

Removing the Mystery of Entropy and Thermodynamics – Part IV

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In Part IV of this five-part series,^{1–3} reversibility and irreversibility are discussed. The question-answer format of Part I is continued and Key Points 4.1–4.3 are enumerated.

Questions and Answers

• **What is a reversible process?** Recall that a reversible process is specified in the Clausius algorithm, $dS = \delta Q_{\text{rev}}/T$. To appreciate this subtlety, it is important to understand the significance of reversible processes in thermodynamics. Although they are *idealized* processes that can only be approximated in real life, they are extremely useful. A reversible process is typically infinitely slow and sequential, based on a large number of small steps that can be reversed in principle. In the limit of an infinite number of vanishingly small steps, all thermodynamic states encountered for all subsystems and surroundings are *equilibrium* states, and the process is reversible.

By definition, a process that proceeds solely through equilibrium thermodynamic states is called *quasistatic*, and all reversible processes are quasistatic. Although most quasistatic processes are reversible—namely, can be reversed, with the surroundings also reversing the original path—some are not. Examples that are nearly quasistatic, but clearly irreversible, are air flowing from a slowly leaking tire, and any ultra-slow frictional mechanical process that converts mechanical to internal energy. Reversibility is required in the Clausius algorithm. If nonequilibrium states are encountered and if T is well defined, then $dS \geq \delta Q/T$.¹

Any heat process that transfers energy through a *finite* temperature difference—e.g., heating water on a stove—is irreversible. Suppose energy is transferred from a reservoir with temperature T_A to the system, which is initially at temperature

$T < T_A$. That energy enters through a surface, heats the matter near that surface to a temperature greater than T , and subsequently energy spreads to other parts of the system at lower temperature. The system's temperature is nonuniform during the ensuing energy-spreading process, nonequilibrium thermodynamic states are reached, and the process is irreversible.

To approximate reversible heating, say, at constant pressure, one can put a system in contact with many successively hotter reservoirs. In Fig. 1 this idea is illustrated using only initial, final, and three intermediate reservoirs, each separated by a finite temperature change. Step 1 takes the system from temperature T_A to the next reservoir temperature $T_1 > T_A$. Energy $Q_1 > 0$ is released by the reservoir, whose entropy change is $\Delta S_{\text{res},1} = -Q_1/T_1$, with $Q_1 = \int_{T_A}^{T_1} C_p(T) dT$, where the integrand is the system's heat capacity. The system's entropy change is

$$\Delta S_{\text{sys},1} = \int_{T_A}^{T_1} C_p(T)/T dT.$$

Thus, the total entropy change in step 1 is

$$\Delta S_{\text{sys},1} + \Delta S_{\text{res},1} = \int_{T_A}^{T_1} C_p(T)[1/T - 1/T_1] dT.$$

Because $T \leq T_1$, the integrand and thus $\Delta S_{\text{total},i} \geq 0$. Generalizing to the i^{th} step, we have

$$\begin{aligned} \Delta S_{\text{total},i} &= \Delta S_{\text{sys},i} + \Delta S_{\text{res},i} \\ &= \int_{T_{i-1}}^{T_i} C_p(T)[1/T - 1/T_i] dT \geq 0. \end{aligned} \quad (1)$$

Note that the equality in Eq. (1) holds *only* in the limit as the temperatures T_i and T_{i-1} approach each other. This happens as we increase the number of steps keeping temperatures T_A and T_B fixed. This can be done by doubling the number of intermediate reservoirs from 3 to 6, to 12, . . . , reducing successive temperature differences accordingly. In the limit of an infinite number of steps we have $\sum_{i=1}^{\infty} \Delta S_{\text{total},i} = 0$. In this limit, the system and environment are always in equilibrium states, and the process can, in principle, be reversed.⁴ Some define a reversible process as one for which the entropy of the universe is unchanged.⁵

Extending the discussion to volume changes, the rapid adiabatic expansion or compressions of a gas is *irreversible*.² For a rapid expansion, the gas develops a lower-density region near a receding piston and, subsequently, particles and energy spread spatially, increasing the entropy. For the infinitely slow *reversible* adiabatic expansion, the work done by the gas causes a decrease of internal energy sufficiently large to offset

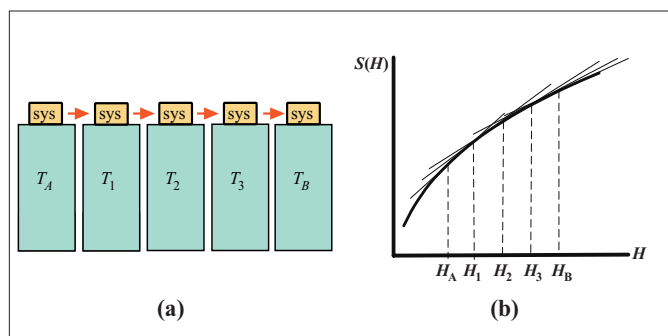


Fig. 1. (a) A system (sys) is heated using five sequential, progressively hotter reservoirs. Each step entails a *finite* temperature difference and is irreversible. (b) Sequentially hotter states (A, 1, 2, 3, B) for a system shown on an S-vs-H plot. Temperatures are the reciprocals of the line slopes. Reversibility is achieved in the limit of an infinite number of reservoirs with successive temperature differences approaching zero.

the effect of energy spreading to a larger volume, and the system's entropy is unchanged.

For a rapid adiabatic compression, a higher-density region is generated near the piston. Subsequently, the “extra” energy in that region spreads spatially, increasing entropy. In the reversible limit, the energy gain from work done on the gas offsets the decrease in spatial spreading because of the volume decrease, leaving the entropy unchanged. A straightforward mathematical treatment linking irreversible compressions and expansions to entropy increase is in Ref. 6.

Key Point 4.1: *Reversible processes do not exist in nature, but are a useful limiting case for envisaged infinitely slow processes that entail only equilibrium states of a system and surroundings. Because $\Delta S_{\text{tot}} = 0$ for a reversible process, the reversed process can be executed without violating the second law of thermodynamics. Irreversible, variable-volume work processes either add internal energy (compression) or spread energy to new spatial regions (expansion), increasing energy spreading and total entropy. When $\Delta S_{\text{total}} > 0$, there is no way to recover the initial entropy values of the system and surroundings because the entropy of an isolated system cannot decrease.*

• **Why are reversible processes important?** Reversible processes are staples of thermodynamics. Because they are quasistatic, they make it possible to draw diagrams of pressure versus volume, temperature versus entropy, and other useful diagrams. And because they can be reversed, they enable the treatment of systems such as refrigerators and heat pumps, simply by running reversible heat engines “backwards.” Reversible processes also give us the ability to establish a limit on the thermal efficiency of heat engines that operate between specified higher and lower constant-temperature reservoirs. Finally, reversible processes are needed in the Clausius entropy calculation algorithm. We may use any reversible path to connect thermodynamic equilibrium states A and B to calculate $\Delta S = S_B - S_A$. Because entropy is a state function, the latter ΔS is valid even when states A and B are connected by any irreversible path.

The importance of reversible processes is evident if one examines the well-known reversible Carnot cycle using the temperature-versus-entropy diagram in Fig. 2. Applying the first law of thermodynamics to the heat engine cycle 12341, we know that $\Delta U = 0$ (initial and final states are the same), so $\Delta U = Q - W$ implies $Q = Q_{\text{in}} - Q_{\text{out}} = W$, where each quantity is defined to be positive. Along isothermal segment 12, $dS = dQ/T_h$, which leads to $Q_{\text{in}} = T_h(S_{\text{max}} - S_{\text{min}})$, the area of the combined white+shaded rectangles. Similarly, along 34, $Q_{\text{out}} = T_c(S_{\text{max}} - S_{\text{min}})$, the area of the shaded rectangle, and the thermal efficiency is

$$\eta \equiv \frac{W}{Q_{\text{in}}} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_c}{T_h}. \quad (2)$$

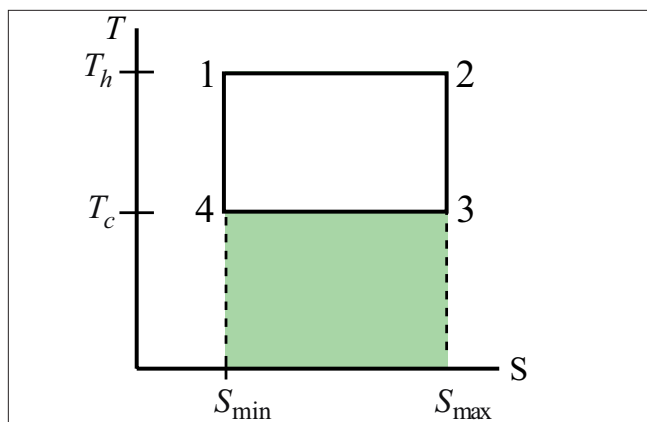


Fig. 2. Reversible Carnot cycle heat engine 12341. Segments 12 and 34 are isothermal, and 23 and 41 are adiabatic processes. The shaded+white area represents the input energy Q_h at the higher temperature T_h , and the shaded area is the output energy Q_c to the colder reservoir at T_c . The work done in one cycle W is the white rectangular area and the thermal efficiency $\eta = W/Q_h$ is (white area)/(white+shaded area).

This is the well-known Carnot efficiency. Note that the temperature-versus-entropy diagram shows clearly that the Carnot engine's efficiency is independent of the minimum and maximum entropy values S_{min} , S_{max} because in calculating η , the ratio of the work (white area) to the input energy (white+shaded areas), the difference $(S_{\text{max}} - S_{\text{min}})$ cancels out. Thus, Carnot cycles producing any amount of work must have the same thermal efficiency for given T_c and T_h . Note that Eq. (2) is independent of the working substance.

If the cycle is run in the reverse order, 43214, it is a refrigerator that removes energy Q_c from the colder region and delivers energy $Q_h = Q_c + W_{\text{ext}}$ to the higher temperature region, where each quantity here is defined to be positive. In particular, $W_{\text{ext}} = -W > 0$, namely the negative of the negative work done by the heat engine's working fluid. There is no violation of the second law of thermodynamics here because external work is needed to move energy “uphill”; it does not occur spontaneously, and the entropy of the universe does not decrease. If the reversed Carnot engine is intended to heat the hotter region, it is called a *heat pump*. If it is intended to cool the colder region, it is called a *refrigerator*.

An important characteristic of reversible heat engines that is not well appreciated is that each cycle must take an infinite amount of time and therefore must generate zero power! In contrast, real heat engines are useful only if they generate sufficient nonzero power levels—e.g., an automobile's internal combustion engine. Similarly a reversible engine run in reverse will have zero heating rate at T_h and zero cooling rate at T_c .

Key Point 4.2: *Reversible processes enable graphs of well-defined thermodynamic paths, consideration of helpful heat engine models, determination of maximum efficiencies for heat engines, and calculations of entropy changes.*

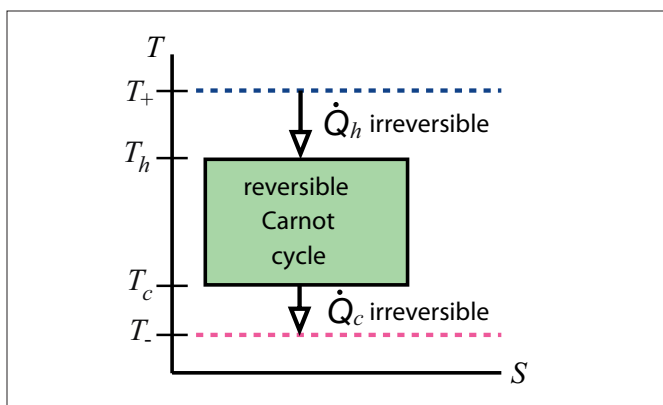


Fig. 3. A reversible Carnot cycle with irreversible heat processes at its hotter and colder temperatures. The temperatures T_c and T_h are assumed to be variable and can be chosen to maximize the output power $\dot{W} = \dot{Q}_h - \dot{Q}_c$.

• **How can irreversibility be taken into account?** To get around the zero power limitation of a reversible heat engine, some have proposed⁷ combining a reversible Carnot cycle with irreversible heat processes at the hotter and colder temperatures, as in Fig. 3. The temperatures T_+ and T_- represent high and low reservoir temperatures. The reversible Carnot cycle runs between hotter and colder temperatures $T_h < T_+$ and $T_c > T_-$. For example, T_+ could be chosen as the temperature of a burning fuel-air mixture in an internal combustion engine; T_- could be the outdoor air temperature.

Each cycle, though treated as reversible, must occur in finite time, with finite rates \dot{Q}_c and \dot{Q}_h (in $J/s = \text{watts}$) that are assumed to be proportional to $(T_c - T_-)$ and $(T_+ - T_h)$, respectively. If T_c approaches T_- and T_h approaches T_+ , the transfer rates \dot{Q}_c and \dot{Q}_h approach zero and the power output vanishes. In this limit the efficiency is maximum, namely, the Carnot efficiency, $\eta_c = 1 - T_-/T_+$. Also, the entropy production rate from the two reservoirs, $\dot{S} = \dot{Q}_c/T_- - \dot{Q}_h/T_+ \rightarrow 0$; i.e., the process becomes reversible.

On the other hand, if T_c approaches T_h , the Carnot cycle's area approaches zero and, again, the power output approaches zero. Here, \dot{Q}_h is finite but $\dot{W} \rightarrow 0$, so the thermal efficiency approaches zero. In this limit, the Carnot cycle "vanishes," there is zero power output, and the heat process takes energy at rate \dot{Q}_h from the reservoir with T_+ and delivers it to the reservoir with T_- , maximizing the entropy production rate, $\dot{S} = \dot{Q}_h(1/T_- - 1/T_+) > 0$.

Between these zero power limits, there is a pair (T_c, T_h) for which the power output is maximum and the thermal efficiency lies between zero and the Carnot efficiency, namely,⁷

$$\eta^* = 1 - (T_-/T_+)^{1/2} \leq 1 - T_-/T_+. \quad (3)$$

The corresponding entropy production rate is between zero and the above maximum entropy production rate.⁸ The efficiency η^* also arises in the context of some reversible heat engine models.⁹

Key Point 4.3: An irreversible heat engine, operating between two reservoirs, has an efficiency less than the corresponding Carnot efficiency. The expression $\eta^* = 1 - (T_-/T_+)^{1/2}$ is a good guide to the efficiencies of electrical generating plants. This seems fortuitous because the model from which it is derived entails a reversible cycle to be operated in finite time. Despite this lack of realism, the irreversible model is valuable because it indicates, albeit roughly, a way that maximum power output can arise.

In Part V, we discuss interpretations of entropy and the concept of "equity" in thermodynamic equilibrium.¹⁰

References

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