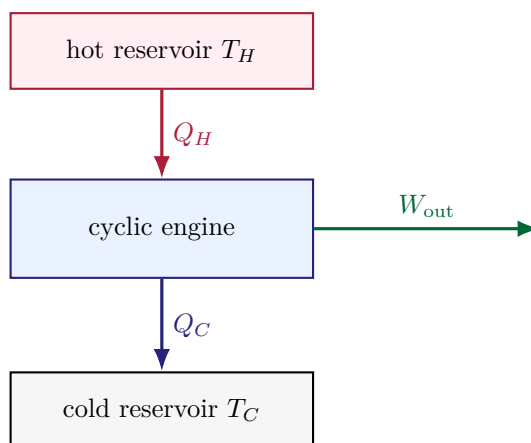
A heat engine operates cyclically. Over one complete cycle, the working substance returns to its initial state, so its changes in internal energy and entropy are zero. Define $Q_H > 0$ as the heat magnitude absorbed from a hot reservoir, $Q_C > 0$ as the heat magnitude rejected to a cold reservoir, and $W_{\text{out}} > 0$ as work delivered. The first law gives

$$W_{\text{out}} = Q_H - Q_C. \quad (20.20)$$

Thermal efficiency is the fraction of hot-side heat converted to work:

$$\eta_{\text{th}} = \frac{W_{\text{out}}}{Q_H} = 1 - \frac{Q_C}{Q_H}. \quad (20.21)$$

The first law alone only requires a consistent energy ledger. It does not tell us the maximum possible efficiency.



$$W_{\text{out}} = Q_H - Q_C \quad \eta = W_{\text{out}}/Q_H$$

Figure 20.12: Cyclic heat-engine ledger. Q_H, Q_C, W_{out} are positive magnitudes; directions belong to the arrows. The working substance has $\Delta E_{\text{int}} = \Delta S = 0$ over a cycle, while both reservoirs change. Arrow widths and object sizes are schematic.

Example 20.10: E20-04: Audit an engine claim with the first law

A cyclic engine is reported to absorb 1.50 kJ per cycle and reject 0.90 kJ per cycle. It is also reported to deliver 0.60 kJ of work.

The energy balance gives

$$Q_H - Q_C = 1.50 - 0.90 = 0.60 \text{ kJ},$$

so the three energy-transfer claims are internally consistent. Its efficiency is

$$\eta_{\text{th}} = 0.60/1.50 = 0.400.$$

This audit does *not* yet prove the engine thermodynamically possible. The reservoir temperatures are needed for the second-law test.

20.4.1 Entropy balance for a cyclic engine

If the engine exchanges heat only with two fixed-temperature reservoirs, the working substance returns to its original entropy each cycle. The reservoirs change by

$$\Delta S_H = -\frac{Q_H}{T_H}, \quad \Delta S_C = +\frac{Q_C}{T_C}. \quad (20.22)$$

For the combined engine plus reservoirs,

$$S_{\text{gen}} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \geq 0. \quad (20.23)$$

This inequality is the route to the Carnot bound.

20.4.2 An inverse audit: what temperatures would make the claim possible?

An engine specification can be used to constrain its reservoirs even when one temperature is unknown. This reverses the usual calculation: the measured heat and work transfers determine an efficiency, and the second law determines which reservoir temperatures could be compatible with that efficiency. The conclusion is a necessary feasibility condition under the two-reservoir cyclic model. It does not identify a particular engine architecture or guarantee that the measured specification can be achieved.

Use the first law before taking a temperature ratio. If the specified transfers give $Q_C = Q_H - W_{\text{out}} > 0$, the entropy inequality becomes

$$T_C \leq T_H \frac{Q_C}{Q_H} = T_H(1 - \eta). \quad (20.24)$$

For a known cold reservoir it instead gives $T_H \geq T_C/(1 - \eta)$. Equality is the reversible boundary. A temperature pair satisfying the strict inequality permits positive entropy generation in the model; it does not establish the magnitude or location of every real loss. If the quoted heat transfers are time averages, the same algebra applies to rates for a periodic steady state with negligible net energy and entropy storage over the reporting interval. Transient start-up data cannot be treated this way without accounting for storage.

Example 20.11: E20-15: Inferring an allowable cold-reservoir temperature

A cyclic model engine absorbs $Q_H = 2.00$ kJ from a reservoir at 650 K and delivers $W_{\text{out}} = 0.800$ kJ per cycle. Determine the largest compatible cold-reservoir temperature. Then audit operation at 300, 390 and 420 K.

System and method. The engine returns to its initial state each cycle. The only heat interactions are with the stated hot reservoir and one cold reservoir, and all quoted transfers are positive magnitudes. Work leaves the combined engine–reservoir system without entropy transfer. First calculate the cold-side rejection, then test the combined reservoir entropy change.

$$Q_C = 2000 - 800 = 1200 \text{ J}, \quad \eta = 800/2000 = 0.400.$$

Equation (20.24) gives

$$T_{C,\text{max}} = 650(1 - 0.400) = 390 \text{ K}.$$

The entropy generation per cycle is

$$S_{\text{gen}}(T_C) = \frac{1200 \text{ J}}{T_C} - \frac{2000 \text{ J}}{650 \text{ K}}.$$

At 300 K it is $+0.9231 \text{ J K}^{-1}$, so the transfers pass this necessary test with irreversibility. At 390 K it is zero, requiring ideal reversible operation. At 420 K it is -0.2198 J K^{-1} , so the claimed combination is impossible within the stated model.

Check and interpretation. Every case has the same balanced energy ledger. The unit of each entropy term is joule per kelvin, and raising T_C reduces the entropy exported with the same rejected heat. The largest permissible T_C is therefore a ceiling, not a lower bound. If a measured device were reported to operate at 420 K, additional heat interactions, net storage, or erroneous measurements would have to be investigated; the negative result cannot be repaired by declaring an efficiency loss elsewhere.

This inverse formulation is useful when discussing thermal design constraints. Cooling a sink raises the allowable efficiency ceiling, but cooling equipment also consumes work. Heating a source raises the ceiling, but source production may itself require resources. A complete installation assessment therefore distinguishes the engine boundary from the boundary of the plant that supplies its hot

and cold conditions. The chapter's two-reservoir audit concerns the former boundary unless an enlarged system is explicitly defined.

20.5 The Carnot limit

From Eq. (20.23),

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}.$$

Substitution into Eq. (20.21) gives

$$\eta_{\text{th}} \leq \eta_C = 1 - \frac{T_C}{T_H}. \quad (20.25)$$

Equality requires zero entropy generation for an ideal reversible engine operating between the same two fixed reservoirs. The bound is independent of working substance. It does not state that a real machine attains the bound, nor that the engine with highest possible efficiency also has highest possible power.

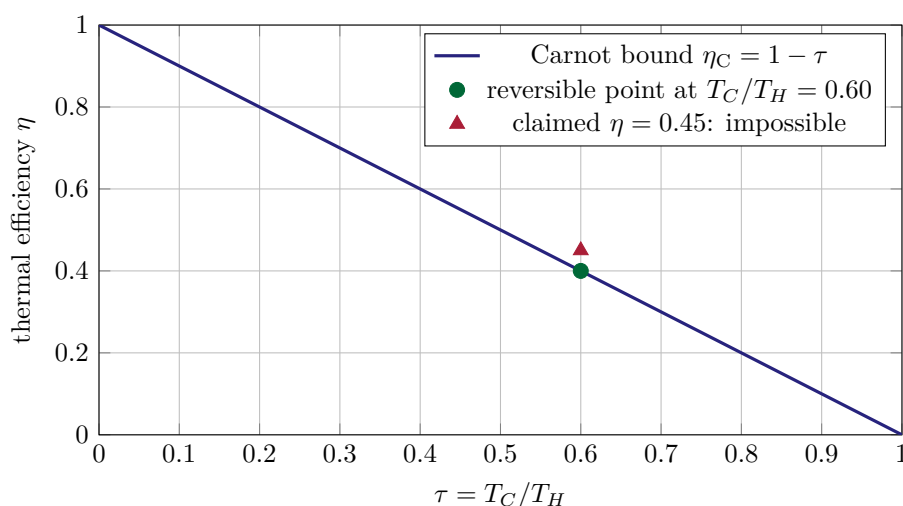


Figure 20.13: F20-05 — Carnot efficiency bound as a function of the absolute-temperature ratio. At any fixed T_C/T_H , points above the line violate the second law for a cyclic engine between those reservoirs.

Example 20.12: E20-05: A first-law-consistent but impossible engine

An engine between reservoirs at $T_H = 500$ K and $T_C = 300$ K absorbs $Q_H = 1000$ J and claims $W_{\text{out}} = 450$ J per cycle. It therefore rejects $Q_C = 550$ J, so the first law is satisfied.

But

$$\eta = 0.450, \quad \eta_C = 1 - \frac{300}{500} = 0.400.$$

Equivalently, the reservoir entropy change is

$$\Delta S_{\text{reservoirs}} = -\frac{1000}{500} + \frac{550}{300} = -0.1667 \text{ J K}^{-1}.$$

The working substance has zero entropy change over a cycle, so this would require negative entropy generation. The claim is impossible even though its energy ledger balances.

20.5.1 Constructing a complete ideal-gas Carnot cycle

The reservoir entropy derivation of the Carnot limit did not require a particular working substance. A concrete ideal-gas construction now makes its physical meaning visible. Consider n moles of ideal gas in a frictionless piston–cylinder, with constant molar heat capacities satisfying $C_{P,m} - C_{V,m} = R$ and $\gamma = C_{P,m}/C_{V,m} > 1$. The four legs are reversible isothermal expansion at T_H , reversible adiabatic expansion from T_H to T_C , reversible isothermal compression at T_C , and reversible adiabatic compression back to T_H . Each leg is traversed through equilibrium states in the ideal model.

The isothermal legs exchange heat with the reservoirs. The adiabatic legs are insulated. They exchange work and change internal energy but exchange no heat. A drawing that places heat arrows on all four legs would describe a different cycle. Likewise, merely drawing two isotherms does not close a Carnot cycle: the connecting curves must satisfy the same reversible adiabatic relation, and the state variables must return to their starting values.

Label the corners $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$. States 1 and 2 have temperature T_H and volumes V_1, V_2 ; states 3 and 4 have temperature T_C and volumes V_3, V_4 . During a reversible adiabatic leg, $\delta Q = 0$, so the first law and ideal-gas equation give

$$nC_{V,m} dT = -p dV = -\frac{nRT}{V} dV.$$

Dividing by $nC_{V,m}T$ and integrating produces

$$\begin{aligned} \ln \frac{T}{T_0} + (\gamma - 1) \ln \frac{V}{V_0} &= \text{constant}, \\ TV^{\gamma-1} &= \text{constant}, \quad pV^\gamma = \text{constant}. \end{aligned} \quad (20.26)$$

Here T_0 and V_0 are arbitrary fixed positive reference values, so both logarithms have dimensionless arguments; the power laws are the convenient finite-state forms. Applying them to both connecting legs gives

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} = \left(\frac{T_H}{T_C} \right)^{1/(\gamma-1)} \equiv a, \quad \frac{V_3}{V_4} = \frac{V_2}{V_1} \equiv r. \quad (20.27)$$

The common expansion ratio a closes the two adiabats, while the common isothermal ratio $r > 1$ makes the entropy gains and losses cancel. Pressures at all corners then follow from $p_i = nRT_i/V_i$; they cannot be chosen independently after the temperatures and volumes are fixed.

For an isothermal ideal-gas leg, $\Delta U = 0$ because internal energy depends only on temperature. Reversible work is $\int p dV$, and its value equals the signed heat received. Hence

$$Q_{12} = W_{12} = nRT_H \ln r = Q_H, \quad (20.28)$$

$$Q_{34} = W_{34} = nRT_C \ln(V_4/V_3) = -nRT_C \ln r = -Q_C. \quad (20.29)$$

On each adiabat, $Q = 0$ and $W_{\text{by}} = -\Delta U$:

$$W_{23} = nC_{V,m}(T_H - T_C), \quad (20.30)$$

$$W_{41} = -nC_{V,m}(T_H - T_C). \quad (20.31)$$

The adiabatic works are nonzero but cancel when added. Thus

$$W_{\text{cycle}} = nR(T_H - T_C) \ln r, \quad \eta = \frac{W_{\text{cycle}}}{Q_H} = 1 - \frac{T_C}{T_H}. \quad (20.32)$$

This construction attains the bound in the reversible limit. It also explains why the work depends on the amount of gas and on r , even though the efficiency depends only on the reservoir temperatures. Increasing r at fixed temperatures increases both heat uptake and work per cycle in this ideal model.

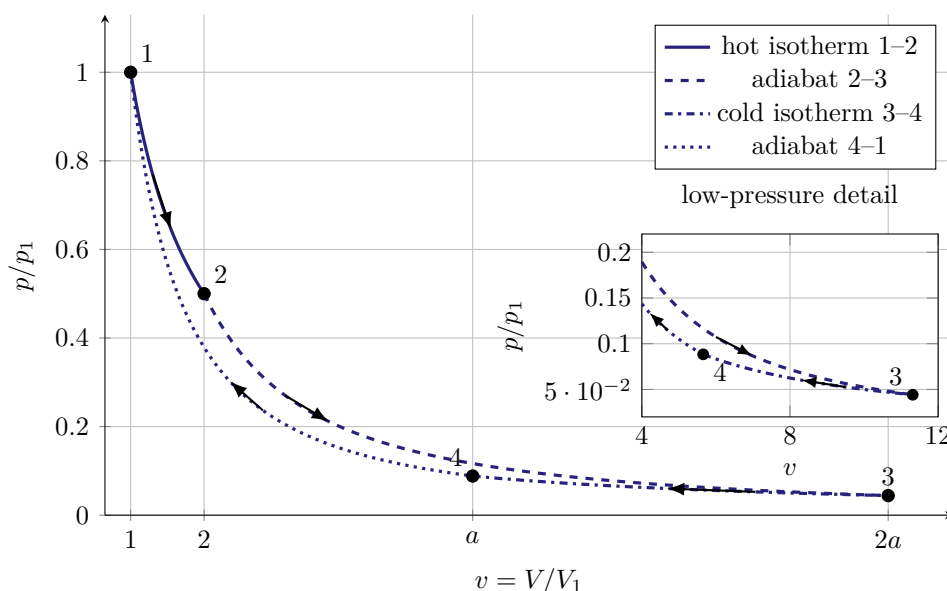


Figure 20.14: C20-V016 — A closed ideal-gas Carnot engine cycle with $T_H = 600$ K, $T_C = 300$ K, $\gamma = 1.4$, $n = 1$ mol, $V_1 = 0.0100$ m³ and $V_2 = 0.0200$ m³. The adiabatic expansion factor is $a = 2^{2.5} = 5.65685$, so $V_3 = 2aV_1$ and $V_4 = aV_1$. The four curves satisfy the equation of state and meet at identical corner states. Arrows indicate the clockwise engine direction; the area inside the loop represents positive net work. The inset enlarges the low-pressure region to distinguish states 3 and 4 and the return isotherm. One colour with four line styles preserves the leg distinction in grayscale.

The entropy changes can be checked without using any plotted area. On the hot isotherm $\Delta S_{12} = Q_H/T_H = nR \ln r$; on the cold isotherm $\Delta S_{34} = -Q_C/T_C = -nR \ln r$. Both reversible adiabats have constant entropy. The two isotherms therefore occupy the same entropy interval $\Delta S_* = nR \ln r$. The T - S representation is a rectangle whose clockwise area is $(T_H - T_C)\Delta S_*$. Its equality with the p - V work follows from the cycle's zero net internal-energy change, not from a general claim that heat and work are interchangeable on every individual leg.

A T - S area represents $\int T dS = Q_{\text{rev}}$ for a reversible path. For an irreversible path, the entropy balance includes generation, so the same graphical prescription is generally not the actual heat. Similarly, the equilibrium p - V area gives boundary work only when the pressure used is the appropriate reversible boundary pressure. These qualifications matter: diagrams are compact representations of the model equations, not replacements for their assumptions.

Example 20.13: E20-16: Verifying every leg of a numerical Carnot cycle

Use the model parameters in Figs. 20.14–20.15. Find all four corner volumes and pressures, the heat and work on each leg, the net work and efficiency, and verify cycle closure and the reservoir entropy balance.

Corner states. With $\gamma = 1.4$, $C_{V,m} = R/(\gamma - 1) = 20.7862$ J mol⁻¹K⁻¹. The adiabatic factor is

$$a = (600/300)^{1/0.4} = 5.656854,$$

so $V_3 = 0.113137$ m³ and $V_4 = 0.0565685$ m³. Using $p = nRT/V$ gives

$$(p_1, p_2, p_3, p_4) = (498.868, 249.434, 22.0470, 44.0941) \text{ kPa}.$$

Both $T_2V_2^{0.4} = T_3V_3^{0.4}$ and $T_4V_4^{0.4} = T_1V_1^{0.4}$ hold; $V_3/V_4 = V_2/V_1 = 2$ verifies the required isothermal ratio. The last leg ends at the starting temperature and volume, and therefore at the starting pressure.

Transfers, positive heat into and positive work by the gas.

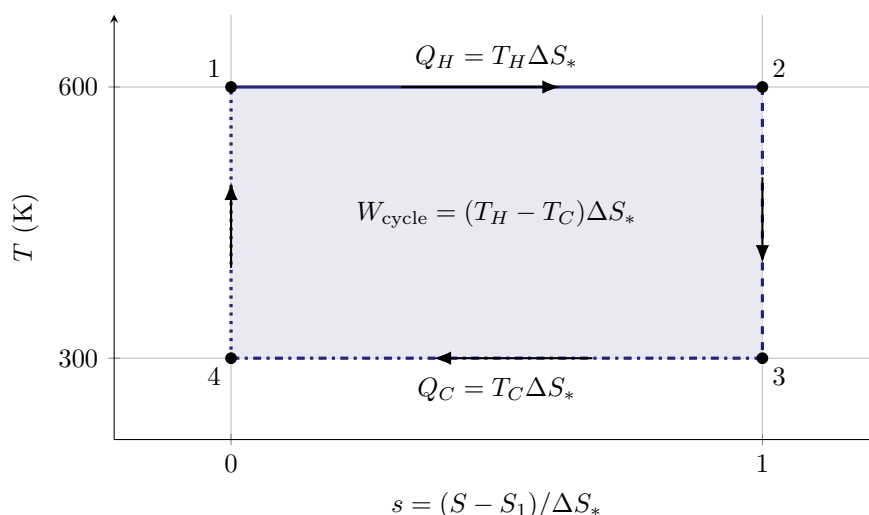


Figure 20.15: C20-V017 — The same cycle as Fig. 20.14 in temperature–entropy coordinates. Here $\Delta S_* = nR \ln 2 = 5.76315 \text{ J K}^{-1}$, and the horizontal coordinate is a dimensionless entropy difference, so an area measured on this normalized plot must be multiplied by ΔS_* to obtain joules. Heat enters only on $1 \rightarrow 2$ and leaves only on $3 \rightarrow 4$; the vertical adiabats exchange no heat. The shaded rectangle gives 1728.94 J of net work.

Leg	Q (J)	W_{by} (J)	ΔU (J)
$1 \rightarrow 2$	+3457.888	+3457.888	0
$2 \rightarrow 3$	0	+6235.847	−6235.847
$3 \rightarrow 4$	−1728.944	−1728.944	0
$4 \rightarrow 1$	0	−6235.847	+6235.847

The signs satisfy $\Delta U = Q - W_{\text{by}}$ on every leg. The net heat and work are both 1728.944 J, while the four internal-energy changes sum to zero. The efficiency is $1728.944/3457.888 = 0.500$, equal to $1 - 300/600$.

Independent entropy check. The gas changes entropy by +5.763146, 0, −5.763146, 0 J K^{−1} on the respective legs. The reservoirs change by

$$\Delta S_H = -3457.888/600 = -5.763146 \text{ J K}^{-1}, \quad \Delta S_C = 1728.944/300 = +5.763146 \text{ J K}^{-1}.$$

Thus both the working substance and the combined reservoirs return zero net entropy change, as required for a reversible cycle. Rounded values can leave a small displayed residual; the algebraic expressions cancel exactly.

Integral check. Integrating the four analytic $p(V)$ curves gives the same leg works as the first-law calculation. In particular, $\int_{V_2}^{V_3} KV^{-\gamma} dV = (p_2 V_2 - p_3 V_3)/(\gamma - 1) = 6235.847 \text{ J}$. Reversing limits on $4 \rightarrow 1$ makes its work negative. Agreement among corner states, energy sums, entropy sums and curve integrals is a stronger verification than matching the final efficiency alone.

20.5.2 Reversing the ideal cycle and approaching the equal-temperature limit

If every leg is reversed, the same closed curve runs counterclockwise. The working gas removes Q_C from the cold reservoir, receives work input $Q_H - Q_C$, and delivers Q_H to the hot reservoir. This is the reversible refrigerator or heat-pump benchmark developed below. Reversal changes the signs of heat and work on each leg while retaining the same four equilibrium corner states. It does not mean an arbitrary irreversible engine can be run backward with all of its original transfers simply reversed.

When T_C approaches T_H at fixed r , a approaches one and the adiabatic connectors shrink. The net work tends to zero because the two isothermal work contributions cancel, even though $Q_H = nRT_H \ln r$ can remain finite. At exactly equal temperatures the cycle degenerates; it does not convert single-reservoir heat into work. At the opposite formal limit $T_C \rightarrow 0$, the efficiency expression tends to one, but constant heat capacities, ideal-gas behaviour and accessible zero-temperature reservoirs cannot be assumed down to that limit. A limiting algebraic expression should therefore be distinguished from a physically realizable engineering procedure.

20.5.3 Kelvin–Planck and Clausius perspectives

A second-law statement equivalent to the engine limit is that no cyclic device can have the sole effect of absorbing heat from a single reservoir and converting it completely into work. An equivalent Clausius form states that no cyclic device can have the sole effect of transferring heat from a colder body to a hotter one without work input. These are not separate empirical laws; they are different operational statements of the same second-law restriction.

Caution

Carnot formulas use absolute temperature. Substituting Celsius readings directly into $1 - T_C/T_H$ changes the physical ratio and can produce nonsensical results. Convert temperatures to kelvin first.

20.5.4 Why the two impossible-device statements are equivalent

The equivalence of the Kelvin–Planck and Clausius statements can be proved by combining devices and cancelling transfers at shared boundaries. The proof concerns sole effects: every component is cyclic, no energy or entropy remains stored after the combined cycle, and any work interaction is included explicitly. It never assumes that heat cannot move from cold to hot; a refrigerator does that routinely with work input. It forbids achieving that transfer as the sole uncompensated effect.

First suppose a Kelvin–Planck violating device absorbs Q from the hot reservoir and delivers exactly Q of work without rejecting heat. Use that work to drive an ordinary cyclic refrigerator. Let the refrigerator remove $q > 0$ from the cold reservoir and reject $q + Q$ to the hot reservoir. The work interactions cancel internally. The hot reservoir loses Q to the hypothetical device and gains $q + Q$ from the refrigerator, for a net gain q . The cold reservoir loses q . The sole external effect is therefore transfer of q from cold to hot without external work: a Clausius violation.

Conversely, suppose a Clausius violating transfer device removes q from the cold reservoir and delivers q to the hot reservoir without work. Pair it with an ordinary engine that absorbs Q_H from the hot reservoir, rejects $q = Q_C$ to the cold reservoir, and delivers $W = Q_H - q$. The cold-reservoir interactions cancel. The hot reservoir supplies a net heat $Q_H - q = W$, which appears completely as work. That is a Kelvin–Planck violation. Scaling the operating durations or number of cycles allows the heat magnitudes to be matched; no assumption of identical components is required.

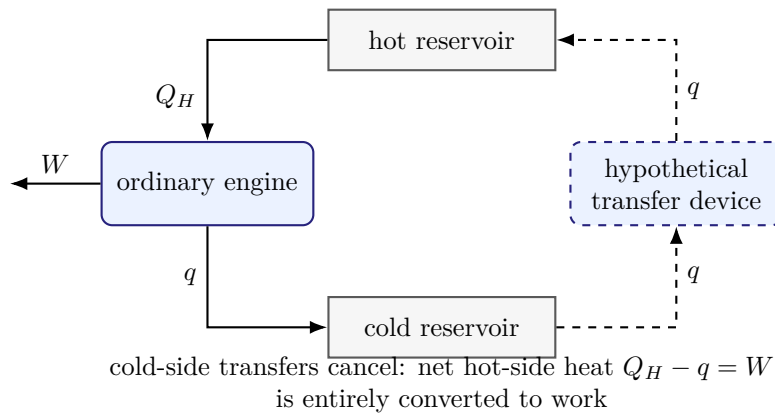
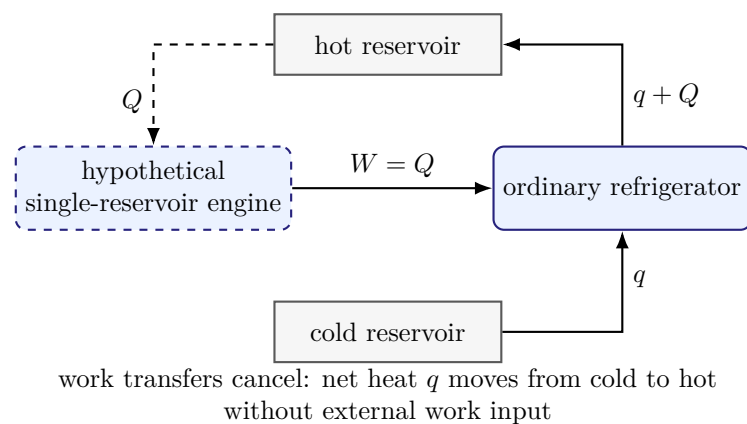
(a) Assume a Clausius violation**(b) Assume a Kelvin–Planck violation**

Figure 20.16: C20-V018 — Constructive equivalence of the second-law device statements. Dashed device borders and arrows mark the assumed impossible component; solid components obey ordinary first-law balances. All symbols are positive transfer magnitudes. Panel (a) cancels the cold-reservoir transfers; panel (b) cancels the work transfers. The combined sole effect violates the other statement in each case. No geometric scale represents transfer magnitude.

Example 20.14: E20-17: Cancelling internal transfers in an impossible composite

An ordinary reversible engine operates between 600 and 300 K with $Q_H = 1200$ J, $Q_C = 600$ J and $W = 600$ J per cycle. Test a hypothetical work-free device that transfers 600 J from the cold reservoir back to the hot reservoir. Then show the converse using an impossible single-reservoir engine supplying the same work to a refrigerator.

First construction. The ordinary engine's reservoir entropy sum is $-1200/600 + 600/300 = 0$. The hypothetical transfer's sum is $+600/600 - 600/300 = -1.00$ J K⁻¹. Combining the devices cancels the 600 J exchanges at the cold side. The hot reservoir loses a net $1200 - 600 = 600$ J, and 600 J of work leaves the composite. Energy is conserved, but the sole effect is complete conversion of single-reservoir heat into work. The entropy decrease remains -1.00 J K⁻¹.

Converse construction. An impossible single-reservoir engine takes 600 J from the 600 K reservoir and delivers 600 J of work. Drive an ordinary reversible refrigerator, which consumes that work, removes 600 J from the 300 K reservoir, and rejects 1200 J to the 600 K reservoir. The external work is zero. The hot reservoir gains $1200 - 600 = 600$ J while the cold reservoir loses 600 J. This is a work-free cold-to-hot transfer with entropy change $600/600 - 600/300 = -1.00$ J K⁻¹.

Check. Each ordinary reversible component has zero total entropy change. The negative entropy contribution belongs to the hypothesized component and survives every cancellation. Listing only one device's heat arrows would conceal the composite sole effect; keeping the full ledger makes the contradiction explicit in both directions.

20.5.5 Regeneration and the meaning of a two-reservoir comparison

The Carnot bound is a bound on external interactions and irreversibility, not a requirement that every reversible engine must have exactly the Carnot cycle's four branches. Consider an ideal Stirling cycle: isothermal expansion at T_H , constant-volume cooling, isothermal compression at T_C , and constant-volume reheating. A perfect regenerator stores the heat released during cooling and returns it during reheating at matching temperatures. In the ideal reversible limit it returns to its initial state each cycle. External heat is then received only at T_H and rejected only at T_C , so the efficiency attains $1 - T_C/T_H$.

Without regeneration, the constant-volume heating requires additional external heat $nC_{V,m}(T_H - T_C)$. Returning that heat over a finite temperature difference generates entropy. Some elementary descriptions call a Stirling engine less efficient than Carnot without specifying the regenerator; that comparison applies to the unregenerated model, not to every ideal Stirling cycle. This is an example of why the system boundary and heat-transfer assumptions belong beside an efficiency statement.

Example 20.15: E20-23: The same cycle with and without regeneration

A model Stirling cycle uses one mole of ideal gas with $C_{V,m} = 5R/2$, $T_H = 600$ K, $T_C = 300$ K and volume ratio $r = 2$. Compare ideal perfect regeneration with no regeneration.

Work. Isochores perform no boundary work. The two isotherms give $W = nR(T_H - T_C) \ln r = 1.72894$ kJ per cycle. With perfect reversible regeneration, $Q_{H,\text{ext}} = nRT_H \ln r = 3.45789$ kJ and $Q_{C,\text{ext}} = 1.72894$ kJ, so $\eta = 0.500$. The external reservoir entropy changes cancel exactly. Without regeneration, reheating adds $nC_{V,m}(T_H - T_C) = 6.23585$ kJ to the required hot-side heat. Thus $Q_{H,\text{ext}} = 9.69373$ kJ and $\eta = 1.72894/9.69373 = 0.1784$. The work remains the same because the specified p - V loop remains the same. The input heat changes because the heat that was internally recovered must now be supplied externally. The energy balance gives $Q_{C,\text{ext}} = 7.96479$ kJ; for external baths fixed at 600 and 300 K this corresponds to $S_{\text{gen}} = 10.3931$ J K⁻¹ > 0 .

Check and limitation. Both efficiencies are below or equal to the two-reservoir bound. Perfect regeneration is an ideal benchmark; finite exchanger temperature differences, storage losses and pressure losses lower actual performance. No commercial device performance is implied by the calculation.

20.6 Refrigerators and heat pumps

A refrigerator and a heat pump describe the same energy transfers but emphasize different useful outputs. A cyclic device removes heat magnitude Q_C from a cold region, receives work input W_{in} , and rejects heat magnitude Q_H to a hot region:

$$Q_H = Q_C + W_{\text{in}}. \quad (20.33)$$

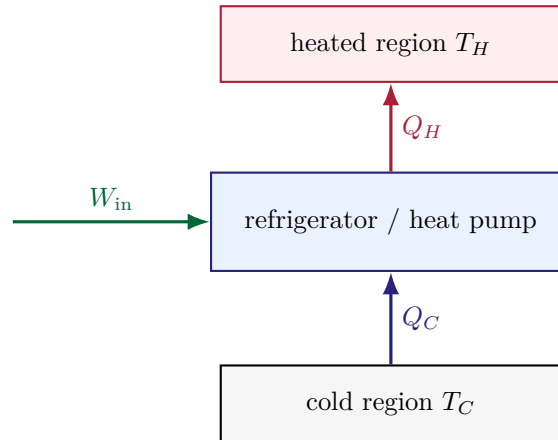
For refrigeration the desired transfer is Q_C ,

$$\text{COP}_R = \frac{Q_C}{W_{\text{in}}}, \quad (20.34)$$

whereas for heating the desired transfer is Q_H ,

$$\text{COP}_{HP} = \frac{Q_H}{W_{\text{in}}} = \text{COP}_R + 1. \quad (20.35)$$

A coefficient of performance can exceed one because it compares a heat transfer with work input; it is not a thermal efficiency.



$$Q_H = Q_C + W_{\text{in}} \quad \text{COP}_{HP} = \text{COP}_R + 1$$

Figure 20.17: Energy flows for the same cyclic device assessed as a refrigerator or heat pump. Work input permits heat to move from cold to hot. Q_C is the useful cooling transfer; Q_H is the useful heating transfer. Magnitudes are positive and schematic arrows do not encode a numerical scale.

For a cyclic device operating between fixed temperatures, the combined reservoir entropy change is

$$S_{\text{gen}} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} \geq 0. \quad (20.36)$$

Substitute the cyclic energy balance into the entropy inequality:

$$\frac{Q_C + W_{\text{in}}}{T_H} - \frac{Q_C}{T_C} \geq 0 \quad \implies \quad W_{\text{in}} \geq Q_C \frac{T_H - T_C}{T_C}.$$

For $T_H > T_C > 0$, division by the positive work input gives the refrigerator bound. Using $Q_H = Q_C + W_{\text{in}}$ then gives the heat-pump bound. The reversible limits are therefore

$$\boxed{\text{COP}_{R,\text{rev}} = \frac{T_C}{T_H - T_C}}, \quad \boxed{\text{COP}_{HP,\text{rev}} = \frac{T_H}{T_H - T_C}}. \quad (20.37)$$

Real COPs must be lower under the same ideal two-reservoir comparison.

Example 20.16: E20-06: Heating and cooling performance of the same device

A model heat-pump cycle operates between $T_C = 275$ K and $T_H = 295$ K. In one reporting interval it consumes $W_{\text{in}} = 2.0$ MJ and extracts $Q_C = 8.0$ MJ from the cold side. The heat delivered is $Q_H = 10.0$ MJ, so

$$\text{COP}_R = 4.0, \quad \text{COP}_{HP} = 5.0.$$

The reversible limits are

$$\text{COP}_{R,\text{rev}} = \frac{275}{20} = 13.75, \quad \text{COP}_{HP,\text{rev}} = \frac{295}{20} = 14.75.$$

The model performance is below the reversible bounds. That establishes consistency with this necessary second-law test; it does not certify a specific real device or installation.

20.6.1 Engineering interpretation

The temperature lift $T_H - T_C$ strongly affects the reversible COP. Reducing that lift raises the thermodynamic upper bound. In real systems, finite heat-exchanger temperature differences, compressor inefficiency, pressure losses, frosting, defrost cycles and auxiliary electrical loads all generate entropy and reduce system COP. A Carnot COP is therefore a benchmark, not a product-performance prediction.

20.6.2 Finite temperature lift, cooling load, and reporting boundaries

The reversible COP depends on reservoir temperatures, not on a specified cooling load. A load determines how much heat must be removed per unit time, while a COP relates that heat removal to required work. For a periodic steady device, define $\dot{Q}_C$ as cooling power and $\dot{W}_{\text{in}}$ as input power. The refrigerator COP is $\dot{Q}_C/\dot{W}_{\text{in}}$ when both powers are averaged over the same interval. Dividing an instantaneous cooling rate by an unrelated daily electrical total has no consistent physical meaning.

At fixed T_C , write the lift as $\Delta T = T_H - T_C > 0$. Then $\text{COP}_{R,\text{rev}} = T_C/\Delta T$ and $\text{COP}_{HP,\text{rev}} = 1 + T_C/\Delta T$. Their difference is exactly one for the same device and reporting boundary. Figure 20.18 shows the rapid deterioration of the bound as lift rises. The asymptote at zero lift concerns an ideal ratio with vanishing reversible work per unit heat transfer. It does not predict infinite cooling capacity or infinite actual performance at finite heat-transfer rate: real exchangers require driving temperature differences and auxiliaries require power.

A simple synthetic model illustrates a separate load effect. Suppose a cooling installation requires an auxiliary power P_0 independent of load and a variable input $\dot{Q}_C/C_*$, where C_* is a stipulated constant cooling COP for the variable part. Then

$$\dot{W}_{\text{in}} = P_0 + \frac{\dot{Q}_C}{C_*}, \quad \text{COP}_{R,\text{system}} = \frac{\dot{Q}_C}{P_0 + \dot{Q}_C/C_*}. \quad (20.38)$$

At small loads the fixed input strongly reduces the reported ratio. At large loads the ratio approaches C_* from below. This is an illustrative balance model, not a compressor correlation: actual partial-load

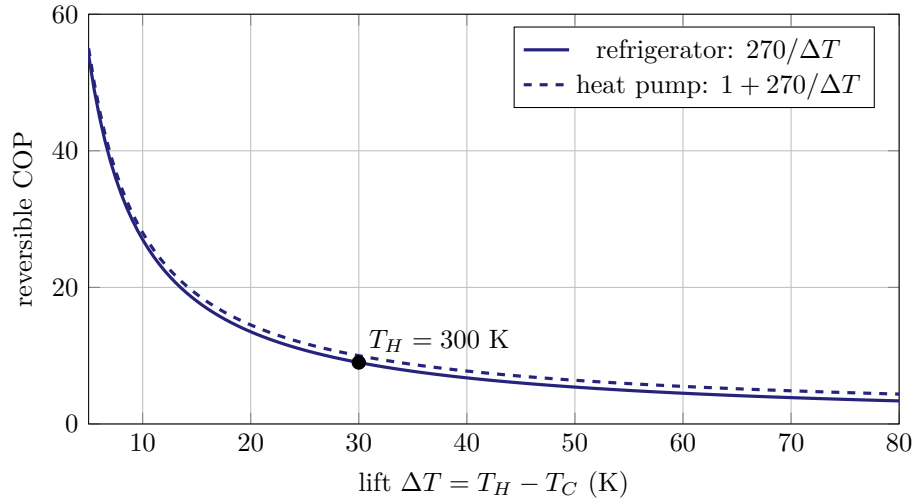


Figure 20.18: C20-V019 — Reversible two-reservoir performance bounds for a fixed cold temperature $T_C = 270$ K and hot temperature $T_H = 270$ K + ΔT . The plotted interval is $5 \leq \Delta T \leq 80$ K; zero lift is deliberately excluded. At $\Delta T = 30$ K the refrigerator bound is 9 and the heat-pump bound is 10. Solid and dashed curves share one colour and differ exactly by one. These are thermodynamic ceilings, not measured device curves.

behaviour may include cycling losses, variable-speed controls and changing exchanger temperatures. Its assumptions must be stated whenever the curve is used.

The auxiliary term may be treated as work dissipated into the hot region for a closed whole-installation boundary. Under that model the total hot-side rate is $\dot{Q}_H = \dot{Q}_C + \dot{W}_{\text{in}}$, and the installation entropy-generation rate is $\dot{Q}_H/T_H - \dot{Q}_C/T_C$. A fan outside the chosen boundary, a motor rejecting heat elsewhere, or a third thermal interaction would require a different balance. This is why system COP and component COP should not be silently interchanged.

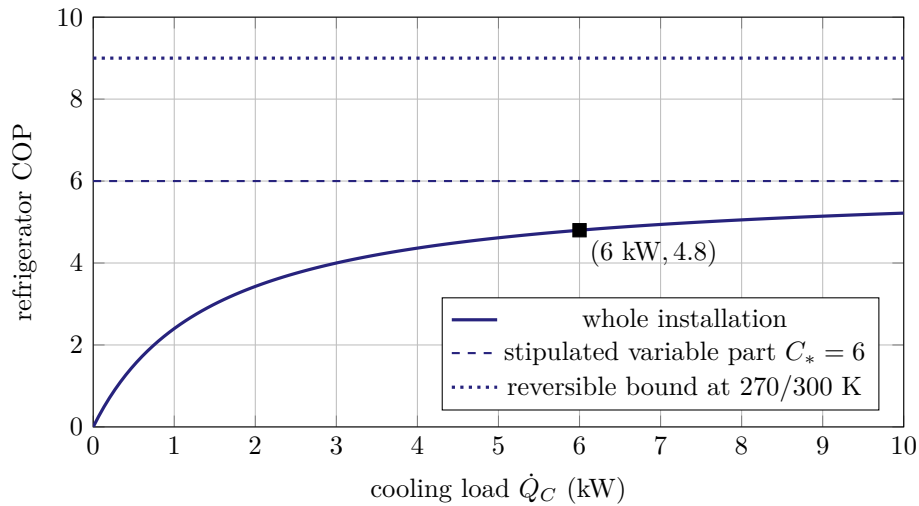


Figure 20.19: C20-V020 — Synthetic load dependence from Eq. (20.38) with $P_0 = 0.250$ kW and $C_* = 6.00$ at fixed reservoir temperatures $T_C = 270$ K, $T_H = 300$ K. All auxiliary input is assumed ultimately rejected to the hot region. The system curve lies below its variable-part ratio and below the reversible bound of 9 at every plotted positive load. The zero-load endpoint has zero heat removal and a finite auxiliary input, so its system COP is zero.

Example 20.17: E20-18: A complete cooling-load and entropy-rate audit

For the synthetic installation in Fig. 20.19, a cooling load of 6.00 kW is maintained between 270 and 300 K. Find the total electrical input, heat rejection, refrigerator COP, corresponding heating COP and entropy-generation rate. Find the reversible minimum input for the same cooling load.

Boundary and assumptions. Include the variable cooling machine and auxiliaries inside a periodic steady boundary. Treat work as the electrical energy entering, neglect net storage over the reporting interval, and let all rejected heat enter the 300 K reservoir. Cooling heat enters from the 270 K reservoir.

$$\dot{W}_{\text{in}} = 0.250 + 6.00/6.00 = 1.250 \text{ kW}, \quad \dot{Q}_H = 6.00 + 1.250 = 7.250 \text{ kW}.$$

Therefore $\text{COP}_R = 6.00/1.250 = 4.80$ and $\text{COP}_{HP} = 7.250/1.250 = 5.80$. Their difference is one, verifying the same-device energy identity. Converting powers to watt gives

$$\dot{S}_{\text{gen}} = \frac{7250}{300} - \frac{6000}{270} = 1.94444 \text{ W K}^{-1} > 0.$$

The reversible minimum input is

$$\dot{W}_{\text{min}} = \frac{\dot{Q}_C}{\text{COP}_{R,\text{rev}}} = \frac{6.00}{270/(300 - 270)} = 0.666667 \text{ kW}.$$

The actual input exceeds this minimum by 0.583333 kW. The fixed-reservoir equality $\dot{W}_{\text{in}} - \dot{W}_{\text{min}} = T_H \dot{S}_{\text{gen}}$ gives $(300)(1.94444) = 583.333 \text{ W}$, an independent check for this matched cooling-load comparison.

Interpretation. The positive generation includes the losses of the stipulated variable part and the hot-side dissipation of auxiliaries. At the same temperatures and half the load, $\dot{W}_{\text{in}} = 0.250 + 3.00/6.00 = 0.750 \text{ kW}$ and the system COP falls to 4.00, although the reservoir Carnot bound remains 9. This answers the load question without attributing the change to a changing temperature lift.

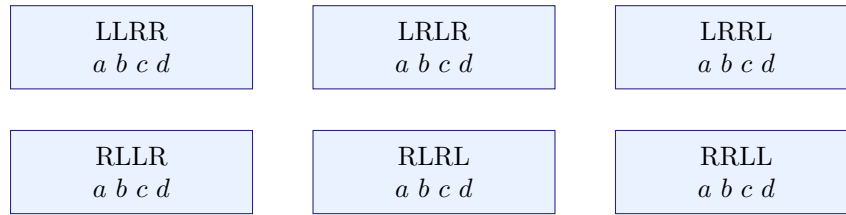
20.7 Statistical interpretation of entropy

Thermodynamics describes macrostates with variables such as T , p , V and S . Statistical mechanics connects such macrostates with possible microscopic configurations. For a deliberately constrained model in which the accessible microstates belonging to a macrostate are equiprobable,

$$S = k_B \ln \Omega, \quad (20.39)$$

where Ω is the multiplicity of the macrostate. This statement requires a specified set of accessible microstates and an equiprobability assumption. It is not a license to count arbitrary arrangements.

The microstate is finer than the macrostate. Label the four particles a, b, c, d in a small illustration and record for each one whether it is left or right. The strings LLRR and LRLR are different microstates even though both belong to the macrostate “two left”. Figure 20.20 lists all six strings in that macrostate; listing only one picture of two particles in each half would miss the combinatorial weight. The labels are a bookkeeping device for this independent classical model. They do not establish that quantum identical particles can always be counted this way.



six equiprobable microstates
one macrostate: $n_L = 2$

Figure 20.20: Explicit assignments for four distinguishable particles, each with left/right probability $1/2$. There are 16 microstates in total; these six give $P(n_L = 2) = 6/16$. Spatial arrangement within either half is deliberately excluded from this constrained counting model.

20.7.1 Two-compartment counting model

Take N distinguishable particles that independently have equal probability of occupying the left or right half of a box. A macrostate can be specified by the number n on the left. Its multiplicity is

$$\Omega(n) = \binom{N}{n} = \frac{N!}{n!(N-n)!}, \quad (20.40)$$

and the total number of left/right microstates is 2^N . The probability of a given n is

$$P(n) = \frac{\Omega(n)}{2^N}. \quad (20.41)$$

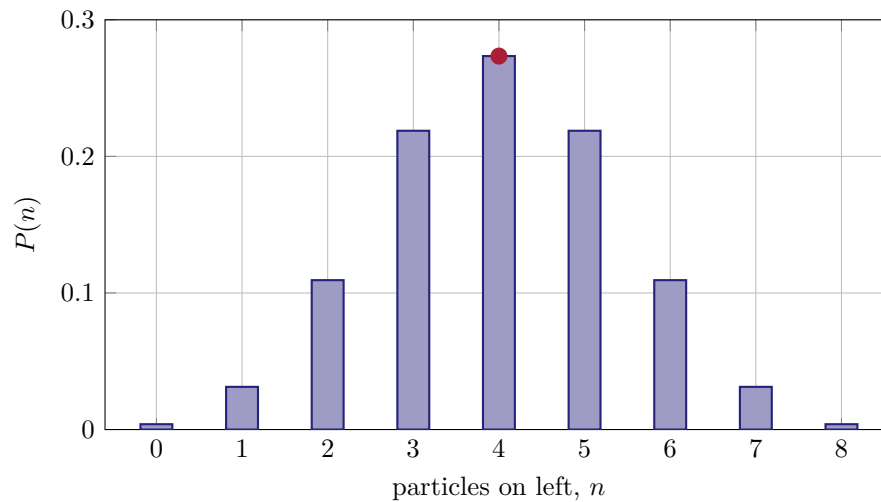


Figure 20.21: F20-07 — Exact probability distribution for $N = 8$ independent distinguishable particles with equal left/right probability. The central macrostate has multiplicity $\binom{8}{4} = 70$ and is most probable, while every individual left/right microstate has probability $1/256$.

Example 20.18: E20-07: A small multiplicity model

For $N = 8$, the multiplicities are

$$1, 8, 28, 56, 70, 56, 28, 8, 1.$$

They sum to $256 = 2^8$. The most probable macrostate is $n = 4$ with

$$P(4) = 70/256 = 0.2734.$$

The two extreme macrostates $n = 0$ and $n = 8$ each have multiplicity one and probability $1/256$.

The entropy associated with the $n = 4$ macrostate in this constrained counting model differs from the $n = 0$ macrostate by

$$S_4 - S_0 = k_B \ln(70/1).$$

The result compares multiplicities under the same constraints; it does not define an absolute entropy for every degree of freedom of a real gas.

Caution

Entropy is not defined as “disorder.” That slogan is too vague to support calculations and can mislead when comparing systems of different sizes or different constraints. The statistical statement used here is precise: under specified accessible equiprobable microstates, entropy varies as the logarithm of multiplicity.

20.7.2 Why the logarithm is natural

For two independent subsystems with multiplicities Ω_A and Ω_B , the combined multiplicity is $\Omega_A \Omega_B$. Entropy is additive for the independent composite system:

$$S_{AB} = k_B \ln(\Omega_A \Omega_B) = k_B \ln \Omega_A + k_B \ln \Omega_B = S_A + S_B.$$

The logarithm converts multiplicative counting into additive thermodynamic entropy.

20.7.3 The large-system tendency

For the equal left/right model, the mean occupancy is $N/2$ and the standard deviation is $\sqrt{N}/2$. Therefore the relative width $\sigma_n/N = 1/(2\sqrt{N})$ becomes very small for large N . Macroscopic equilibrium does not mean that every particle freezes into one configuration; microscopic states keep changing, while overwhelmingly many accessible microstates correspond to macroscopic occupancies close to the most probable range.

20.7.4 Normalization, fractional fluctuations, and the meaning of typical

The central macrostate is the most probable single occupancy, but it is not the only likely occupancy. For $N = 8$, its probability is only $70/256$, whereas a range of neighbouring occupancies has a much larger total probability. For very large N , the probability of any one exact central occupancy actually decreases approximately as $N^{-1/2}$. What becomes overwhelming is the probability of a narrow *fractional range* around one half. This distinction resolves an apparent tension between the phrase “equilibrium is overwhelmingly likely” and a central bin whose individual probability decreases.

Normalization follows directly from the binomial theorem:

$$\sum_{n=0}^N P(n) = 2^{-N} \sum_{n=0}^N \binom{N}{n} = 2^{-N} (1+1)^N = 1. \quad (20.42)$$

The same identity shows that probabilities are obtained from multiplicities only after dividing by the total number of accessible microstates. Multiplicity is an integer count; probability is a dimensionless normalized number. Replacing one with the other without tracking the normalization would corrupt both the plotted distribution and any entropy comparison.

To derive the fluctuation scale, write $n = X_1 + \dots + X_N$, where $X_i = 1$ for a particle on the left and zero otherwise. Independence and equal left/right probabilities give $\langle X_i \rangle = 1/2$ and $\text{var}(X_i) = 1/4$. Consequently $\langle n \rangle = N/2$ and $\text{var}(n) = N/4$. For the fractional occupancy $f = n/N$,

$$\langle f \rangle = \frac{1}{2}, \quad \sigma_f = \frac{\sigma_n}{N} = \frac{1}{2\sqrt{N}}. \quad (20.43)$$

The fractional standard deviation falls while the absolute particle-number standard deviation grows. Relative to the mean particle count, the standard deviation is $\sigma_n/\langle n \rangle = 1/\sqrt{N}$; relative to the full count it is $\sigma_n/N = 1/(2\sqrt{N})$. Stating the denominator avoids a factor-of-two ambiguity in the word “relative.”

Figure 20.22 compares exact distributions on the fractional axis. Their grid spacing is $\Delta f = 1/N$, so the plotted height is $NP(n)$ rather than $P(n)$. This is a discrete density convention: each height times its fractional bin width equals the actual probability mass, and their sum is one. Joining the points helps trace the shape but does not turn the finite counting model into a continuous distribution.

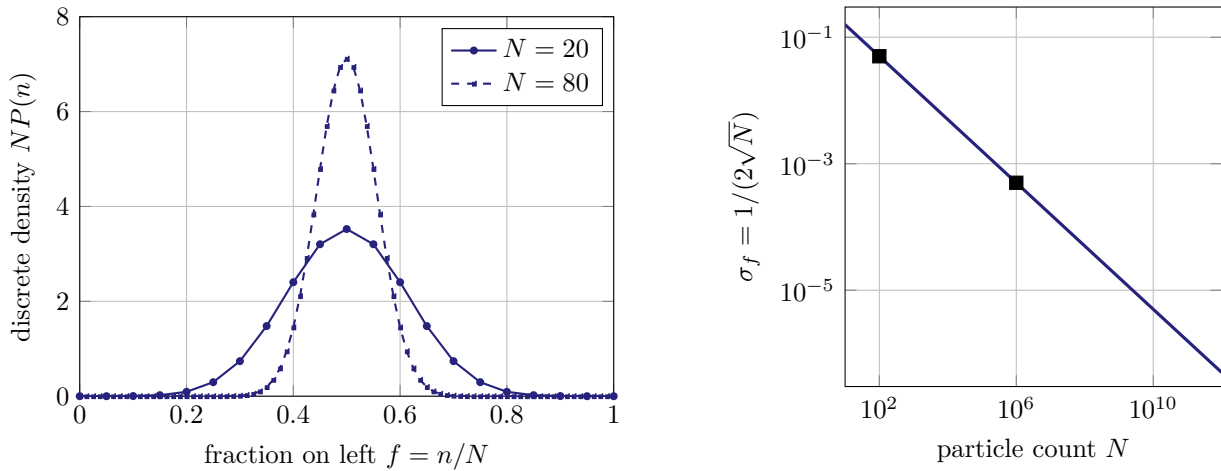


Figure 20.22: C20-V021 — Left: exact binomial distributions for $N = 20$ and 80 independent distinguishable particles with equal compartment probabilities, shown as a discrete density on $f = n/N$. Every full inline table includes $n = 0, \dots, N$ and obeys $\sum[NP(n)]/N = 1$; line segments are guides between discrete values. Increasing N narrows the fractional distribution. Right: the exact fractional standard deviation decreases as $N^{-1/2}$; the plotted interval is $10 \leq N \leq 10^{12}$. Solid circles and dashed squares distinguish the distributions without relying on colour.

Optional enrichment: large-number approximations

The exact counting model above is sufficient for the core discussion. The following asymptotic approximation and the variance bound in E20-19 are enrichment; they are not prerequisites for the finite-body thermodynamic extension. Stirling's formula is

$$\ln M! = M \ln M - M + \frac{1}{2} \ln(2\pi M) + O(M^{-1}).$$

Apply it only when the factorial arguments are large. In a binomial coefficient, both n and $N - n$ must be large; this route does not justify endpoint-tail estimates.

An approximate continuous density follows by using this large-factorial approximation near the centre:

$$P(n) \simeq \sqrt{\frac{2}{\pi N}} \exp \left[-\frac{2(n - N/2)^2}{N} \right]. \quad (20.44)$$

This is a local large- N approximation for occupancy probabilities near $N/2$, not an exact tail formula. The central value scales as $N^{-1/2}$, while the corresponding density on the fractional axis scales as $\sqrt{N}$. The widening count distribution and narrowing fraction distribution are therefore different descriptions of the same statistical behaviour. Exact binomial counting is preferable for the small models plotted here.

The entropy interpretation is also clearer on the fractional axis. Stirling's approximation gives the leading term

$$\ln \Omega(n) \simeq N[-f \ln f - (1 - f) \ln(1 - f)], \quad (20.45)$$

with subleading logarithmic corrections suppressed here. The bracket has its maximum at $f = 1/2$. Writing $f = 1/2 + \epsilon$ and expanding around the maximum gives $\ln \Omega \simeq N \ln 2 - 2N\epsilon^2$ at leading order in ϵ . Since P is proportional to Ω , this reproduces the Gaussian exponent in Eq. (20.44). A small fractional deviation has a multiplicity penalty that grows with N , explaining why the same percentage imbalance is much less likely in a larger independent-particle system.

Neither the binomial formula nor this approximation describes every fluctuation in a real material. Interparticle correlations, unequal compartment volumes, conservation constraints, quantum indistinguishability and long-range interactions can change the accessible states and probabilities. The model nevertheless isolates a useful mechanism: many nearly equivalent microscopic choices can produce highly reproducible macroscopic fractions. A statistical tendency toward typical macrostates is a probabilistic statement, not a claim that all microscopic transitions increase the coarse-grained entropy on every occasion.

Example 20.19: E20-19: A typical range is more likely than one exact occupancy

For the independent equal-compartment model, calculate the exact central-bin probability and the probability of $8 \leq n \leq 12$ for $N = 20$. Compare the central-bin probability for $N = 80$. Then find the count and fractional standard deviations for $N = 10^6$ and give a conservative bound on an imbalance satisfying $|f - 1/2| \geq 0.01$. Finally compare the $N = 20$, $n = 10$ macrostate entropy with the $n = 0$ macrostate entropy.

Exact small-system probabilities. There are 2^{20} equally probable left/right microstates. Therefore

$$P_{20}(10) = \frac{\binom{20}{10}}{2^{20}} = \frac{184756}{1048576} = 0.176197.$$

The range probability requires a sum, not five copies of the central value:

$$P_{20}(8 \leq n \leq 12) = 2^{-20} \sum_{j=8}^{12} \binom{20}{j} = 0.736824.$$

The central-bin probability for $N = 80$ is $\binom{80}{40}/2^{80} = 0.0889279$, smaller than for $N = 20$. This is consistent with a narrower fractional distribution because the fractional bins are also four times narrower.

Large-system fluctuation scale. At $N = 10^6$, $\sigma_n = \sqrt{N}/2 = 500$ particles, while $\sigma_f = 500/10^6 = 5.00 \times 10^{-4}$. A one-percentage-point imbalance is 20 fractional standard deviations. Without treating a Gaussian approximation as an exact extreme-tail probability, use the variance inequality

$$P(|f - \langle f \rangle| \geq \epsilon) \leq \frac{\text{var}(f)}{\epsilon^2}.$$

With $\epsilon = 0.01$ and $\text{var}(f) = 1/(4N) = 2.50 \times 10^{-7}$, the bound is 0.00250. This is a conservative upper bound, not the exact tail probability; the assumptions establishing the variance are independence and equal probabilities.

Entropy comparison. Under the same constrained counting model, $\Omega(0) = 1$ and $\Omega(10) = 184756$. Thus

$$S_{10} - S_0 = k_B \ln 184756 = 1.67428 \times 10^{-22} \text{ J K}^{-1}.$$

The positive sign agrees with the larger multiplicity. The logarithm contains a ratio of counts and is dimensionless. The very small numerical entropy belongs to a 20-particle positional counting model; it does not include the momentum states or all other degrees of freedom of a macroscopic gas.

The examples also clarify what is meant by a spontaneous return after free expansion. A small system can fluctuate toward less typical occupancies. For a specified extreme occupancy in the independent model its probability is 2^{-N} , which falls much faster than the fractional fluctuation width. Turning that probability into a waiting time would additionally require a dynamical model of statistically independent trials. Counting alone supplies no trial frequency, so this chapter does not infer a physical recurrence time from the distribution.

20.8 Real cycles, irreversibility, and lost work

Entropy generation is a diagnostic of degraded work potential. A carefully bounded relation is the Gouy–Stodola form

$$W_{\text{lost}} = T_0 S_{\text{gen}}, \quad (20.46)$$

when an irreversible process is compared with a reversible process between the same relevant end states and with the same environment at temperature T_0 . The relation is powerful only when the comparison basis is held fixed; “energy dissipated” is not automatically equal to lost useful work in every context.

For $T_H > T_C \geq T_0 > 0$, the direct-use reversible work is $W_a = Q(1 - T_0/T_H)$, while work after degradation is $W_b = Q(1 - T_0/T_C)$. Subtracting gives

$$W_a - W_b = T_0 Q \left(\frac{1}{T_C} - \frac{1}{T_H} \right) = T_0 S_{\text{gen}}.$$

The source loses the same heat in both routes and the intermediate reservoir has no net change. The environment receives more rejected heat in the degradation route by exactly the lost work amount. This identifies the matching comparison explicitly; it does not assign a universal work loss to every entropy increase.

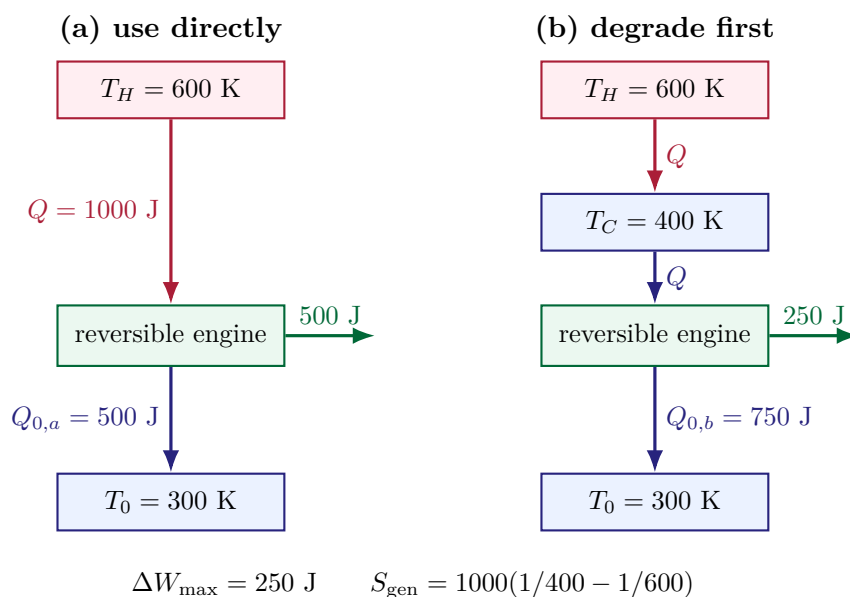


Figure 20.23: Correct work-potential comparison for the same source heat quantity and environment. In (b), direct transfer to the intermediate reservoir generates entropy; a reversible engine then extracts less work. Heat rejection to the environment is 500 J in (a) and 750 J in (b). The intermediate reservoir gains and then loses the same Q . Reservoir blocks are schematic, not finite bodies.

Example 20.20: E20-08: Lost work from thermal degradation

A heat quantity $Q = 1000 \text{ J}$ is available at $T_H = 600 \text{ K}$ but is first degraded to $T_C = 400 \text{ K}$ before being used against an environment at $T_0 = 300 \text{ K}$. Treat the temperatures as fixed reservoirs for this comparison.

The entropy generated in the degradation step is

$$S_{\text{gen}} = Q \left(\frac{1}{T_C} - \frac{1}{T_H} \right) = 0.8333 \text{ J K}^{-1}.$$

The associated decrease in maximum available work against the same T_0 is

$$W_{\text{lost}} = T_0 S_{\text{gen}} = (300)(0.8333) = 250 \text{ J}.$$

Indeed, the reversible work opportunity changes from $Q(1 - T_0/T_H) = 500 \text{ J}$ to $Q(1 - T_0/T_C) = 250 \text{ J}$, a reduction of 250 J.

20.8.1 Computational connection: an entropy-balance checker

A short program can audit a two-reservoir cyclic device. The code is not a substitute for choosing the physical system correctly; it only evaluates the model supplied to it.

Listing 20.1: Minimal cyclic heat-engine balance checker. Positive Q_H and Q_C are magnitudes.

```
def engine_audit(QH, QC, TH, TC):
    if min(QH, QC, TH, TC) <= 0.0:
        raise ValueError("positive magnitudes and absolute temperatures required")
    if TH <= TC or not (0.0 < QC < QH):
        raise ValueError("heat-engine scope requires TH>TC and 0<QC<QH")
    Wout = QH - QC
    eta = Wout / QH
    Sgen = QC/TC - QH/TH
    eta_carnot = 1.0 - TC/TH
```

```
return Wout, eta, Sgen, eta_carnot
```

Useful tests are more informative than a plausible output: set $Q_C/Q_H = T_C/T_H$ and verify $S_{\text{gen}} = 0$; increase Q_C at fixed Q_H and verify $S_{\text{gen}} > 0$ while efficiency falls; then intentionally choose an efficiency above Carnot and verify that $S_{\text{gen}} < 0$ flags the impossible input.

20.9 Advanced Topics for Technical and Engineering Students

The core treated reservoirs whose temperatures were fixed and finite bodies brought into direct contact. Real thermal systems often lie between those idealizations. This advanced section develops a finite-reservoir benchmark: the maximum work obtainable while two finite bodies approach a common equilibrium temperature through an ideal reversible engine. The additional mathematics is modest—logarithmic entropy balances, weighted geometric means, series expansions and numerical quadrature—but the conceptual payoff is substantial. It shows exactly how irreversibility can destroy work opportunity even when total energy is conserved.

20.9.1 Finite reservoirs: direct contact versus reversible work extraction

Take two bodies with the same constant heat capacity C . Initially they are at $T_H > T_C$. If they are placed in direct thermal contact inside an isolated enclosure, no work leaves the pair. Energy conservation gives

$$T_{f,\text{direct}} = \frac{T_H + T_C}{2}. \quad (20.47)$$

The entropy generated is

$$S_{\text{gen,direct}} = C \ln \left(\frac{T_{f,\text{direct}}^2}{T_H T_C} \right) > 0. \quad (20.48)$$

Now insert an ideal reversible cyclic engine between the bodies. Because the pair plus cyclic engine is an adiabatic closed composite, and work carries no entropy transfer in this model, reversibility requires zero total entropy change:

$$C \ln \left(\frac{T_f}{T_H} \right) + C \ln \left(\frac{T_f}{T_C} \right) = 0. \quad (20.49)$$

Hence

$$\boxed{T_{f,\text{rev}} = \sqrt{T_H T_C}.} \quad (20.50)$$

The final temperature is the geometric mean rather than the arithmetic mean. Since $\sqrt{T_H T_C} \leq (T_H + T_C)/2$, the reversible path leaves less internal energy in the pair; the difference emerges as maximum work:

$$\boxed{W_{\text{max}} = C \left(T_H + T_C - 2\sqrt{T_H T_C} \right) = C \left(\sqrt{T_H} - \sqrt{T_C} \right)^2.} \quad (20.51)$$

Example 20.21: E20-09: Maximum work from two finite bodies

Two bodies each have constant heat capacity $C = 1.00 \text{ kJ K}^{-1}$. Initially $T_H = 500 \text{ K}$ and $T_C = 300 \text{ K}$.

Reversible path.

$$T_{f,\text{rev}} = \sqrt{(500)(300)} = 387.30 \text{ K}.$$

The hot body releases 112.70 kJ and the cold body receives 87.30 kJ. Their difference is

$$W_{\text{max}} = 25.40 \text{ kJ}.$$

Their entropy changes are equal and opposite:

$$\Delta S_H = -255.41 \text{ J K}^{-1}, \quad \Delta S_C = +255.41 \text{ J K}^{-1}.$$

Direct contact. The arithmetic-mean final temperature is 400.0 K and no work leaves the pair. The entropy generated is

$$S_{\text{gen,direct}} = 64.54 \text{ J K}^{-1}.$$

Both paths conserve energy. Only the reversible path extracts the maximum work allowed by the stated constraints while preserving zero total entropy generation.

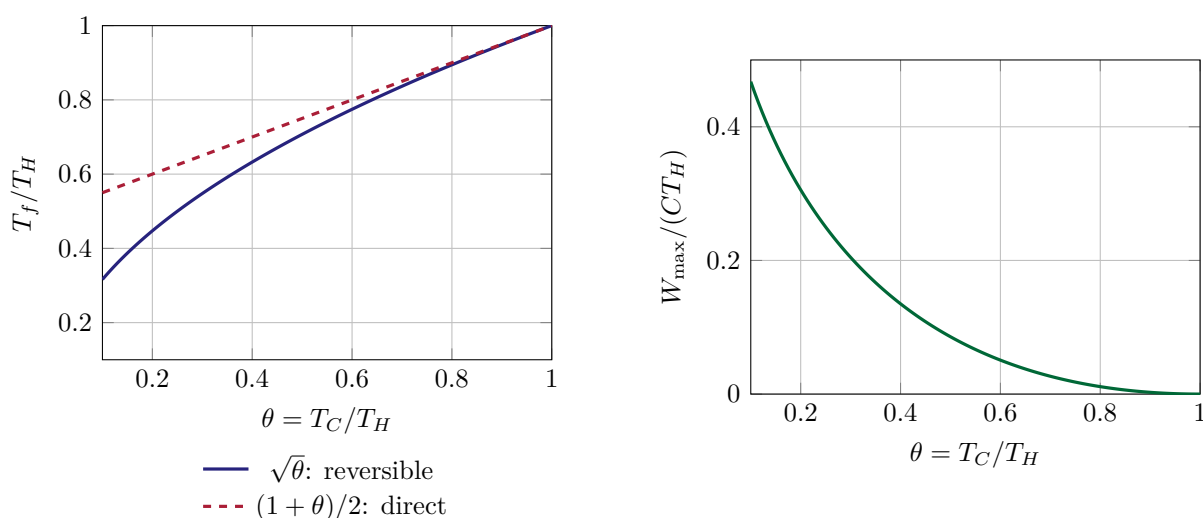


Figure 20.24: F20-09 — Finite-reservoir benchmark for equal heat capacities. Left: the reversible common temperature is the geometric mean, below the direct-contact arithmetic mean. Right: the energy difference appears as maximum work, normalized by CT_H . Neither body is a fixed-temperature reservoir.

20.9.2 Following a finite-body engine through its changing temperatures

For a finite hot body, an increment of heat removal changes its temperature. Thus using the initial Carnot efficiency for the whole process would overestimate the work. Let q_H denote cumulative heat removed from the hot body, and let T_h, T_c denote the instantaneous temperatures. With equal constant capacities, $q_H = C(T_H - T_h)$. Reversible heat transfer to the cold body satisfies $\delta q_C/T_c = \delta q_H/T_h$. Since $\delta q_H = -C dT_h$ and $\delta q_C = C dT_c$, we obtain

$$\frac{dT_c}{T_c} = -\frac{dT_h}{T_h}, \quad T_h T_c = T_H T_C.$$

The product, rather than the sum, stays constant. The instantaneous work output is

$$\delta W = \delta q_H - \delta q_C = \left(1 - \frac{T_c}{T_h}\right) \delta q_H.$$

Integrating this equation until $T_h = T_c$ recovers Eq. (20.51); it supplies a second route to the endpoint result. In Figure 20.25, compare the cold-body temperature after a fixed hot-side heat withdrawal, rather than after an unspecified common time. A reversible engine sends part of the withdrawn energy out as work, so the cold body warms less than it would in direct contact.

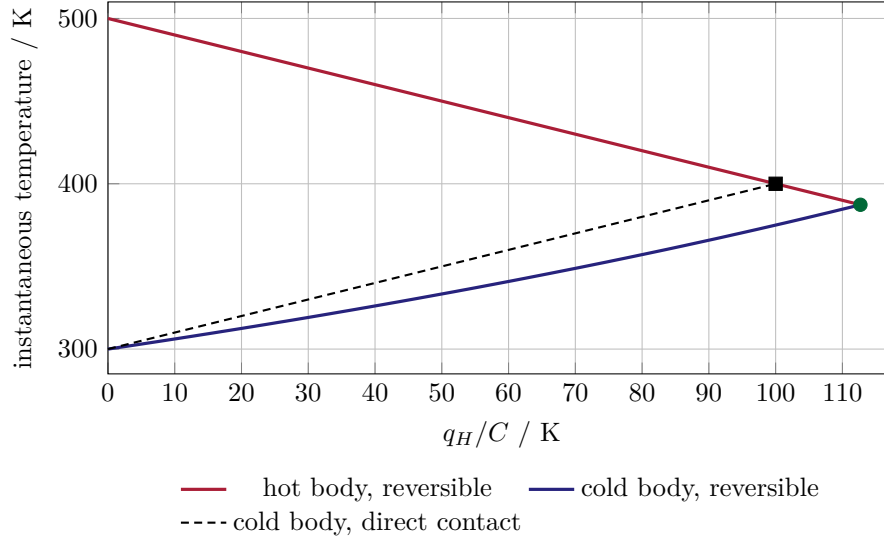


Figure 20.25: Two finite-body processes beginning at 500 and 300 K. The horizontal axis measures energy withdrawn from the hot body divided by its constant heat capacity, not elapsed time. The direct-contact hot curve coincides with $500 - q_H/C$ but terminates at the square. Reversible operation continues to the circular endpoint at 387.30 K.

There is no claim that the reversible engine operates at appreciable power. Reversibility requires infinitesimal temperature mismatches at the contacts and no dissipative work loss. The endpoint calculation gives an energy limit, not a duration, a power rating or a mechanical design.

The cumulative work at an intermediate hot temperature follows directly from energy conservation:

$$\frac{W(q_H)}{C} = T_H + T_C - \left(T_H - \frac{q_H}{C}\right) - \frac{T_H T_C}{T_H - q_H/C}. \quad (20.52)$$

Its derivative with respect to q_H is $1 - T_c/T_h$, exactly the instantaneous efficiency. The slope tends to zero at the common-temperature endpoint. This diminishing slope is the reason a final increment of heat cannot be assigned the initial efficiency.

20.9.3 Unequal heat capacities

For constant but unequal heat capacities C_H and C_C , reversible operation imposes

$$C_H \ln \frac{T_f}{T_H} + C_C \ln \frac{T_f}{T_C} = 0,$$

so

$$T_{f,\text{rev}} = T_H^{C_H/(C_H+C_C)} T_C^{C_C/(C_H+C_C)}. \quad (20.53)$$

This is a weighted geometric mean. The maximum work is the decrease in total internal energy for the constant- C model:

$$W_{\text{max}} = C_H T_H + C_C T_C - (C_H + C_C) T_{f,\text{rev}}. \quad (20.54)$$

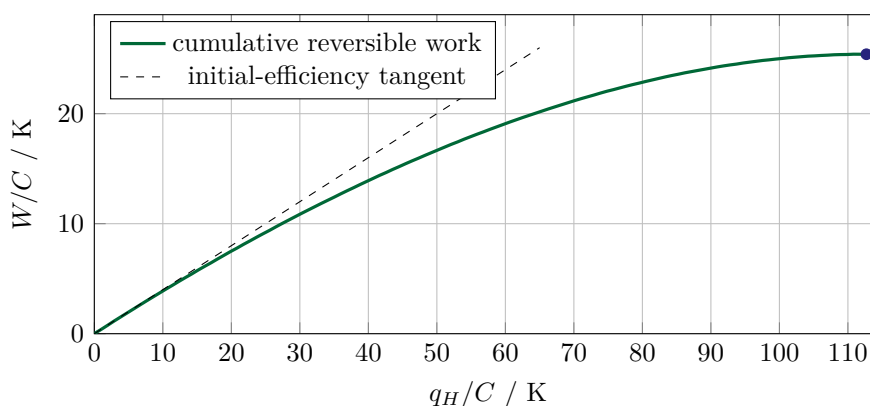


Figure 20.26: Accumulated work for the reversible process in Figure 20.25. The initial slope is 0.4; it decreases continuously to zero. For $C = 1.00 \text{ kJ K}^{-1}$, the final ordinate corresponds to 25.40 kJ, not 0.4 times the total heat withdrawal. The dashed tangent is a local estimate, not a physical path.

The direct-contact temperature remains the weighted arithmetic mean of Eq. (20.17). The difference between arithmetic and geometric means is the mathematical signature of the work opportunity created by the temperature difference under these assumptions.

20.9.4 Why the reversible endpoint maximizes work

The word “maximum” needs a constraint argument. Assume the two bodies and a cyclic engine form an adiabatic closed composite; no external heat enters, and work is the only energy crossing its boundary. It is not an isolated system, because work leaves. For any admissible process that ends with both bodies at a common temperature T_f , the entropy balance is

$$(C_H + C_C) \ln T_f - C_H \ln T_H - C_C \ln T_C = S_{\text{gen}} \geq 0,$$

where a common reference temperature is implicit inside the logarithms and cancels. Consequently

$$T_f \geq T_H^{C_H/(C_H+C_C)} T_C^{C_C/(C_H+C_C)}.$$

Energy conservation gives $W = C_H T_H + C_C T_C - (C_H + C_C) T_f$, with any reference energy canceling. Since both capacities are positive, the smallest allowed T_f gives the largest work. Equality in the entropy inequality is achieved by the reversible limiting path, which proves the claim within this model.

Example 20.22: E20-20: Unequal finite thermal stores

An ideal reversible engine draws work from two finite bodies with constant capacities $C_H = 1.00 \text{ kJ K}^{-1}$ and $C_C = 2.00 \text{ kJ K}^{-1}$, initially at 600 and 300 K. Determine their common final temperature, the heat removed from each body or delivered to it, and the work. Compare with direct contact.

Strategy. The temperatures vary, so a fixed-reservoir Carnot efficiency cannot be applied to the entire run. Use zero total entropy change to find the final state, then use energy to find transfers.

$$\ln(T_f/600) + 2 \ln(T_f/300) = 0, \quad T_f = 600^{1/3} 300^{2/3} = 377.976 \text{ K}.$$

The hot body supplies $Q_H = C_H(600 - T_f) = 222.024 \text{ kJ}$; the cold body receives $Q_C = C_C(T_f - 300) = 155.953 \text{ kJ}$. Thus $W = 66.071 \text{ kJ}$. These positive transfers add up correctly: $222.024 = 155.953 + 66.071$ to rounding accuracy.

Direct contact ends at $(600 + 2 \times 300)/3 = 400 \text{ K}$ and exports no work. Its total entropy increase is $1000 \ln(400/600) + 2000 \ln(400/300) = 169.899 \text{ J K}^{-1}$. The reversible final temperature is

lower because some energy has left as work. The inequality between weighted arithmetic and geometric means is the mathematical check; neither endpoint is below 300 K or above 600 K.

Caution

Do not equate the finite-body $W_{\max}$ with T_0 times the entropy generated by direct contact without specifying a matching environment and matching endpoints. Direct contact and reversible work extraction leave different final temperatures. For the equal-capacity 500/300 K case, $W_{\max} = 25.40$ kJ, whereas an arbitrary $T_0 = 300$ K times the direct-contact entropy generation is 19.36 kJ. The mismatch is a difference in comparison constraints, not a failure of the second law.

20.9.5 Temperature-dependent heat capacities and numerical solution

If $C_H(T)$ and $C_C(T)$ vary appreciably, the reversible final temperature solves

$$\int_{T_H}^{T_f} \frac{C_H(T)}{T} dT + \int_{T_C}^{T_f} \frac{C_C(T)}{T} dT = 0. \quad (20.55)$$

Once T_f is found, maximum work follows from the decrease in total internal energy,

$$W_{\max} = - \left[\int_{T_H}^{T_f} C_H(T) dT + \int_{T_C}^{T_f} C_C(T) dT \right]. \quad (20.56)$$

A numerical root finder should be bracketed by physically meaningful temperatures and tested on a constant- C case for which the exact geometric-mean result is known. Numerical convergence cannot repair a wrong entropy balance or an invalid heat-capacity model.

For example, if $C(T) = A + BT$, then

$$\Delta S = A \ln \frac{T_f}{T_i} + B(T_f - T_i). \quad (20.57)$$

This analytic result is a useful benchmark for quadrature code.

20.9.6 A reproducible variable-capacity calculation

The reversible entropy residual in Eq. (20.55) is a scalar function $F(T)$. When both heat capacities are positive and continuous, $F'(T) = [C_H(T) + C_C(T)]/T > 0$. Furthermore $F(T_C) < 0$ and $F(T_H) > 0$. There is therefore one and only one root in the physical interval (T_C, T_H) . Bisection is especially transparent: its sign bracket prevents an unphysical root and its interval width gives a rigorous temperature error bound. A faster method may be used, but speed is not a substitute for a valid bracket.

Method

Given positive functions $C_H(T)$, $C_C(T)$ and $T_H > T_C > 0$: set $a = T_C$, $b = T_H$; evaluate the two entropy integrals at $m = (a + b)/2$; replace a by m if $F(m) < 0$, otherwise replace b . Repeat until $b - a$ is smaller than the required temperature tolerance. Evaluate the energy integrals at the root. For numerical quadrature, repeat with a finer mesh and compare both T_f and W . First reproduce the exact constant-capacity geometric mean and the analytic $A + BT$ integrals.

Example 20.23: E20-21: Variable-capacity finite bodies

Two stipulated model bodies have capacities $C_H(T) = 400 + 0.200T$ and $C_C(T) = 600 + 0.100T$ in J K^{-1} when T is inserted in kelvin. The slope coefficients have units J K^{-2} . Initially $T_H = 500 \text{ K}$ and $T_C = 300 \text{ K}$. Find the reversible common temperature and work.

Model and calculation. No phase change occurs; capacities remain positive throughout the interval. Analytical entropy integration gives

$$F(T) = 400 \ln(T/500) + 0.200(T - 500) + 600 \ln(T/300) + 0.100(T - 300).$$

Bracketed solution yields $T_f = 374.557549 \text{ K}$. The energy primitives are $400T + 0.100T^2$ and $600T + 0.050T^2$. Subtracting their final sum from their initial sum gives $W_{\max} = 13.89845 \text{ kJ}$. In direct contact, the energy residual instead vanishes at $T_{f,\text{direct}} = 387.03105 \text{ K}$; that path generates 36.5015 J K^{-1} and exports no work.

Checks. The reversible root lies between 300 and 500 K. The analytic entropy residual at the quoted root is smaller than $3 \times 10^{-6} \text{ J K}^{-1}$ after decimal rounding. Independent quadrature of $C(T)/T$ and $C(T)$ reproduces the root and work. The final work is positive and smaller than the heat withdrawn from the hot body. The values describe these model functions, not a named material property measurement.

Figure 20.27 makes the unique-root argument visible. It also shows why an entropy root and an energy root solve different questions. A direct-contact endpoint cannot be substituted into the reversible engine calculation merely because both bodies have equal final temperatures.

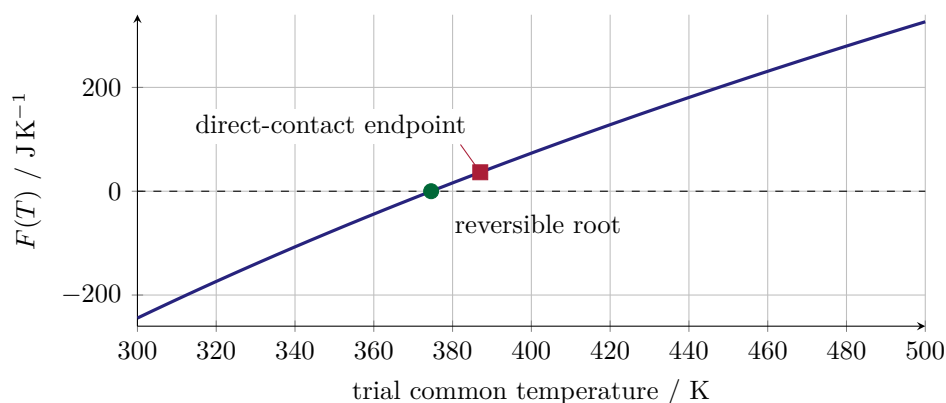


Figure 20.27: Entropy residual for the model in E20-21. The strictly increasing curve crosses zero once. The square is the energy-conserving direct-contact endpoint; its positive ordinate is the generated entropy of that process.

For this analytic residual a 200-K bisection bracket is at most $200/2^{20} = 1.91 \times 10^{-4} \text{ K}$ wide after 20 iterations and $200/2^{30} = 1.86 \times 10^{-7} \text{ K}$ wide after 30. These are guaranteed bracket widths, not measured material accuracy. If the integral is itself approximated, its error must also be small enough to establish the sign. For the hot-body entropy integral from 500 K to the quoted root, composite trapezoidal meshes of 50, 100 and 200 intervals give absolute errors of about 6.56×10^{-4} , 1.64×10^{-4} and $4.10 \times 10^{-5} \text{ J K}^{-1}$, respectively. The factor-of-four decrease is consistent with second-order convergence. It certifies this smooth numerical integration benchmark, not every possible heat-capacity model.

20.9.7 Small temperature differences

Write $T_H = \bar{T} + \Delta T/2$ and $T_C = \bar{T} - \Delta T/2$ with $|\Delta T| \ll \bar{T}$. Expanding Eq. (20.51) gives

$$W_{\max} \simeq \frac{C(\Delta T)^2}{4\bar{T}} \quad (|\Delta T| \ll \bar{T}). \quad (20.58)$$

There is no term linear in ΔT : exchanging the labels hot and cold changes the sign of ΔT but cannot change the nonnegative maximum work. The leading behaviour must therefore be even in the temperature difference.

20.9.8 Fluctuation scale in the two-compartment model

For equal left/right probability, the binomial distribution has

$$\langle n \rangle = \frac{N}{2}, \quad \sigma_n = \frac{\sqrt{N}}{2}. \quad (20.59)$$

The absolute fluctuation grows as $\sqrt{N}$ while the relative fluctuation σ_n/N falls as $N^{-1/2}$. Near $n = N/2$, the multiplicity may be approximated by a Gaussian form. This is the mathematical reason macroscopic equilibrium variables can be extremely stable even though microscopic configurations fluctuate continually.

Pedagogical boundary

This fluctuation discussion is a bridge, not a full statistical-mechanics treatment. It does not introduce canonical ensembles, partition functions or quantum statistics as prerequisites for the core second-law material.

20.10 Chapter summary and working formula sheet

Summary

The first law constrains energy accounting; the second law constrains process direction and attainable performance. Entropy is a state function, so an irreversible process may be assigned an entropy change by integrating $\delta Q_{\text{rev}}/T$ along any reversible comparison path with the same endpoints. Entropy can cross a boundary with heat and can be generated by irreversibility; $S_{\text{gen}} \geq 0$. For an isolated system, $\Delta S = S_{\text{gen}}$.

A cyclic engine obeys $W_{\text{out}} = Q_H - Q_C$ and $\eta = W_{\text{out}}/Q_H$, but the second law limits $\eta \leq 1 - T_C/T_H$. A refrigerator and heat pump obey $Q_H = Q_C + W_{\text{in}}$ with reversible COP bounds determined by the same two temperatures. Under specified equiprobable microscopic constraints, $S = k_B \ln \Omega$ links thermodynamic entropy to multiplicity without defining entropy as vague “disorder.”

Formula summary

Entropy as a state function

$$\Delta S = \int_i^f \frac{\delta Q_{\text{rev}}}{T}, \quad \Delta S = C \ln \frac{T_f}{T_i}, \quad \Delta S_{\text{ideal gas}} = nC_{V,m} \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}.$$

Closed-system entropy balance

$$\Delta S_{\text{sys}} = \sum_j \int \frac{\delta Q_j}{T_{b,j}} + S_{\text{gen}}, \quad S_{\text{gen}} \geq 0.$$

Heat engine

$$W_{\text{out}} = Q_H - Q_C, \quad \eta = 1 - \frac{Q_C}{Q_H}, \quad \eta \leq 1 - \frac{T_C}{T_H}.$$

Refrigerator / heat pump

$$Q_H = Q_C + W_{\text{in}}, \quad \text{COP}_R = \frac{Q_C}{W_{\text{in}}} \leq \frac{T_C}{T_H - T_C},$$

$$\text{COP}_{HP} = \frac{Q_H}{W_{\text{in}}} \leq \frac{T_H}{T_H - T_C}.$$

Statistical interpretation under stated equiprobable constraints

$$S = k_B \ln \Omega, \quad \Omega(n) = \binom{N}{n}.$$

20.11 Exercises and problems

The following sequence moves from system boundaries and conceptual distinctions to numerical entropy balances, cycle audits, a constrained statistical model, and advanced engineering comparisons. Problems 1–30 use the core material; Problems 31–44 draw on the finite-body extension or combine several core ideas. A complete solution to every part follows the statements. Show the system boundary, heat/work directions, assumptions, and an independent physical check; a numerical result alone is not a complete answer.

Use $R = 8.314462618 \text{ J mol}^{-1}\text{K}^{-1}$ and $k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$. Heat quantities labelled Q_H, Q_C are positive magnitudes; a signed Q is positive into the chosen closed system. All entropy and Carnot temperatures are absolute. Treat stipulated heat capacities as model parameters rather than exact material data.

A. Concepts, reversibility and entropy meaning

Problem 1: direction beyond energy conservation

A rigid insulated box contains two metal blocks initially at different temperatures. **(a)** Explain why the first law cannot decide which block warms and which cools. **(b)** State the second-law information that decides the direction, including the relevant system boundary.

Problem 2: slow versus reversible

(a) Distinguish a reversible process from a quasi-static process. **(b)** Give a quasi-static but irreversible example and identify its entropy-generation mechanism.

Problem 3: decreasing subsystem entropy

A closed system loses entropy during a process. Must the second law be violated? Explain using separate entropy-transfer and entropy-generation terms, and give a consistent physical example.

Problem 4: adiabatic and zero entropy change

A closed system is adiabatic and has $\Delta S = 0$. **(a)** What follows about S_{gen} ? **(b)** What can be inferred about reversibility within the entropy-balance model, and what has not been established about external processes?

Problem 5: free expansion

Explain why substituting the actual $Q = 0$ of adiabatic ideal-gas free expansion into $\Delta S = Q/T$ is invalid. Identify a reversible comparison path that computes the correct entropy change.

Problem 6: an operational definition

A student says, “Entropy is the amount of disorder.” Give two distinct reasons why this is an inadequate operational definition here. Replace it with precise thermodynamic and statistical statements, identifying the statistical model’s constraints.

Problem 7: three different conditions

(a) Define isolated, adiabatic and isentropic for a closed system. (b) Identify valid implications among these conditions and reversibility; explain two implications that fail without an additional assumption.

B. Entropy changes and balances**Problem 8: reversible isothermal heat**

A system receives 2.40 kJ reversibly and isothermally at 400 K. Find its entropy change.

Problem 9: heating a finite body

A model body of mass 0.500 kg has constant $c = 900 \text{ J kg}^{-1}\text{K}^{-1}$ and is heated from 300 to 360 K. Find its entropy change. Explain whether these data also determine the entropy generated during the actual heating process.

Problem 10: melting at fixed temperature

A 0.250 kg sample melts reversibly at 273.15 K. Use stipulated latent heat $L = 334 \text{ kJ kg}^{-1}$. Find the sample’s entropy change and the compensating reservoir change.

Problem 11: gas endpoint calculation

Two moles of an ideal monatomic gas go from $(T_i, V_i) = (300 \text{ K}, 5.0 \text{ L})$ to $(450 \text{ K}, 10.0 \text{ L})$. Use $C_{V,m} = 3R/2$. (a) Find ΔS . (b) Describe a reversible two-step comparison path and separate its two entropy contributions.

Problem 12: finite-body direct contact

Two bodies, each with constant $C = 400 \text{ J K}^{-1}$, initially at 350 and 290 K are placed in direct contact in an isolated enclosure. (a) Find T_f . (b) Calculate both body entropy changes and S_{gen} .

Problem 13: entropy received and generated

A closed system receives 500 J through a boundary at 400 K and its entropy rises by 1.80 J K^{-1} . Find the entropy generated inside the chosen boundary and classify the process under this model.

Problem 14: adiabatic irreversibility

An adiabatic closed process has $\Delta S = 3.0 \text{ J K}^{-1}$. Find S_{gen} and classify the process as reversible or irreversible within the stated model.

C. Engines, refrigerators and heat pumps

Problem 15: cyclic energy accounting

A cyclic engine absorbs 2.0 kJ and rejects 1.3 kJ per cycle. (a) Find W_{out} and thermal efficiency. (b) Explain why these two heat data alone do not establish second-law feasibility.

Problem 16: testing an engine claim

An engine between fixed reservoirs at 700 and 300 K absorbs 2.00 kJ and claims to deliver 1.25 kJ per cycle. (a) Find Q_C , η and η_C . (b) Calculate the reservoir entropy change and test both laws.

Problem 17: a feasible irreversible engine

An engine between 800 and 320 K absorbs 1.50 kJ and has $\eta = 0.500$. Find (a) W_{out} and Q_C , and (b) the Carnot bound and entropy generation per cycle for the cyclic device plus reservoirs.

Problem 18: refrigerator performance

A refrigerator between 270 and 300 K consumes 0.50 kWh while removing 4.0 kWh from the cold region. Find (a) Q_H and COP_R , and (b) the reversible COP bound and reservoir entropy generation over this operation.

Problem 19: heating objective

A heat pump operates between 280 K outdoors and 300 K indoors. Find (a) the minimum reversible work to deliver 12 MJ indoors, and (b) the work required by a device with $\text{COP}_{HP} = 4.0$. For each case find the heat extracted outdoors.

Problem 20: rejecting a proposal

A proposed engine has $\eta = 0.40$ between $T_H = 500$ K and $T_C = 350$ K. Without further device data, can it satisfy the second law? Demonstrate the conclusion using both an efficiency bound and a symbolic entropy balance.

D. Statistical interpretation

Problem 21: six particles

Six distinguishable particles independently occupy two equal halves of a box, with probability $1/2$ for either half. Find the probability that exactly three are on the left. Specify what a microstate and a macrostate mean in this model.

Problem 22: ten particles

For ten particles in the same model, find (a) the probability of exactly five on the left, (b) the probability that all ten occupy one specified half, and (c) the multiplicity ratio of the 5–5 and specified 10–0 macrostates. Distinguish “specified half” from “either half.”

Problem 23: an entropy difference

For $N = 8$, compare the configurational entropies of the $n = 4$ and $n = 2$ macrostates. Calculate $S_4 - S_2$ and explain the sign.

Problem 24: independent subsystems

Independent subsystems have multiplicities $\Omega_A = 20$ and $\Omega_B = 50$. Find the combined multiplicity and verify entropy additivity using $S = k_B \ln \Omega$. State why independence matters.

Problem 25: extra accessible volume

In a stipulated spatial model, every molecule gains a factor of three in accessible positional microstates when a partition is removed. For N molecules, find (a) Ω_f/Ω_i and (b) the entropy change. Express the result for n moles and connect it to ideal-gas free expansion.

E. Measurement, engineering and computation**Problem 26: a mixing prediction**

Two water samples have model constant $c = 4180 \text{ J kg}^{-1}\text{K}^{-1}$: 0.200 kg at 330 K and 0.300 kg at 290 K. Assume isolated mixing and neglect the calorimeter. Find (a) T_f and (b) S_{gen} . (c) List two experimental effects that could invalidate this numerical model and specify how to investigate each.

Problem 27: reservoir transfer

A fixed heat quantity $Q = 1.50 \text{ kJ}$ flows directly from a 450 K reservoir to a 300 K reservoir. Find both reservoir entropy changes and total entropy generation.

Problem 28: computational audit

A cyclic engine absorbs 900 J from a 600 K reservoir and rejects 550 J to a 300 K reservoir. Find work, efficiency and entropy generation. Specify energy and entropy residuals that software should check, including their units.

Problem 29: temperature scales

Explain why using the number 25 for 25°C directly in Q/T or $1 - T_C/T_H$ is physically invalid. Give a numerical example showing the mistake, and explain why a temperature *difference* in degrees Celsius may nevertheless be used in $Q = mc\Delta T$.

Problem 30: designing a unit test

Design a numerical unit test that distinguishes adiabatic reversible and adiabatic irreversible closed processes through the entropy balance, rather than through $Q = 0$ alone. Include one case that should be rejected, a justified numerical tolerance, and the expected classifications.

F. Advanced challenges**Problem 31: two equal finite bodies**

Two bodies each have $C = 2.00 \text{ kJ K}^{-1}$ and initial temperatures 600 and 300 K. Find (a) the direct-contact final temperature and entropy generation and (b) the reversible final temperature and maximum work. Explain why the endpoints differ.

Problem 32: unequal finite bodies

(a) Derive the weighted-geometric-mean formula for two constant but unequal heat capacities. (b) Evaluate it for $C_H = 1.00 \text{ kJ K}^{-1}$, $C_C = 2.00 \text{ kJ K}^{-1}$, $T_H = 600 \text{ K}$ and $T_C = 300 \text{ K}$. Find maximum work and compare with direct-contact temperature.

Problem 33: auditing the finite-body example

Use two bodies with $C_H = C_C = 1.00 \text{ kJ K}^{-1}$, initially at 500 and 300 K. **(a)** Find reversible hot-side heat loss, cold-side heat gain and maximum work. **(b)** Verify zero total entropy change. **(c)** Compare direct contact and explain where the work opportunity is lost. These are the parameters of the chapter's finite-body worked example; the restatement makes this task independent of example numbering.

Problem 34: a matched lost-work comparison

A quantity 2.00 kJ degrades from a 700 K reservoir to a 350 K reservoir before use against an environment at 300 K. Under the matched fixed-reservoir comparison, find **(a)** S_{gen} and **(b)** lost work. Verify the latter by comparing reversible work obtainable before and after this heat transfer.

Problem 35: temperature-dependent heat capacity

A model body has $C(T) = a + bT$, where $a = 400 \text{ J K}^{-1}$ and $b = 0.200 \text{ J K}^{-2}$. **(a)** Derive and evaluate its entropy change from 300 to 500 K. **(b)** Explain how quadrature should be checked against the analytic result, including a convergence criterion.

Problem 36: a small temperature difference

Two equal finite bodies start at $T_H = \bar{T} + \Delta T/2$ and $T_C = \bar{T} - \Delta T/2$, with $|\Delta T| \ll \bar{T}$. **(a)** Expand the exact maximum-work formula through leading nonzero order. **(b)** Explain why the first-order term is absent and identify the approximate relative error's scaling.

G. Graph, data and combined-model tasks**Problem 37: reading entropy-transfer slopes**

Figure 20.28 shows direct heat transfer Q from a 500 K reservoir to a 300 K reservoir. **(a)** Identify each line from its sign and slope and write its equation. **(b)** Read the total entropy change at $Q = 6.0 \text{ kJ}$, then verify it algebraically. **(c)** Determine the maximum heat transfer allowed if a specified entropy-generation budget is 5.0 J K^{-1} .

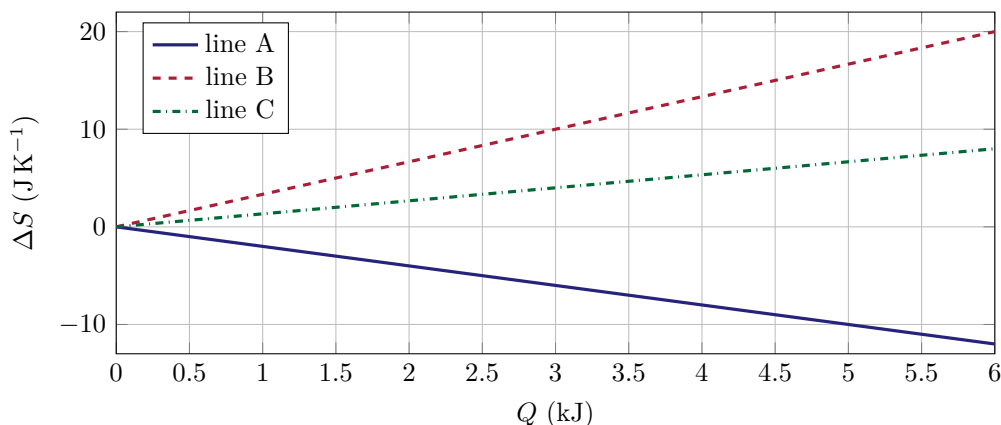


Figure 20.28: C20-V022 — Reservoir entropy changes and their sum for a common heat-transfer magnitude. Reservoir temperatures are fixed; the horizontal unit is kilojoules, so the plotted slopes include the factor 1000 J/kJ. Lines encode the same transfer, not three different processes.

Problem 38: a reversible T – S cycle

A cyclic working substance follows the rectangle in Fig. 20.29; all four branches are reversible. Vertical branches are adiabatic and the indicated arrow sequence is $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$. **(a)**

Calculate heat on each branch using the graph. **(b)** Determine net work and engine efficiency. **(c)** Reverse the cycle and calculate both refrigeration and heat-pump COPs. Explain why the entropy-coordinate origin does not affect any result.

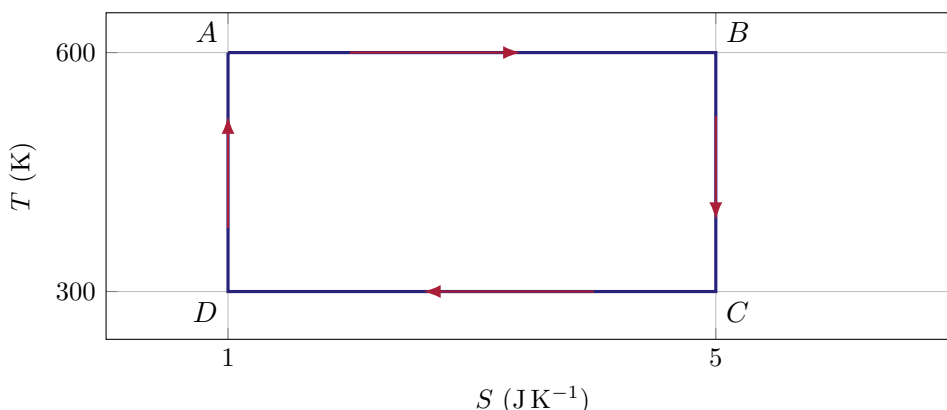


Figure 20.29: C20-V023 — A reversible cycle with a 4.0 J K^{-1} entropy span between 300 and 600 K. The enclosed area is work only after reversible heat and the cyclic first law are applied. Absolute entropy values are unnecessary; the differences determine the heat transfers.

Problem 39: locating entropy generation

A cyclic engine receives 12.0 kJ per cycle through a hot exchanger from a 600 K reservoir; the engine-side transfer boundary is 550 K . It rejects 8.00 kJ through a cold exchanger; its engine-side boundary is 330 K and the cold reservoir is at 300 K . Model each exchanger as cyclic with no work or energy storage. **(a)** Find work and overall efficiency. **(b)** Find entropy generated separately in the hot exchanger, engine core and cold exchanger, and verify the sum against the reservoir balance. **(c)** Find work lost relative to a reversible engine receiving the same Q_H from the same fixed reservoirs.

Problem 40: inverse reading of a finite-body curve

In Fig. 20.30, two equal bodies have $C = 2.00 \text{ kJ K}^{-1}$. The initially hot body is at 600 K ; the initially cold body's temperature is variable. **(a)** Read and then calculate maximum work for $T_C = 400 \text{ K}$. **(b)** Estimate from the curve the initial T_C that gives $W_{\max} = 40.0 \text{ kJ}$, then solve the inverse problem exactly. **(c)** Explain the horizontal tangent as $T_C \rightarrow 600 \text{ K}$ and why the graph does not describe a constant-efficiency engine.

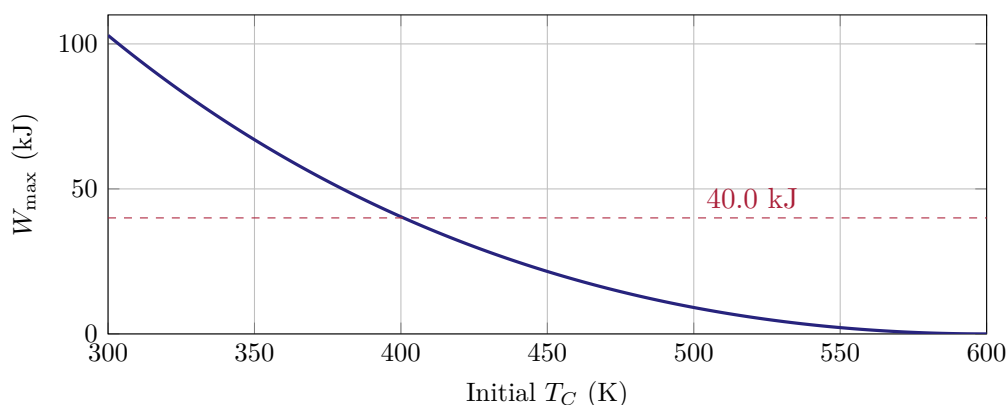


Figure 20.30: C20-V025 — Maximum reversible work from two finite bodies as their initial temperature contrast varies. Both bodies change temperature during extraction; heat capacity, hot initial temperature, and stopping condition are held fixed. The dashed line defines an inverse graph-reading task.

Problem 41: testing a calorimeter model

The synthetic observations in Fig. 20.31 describe mixing 0.200 kg of hot water at initial T_H with 0.300 kg at 290.0 K. Each final-temperature uncertainty is an independent standard uncertainty of 0.40 K. Use constant $c = 4180 \text{ J kg}^{-1} \text{ K}^{-1}$ and treat initial quantities as exact in this task. The measured pairs are $(T_H, T_f) = (310, 297.3), (320, 300.8), (330, 304.7), (340, 308.2)$ in kelvin. **(a)** Calculate the final temperatures predicted if the calorimeter has zero heat capacity and find the four residuals. **(b)** Test instead an insulated calorimeter with $C_{\text{cal}} = 200 \text{ J K}^{-1}$, initially at 290.0 K; compare residuals in uncertainty units. **(c)** For $T_H = 330 \text{ K}$, calculate predicted total entropy generation including the calorimeter. State what these observations can and cannot establish about the model.

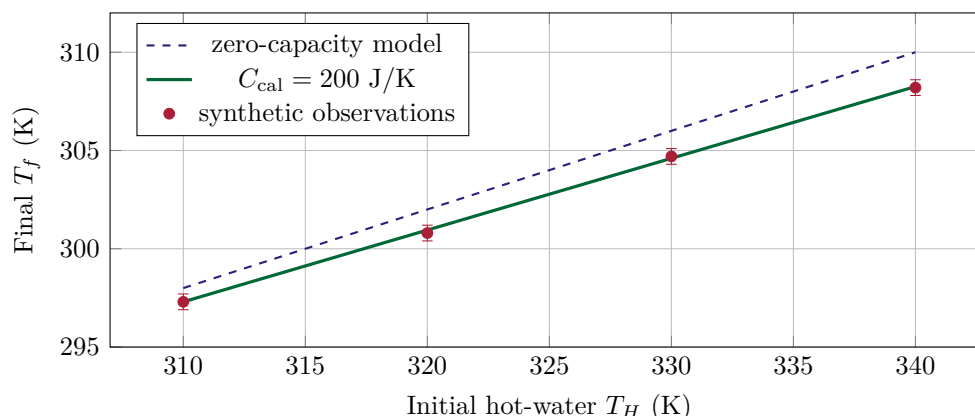


Figure 20.31: C20-V026 — Synthetic mixing observations and two physically specified energy-balance predictions. Vertical bars represent one standard uncertainty of 0.40 K, not a guaranteed bound. The comparison illustrates model testing; it is not experimental evidence about real water or a particular instrument.

Problem 42: a fluctuation event

In the independent two-half model, $N = 20$ particles have equal left/right probabilities. **(a)** Find the probability that at least 16 particles are in either half; include every macrostate in this event. **(b)** Find $S_{10} - S_{16}$ for specified-left macrostates. **(c)** Explain why a fluctuation to the less numerous macrostate does not imply a macroscopic engine can violate the second law.

Problem 43: a variable-capacity root

Two finite bodies both have $C(T) = 400 + 0.200T$ in J K^{-1} , initially at 500 and 300 K. A reversible engine extracts work until they share a temperature. **(a)** Derive a scalar equation for T_f and prove that it has one root between the initial temperatures. **(b)** Find that root numerically and calculate maximum work by integrating the energy changes. **(c)** Describe two independent checks on the root and work calculation.

Problem 44: two paths, identical gas endpoints

One mole of ideal gas initially at 300 K expands from 2.00 to 6.00 L. Compare **(a)** free expansion into vacuum inside a rigid insulated enclosure with **(b)** reversible isothermal expansion against a movable boundary while in contact with a 300 K reservoir. Find Q , work done by the gas, gas entropy change and total entropy generation for each. **(c)** Explain why the gas endpoint entropy agrees while heat and work differ; specify the combined boundary used for each second-law test.

20.12 Complete reasoned solutions

The calculations below retain extra digits where cancellation occurs and round final reported results. An entropy generation can be interpreted only after the boundary is fixed. Endpoint entropy calculations use reversible comparison paths even when the physical event is irreversible. Unless stated otherwise, an enclosure including the device and its reservoirs is adiabatic and closed, with work as its only external energy transfer; work transfers no entropy in this model.

Problem 1: direction beyond energy conservation

(a) Choose the two blocks plus their insulated rigid enclosure. With negligible enclosure heat capacity, neither heat nor work crosses its outer boundary, so $\Delta U_H + \Delta U_C = 0$. This equation admits both $\Delta U_H = -q, \Delta U_C = q$ and the reverse sign. It constrains the energy exchanged, but by itself does not select a direction.

(b) For the isolated composite, $\Delta S = S_{\text{gen}} \geq 0$. For an infinitesimal heat transfer $q > 0$ from the warmer block at T_H to the colder at T_C , its entropy change is $q(1/T_C - 1/T_H) > 0$. Reversing that transfer gives a negative total change and is excluded as an unassisted event. Thermal equilibrium is the common-temperature endpoint. A complete response names the composite boundary, distinguishes conservation from direction, and uses the reciprocal *absolute* temperatures; saying only “heat goes from hot to cold” does not explain the first law’s insufficiency.

Problem 2: slow versus reversible

(a) A quasi-static process passes through a sequence of states close enough to equilibrium for state variables to be defined. A reversible process can be retraced with system and surroundings both restored and no residual change; in the ideal entropy balance, all entropy-generation mechanisms vanish. The smallness of a driving rate does not prove this stronger condition.

(b) Compress gas slowly with a piston that has sliding friction. Gas pressure can remain almost uniform, making the gas path quasi-static, while friction converts mechanical energy into heat. If frictional work $W_f > 0$ is dissipated at approximately uniform temperature T , its entropy-generation contribution is $W_f/T > 0$. Reversing piston motion dissipates further work instead of undoing the original dissipation. Alternatively, a body heated slowly across a finite maintained temperature difference is quasi-static internally but creates entropy at the heat-transfer interface. Credit requires identifying the actual irreversible mechanism and why a slower rate does not remove its integrated effect under the specified constraints.

Problem 3: decreasing subsystem entropy

No. For the chosen closed system,

$$\Delta S_{\text{sys}} = S_{\text{transfer}} + S_{\text{gen}} = \int \frac{\delta Q}{T_b} + S_{\text{gen}}, \quad S_{\text{gen}} \geq 0.$$

Entropy may leave with heat, making the transfer term negative and larger in magnitude than the positive generation. For example, a body cools reversibly from 360 to 300 K using infinitesimally matched external reservoirs. Its change is $C \ln(300/360) < 0$, while the reservoirs gain exactly the opposite entropy; generation is zero. Cooling across a finite temperature difference produces a larger combined entropy increase. The second law constrains generation and the isolated composite, rather than the sign of each subsystem’s entropy change. The example also distinguishes a state change from a statement about the mechanism causing it.

Problem 4: adiabatic and zero entropy change

(a) Closed means no mass transports entropy; adiabatic means the heat-transfer integral vanishes. Thus $\Delta S = S_{\text{gen}}$. With $\Delta S = 0$, the model gives $S_{\text{gen}} = 0$ exactly.

(b) Under the stated balance and complete accounting of internal mechanisms, the process is internally reversible in the entropy-generation sense. No frictional dissipation, unrestrained expansion or other represented mechanism generates entropy within this boundary. This inference does not certify every external device as reversible: a separate brake outside the system could dissipate its exported work. Nor does adiabatic alone imply reversibility. A satisfactory answer distinguishes the exact ideal inference from measurement: an experimentally unresolved small ΔS establishes a bound at the measurement resolution, not mathematically exact zero.

Problem 5: free expansion

The definition is $dS = \delta Q_{\text{rev}}/T$ along a reversible comparison path, not the actual heat divided by an arbitrary temperature for every event. In ideal-gas free expansion, the outer enclosure is adiabatic, work against vacuum is zero, and $\Delta U = 0$; ideal-gas $U(T)$ then implies $T_f = T_i$. The expansion is nevertheless irreversible. Connect the same gas endpoints by reversible isothermal expansion. Its heat is $Q_{\text{rev}} = nRT \ln(V_f/V_i)$, yielding

$$\Delta S = nR \ln(V_f/V_i) > 0.$$

For the actual adiabatic event, this entropy change is generation, not entropy carried by heat. The reversible path is a calculation device and is not claimed to be the actual expansion history.

Problem 6: an operational definition

First, “disorder” supplies neither a numerical measurement rule nor units. A reversible heating process at fixed volume increases entropy through $\int C(T)dT/T$ without a unique visible geometric disorder. Second, it ignores constraints and system boundaries: a subsystem can lose entropy, and a visually mixed state need not have the same microstate count under different energy or particle restrictions.

Thermodynamically, entropy is a state function whose difference can be calculated from $\int \delta Q_{\text{rev}}/T$; its balance separates transfer from nonnegative generation. Statistically, within the equiprobable constrained model, $S = k_B \ln \Omega$ counts accessible microstates compatible with the macrostate. For the two-half model, a microstate assigns each distinguishable particle to a half, and $\Omega(n) = \binom{N}{n}$ for exactly n on the left. Positions beyond this coarse binary information, velocities and interactions are excluded from that model. Both replacements are quantitative and state their domain; neither is a universal visual metaphor.

Problem 7: three different conditions

(a) An isolated system exchanges neither energy nor matter with its environment. An adiabatic closed system exchanges no heat, but may exchange work. An isentropic process has $\Delta S = 0$ between its states; this describes entropy rather than which energy transfers occur.

(b) Isolation implies adiabatic closure and $\Delta S = S_{\text{gen}} \geq 0$. Closed, adiabatic and reversible together imply isentropic. Conversely, closed, adiabatic and isentropic imply zero internal generation under the complete entropy balance. Isolation does *not* imply isentropy: two contacting unequal-temperature bodies in an insulated enclosure generate entropy. Isentropy alone does *not* imply adiabatic reversibility: a system may generate entropy while exporting precisely the same amount through heat. A quasi-static process need not be reversible because friction or a finite transfer gradient can remain. Award full credit for correct definitions plus examples for the failed implications; a list of labels without entropy accounting leaves the key distinction unresolved.

Problem 8: reversible isothermal heat

Choose the heat-receiving system. Reversibility and constant T allow the temperature to be taken outside the entropy integral:

$$\Delta S = \frac{Q_{\text{rev}}}{T} = \frac{2400 \text{ J}}{400 \text{ K}} = 6.00 \text{ J K}^{-1}.$$

The sign is positive because heat enters. Its entropy generation is zero; the reservoir supplying heat reversibly loses 6.00 J K^{-1} . Reversing the direction changes both signs but still gives zero composite generation. Converting kilojoules before dividing prevents a factor-of-1000 unit error.

Problem 9: heating a finite body

The body's heat capacity is $C = mc = (0.500)(900) = 450 \text{ J K}^{-1}$. Along a reversible comparison heating path, $\delta Q_{\text{rev}} = C dT$, hence

$$\Delta S = \int_{300}^{360} \frac{450}{T} dT = 450 \ln \frac{360}{300} = 82.0447 \text{ J K}^{-1} \simeq 82.0 \text{ J K}^{-1}.$$

The logarithm is dimensionless and the positive sign matches heating. The actual energy received is $C(360 - 300) = 27.0 \text{ kJ}$ if there is no work. The endpoint data do not specify the heat-transfer boundary history and therefore do not determine actual entropy generation. Reversible heating gives zero generation; heating from one 360 K reservoir gives composite generation $82.0447 - 27000/360 = 7.0447 \text{ J K}^{-1}$. Both produce the same body entropy difference, illustrating why ΔS and S_{gen} must be distinguished.

Problem 10: melting at fixed temperature

The reversible latent heat is $Q = mL = (0.250)(334000) = 83500 \text{ J}$. During the stipulated phase change $T = 273.15 \text{ K}$ is constant, so

$$\Delta S_{\text{sample}} = \frac{83500}{273.15} = 305.693 \text{ J K}^{-1} \simeq 305.7 \text{ J K}^{-1}.$$

The matched supplying reservoir has $\Delta S_{\text{res}} = -305.693 \text{ J K}^{-1}$; total generation is zero. Constant temperature does not imply constant entropy: the phase change receives latent heat while its internal state changes. The stipulated value of L and reversible coexistence temperature are essential; sensible heating before melting would add a separate $mc \ln(T_f/T_i)$ contribution.

Problem 11: gas endpoint calculation

(a) For the ideal gas with constant molar capacity,

$$\Delta S = nC_{V,m} \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i} = 3R \ln(1.5) + 2R \ln 2 = 21.6400 \text{ J K}^{-1}.$$

Both temperature increase and expansion increase entropy. Litres need not be converted here because only a ratio appears.

(b) Heat reversibly at fixed 5.0 L from 300 to 450 K , then expand reversibly at 450 K to 10.0 L . The heating contribution is $3R \ln 1.5 = 10.1137 \text{ J K}^{-1}$; the expansion contribution is $2R \ln 2 = 11.5263 \text{ J K}^{-1}$. Their sum matches the endpoint formula. Choosing a different reversible route would change heat and work branch by branch but not this sum. No entropy-generation value for the unspecified actual path follows from these endpoints alone.

Problem 12: finite-body direct contact

(a) The enclosure is isolated and no work leaves. Constant capacities give $400(T_f - 350) + 400(T_f - 290) = 0$, hence $T_f = 320$ K, between the initial values. Energy lost by the hot body equals $400(30) = 12000$ J, the cold body's gain.

(b) Calculate each endpoint entropy using a reversible comparison path:

$$\Delta S_H = 400 \ln(320/350) = -35.8449 \text{ J K}^{-1}, \quad \Delta S_C = 400 \ln(320/290) = 39.3760 \text{ J K}^{-1}.$$

Thus $S_{\text{gen}} = \Delta S_H + \Delta S_C = 3.53116 \text{ J K}^{-1}$. The hot body loses entropy but the cold gain is larger. Retain unrounded values in the subtraction; rounding two large opposite terms prematurely can obscure the small positive generation. Nonnegativity is also guaranteed by the arithmetic-mean/geometric-mean inequality applied to $\ln[T_f^2/(350 \cdot 290)]$.

Problem 13: entropy received and generated

Entropy entering with the heat is $500/400 = 1.250 \text{ J K}^{-1}$. For the chosen closed boundary,

$$S_{\text{gen}} = \Delta S - \frac{Q}{T_b} = 1.80 - 1.25 = 0.550 \text{ J K}^{-1} > 0.$$

It is internally irreversible under the specified balance. The boundary temperature, rather than a guessed average system temperature, determines entropy transfer. The total entropy rise is not wholly generation: 1.250 J K^{-1} entered from outside. If an external heat-transfer interface is excluded from the boundary, its additional generation would need a separate balance.

Problem 14: adiabatic irreversibility

For a closed adiabatic system, no heat or matter carries entropy through the boundary. Therefore $S_{\text{gen}} = \Delta S = 3.0 \text{ J K}^{-1}$. Positive generation establishes irreversibility within the model. Work may still cross the boundary, but work itself carries no entropy in this balance. This result is consistent with adiabatic free expansion or dissipation and directly refutes the claim that every adiabatic process is isentropic.

Problem 15: cyclic energy accounting

(a) The working substance returns to its initial state, so $\Delta U = 0$ each cycle. With positive absorbed/rejected heat magnitudes,

$$W_{\text{out}} = Q_H - Q_C = 2.0 - 1.3 = 0.70 \text{ kJ}, \quad \eta = \frac{W_{\text{out}}}{Q_H} = 0.350.$$

This is 35.0%, not a COP; it compares useful work with heat absorbed.

(b) Second-law feasibility needs reservoir temperatures, or enough boundary entropy-transfer data to evaluate generation. For two fixed reservoirs, $S_{\text{gen}} = Q_C/T_C - Q_H/T_H$. The same heat data could be feasible for $T_H = 600, T_C = 300$ K but impossible for reservoirs whose Carnot limit is below 0.350. Energy conservation is satisfied by the stipulated heat/work values, yet conservation alone supplies no temperature-dependent performance limit.

Problem 16: testing an engine claim

(a) The proposed cyclic first law gives $Q_C = 2000 - 1250 = 750$ J and $\eta = 1250/2000 = 0.625$. The reservoir bound is $\eta_C = 1 - 300/700 = 0.571429$, already below the claim.

(b) The hot reservoir loses $2000/700 = 2.85714 \text{ J K}^{-1}$; the cold gains $750/300 = 2.50000 \text{ J K}^{-1}$. Since the device has zero cyclic entropy change,

$$\Delta S_{\text{reservoirs}} = -0.357143 \text{ J K}^{-1}$$

would have to equal negative generation for the adiabatic closed device-plus-reservoir composite. The first law can be satisfied with the calculated heat rejection, but the second law cannot. A reversible engine with this Q_H could deliver only $2000(4/7) = 1142.86$ J. The claim exceeds that value by 107.14 J; changing an internal design cannot repair the reservoir-level contradiction.

Problem 17: a feasible irreversible engine

(a) $W_{\text{out}} = \eta Q_H = (0.500)(1500) = 750$ J and $Q_C = 1500 - 750 = 750$ J. Absorption equals rejection plus work, confirming cyclic energy accounting.

(b) $\eta_C = 1 - 320/800 = 0.600$. The stipulated 0.500 is below this ceiling. The composite entropy generation is

$$S_{\text{gen}} = \frac{750}{320} - \frac{1500}{800} = 2.34375 - 1.87500 = 0.468750 \text{ J K}^{-1}.$$

A positive value makes this reservoir-level engine model feasible and irreversible; it does not specify which internal mechanism generates entropy. As a further check, $Q_H(\eta_C - \eta) = 150 \text{ J} = T_C S_{\text{gen}}$, the work shortfall for the matched two-reservoir comparison.

Problem 18: refrigerator performance

(a) For cyclic refrigeration $Q_H = Q_C + W_{\text{in}} = 4.0 + 0.50 = 4.50$ kWh. The cooling objective gives $\text{COP}_R = Q_C/W_{\text{in}} = 8.0$; heat delivered on the warm side is nine times input work, so the corresponding heating COP would be 9.0.

(b) The reversible cooling ceiling is $270/(300 - 270) = 9.0$, above the actual COP. Convert energy for the entropy calculation: $Q_C = 14.4$ MJ and $Q_H = 16.2$ MJ. Then

$$S_{\text{gen}} = \frac{16.2 \times 10^6}{300} - \frac{14.4 \times 10^6}{270} = 666.667 \text{ J K}^{-1}.$$

Heat extraction reduces cold-region entropy, while rejection gives a larger warm-region increase. A COP greater than one is consistent with the first law because input work supplements transported heat; it is not an engine efficiency.

Problem 19: heating objective

(a) The reversible heating bound is $\text{COP}_{HP} = 300/(300 - 280) = 15.0$. For fixed delivered heat $Q_H = 12$ MJ, minimum work is $W_{\text{in}} = Q_H/15 = 0.800$ MJ. The outdoor extraction is $Q_C = 12 - 0.800 = 11.2$ MJ. The reservoir entropy check is $12 \times 10^6/300 - 11.2 \times 10^6/280 = 0$.

(b) With $\text{COP}_{HP} = 4.0$, work is $12/4 = 3.00$ MJ and outdoor extraction is 9.00 MJ. This is feasible because $4.0 < 15.0$, and generation is $12 \times 10^6/300 - 9 \times 10^6/280 = 7857.14 \text{ J K}^{-1} > 0$. Delivering the same heat requires more work and less outdoor heat than in the reversible limit. Using the refrigeration numerator would answer a different objective and produce an incorrect work requirement.

Problem 20: rejecting a proposal

The maximum two-reservoir engine efficiency is $1 - 350/500 = 0.300$. Hence 0.40 is impossible irrespective of the unknown cycle's detailed working fluid or shape. For any absorbed heat $Q_H > 0$, the claimed efficiency requires $Q_C = (1 - 0.40)Q_H = 0.60Q_H$. Its entropy balance would be

$$S_{\text{gen}} = Q_H \left(\frac{0.60}{350} - \frac{1}{500} \right) = -\frac{Q_H}{3500 \text{ K}} < 0.$$

The negative sign is independent of cycle size. More device information might locate an incorrect measurement or missing heat source, but cannot make this stated two-reservoir proposal feasible. The efficiency and entropy tests are equivalent consequences of the same second-law constraint.

Problem 21: six particles

A binary microstate specifies which half each of six labelled particles occupies. There are $2^6 = 64$ equiprobable assignments. The macrostate specifies only the left count $n = 3$, with multiplicity $\binom{6}{3} = 6!/(3!3!) = 20$. Therefore $P(3) = 20/64 = 0.3125$. This is an exactly equal count event, not the probability of being “near” equal occupancy; a broader event would include additional counts. Summing $\binom{6}{n}/64$ over $n = 0, \dots, 6$ gives 1 by the binomial theorem, checking the denominator and normalization.

Problem 22: ten particles

- (a) $\Omega(5) = \binom{10}{5} = 252$ and total assignments are $2^{10} = 1024$, so $P(5) = 252/1024 = 0.24609375$.
- (b) All particles in a specified half gives just one assignment, probability $1/1024 = 9.765625 \times 10^{-4}$. If the event instead means either all left or all right, its two disjoint assignments give $2/1024 = 1.953125 \times 10^{-3}$.
- (c) The specified 10–0 multiplicity is one, so the ratio to 5–5 is $252 : 1$. A single all-left microstate is no less probable than a single balanced microstate; the balanced *macrostate* is more probable because it contains many assignments. This distinction prevents confusing equal microstate probabilities with equal macrostate probabilities.

Problem 23: an entropy difference

The multiplicities are $\Omega(4) = \binom{8}{4} = 70$ and $\Omega(2) = \binom{8}{2} = 28$. The entropy difference is

$$S_4 - S_2 = k_B \ln \frac{70}{28} = k_B \ln 2.5 = 1.26508 \times 10^{-23} \text{ J K}^{-1}.$$

Its positive sign says the balanced macrostate contains more configurations. The microscopic scale is expected because only eight particles are counted. An arbitrary common entropy offset cancels; taking a difference of raw multiplicities would neither have entropy units nor satisfy the logarithmic state-counting rule.

Problem 24: independent subsystems

Every allowed state of A can be paired with every allowed state of B when their constraints are independent. Thus $\Omega_{AB} = 20 \cdot 50 = 1000$. Consequently

$$S_{AB} = k_B \ln 1000 = k_B (\ln 20 + \ln 50) = S_A + S_B.$$

Numerically $S_A = 4.13605 \times 10^{-23}$, $S_B = 5.40113 \times 10^{-23}$ and $S_{AB} = 9.53719 \times 10^{-23} \text{ J K}^{-1}$ (with sums checked using unrounded logarithms). If a shared constraint prevents some pairs, the multiplicity need not equal $20 \cdot 50$ and this simple derivation of additivity cannot be used. The multiplication counts independent combinations; the logarithm converts that multiplication into an extensive sum.

Problem 25: extra accessible volume

- (a) Under the stipulated independent positional counting, N molecules each obtain a factor three, so $\Omega_f/\Omega_i = 3^N$. It is not $3N$: choices multiply across independent molecules.
- (b) The entropy change is $k_B \ln(3^N) = Nk_B \ln 3$. Since $N = nN_A$ and $N_A k_B = R$, it is $nR \ln 3$, or $9.13437n \text{ J K}^{-1}$ when n is the number of moles. This matches ideal-gas isothermal endpoint expansion with $V_f/V_i = 3$. In adiabatic ideal-gas free expansion the same temperature follows from $Q = W = 0$, so this endpoint increase equals generation. The counting model’s positional constraint supports this comparison without introducing a complete microscopic gas theory.

Problem 26: a mixing prediction

(a) Choose both water samples as the isolated composite. With equal constant c and no work, $m_H c(T_f - 330) + m_C c(T_f - 290) = 0$. Therefore

$$T_f = \frac{0.200(330) + 0.300(290)}{0.500} = 306.0 \text{ K.}$$

The hot loss and cold gain are each 20.064 kJ, checking energy conservation.

(b) Capacities are $C_H = 836$ and $C_C = 1254 \text{ J K}^{-1}$. Their entropy changes are $836 \ln(306/330) = -63.1243$ and $1254 \ln(306/290) = 67.3450 \text{ J K}^{-1}$, giving $S_{\text{gen}} = 4.22073 \text{ J K}^{-1}$. This is thermal equilibration of identical water, so no additional compositional mixing entropy is added under the model.

(c) A initially cool calorimeter absorbs energy, reducing T_f below this prediction. Measure its effective heat capacity in an independent calibration and include it in the energy/entropy balances. Heat loss to the room also usually lowers the observed final temperature: monitor drift versus time and repeat with improved insulation or extrapolate to the mixing time using a justified loss model. Evaporation, incomplete mixing and sensor lag are further possibilities. Full-credit experimental reasoning proposes a test that distinguishes mechanisms; simply fitting any discrepancy to an invented heat capacity does not uniquely identify its cause.

Problem 27: reservoir transfer

The hot reservoir has signed heat input $Q = -1500 \text{ J}$, so $\Delta S_H = -1500/450 = -3.33333 \text{ J K}^{-1}$. The cold reservoir receives that heat and gains $1500/300 = 5.00000 \text{ J K}^{-1}$. The combined fixed-reservoir transfer gives

$$S_{\text{gen}} = 1500 \left(\frac{1}{300} - \frac{1}{450} \right) = 1.66667 \text{ J K}^{-1}.$$

No energy is lost: the two heat changes cancel. The positive entropy generation records degradation of the work opportunity associated with the temperature difference, not destruction of the heat energy.

Problem 28: computational audit

Cyclic energy accounting gives $W_{\text{out}} = 900 - 550 = 350 \text{ J}$ and $\eta = 350/900 = 0.388889$. Reservoir accounting gives

$$S_{\text{gen}} = 550/300 - 900/600 = 0.333333 \text{ J K}^{-1}.$$

This is positive, and $\eta < 1 - 300/600 = 0.500$, so both checks agree. A program can form the energy residual $r_E = Q_H - Q_C - W_{\text{out}}$ in joules and the entropy residual $r_S = S_{\text{gen}} - (Q_C/T_C - Q_H/T_H)$ in J K^{-1} . Here both should vanish within numerical tolerance. Also test $T_H > T_C > 0$, $Q_H, Q_C, W_{\text{out}} \geq 0$ for the specified engine mode and $S_{\text{gen}} \geq 0$. Residual closure alone cannot validate physics if all outputs derive from the same incorrect equation; the independent Carnot inequality provides an additional model-level check.

Problem 29: temperature scales

Absolute temperature has a physical zero and is required in reciprocal-temperature entropy balances and temperature ratios. Celsius adds an arbitrary offset: $25^\circ\text{C} = 298.15 \text{ K}$. For $Q = 1000 \text{ J}$ delivered reversibly at that temperature, the correct entropy is $1000/298.15 = 3.35402 \text{ J K}^{-1}$, whereas using 25 gives 40 J K^{-1} . At 0°C the erroneous calculation would even diverge, despite the actual temperature being 273.15 K .

For an engine between 100°C and 25°C , $\eta_C = 1 - 298.15/373.15 = 0.200992$, not $1 - 25/100 = 0.75$. By contrast, ΔT in kelvin and Celsius has the same numerical value because their offsets cancel. Thus

$Q = mc\Delta T$ may use a Celsius difference with consistent heat-capacity units. The rubric requires an offset argument, a numerical consequence, and this valid difference/invalid ratio distinction.

Problem 30: designing a unit test

A worked test accepts signed heat-transfer entropy S_Q , endpoint ΔS , and computes $S_{\text{gen}} = \Delta S - S_Q$. For all three test cases set $Q = 0$ and therefore $S_Q = 0$: (i) $\Delta S = 0$ should yield zero generation and the ideal internally reversible classification; (ii) $\Delta S = 2.0 \text{ J K}^{-1}$ should yield positive generation and the irreversible classification; (iii) $\Delta S = -1.0 \text{ J K}^{-1}$ should be rejected as inconsistent for a closed adiabatic model. A test that merely sees $Q = 0$ would misclassify case (ii).

For double-precision values of order 1 J K^{-1} , a declared absolute numerical tolerance $10^{-10} \text{ J K}^{-1}$ is generous relative to arithmetic rounding and small relative to the test distinctions. Use a scale-aware tolerance if inputs become very large; keep measurement uncertainty separate from computational tolerance. Verify expected generation and classification independently rather than comparing an implementation with itself. A defensible alternative earns full credit if it includes a zero-generation case, a positive case, a forbidden negative case, units and an explicit tolerance policy.

Problem 31: two equal finite bodies

(a) Direct contact extracts no work. Constant equal capacities and isolated energy conservation give $T_{f,\text{direct}} = (600 + 300)/2 = 450 \text{ K}$. The generated entropy is

$$S_{\text{gen}} = 2000 \ln \frac{450}{600} + 2000 \ln \frac{450}{300} = 2000 \ln(1.125) = 235.566 \text{ J K}^{-1}.$$

(b) Reversible engine-mediated equilibration generates no entropy, so $2000 \ln[T_f^2/(600 \cdot 300)] = 0$ and $T_f = \sqrt{180000} = 424.264 \text{ K}$. The pair loses internal energy as external work:

$$W_{\text{max}} = 2.00[600 + 300 - 2(424.264)] = 102.944 \text{ kJ}.$$

The hot body supplies 351.472 kJ and the cold receives 248.528 kJ; their difference verifies the work. These paths have different common-temperature endpoints because one exports energy as work and the other keeps all energy inside. Equating their final temperatures would impose incompatible endpoint constraints and erase the extractable work.

Problem 32: unequal finite bodies

(a) Reversible operation of a cyclic intermediate engine imposes zero total entropy change:

$$C_H \ln(T_f/T_H) + C_C \ln(T_f/T_C) = 0.$$

Divide by $C_H + C_C$ and exponentiate the dimensionless ratios to obtain

$$T_f = T_H^{C_H/(C_H+C_C)} T_C^{C_C/(C_H+C_C)}.$$

The weights are heat-capacity fractions. Temperature ratios ensure no dimensionful logarithm enters the derivation; the displayed product has temperature dimension because the powers sum to one.

(b) $T_f = 600^{1/3} 300^{2/3} = 377.976 \text{ K}$. The energy decrease is $W_{\text{max}} = 1.00(600) + 2.00(300) - 3.00(377.976) = 66.0711 \text{ kJ}$. The hot loss is 222.024 kJ, the cold gain 155.953 kJ, and the difference matches. Direct contact gives the weighted arithmetic mean $(600 + 2 \cdot 300)/3 = 400.0 \text{ K}$, higher than the reversible endpoint. The reversible entropy changes are -462.098 and $+462.098 \text{ J K}^{-1}$, verifying cancellation independently of the energy equation.

Problem 33: auditing the finite-body example

(a) For the restated 1.00 kJ K^{-1} capacities, reversible common temperature is $\sqrt{500 \cdot 300} = 387.298 \text{ K}$. Thus

$$Q_H = 1.00(500 - 387.298) = 112.702 \text{ kJ}, \quad Q_C = 1.00(387.298 - 300) = 87.2983 \text{ kJ},$$

with $W_{\max} = 25.4033 \text{ kJ}$. The heat quantities are integrated changes of finite bodies, not heat from fixed-temperature reservoirs.

(b) The separate endpoint changes are

$$\begin{aligned} \Delta S_H &= 1000 \ln(387.298/500) = -255.413 \text{ J K}^{-1}, \\ \Delta S_C &= 1000 \ln(387.298/300) = +255.413 \text{ J K}^{-1}. \end{aligned}$$

Their sum is zero, while their energy changes sum to negative work.

(c) Direct contact gives 400.0 K and $S_{\text{gen}} = 1000 \ln[400^2/(500 \cdot 300)] = 64.5385 \text{ J K}^{-1}$, with zero work extracted. The temperature difference is dissipated through irreversible contact; the pair retains the extra internal energy that could have left as work along reversible engine-mediated equilibration. Without a specified reference environment, identifying this lost opportunity with an arbitrary $T_0 S_{\text{gen}}$ would impose an additional comparison not supplied here.

Problem 34: a matched lost-work comparison

(a) Direct degradation from 700 to 350 K generates $S_{\text{gen}} = 2000(1/350 - 1/700) = 2.85714 \text{ J K}^{-1}$.

(b) With the specified common environment $T_0 = 300 \text{ K}$, $W_{\text{lost}} = T_0 S_{\text{gen}} = 857.143 \text{ J}$. Independently, reversible use of 2000 J supplied at 700 K could provide $W_1 = 2000(1 - 300/700) = 1142.857 \text{ J}$. After degradation, the same heat supplied at 350 K could provide only $W_2 = 2000(1 - 300/350) = 285.714 \text{ J}$. Their difference is 857.143 J , matching the entropy calculation. Energy remains 2000 J at the degraded temperature, but its attainable work is reduced. This result depends on matching heat quantities, reservoirs and the environment; it is not a universal identity for arbitrary paths ending at different states.

Problem 35: temperature-dependent heat capacity

(a) Use a reversible heating comparison and the stated positive capacity:

$$\Delta S = \int_{300}^{500} \frac{a + bT}{T} dT = a \ln(500/300) + b(500 - 300) = 244.330 \text{ J K}^{-1}.$$

The two contributions are 204.330 and 40.000 J K^{-1} . Capacity increases from 460 to 500 J K^{-1} , and the entropy remains positive. A useful crude check bounds the integral between $460 \ln(5/3)$ and $500 \ln(5/3)$; the answer lies inside these bounds.

(b) Integrate $f(T) = 400/T + 0.200$ numerically over the same kelvin interval. For composite trapezoidal quadrature, halving the spacing should reduce the leading error by approximately four for this smooth integrand; Simpson quadrature gives a factor near sixteen when its assumptions apply. A worked acceptance target is relative error below 10^{-8} against $244.3302495 \text{ J K}^{-1}$ with refinement continuing until that target and the expected convergence behavior are reached. Checking only successive estimates risks accepting a stable but incorrectly specified integrand; the analytic benchmark checks both model and implementation.

Problem 36: a small temperature difference

(a) Write the exact result as

$$W_{\max} = 2C\bar{T} \left[1 - \sqrt{1 - \frac{(\Delta T)^2}{4\bar{T}^2}} \right].$$

With $x = (\Delta T)^2/(4\bar{T}^2)$ and $\sqrt{1-x} = 1 - x/2 - x^2/8 + \dots$,

$$W_{\max} = \frac{C(\Delta T)^2}{4\bar{T}} + \frac{C(\Delta T)^4}{64\bar{T}^3} + \dots.$$

The leading term has units $\text{J/K} \times \text{K}^2/\text{K} = \text{J}$ and tends to zero as temperatures become equal.

(b) Swapping the two initial bodies changes ΔT to $-\Delta T$ without changing the available work, so the exact function is even and no linear term exists. The first omitted term divided by the leading term is $(\Delta T)^2/(16\bar{T}^2)$; the leading formula slightly underestimates the exact work. For $\bar{T} = 400 \text{ K}$ and $\Delta T = 20 \text{ K}$, the estimated relative correction is 1.5625×10^{-4} , verifying the approximation's usefulness without claiming validity for a large temperature contrast.

Problem 37: reading entropy-transfer slopes

(a) The hot reservoir loses entropy, so line A is $\Delta S_H = -Q/500$. The cold reservoir gains more entropy for the same heat, giving line B, $\Delta S_C = Q/300$. Line C is their sum $S_{\text{gen}} = Q(1/300 - 1/500)$. With $q = Q/(1 \text{ kJ})$, the plotted equations in J K^{-1} are $-2q$, $(10/3)q$ and $(4/3)q$. The less steep negative line reflects the higher temperature.

(b) At $Q = 6.0 \text{ kJ}$ the graph gives -12 , $+20$ and $+8 \text{ J K}^{-1}$. Algebra gives $6000(1/300 - 1/500) = 8.00 \text{ J K}^{-1}$. Their energy transfers still cancel; entropy transfers do not cancel because the receiving temperature is lower.

(c) The budget sets $Q(1/300 - 1/500) \leq 5.0 \text{ J K}^{-1}$, hence $Q \leq 3750 \text{ J} = 3.75 \text{ kJ}$. Equality exhausts the budget. The result is a limit for this stipulated direct-transfer mechanism, not a universal heat limit: a reversible engine could transport a different heat amount while extracting work and altering the destination heat.

Problem 38: a reversible T - S cycle

(a) Reversible heat is $Q = \int T dS$. The horizontal entropy span is $5 - 1 = 4.0 \text{ J K}^{-1}$. On $A \rightarrow B$, $Q = 600(4) = +2400 \text{ J}$; on $C \rightarrow D$, $Q = 300(-4) = -1200 \text{ J}$. The vertical branches have $dS = 0$ and are stipulated reversible adiabatic, so both have zero heat. Reversibility is necessary: a general irreversible T - S trace cannot be read as actual heat by this rule.

(b) Cyclic $\Delta U = 0$ gives $W_{\text{out}} = Q_{\text{net}} = 2400 - 1200 = 1200 \text{ J}$. It equals the rectangle's area $(600 - 300)(5 - 1)$ in joules. Efficiency is $1200/2400 = 0.500$, equal to $1 - 300/600$ as expected for this reversible two-temperature cycle.

(c) Reversal removes $Q_C = 1200 \text{ J}$ at 300 K , delivers $Q_H = 2400 \text{ J}$ at 600 K and consumes $W_{\text{in}} = 1200 \text{ J}$. Therefore $\text{COP}_R = 1.00$ and $\text{COP}_{HP} = 2.00$, satisfying $\text{COP}_{HP} = \text{COP}_R + 1$. Adding any constant to all entropy coordinates leaves ΔS unchanged; heat, area, work and both COPs remain unchanged. The graph therefore needs an entropy difference, not an absolute entropy calibration.

Problem 39: locating entropy generation

(a) Cyclic energy balance for the entire apparatus gives $W_{\text{out}} = 12.0 - 8.00 = 4.00 \text{ kJ}$ and $\eta = 1/3 = 0.333333$.

(b) Each exchanger has no cyclic entropy storage. The hot exchanger takes entropy $12000/600$ from the hot reservoir and passes $12000/550$ to the core, so its generation is the difference. The engine core receives heat at 550 K and rejects it at 330 K. The cold exchanger carries that rejected heat onward to 300 K. Thus

$$\begin{aligned} S_{\text{gen,HX}_H} &= 12000(1/550 - 1/600) = 1.81818 \text{ J K}^{-1}, \\ S_{\text{gen,core}} &= 8000/330 - 12000/550 = 2.42424 \text{ J K}^{-1}, \\ S_{\text{gen,HX}_C} &= 8000(1/300 - 1/330) = 2.42424 \text{ J K}^{-1}. \end{aligned}$$

Their sum 6.66667 J K^{-1} matches $8000/300 - 12000/600$; internal transfer terms cancel exactly. Figure 20.32 partitions this total without implying that any component's entropy generation is an energy loss.

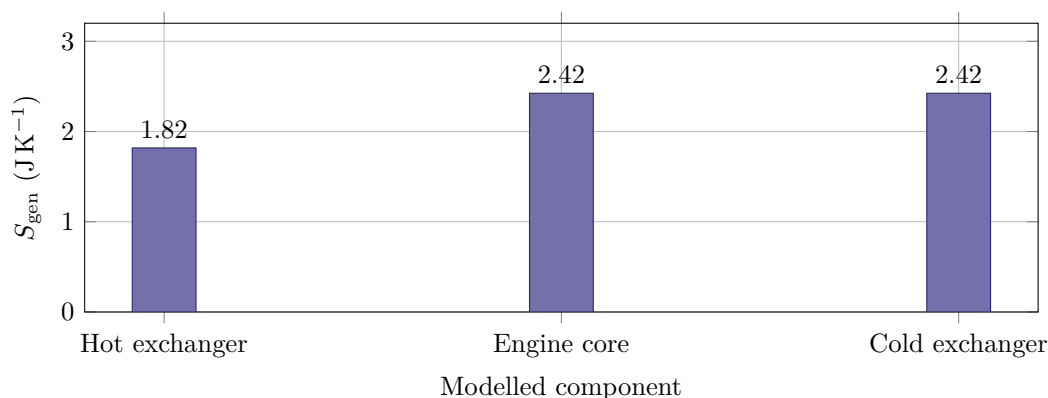


Figure 20.32: C20-V024 — Entropy-generation budget for the explicitly bounded components in Problem 39. The three positive contributions sum to the adiabatic closed apparatus-and-reservoir entropy increase; internal heat-transfer entropy terms cancel when component balances are added. The values are per cycle, not rates.

(c) A reversible engine receiving 12.0 kJ between the original reservoirs would provide $W_{\text{rev}} = 12.0(1 - 300/600) = 6.00$ kJ. The work shortfall is 2.00 kJ, also $T_C S_{\text{gen}} = 300(6.66667) = 2000$ J. Reservoir temperatures determine the overall limit; the intermediate temperatures identify additional irreversible transfer mechanisms and must not replace those reservoirs in the overall Carnot comparison.

Problem 40: inverse reading of a finite-body curve

(a) At $T_C = 400$ K, the graph gives about 40 kJ. The exact finite-body formula is

$$W_{\text{max}} = 2.00(\sqrt{600} - \sqrt{400})^2 = 40.4082 \text{ kJ}.$$

The reversible endpoint is $\sqrt{600 \cdot 400} = 489.898$ K, which lies between the initial temperatures and verifies the energy-derived work.

(b) The dashed 40.0 kJ line crosses near 401 K. Solve the monotone relation with $T_C \leq T_H$:

$$\sqrt{T_C} = \sqrt{600} - \sqrt{40.0/2.00}, \quad T_C = \left(\sqrt{600} - \sqrt{20.0}\right)^2 = 400.911 \text{ K}.$$

The opposite square-root branch would violate the cold/hot ordering; retaining the physical branch is part of solving the inverse problem.

(c) Differentiation gives $dW_{\text{max}}/dT_C = C[1 - \sqrt{T_H/T_C}]$, zero at equality. Near equality work scales quadratically with the small temperature difference, so the curve approaches zero with a horizontal tangent. During each extraction both bodies change temperature and the instantaneous Carnot factor changes. The plotted ordinate is integrated maximum work, not the efficiency at a fixed pair of temperatures.

Problem 41: testing a calorimeter model

(a) Ignoring the calorimeter gives $T_f = 0.4T_H + 0.6(290)$, so predictions at the four T_H values are 298.0, 302.0, 306.0, 310.0 K. Observed-minus-predicted residuals are $-0.7, -1.2, -1.3, -1.8$ K, or $-1.75, -3.00, -3.25, -4.50$ standard-uncertainty units. All are negative and their magnitude generally increases with the hot initial temperature. That structured disagreement is evidence against this zero-capacity isolated model under the stipulated uncertainty assumptions.

(b) The cold-water capacity is 1254 J K^{-1} and the initially cold calorimeter adds 200, while the hot-water capacity is 836. Energy balance predicts

$$T_f = \frac{836T_H + (1254 + 200)290}{836 + 1254 + 200} = \frac{836T_H + 1454(290)}{2290}.$$

The corresponding predictions and observed-minus-predicted residuals are:

T_H (K)	Predicted T_f (K)	Residual r (K)	$r/(0.40 \text{ K})$
310	297.3013	-0.0013	-0.003
320	300.9520	-0.1520	-0.380
330	304.6026	$+0.0974$	$+0.243$
340	308.2533	-0.0533	-0.133

A simple weighted residual sum is $\chi^2 = \sum(r_i/0.40)^2 = 0.22135$, compared with 42.875 for the zero-capacity prediction. These are comparisons to specified models, with no fitted parameters here; they do not establish a uniquely correct mechanism.

(c) At $T_H = 330 \text{ K}$, use the predicted $T_f = 304.602620 \text{ K}$, not a fluctuating measurement substituted into an otherwise exact isolated energy balance. The total change is

$$S_{\text{gen}} = 836 \ln \frac{304.602620}{330} + (1254 + 200) \ln \frac{304.602620}{290} = 4.48010 \text{ J K}^{-1}.$$

The calorimeter contribution is $200 \ln(304.602620/290) > 0$ and is included in the second term. All reservoirs are finite here. The observations are consistent with the supplied calorimeter correction at this resolution, but could also be influenced by heat leakage or a correlated thermometer bias. Repeated runs, independent calorimeter calibration and drift measurements would test that interpretation. Very small residual scatter can reflect generous uncertainties as well as a good model; it does not warrant claiming exact physics from four synthetic points.

Problem 42: a fluctuation event

(a) “At least 16 in either half” means left count $n \geq 16$ or $n \leq 4$. These disjoint events are symmetric. Therefore

$$P = \frac{2 \sum_{n=16}^{20} \binom{20}{n}}{2^{20}} = \frac{2(4845 + 1140 + 190 + 20 + 1)}{1048576} = 0.0118179.$$

Including only $n = 16$ would omit the more extreme counts and answer a different event.

(b) $\Omega(10) = 184756$ and $\Omega(16) = 4845$, giving $S_{10} - S_{16} = k_B \ln(184756/4845) = 5.02707 \times 10^{-23} \text{ J K}^{-1} > 0$. The probability above concerns a union of macrostates, whereas this entropy difference compares two specified-left macrostates; these objects must not be conflated.

(c) The statistical model allows rare finite-number occupancy fluctuations; it does not assert that each random realization increases this coarse configurational entropy. A less numerous macrostate is possible but not a repeatable source of unassisted macroscopic cyclic work. As particle number grows, large relative count imbalances become overwhelmingly improbable in the independent model. Extracting a usable cycle also requires accounting for apparatus and its interactions, which this binary occupancy model does not describe. This restrained interpretation connects fluctuation probability with macroscopic behavior without introducing an unsupported universal rule about every microscopic trajectory.

Problem 43: a variable-capacity root

(a) Reversibility of the adiabatic closed two-body-plus-cyclic-engine composite gives

$$F(T) = 400 \ln \frac{T}{500} + 0.200(T - 500) + 400 \ln \frac{T}{300} + 0.200(T - 300) = 0,$$

or $F(T) = 400 \ln[T^2/(150000)] + 0.400T - 160$. Its units are J K^{-1} . At 300 K, $F < 0$; at 500 K, $F > 0$. Moreover $F'(T) = 800/T + 0.400 > 0$ on the interval, so continuity and strict monotonicity establish exactly one physical root. The derivative has units J K^{-2} .

(b) A bracketed numerical solve gives $T_f = 389.363559$ K. The energy primitive is $U(T) = 400T + 0.100T^2 + \text{constant}$ in joules, so

$$W_{\max} = 400(500 + 300 - 2T_f) + 0.100(500^2 + 300^2 - 2T_f^2) = 12188.4 \text{ J} = 12.1884 \text{ kJ}.$$

The heat released by the hot body exceeds the cold body's energy gain by precisely this amount. The root is slightly above the constant-capacity geometric mean 387.298 K because the higher-temperature capacity is larger; using the constant- C formula without amendment would violate the stipulated entropy balance.

(c) Check the signed entropy residual $F(T_f)$ against a numerical tolerance, using the original two separate integrals as well as the simplified expression. Independently integrate each body's $C(T)$ numerically and compare their summed energy decrease with the analytic primitive. Also verify $300 < T_f < 500$ and $W_{\max} > 0$, and recover $T_f = \sqrt{500 \cdot 300}$ when b is set to zero. These tests examine bracketing, integral signs and model limiting behavior rather than relying only on the root finder's convergence flag.

Problem 44: two paths, identical gas endpoints

(a) For free expansion, choose gas inside its rigid insulated outer enclosure. Heat across the outer wall is zero and work against vacuum is zero. Thus $\Delta U = 0$; for ideal gas this leaves $T_f = 300$ K. Endpoint entropy is

$$\Delta S_{\text{gas}} = R \ln(6.00/2.00) = 9.13437 \text{ J K}^{-1}.$$

No entropy is transferred across the adiabatic boundary, so total generation is this positive value. The final temperature statement uses the ideal-gas internal-energy model; it is not a universal claim for every real gas.

(b) Reversible isothermal expansion has $W_{\text{by}} = \int_{2L}^{6L} nRTdV/V = RT \ln 3 = 2740.31 \text{ J}$. Since $\Delta U = 0$, heat entering equals 2740.31 J. The gas entropy change is again $Q_{\text{rev}}/T = 9.13437 \text{ J K}^{-1}$. The 300 K reservoir loses the same entropy; the gas-plus-reservoir-plus-ideal-work-receiver composite generates zero entropy. The work receiver's ideal energy increase is included, but it contributes no entropy transfer or dissipation.

(c) Gas entropy is a state function and the gas endpoints are identical, while heat and work describe paths. The free-expansion composite has no exported work and positive generation. In the reversible comparison the gas receives reservoir heat and delivers work to the ideal work receiver; the expanded composite stores that work and generates no entropy. Using the gas alone for one entropy change and then comparing it with the composite for the other would confuse system boundaries. The consistent comparison identifies each boundary explicitly and demonstrates both energy conservation and the correct entropy balance.

20.13 Volume I synthesis and bridge to further study

Volume I began with measurement and modelling, developed Newtonian mechanics and conservation laws, extended them to rotation, gravitation and fluids, introduced oscillations and waves, and ended

with thermal physics. The second law completes an important conceptual progression: conservation laws tell us what cannot be created or destroyed within a model, while entropy generation tells us why many energy-conserving transformations have a preferred direction and why useful work has limits.

The ideas developed here are also bridges. Statistical mechanics deepens the multiplicity interpretation and treats fluctuations systematically. Thermodynamic potentials and chemical potentials extend second-law reasoning to matter exchange, phase and chemical equilibrium. Exergy analysis formalizes work potential in engineering systems. Quantum statistics explains low-temperature and high-density regimes beyond classical counting. None of those extensions changes the discipline established here: define the system, identify constraints, keep energy and entropy accounts distinct, and test limiting cases before trusting a calculation.

Take-home message

Energy is conserved; usefulness is not. Irreversibility can preserve total energy while reducing the maximum work that can be extracted from it. Entropy generation is the quantitative signature of that loss of thermodynamic opportunity.

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