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Reversible and irreversible heat engine and refrigerator cycles

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Although no reversible thermodynamic cycles exist in nature, nearly all cycles covered in textbooks are reversible. This is a review, clarification, and extension of results and concepts for quasistatic, reversible and irreversible processes and cycles, intended primarily for teachers and students. Distinctions between the latter process types are explained, with emphasis on clockwise (CW) and counterclockwise (CCW) cycles. Specific examples of each are examined, including Carnot, Kelvin and Stirling cycles. For the Stirling cycle, potentially useful task-specific efficiency measures are proposed and illustrated. Whether a cycle behaves as a traditional refrigerator or heat engine can depend on whether it is reversible or irreversible. Reversible and irreversible-quasistatic CW cycles both satisfy Carnot's inequality for thermal efficiency, $\eta \leq \eta_{Carnot}$. Irreversible CCW cycles with two reservoirs satisfy the coefficient of performance inequality $K \leq K_{Carnot}$. However, an arbitrary reversible cycle satisfies $K \geq K_{Carnot}$ when compared with a reversible Carnot cycle operating between its maximum and minimum temperatures, a potentially counterintuitive result. © 2018 American Association of Physics Teachers. <https://doi.org/10.1119/1.5020985>

I. INTRODUCTION

Historically, advances in thermodynamics were closely linked to the study of thermodynamic cycles and the limitations on their efficiency for performing work, cooling or heating. This was of interest to engineers and physicists initially for clockwise heat engine cycles in connection with efficiency limits imposed by the second law of thermodynamics. Ultimately both clockwise (CW) and counterclockwise (CCW) thermodynamic cycles were studied and both are covered in introductory physics textbooks.

The question of whether all CCW cycles are refrigerators was addressed by Dickerson and Mottmann.¹ That question can be posed for heat engines as well. The answers depend critically not only on the definitions of a refrigerator and heat engine (which are to some extent arbitrary) but also on the important physics-related issue of whether a cycle is reversible or irreversible. This article is intended to clarify these points for physics teachers and students. Additionally it is a review, clarification and elaboration, with some new results for reversible and quasistatic-irreversible processes. Because it is part a review, some standard textbook material is revisited. To my knowledge, no existing source synthesizes these concepts, which are fundamental in physics teaching.

Section II is devoted to important distinctions between reversibility and irreversibility, and Sec. III clarifies characteristics of reversible and irreversible work and heat processes. Distinctions between quasistatic and reversible processes are explained and a pulsed model for quasistatic-irreversible heat processes is proposed. Section IV is a brief review of heat engines and refrigerators and their efficiency measures. Inclusion of temperature vs. entropy graphs is to show the temperature behavior along each cycle and also to reveal heat quantities as areas under curves.

Section V is devoted to Kelvin three-legged cycles, Sec. VI covers the well known Carnot cycles, and Sec. VII focuses on Stirling cycles. Sections VIII and IX are dedicated to thermal efficiency and coefficient of performance inequalities for reversible and irreversible cycles. Section X

contains related final remarks. Throughout the manuscript, main findings are expressed in "Key Points."

II. DISTINCTION BETWEEN REVERSIBLE AND IRREVERSIBLE CYCLES

Rudolf Clausius^{2,3} used the distinction between reversible and irreversible CW cycles in his *tour de force* derivation of the so-called Clausius inequality. Using cycles as a mathematical tool rather than a device for doing work, heating or cooling, Clausius was led to the concept and definition of entropy, including the principle of entropy increase. Specifically, he examined a CW cycle on a pressure vs. volume diagram such as that in Fig. 1. Define dQ to be an inexact differential that represents the energy added to the working substance from a reservoir at temperature T ; i.e., $dQ > 0$ when the working substance receives energy and $dQ < 0$ when the working substance sends energy to the reservoir. Clausius showed that for a cyclic process of the working substance,⁴

$$\oint \frac{dQ}{T} \leq 0, \quad \text{the Clausius inequality.} \quad (1)$$

The inequality holds for an irreversible cycle and the equality holds for a reversible cycle. Clausius assumed that a (possibly infinite) number of reservoirs guide the system through the cycle. During the cycle, the working substance can deviate from thermodynamic equilibrium, but by definition the reservoir cannot. Figure 1 assumes the cycle can be split into two segments, one irreversible, the other reversible, and Eq. (1) can be rewritten $\int_{irrev(1 \rightarrow 2)} dQ/T + \int_{rev(2 \rightarrow 1)} dQ/T \leq 0$. Reversing the sense of the integral along the reversible path, the latter equation becomes $\int_{irrev(1 \rightarrow 2)} dQ/T - \int_{rev(1 \rightarrow 2)} dQ/T \leq 0$. The second term is defined to be $\Delta S \equiv S(2) - S(1)$ and thus,

$$\Delta S \geq \int_{irrev(1 \rightarrow 2)} dQ/T. \quad (2)$$

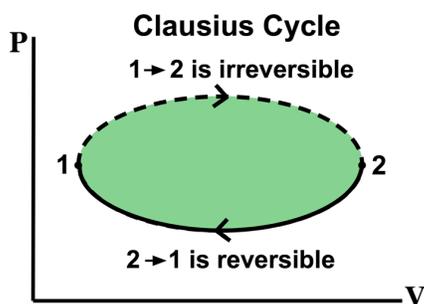


Fig. 1. Clockwise cycle with an irreversible segment $1 \rightarrow 2$ and a reversible segment $2 \rightarrow 1$. The dashed line $1 \rightarrow 2$ is purely symbolic because pressure P might not be well defined along this path, so the path cannot be graphed.

The equality holds only if the irreversible path is replaced by a reversible one. Indeed, for a reversible cycle if the inequality held, then reversing the cycle would lead to the opposite inequality—thus only the zero value is mathematically possible. Reversibility and irreversibility are clarified further in Sec. III.

For an irreversible adiabatic path, $dQ = 0$ and Eq. (2) implies

$$\Delta S \geq 0 \quad \text{for adiabatically insulated or isolated systems.} \quad (3)$$

Note that a pure work process cannot decrease the entropy of an adiabatically insulated system. The following points are worth emphasizing:

Key Point 1. Equation (3) is a form of the second law of thermodynamics, namely, the principle of entropy increase. For an isolated “universe,” $\Delta S_{\text{universe}} \geq 0$.

Key Point 2. It is essential to carefully distinguish between reversible and irreversible processes when examining thermodynamic cycles. Non-equilibrium states, for which temperature and other variables are not well defined, can occur for irreversible processes. In Clausius’s arguments leading to Eq. (2), T refers to the temperatures of the constant-temperature reservoirs that generate the cycle. By definition, reservoirs have infinitesimally small relaxation times and are always in equilibrium.

No reversible processes exist in the real world. If one existed, it would take an infinite amount of time because approaching reversibility in a laboratory requires an ultra-slow process with minimal deviations from equilibrium, just enough to make the process proceed. This entails *near equilibrium* states, which lie outside the domain of classical thermodynamics, and which are arbitrarily close to the equilibrium states on the reversible path.

John Norton⁵ summed up the issue neatly as follows: “...a reversible process is, loosely speaking, one whose driving forces are so delicately balanced around equilibrium that only a very slight disturbance to them can lead the process to reverse direction. Because such processes are arbitrarily close to a perfect balance of driving forces, they proceed arbitrarily slowly while their states remain arbitrarily close to equilibrium states. They can never become equilibrium states, for otherwise there would be no imbalance of driving forces, no change, and no process. Equilibrium states remain as they are.”

Key Point 3. A quasistatic path is a continuum of equilibrium states. An infinite number of reservoirs is needed to take a working substance through paths with variable-temperature heat processes. Real paths must deviate from equilibrium states, and can only approximate quasistatic work and heat processes.

Key Point 4. When taken from thermodynamic state a to state b quasistatically, a system can traverse those states in reverse order, and its entropy change is $\Delta S_{ab} = \int_a^b dQ/T = -\Delta S_{ba}$. A quasistatic process is reversible only if it can be run backwards such that both the system and environment follow their same paths in reverse order. All reversible processes are quasistatic but a quasistatic process need not be reversible.

Key Point 5. It takes a reversible heat engine an infinite amount of time to complete each cycle and thus, the power output of such a cycle is zero. Similarly, a reversible refrigerator would have a cooling rate of zero. The same is true for quasistatic cycles.

Despite the practical limitations of reversible cycles, their ease of treatment and use in establishing profound efficiency limits are important. Actual heat engines and refrigerators have unavoidable sources of irreversibility like friction and heat leaks. They typically operate so fast that their working substances, e.g., steam, do not have uniform temperatures and pressures. Nonequilibrium states are involved and such processes are irreversible.⁶

III. CHARACTERISTICS OF REVERSIBLE AND IRREVERSIBLE PROCESSES

A. Finite-speed work processes

Thermodynamic processes depend critically on process speed. For sufficiently *slow* processes, the path of thermodynamic states followed can be approximated using equilibrium states and quasistatic processes, which can be represented on a pressure-volume or temperature-volume graph such as the lower path $2 \rightarrow 1$ in Fig. 1. The upper path $1 \rightarrow 2$ cannot be graphed because the irreversibility leads to nonequilibrium states without well defined pressures and/or volumes.

For an example, consider an external force on a piston, which induces external pressure P_{ext} on a gas whose equilibrium pressure is initially P . If $P_{\text{ext}} \gg P$, the gas molecules bunch up near the quickly moving piston, and gas pressure near the piston exceeds that farther away; i.e., there is a non-equilibrium situation without a well defined pressure, as in Fig. 2(a). If $P_{\text{ext}} \ll P$, the piston moves in the opposite direction, and the gas pressure near the piston is *less* than that farther away, as in Fig. 2(b). If the receding piston moves faster than any of the gas molecules, the gas expands freely and a P-V plot is not possible.

Key Point 6. Only if the external pressure differs infinitesimally from P , will a volume change approach the quasistatic ideal, and an infinitesimal external pressure change can reverse the path. If the work sources (e.g., a weight hanging from a pulley) and reservoirs also retrace their paths, the process is reversible. Clearly, a quick compression followed by a quick expansion does not lead to the initial gas state.

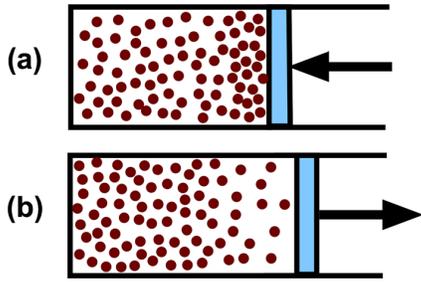


Fig. 2. Symbolic view of an irreversible quick (a) compression and (b) expansion of a gas.

B. Finite-speed heat processes

For a reversible adiabatic (zero heat) process, the work process involved induces temperature changes of a gas without reservoirs. More generally, there can be temperature variations associated with a combination of work and heat processes. To approach reversibility, such temperature changes must be extremely slow. It is helpful to imagine successive, constant-temperature energy reservoirs, as illustrated in Fig. 3(a). In principle, the limiting case of an infinite number of reservoirs with vanishing successive temperature differences achieves reversibility.⁷ As successive temperature differences get smaller, the entropy produced does too, approaching zero in the *reversible* limit. The energy transferred to the system is $Q_{\text{sys}} = \int_{T_1}^{T_n} C_p dT$, where C_p is the system's constant-pressure heat capacity at an assumed constant atmospheric pressure. The system's entropy gain $\Delta S_{\text{sys}} = \int_{T_1}^{T_n} (C_p/T) dT$ is the negative of that for the reservoirs.

Key Point 7. *Reversible heating can be done with a sequence of reservoirs, each with an infinitesimally higher temperature than the last and reversal is possible.*

If instead, heating or cooling results from an energy transfer through a *finite* temperature difference such as $T_n - T_1 > 0$ in Fig. 3(b), the process is *irreversible*. The energy transfer to the system and its entropy change are the same as in the previous paragraph. Thus the total entropy change is positive which signals irreversibility,

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{res}} \\ &= \int_{T_1}^{T_n} C_p \left(\frac{1}{T} - \frac{1}{T_n} \right) dT > 0 \quad \text{for } T_1 \leq T_n. \end{aligned} \quad (4)$$

Although this process is irreversible, the calculation of ΔS_{sys} takes advantage of the state function property of entropy,

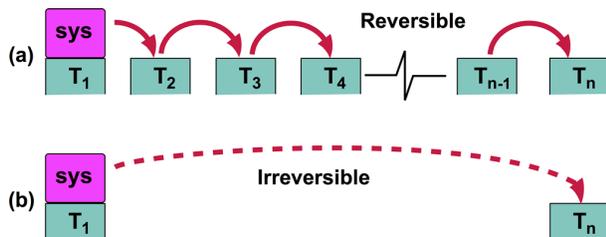


Fig. 3. (a) Heating by thermal contact with a sequence of n constant-temperature energy reservoirs, with $T_j = T_1 + j\epsilon$, $j = 0, 1, \dots, (n-1)$. Reversibility is achieved as $\epsilon \rightarrow 0$ and $n \rightarrow \infty$ with $n\epsilon$ fixed. (b) Irreversible energy transfer, bringing the system directly from the first to n th reservoir.

using a convenient reversible path that connects the system's initial and final states.

It is possible to transfer energy from higher to lower temperature *quasistatically*, but *not* reversibly, as shown in Fig. 4. Connect the cycle's working substance, with temperature reservoirs using ultra-thin low-conductivity fibers. If the connection is closed, opened, and closed again at quick intervals, this creates arbitrarily small, irreversible energy transfers by thermal conduction. Repeating this procedure generates a quasistatic, irreversible heat process. Although pulsing through narrow fibers provides a pleasing mental model, in fact pulsing through larger surfaces can achieve the same result.

When the working substance undergoes a cyclic process, its entropy change per cycle is zero. Because the pulsed energy transfers between the working substance and reservoirs are through finite temperature differences, there is a net entropy gain by the reservoirs during each cycle—i.e., outside the working substance—consistent with the second law of thermodynamics.

Key Point 8. *Quasistatic-irreversible cycles with two reservoirs can be effected via ultra slow work and pulsed heat processes. Reversal using only the same reservoirs is impossible.*

Key Point 9. *A variable temperature path can be achieved for a quasistatic irreversible cycle with two reservoirs, as in Fig. 4, using an ultra-slow heat process together with a simultaneous slow work process.*

There are other ways a quasistatic-irreversible process can occur. One is by friction between a slowly moving piston and its cylinder wall, which converts mechanical energy of the moving piston to internal energy of the piston and cylinder. If the piston's motion is reversed, again ultra-slowly, friction converts *more* mechanical to internal energy. Such processes dissipate energy and are *not* reversible.

C. Quasistatic volume changes

In this section, I address isothermal, isobaric and adiabatic quasistatic volume change. Although a heat process unaccompanied by a work process requires a temperature gradient, an isothermal volume change has no such gradient.

Key Point 10. *An ultra-slow volume change of a gas in contact with a reservoir generates an isothermal process through a sequence of near equilibrium states.⁵ Throughout the process energy is exchanged between the gas and reservoir, keeping the gas temperature constant.*

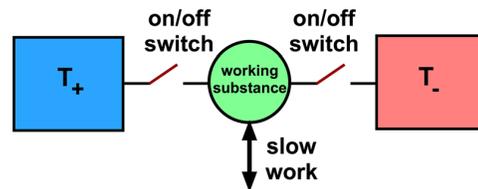


Fig. 4. Depiction of an irreversible cyclic process with a working substance (circle) using ultra-slow, pulsed heat processes through narrow low-conductivity fibers connected to hot (T_+) and cold (T_-) reservoirs. Either positive or negative work can be done on the working substance, which goes through a quasistatic cycle, with zero entropy change of the working substance, but non-zero net entropy increase of the reservoirs.

Key Point 11. A quasistatic process at constant pressure can be induced using a succession of constant-temperature reservoirs. This results in a combination of work and heat processes that redistribute energy between the system and reservoirs, leading to a desired final volume or temperature.

Key Point 12. A reversible, adiabatic ultra-slow work process on an insulated system alters its internal energy and temperature at constant entropy. Examples are (i) a volume change resulting from ultra-slow, variable-pressure piston work and (ii) magnetization or demagnetization of a paramagnet slowly and adiabatically, altering its temperature.

Key Point 13. Adiabatic work processes are central to thermodynamics, from connecting higher and lower temperature regions of heat engines and refrigerators to reaching ultra-low temperatures not reachable otherwise.

IV. HEAT ENGINES, REFRIGERATORS, AND EFFICIENCY MEASURES

The focus here is on quasistatic cycles with gaseous working substances that can be represented on pressure-volume and temperature-entropy graphs.

What is a heat engine? A general definition of a heat engine is a cyclic device that takes a working substance through a CW thermodynamic cycle, receiving energy Q_{in} from a range of high temperature reservoirs, delivering positive work energy W to an external load and the remaining energy $Q_{out} = Q_{in} - W$ to a range of low temperature reservoirs. A special case is a “traditional” heat engine with narrow high and low temperature ranges relative to the temperature difference between those ranges. An example is an electric generating plant, where the high temperature range is that of the burner and the low temperature range is that of the outdoor environment.

What is a refrigerator? A general definition of a refrigerator is a cyclic device that takes a working substance through a CCW thermodynamic cycle, receiving positive external work energy W and heat energy Q_{in} from a range of low temperatures, delivering energy $Q_{out} = Q_{in} + W$ to a range of higher temperatures. The special case of a “traditional” refrigerator has narrow high and low temperature ranges relative to the temperature difference between those ranges. An example is a household refrigerator, where the high temperature range is that of the kitchen and the low temperature range is that of the food compartment.

Q_{in} and Q_{out} represent net energy input and output magnitudes for the working substance during a cycle. Subscripts $-$ and $+$ are reserved for the highest and lowest cycle temperatures. The irreversible-quasistatic cycles considered in the remainder of this article are limited to irreversibilities achievable using pulsed energy exchanges with reservoirs.

Efficiency measures. Applying the first law of thermodynamics to one complete CW cycle, $\Delta U = Q_{in} - Q_{out} - W = 0$, and the work done by the working substance is $W = Q_{in} - Q_{out} > 0$. Doing the same for one complete CCW cycle, the latter equation holds with W being the external work on the working substance.

Because the objective of a heat engine is to use energy from a high-temperature region to perform external work, it is common to compare CW cycles according to their thermal efficiency η

$$\eta \equiv \frac{W}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}. \quad (5)$$

Similarly, a refrigerator cycle’s purpose is to remove energy from a lower temperature region, and it is common to define a coefficient of performance K for such CCW cycles,

$$K \equiv \frac{Q_{in}}{W} = \frac{1}{Q_{out}/Q_{in} - 1}. \quad (6)$$

The general efficiency measures, η and K , exist for any CW and CCW cycles, but are of most practical interest for “traditional” model heat engines or refrigerators defined above.

For a reversible cycle, Q_{in} in η equals Q_{out} in K and vice versa, and Eqs. (5) and (6) together imply

$$K = \frac{1 - \eta}{\eta} \quad (\text{reversible cycle}). \quad (7)$$

In Secs. V–VII, I use the Kelvin, Carnot and Stirling cycles to illustrate some implications of reversibility and irreversibility for CW and CCW cycles.

V. KELVIN CYCLE

A. CCW Kelvin cycle

One of the earliest studies of CCW cycles was by William Thomson (Lord Kelvin) who was interested in a novel way to heat buildings by extracting energy from the outdoor environment, thereby in essence inventing the concept of the *heat pump*.^{8,9} His idea, modeled (roughly) in Figs. 5(a) and 5(b), was to take outdoor air into a conducting cylinder located outdoors, and to expand that air isothermally at the winter outdoor temperature T_- (path ab), reducing its pressure. The second step was an adiabatic compression (path bc) in a now insulated cylinder, raising the gas temperature from T_- to $T_+ > T_-$.

Kelvin’s proposed machine did *not* execute a closed cycle; i.e., one with zero exchange of working substance with the environment. Rather, he specified that the warmed air in state c was to be transferred at constant pressure to the space being heated, with an equal amount of somewhat cooler air being transferred from that space to the outdoors. Simultaneously, *new*, lower-temperature air in state a was to be taken into the Kelvin warming machine from the outdoors, and the latter set of steps was to be repeated *ad infinitum*.

The closed cycle in Fig. 5, which is dubbed the “Kelvin cycle,” approximates Kelvin’s proposed machine

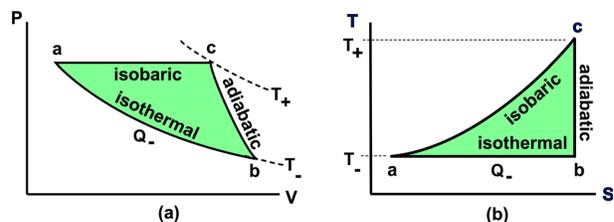


Fig. 5. (a) Pressure vs. volume for a Kelvin Cycle. (b) Temperature vs. entropy for the same cycle. Work on the system (CCW cycle) or by the system (CW cycle) is the shaded area $abca$.

with the quasistatic paths ab and bc , plus a quasistatic, isobaric path leading from state c back to a . This captures the spirit, but not the letter, of Kelvin's warming machine proposal.

1. Reversible CCW Kelvin cycle

The reversible CCW Kelvin cycle $abca$ in Fig. 5 uses an infinite number of reservoirs along ca , covering the temperature interval (T_-, T_+) .

Key Point 14. For the reversible CCW Kelvin cycle, energy $Q_{in} = Q_-$ is taken in at temperature T_- and Q_{out} is rejected over the interval (T_-, T_+) , which includes T_- . The absorption and ejection temperature regions are not separated. Although this is not a traditional refrigerator, it does refrigerate, removing net energy from the reservoir at T_- in Fig. 5.

Figure 6 shows the reversible Kelvin cycle embedded in a graph of a reversible Carnot cycle with isothermal segments at T_+ and T_- alternated with adiabatic segments. That figure shows that for CCW cycles, the same heat input $Q_{in} = Q_-$ occurs at T_- for the Kelvin and Carnot cycles. The Kelvin cycle's highest and lowest reservoir temperatures are the Carnot cycle temperatures and the Carnot cycle's adiabatic segments contain states a and c , so the external work W_{Kelvin} for the Kelvin cycle (area $abca$) is less than W_{Carnot} (shaded plus hatched areas, $abcda$). Equation (6), $K_{Carnot} \equiv Q_{in}/W_{Carnot}$, gives us

$$K_{Kelvin} > K_{Carnot} \text{ when Carnot cycle temperatures are } T_-, T_+. \quad (8)$$

Figure 6(b) makes clear that the magnitude $Q_{+}^{Carnot} = \int_a^c T dS > Q_p^{Kelvin} = \int_a^c T dS$, which also leads to Eq. (8), using Eq. (6). Equation (8) is generalized in Sec. IX A.

2. Irreversible CCW Kelvin cycle

No reservoir is needed at T_+ because that temperature is reached via adiabatic compression. Only the T_- reservoir is needed to facilitate the isothermal segment ab . Along isobaric path ca , a pulsed heat process sends energy from the working substance to the T_- reservoir.

Key Point 15. With only one reservoir, the irreversible CCW Kelvin cycle is not a refrigerator. It removes Q_- from the lone reservoir and adds $Q_{in} = Q_- + W_{Kelvin}$ to the same reservoir, generating entropy $\Delta S = W_{Kelvin}/T_-$ each cycle.

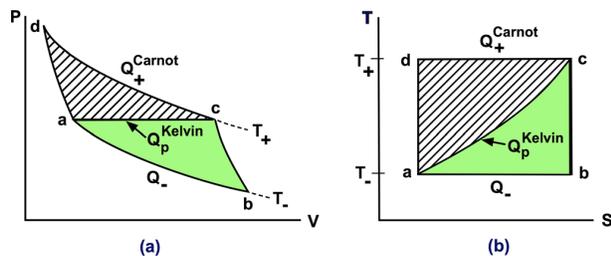


Fig. 6. Kelvin cycle $abca$, embedded in a reversible Carnot cycle. Note that $Q_p^{Kelvin} = \{Q_{out}, Q_{in}\}$ for $\{CCW, CW\}$ cycles, respectively. Subscript p connotes a constant-pressure path.

Application of Eq. (6), intended for a multi-reservoir system, gives a meaningless result.

B. Clockwise Kelvin cycle

Although William Thomson did not consider a CW cycle, one has been studied.¹⁰ There are stark differences between its reversible and irreversible cases.

1. Reversible CW Kelvin cycle

The constant-pressure expansion ac of the reversible Kelvin cycle's working substance requires energy inputs at all temperatures in (T_-, T_+) . Figure 6(b) shows that $Q_- = Q_-^{Kelvin} = Q_-^{Carnot}$ and $Q_p^{Kelvin} < Q_p^{Carnot}$, which with Eq. (5) confirms Carnot's inequality, which is generalized in Sec. VIII,

$$\eta_{Kelvin} < \eta_{Carnot}. \quad (9)$$

Key Point 16. The reversible CW Kelvin cycle has some characteristics of a heat engine: most of Q_p^{Kelvin} is input at the higher temperatures, output is to the lowest temperature, and the cycle does external work. Because energy absorption occurs over the full temperature range $[T_-, T_+]$, this is not a "traditional" heat engine.

2. Irreversible CW Kelvin cycle

For the irreversible CW Kelvin cycle $acba$, a high temperature reservoir at T_+ is needed to execute path ac with ultra-slow pulsed heating of the gas from T_- to T_+ . A low temperature (T_-) reservoir is needed for the isothermal path ba . Energy is received from the T_+ reservoir and is delivered to the T_- reservoir.

Key Point 17. The irreversible CW Kelvin cycle with two reservoirs is a traditional heat engine as described in Sec. IV.

To see an explicit indicator of irreversibility, suppose the working substance is a monatomic classical ideal gas. The energy transferred is $Q_p = (5/2)Nk(T_+ - T_-)$ and along cb the gas does work on the piston, lowering its temperature to T_- . The compression ba delivers energy $Q_- = NkT_- \ln(V_b/V_a)$ to the low temperature reservoir. Along ac , $V_a/T_a = V_c/T_c$ and along cb , $V_b^{2/3}T_b = V_c^{2/3}T_c$ so $V_b/V_a = (T_+/T_-)^{5/2}$, and $Q_- = (5/2)NkT_- \ln(T_+/T_-)$. The entropy change of the gas per cycle is $\Delta S_{ws} = 0$. Because $T_a = T_b = T_-$ and $T_c = T_+$, the net entropy change of the gas plus reservoirs is¹¹

$$\Delta S_{total} = -\frac{Q_p}{T_+} + \frac{Q_-}{T_-} = -\frac{5}{2}Nk \left[\left(1 - \frac{T_-}{T_+}\right) - \ln\left(\frac{T_-}{T_+}\right) \right] > 0$$

with $T_- < T_+$. (10)

More entropy is gained by the low temperature reservoir than is lost from the high temperature reservoir, leading to a net entropy increase, signaling irreversibility and consistency with the second law of thermodynamics.

Notably, the irreversibility does *not* reduce the thermal efficiency η_{Kelvin} relative to the reversible Kelvin cycle because both cycles have the same Q and W energy transfers.

Generally, the connections between entropy increase and thermal efficiency can be complex.¹²

VI. CARNOT CYCLES

A. Clockwise Carnot cycle

The familiar CW Carnot cycle for a classical ideal gas working substance is illustrated on the pressure vs. volume and temperature vs. entropy graphs in Fig. 7.

1. Reversible CW Carnot cycle

The reversible Carnot cycle holds a unique role in thermodynamics. It has two constant-temperature reservoirs, and temperature changes occur only along the adiabatic segments. The work done by the working substance is the shaded area of the cycle $abcd$ in Figs. 6(a) and 6(b). This follows from $\oint dU = \oint TdS - \oint pdV = 0$ for one cycle, implying

$$W = \oint_{abcd} P dV = \oint_{abcd} T dS = \text{positive area bounded by } abcd. \quad (11)$$

Key Point 18. *The reversible CW Carnot cycle in Fig. 6 is a traditional heat engine as described in Sec. IV.*

2. Irreversible CW Carnot cycle

Consider two possible sources of irreversibility: (α) a process that takes the working substance out of equilibrium, e.g., by a rapid, irreversible adiabatic ($Q=0$) expansion; and (β) a quasistatic heat process through a finite temperature difference using the pulsed energy technique in Fig. 4.

Type (α) irreversibility is exemplified by a working substance that undergoes a quick adiabatic expansion as in Fig. 2(b), replacing segment bc with bc' in Fig. 8(a).¹² Because the piston moves away from the gas, less work is done on it per unit of volume expansion than for the reversible case. In order for the working substance to lose sufficient internal energy to lower its temperature to T_- , the piston must move farther. This results in a subsequent isothermal compression $c'd$ with larger output $Q'_- > Q_-$ relative to the reversible case. According to the definition in Eq. (5), the thermal efficiency is $\eta = 1 - Q'_-/Q_+ < \eta_{Carnot}$. In similar fashion, a quick compression, depicted in Fig. 2(b),

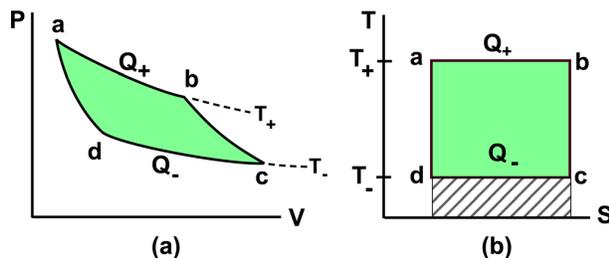


Fig. 7. Carnot cycle (CW or CCW) on (a) pressure–volume (P-V) and (b) temperature–entropy (T-S) plots for a gas working substance. Paths ab and cd are isothermal while bc and da are adiabatic. The areas $abcd$ in (a) and (b) equal the work magnitude by or on the gas. The (shaded + hatched, hatched) areas in (b) equal (Q_+, Q_-) .

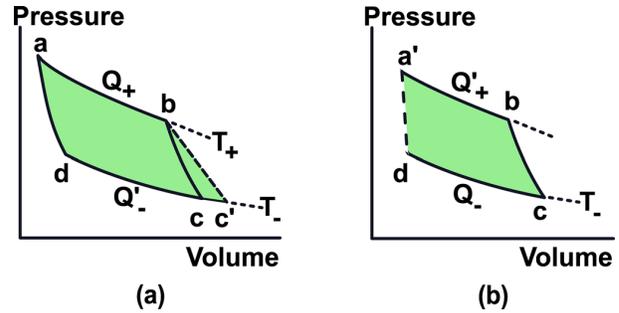


Fig. 8. Carnot cycle with (a) rapid, irreversible expansion starting in state b , leading to c' rather than c ; and (b) a rapid compression starting in state d , leading to a' rather than a . The dashed lines in (a) and (b) are symbolic, representing paths that cannot be graphed because pressure is not well defined between states b and c' and states d and a' . The latter four states are well defined.

leads to the modified path da' in Fig. 8(b). This results in $Q'_+ < Q_+$ and $\eta < \eta_{Carnot}$ again.

Key Point 19. *Internal irreversibilities from rapid volume changes lower the efficiency of a Carnot heat engine relative to the corresponding reversible Carnot cycle.*

Type (β) irreversibility is illustrated by the cycle, shown in Fig. 9, that was introduced to physics teachers by Curzon and Ahlborn in 1975.¹³ The cycle is sometimes referred to as a Novikov-Curzon-Ahlborn cycle.^{14,15} It consists of a reversible Carnot cycle with irreversible energy exchanges with reservoirs at temperatures $T_H > T_L$ as shown in Fig. 9. As normally implemented, this model is internally inconsistent in that the quasistatic Carnot cycle takes infinite time per cycle while the heat processes take finite times. As an approximation, one can envisage long but finite times for all processes, depicted in Fig. 9, which limits the output power.

For fixed reservoir temperatures T_H and T_L , there are two limiting cases in Fig. 9(a). One is $T_+ \rightarrow T_H$ and $T_- \rightarrow T_L$, the reversible Carnot limit with zero power output. The other is, $T_+ \rightarrow T_-$, where the work per cycle and power output approach zero. For intermediate values of (T_-, T_+) there is a power maximum with thermal efficiency¹³

$$\eta^* \equiv \frac{W}{Q_{in}} = 1 - \sqrt{\frac{T_L}{T_H}} < \eta_{Carnot} \quad \text{at maximum power output.} \quad (12)$$

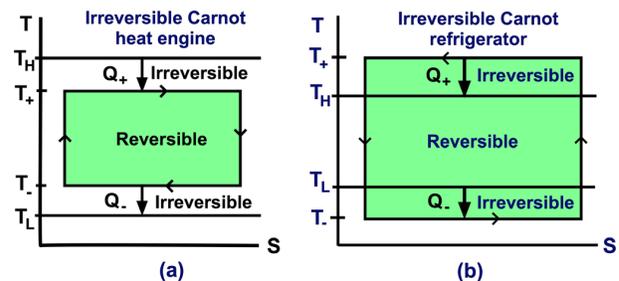


Fig. 9. Temperature–entropy plot of an irreversible-quasistatic Carnot CW (heat engine) cycle with two isothermal and two adiabatic segments. (b) Temperature–entropy plot of the irreversible CCW (refrigerator) cycle. Note: (T_+, T_-) are the working substance’s (maximum, minimum) temperatures while (T_H, T_L) are the high and low reservoir temperatures.

The Novikov-Curzon-Ahlborn model shares a common feature with real life heat engines: there are finite temperature differences between the working substance's highest and lowest temperatures and the respective high and low reservoir temperatures. A (non-Carnot) example is a steam engine used to generate electricity in a power plant.¹⁶ The boiler's flame temperature exceeds the steam temperature and the water temperature in the condenser exceeds the ambient temperature. It turns out that the efficiency η^* in Eq. (12) gives good numerical approximations (likely fortuitous) for electric power plants. The efficiency η^* occurs also under maximum work (not power) conditions for a number of common reversible heat engine models.¹⁷

Key Point 20. *The irreversible Carnot cycle in Fig. 9(a) is a "traditional" heat engine and obeys Carnot's inequality, $\eta^* < \eta_{Carnot}$. Because of this model's rich behavior, it led to a new field called finite-time thermodynamics,¹⁸ and is included in some textbooks.¹⁹ There is positive entropy production during each cycle.*

The "first law efficiency" η does not account for limitations by the second law of thermodynamics. In contrast, a second law efficiency²⁰ ϵ measures performance relative to the maximum possible η using the same reservoirs and input energy; i.e., $\epsilon = \eta / (1 - T_L/T_H) \leq 1$. For example, at maximum power the Novikov-Curzon-Ahlborn engine's second law efficiency is $\epsilon = 1 / (1 + \sqrt{T_L/T_H})$.

B. CCW Carnot cycle

1. Reversible CCW Carnot cycle

Because $Q_{in}/T_+ = Q_{out}/T_-$, the coefficient of performance K can be expressed solely as a function of T_-, T_+ , giving the following result, consistent with Eq. (7):

Key Point 21. *The reversible CCW Carnot cycle, a traditional refrigerator as described in Sec. IV, has coefficient of performance $K_{Carnot} = 1 / (T_+/T_- - 1)$.*

2. Irreversible CCW Carnot cycle

If energy flows from the T_L reservoir and to the T_H reservoir, it is necessary that the Carnot cycle's low and high temperatures satisfy $T_- < T_L$ and $T_+ > T_H$, as in Fig. 9(b). The reservoir temperatures are assumed fixed and the working substance temperatures can be adjusted by design. In the double limit $T_+ \rightarrow T_H, T_- \rightarrow T_L$, the reversible Carnot refrigerator is recovered. Unlike the heat engine, which has a maximum power condition, there is no such optimal operating condition for the refrigerator.

Key Point 22. *Statements such as "heat flows uphill in a CCW cycle" are incorrect. The heat processes for the irreversible cycle in Fig. 9(b) have normal energy flows from higher to lower temperatures, modeling real-life refrigerators; i.e., the hot coil is heated by compressive work, and becomes hotter than the kitchen, while the cold coil is cooled via expansion and is colder than the food compartment.²¹*

Despite irreversibility, the quasistatic Carnot cycle has $Q_{in}/T_+ = Q_{out}/T_-$ and

$$K_{irrCarnot} = \frac{1}{(T_+/T_- - 1)}$$

for an irreversible-quasistatic CCW Carnot cycle.

(13)

Key Point 23. *The irreversible CCW Carnot cycle is a traditional refrigerator as described in Sec. IV. For a given Q_{out} , Fig. 9(b) shows the minimum required input work occurs in the reversible Carnot cycle limit, and Eq. (6) implies $K_{irrCarnot} \leq K_{Carnot}$.*

VII. STIRLING CYCLE

The Stirling cycle has two isothermal segments at temperatures T_+ and T_- , alternated with two constant-volume segments, which have non-isothermal heat processes. Pressure vs. volume and temperature vs. entropy graphs of the Stirling cycle are in Fig. 10.

A. CCW Stirling cycle

1. Reversible CCW Stirling cycle

The reversible Stirling cycle is well known and the CCW refrigerator was discussed recently by Mungan.²² The temperature range for both energy input $Q_{in} = Q_- + Q_{dc}$ and output $Q_{out} = Q_+ + Q_{bc}$ is the full interval (T_-, T_+) . This is inconsistent with the specified narrow temperature range in the definition of a refrigerator and the intended meaning of Eq. (6). From Fig. 10, it is clear that $Q_{in} = Q_- + Q_{dc}$ exceeds the Carnot cycle's input Q_-^{Carnot} at T_- and $W_{Stirling}$, the shaded area $adcb$, is less than W_{Carnot} , the area within the dashed rectangle. From Eq. (6) it follows that $K_{Stirling} \geq K_{Carnot}$. The constant-volume segments "cancel" one another if the specific heat of the gas is volume dependent, with the reservoirs involved returning to their initial states each cycle. If the intended goal for the device being modeled is cooling at temperature T_- , then using $Q_{in} = Q_- + Q_{dc}$ in Eq. (6) is misleading. A more relevant measure of efficiency is the task-specific coefficient of performance, defined as $K_{task} \equiv Q_- / W < K_{Stirling}$.²³

In real-life Stirling cycles, the movements of two pistons are coordinated to approximate the four Stirling cycle segments, and with a regenerator, depicted in Fig. 11(a). As the constant volume gas winds its way through the regenerator

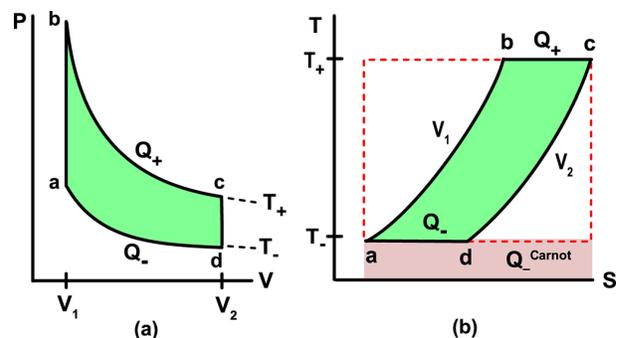


Fig. 10. Two views of the Stirling cycle with alternating constant-temperature and constant-volume segments. (a) Pressure vs. volume. (b) Temperature vs. entropy. The dashed rectangle is for a comparison Carnot cycle and the shaded lower rectangle is the energy exchanged between the gas and reservoir at T_- .

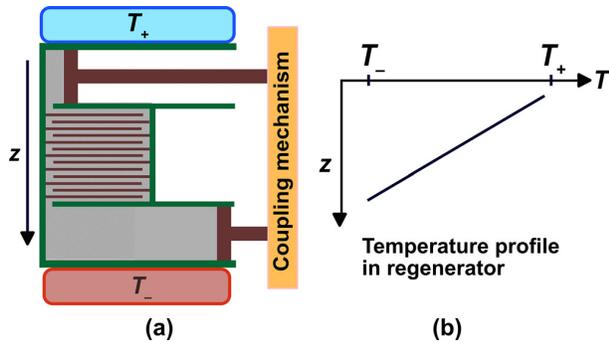


Fig. 11. (a) Depiction of Stirling cycle apparatus with regenerator in which the gas cools as the gas moves from the hot to cold side, and heats as the gas moves oppositely. (b) Temperature profile of the gas in the regenerator, regardless of gas flow direction. Adapted from D. V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley-Longman, 1999), p. 133.

from higher to lower temperature, the regenerator retains a temperature gradient as in Fig. 11(b), generating path ba . This process approximates using a sequence of successively cooler reservoirs, ideally approaching reversibility. Similarly, heating along dc occurs when gas flows in the reverse direction. The CCW reversible Stirling cycle with regeneration uses only two reservoirs and has the same coefficient of performance as the reversible Carnot cycle.

2. Irreversible CCW Stirling cycle

For a quasistatic-irreversible CCW cycle, energy flows (from, to) the cold reservoir along (ad , ba), and (to , from) the hot reservoir along (cb , dc), so this is *not* a traditional refrigerator. The net input from the cold reservoir per cycle is $Q_{in} = Q_- - Q_{ba}$, so $K = (Q_- - Q_{ba})/W$ is more reflective of the energy from the cold reservoir than K_{task} . Irreversibility increases the environment's entropy.

B. CW Stirling cycle

1. Reversible CW Stirling cycle

Analysis of the reversible clockwise Stirling cycle is substantially the same as for the counterclockwise case. Here $Q_{out} = Q_{cd} + Q_- \geq Q_-^{Carnot}$ and $Q_{in} = Q_{ab} + Q_+ \leq Q_+^{Carnot}$, and it follows from Eq. (5) and an area-based argument using Fig. 10(b) that $\eta_{Stirling} \leq \eta_{Carnot}$.

This cycle also can be used with a regenerator to approach reversible heat exchanges along the constant-volume segments, in which case only the T_+ and T_- reservoirs are involved, and the efficiency equals the reversible Carnot efficiency, η_{Carnot} .

In analogy with the CCW case a, task-specific thermal efficiency $\eta_{task} \equiv W/Q_+$ is sensible if the energy exchanges over the constant-volume segments cancel—or nearly do. In this case $\eta_{task}^{Stirling} = \eta_{Carnot}$, the same result obtained with a regenerator.

2. Irreversible CW Stirling cycle

Heating energy flows *to* the gas from the hot reservoir along both ab and bc , and *from* the gas *to* the cold reservoir along cd and da . Although *not* a traditional heat engine, this cycle does supply external work.

VIII. CARNOT'S INEQUALITY FOR CW CYCLES

A. Reversible CW cycles

An interesting geometric demonstration of Carnot's inequality for reversible CW cycles was presented by Tatiana Ehrenfest-Afanaseva in her book on thermodynamics.²⁴ A variant, which incorporates adiabatic segments that separate the upper and lower temperature regions, is illustrated in Fig. 12. An arbitrary²⁵ reversible cycle is represented by a closed path $abcd$ (or $adcb$), circumscribed by a comparison Carnot cycle (dashed rectangle),²⁶ chosen to have the arbitrary cycle's maximum and minimum temperatures.

The thermal efficiency is defined as $\eta = 1 - Q_{out}/Q_{in}$, and $Q_{in} = \int_{\text{upper } a \rightarrow b} T dS$ is the area under the upper path $a \rightarrow b$ of the arbitrary cycle and the S axis. In Fig. 12(a), Q_{out} is the area of the hatched pattern, namely, the area under the lower path dc . Q_-^{Carnot} and Q_+^{Carnot} are the respective areas of the lower shaded rectangle and rectangle $efhg$. Since Q_{in} , Q_{out} are non-negative by definition, it is clear visually that

$$Q_{in} \leq Q_+^{Carnot} \quad \text{and} \quad Q_{out} \geq Q_-^{Carnot}. \quad (14)$$

Using the latter inequalities, we have

$$\eta = 1 - Q_{out}/Q_{in} \leq 1 - Q_-^{Carnot}/Q_+^{Carnot} = \eta_{Carnot}. \quad (15)$$

Key Point 24. Any reversible variable-temperature CW cycle represented in the temperature–entropy diagram in Fig. 12 satisfies $\eta \leq \eta_{Carnot}$, where the comparison Carnot cycle circumscribes the arbitrary cycle.

B. Irreversible CW cycles

For any quasistatic CW cycle receiving Q_+ and delivering Q_- from and to high and low temperature reservoirs, $\Delta S_{cycle} = 0$, and the total entropy change (of the universe) is the net entropy change of the reservoirs

$$\Delta S_{tot} = \Delta S_{cycle} + \frac{Q_-}{T_-} - \frac{Q_+}{T_+} \geq 0. \quad (16)$$

Equation (16) reduces to $Q_-/Q_+ \geq T_-/T_+$, which implies Eq. (15).

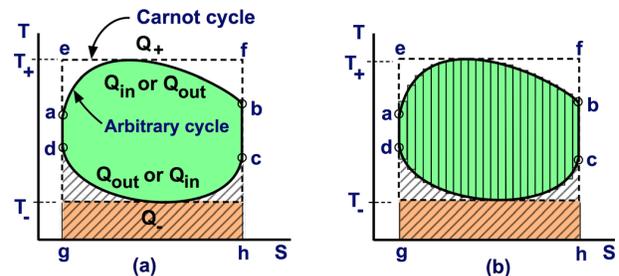


Fig. 12. (a) Temperature vs. entropy plot of an arbitrary CW or CCW reversible cycle ($abcd$ or $adcb$) and a comparison Carnot cycle (dashed rectangle). The vertical segments are quasistatic adiabatic ($Q=0$) paths that separate the high and low temperature heat processes. A traditional heat engine or refrigerator cycle has $|T_b - T_d|$ and $|T_d - T_c|$ much less than T_+ , T_- . For a CW cycle, $Q_{ab} = Q_{in}$, $Q_{dc} = Q_{out}$; for a CCW cycle, $Q_{ab} = Q_{out}$, $Q_{dc} = Q_{in}$. (b) The same plot, with a set of narrow reversible Carnot cycle rectangles whose envelope approximates the arbitrary cycle.

Key Point 25. Any irreversible CW quasistatic cycle, including those represented in Fig. 12 has $\eta \leq \eta_{Carnot}$ where the comparison Carnot cycle operates between the arbitrary cycle's maximum and minimum temperatures.

IX. CARNOT-LIKE COEFFICIENT OF PERFORMANCE INEQUALITIES FOR CCW CYCLES

A. Reversible CCW cycles

I now present three different derivations leading to a generalization of Eq. (8) for the reversible CCW Kelvin cycle. Each leads to Eq. (17), where the comparison Carnot cycle temperatures are the arbitrary cycle's extreme temperatures.

Derivation 1. From Fig. 12(a), $Q_+/Q_- \geq Q_{out}/Q_{in}$, thus Eq. (6) leads to

$$K \geq K_{Carnot}, \text{ generalizing Eq. (8)}. \quad (17)$$

Derivation 2. The inequality (17) can also be obtained using Fig. 12(b), where the i th approximating narrow Carnot rectangle has energy input $Q_{in,i}$ and coefficient of performance K_i . Note that each rectangular approximating Carnot cycle has a larger coefficient of performance than the circumscribing Carnot cycle; i.e., $K_i \geq K_{Carnot}$. This follows from $T_{out,i}/T_{in,i} \leq T_+/T_-$, which implies $K_i = 1/(T_{out,i}/T_{in,i} - 1) \geq 1/(T_+/T_- - 1) = K_{Carnot}$.

For the approximating Carnot rectangles, $K = (\sum_{j=1}^n Q_{in,j}) / (\sum_{\ell=1}^n W_\ell)$, where W_ℓ is the external work for the ℓ th rectangle. Because $Q_{in,j} = W_j K_j$ for the j th Carnot rectangle,

$$K = \sum_{j=1}^n \left(\frac{W_j}{\sum_{\ell=1}^n W_\ell} \right) K_j \geq K_{Carnot}. \quad (18)$$

The first step represents K as a weighted average of the $\{K_j\}$ for the approximating narrow Carnot cycles, and the second step uses the previous result $K_j \geq K_{Carnot}$ and the fact that, $(\sum_{j=1}^n W_j) / (\sum_{\ell=1}^n W_\ell) = 1$. Equation (18) confirms Eq. (8), which was derived for the Kelvin CCW cycle.²⁷

Derivation 3. The third proof of Eq. (17) comes from Eq. (7), which can be rearranged to read $K = 1/\eta - 1$. For a Carnot cycle, $K_{Carnot} = 1/\eta_{Carnot} - 1$. Using Carnot's inequality $\eta \leq \eta_{Carnot}$ for the reversible CW cycle we obtain,

$$K - K_{Carnot} = \frac{\eta_{Carnot} - \eta}{\eta_{Carnot}\eta} \geq 0 \text{ for reversible cycles,} \quad (19)$$

again agreeing with Eq. (8). The Carnot cycle reservoir temperatures here are the maximum and minimum arbitrary cycle temperatures used to obtain $\eta \leq \eta_{Carnot}$.

Key Point 26. Any reversible CCW cycle has coefficient of performance $K \geq K_{Carnot}$. Its CW counterpart satisfies $\eta \leq \eta_{Carnot}$. For both cases, the comparison Carnot cycles operate between the cycle's maximum and minimum temperatures.

B. Irreversible CCW arbitrary cycle

For any quasistatic CCW cycle operating between T_+ and T_- , $\Delta S_{cycle} = 0$ for each cycle, and the net entropy change is

that of the reservoirs, $\Delta S_{tot} = \Delta S_{cycle} + Q_{out}/T_+ - Q_{in}/T_- \geq 0$. The latter inequality together with Eq. (6) implies

$$K \equiv 1/(Q_{out}/Q_{in} - 1) \leq 1/(T_+/T_- - 1). \quad (20)$$

Key Point 27. For any 2-reservoir irreversible CCW cycle, $K \leq K_{Carnot}$, an inequality that appears in some physics books.²⁸

X. FINAL REMARKS

The examples above show how reversible and irreversible cycles that look the same on quasistatic pressure-volume or temperature-entropy graphs can result in very different behavior and entropy changes of the environment. The numbered Key Points provide a capsule summary of major findings. Sections V–VII are illustrative of the differences between irreversible and reversible cycles.

For irreversible cycles, the inequalities $\eta \leq \eta_{Carnot}$ and $K \leq K_{Carnot}$ are imposed by the second law of thermodynamics. The η inequality holds also for non-Carnot reversible CW cycles. The K inequality for reversible CCW cycles, $K \geq K_{Carnot}$, is *not* imposed by the second law because reversible cycles generate zero entropy and always satisfy the second law. For the Stirling and other²⁹ cycles with isothermal segments, a task-specific coefficient of performance K_{task} and efficiency η_{task} can be useful efficiency measures.

We found that the reversible and irreversible CW Kelvin cycles have the same thermal efficiency η_{Kelvin} , which might seem odd at first. However, the thermal efficiency η , which is a ratio of the work output to heat input, is unaffected by entropy-generating irreversibilities involving the reservoirs. For the reversible case, the infinite set of reservoirs undergoes zero net entropy change, but for the irreversible case, the net entropy change of the hot and cold reservoirs is positive, as shown, e.g., in Eq. (10). The point is that the primary difference between the reversible and quasistatic irreversible cases lies in changes to the environment.

In summary, thermodynamic cycles are rich in insights and subtleties. Because there is much more to them than typical textbook expositions indicate, they offer unique opportunities for teachers who would like to stimulate the mental juices of their students.

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- ²³ The task-specific efficiency idea was suggested by a clever AJP referee.
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- ²⁵ This cycle is arbitrary within the class of cycles that transfer energy (*from*, *to*) reservoirs along the upper path and (*to*, *from*) reservoirs along the lower path for (*clockwise*, *CCW*) cycles, and are separated by adiabatic paths.
- ²⁶ For reversible cycles, the maximum and minimum reservoir temperatures coincide with the arbitrary cycle's maximum and minimum working substance temperatures.
- ²⁷ One can derive Eq. (15) for the CW case writing η as a weighted average, $\eta = \sum_j f_j \eta_j \leq \eta_{Carnot}$ with $f_j = T_{in,j} \Delta S_j / \sum_\ell T_{in,\ell} \Delta S_\ell$, $\eta_j = 1 - T_{out,j} / T_{in,j}$, and using $T_{in,j} / T_{out,j} \leq T_{in} / T_{out}$.
- ²⁸ See, for example, p. 128 of Ref. 19.
- ²⁹ The Ericsson cycle (https://en.wikipedia.org/wiki/Ericsson_cycle) has alternating isothermal and constant-pressure segments and an argument similar to that for the Stirling cycle can be made regarding compensation of energy exchanges along the two non-isothermal segments. It can also be operated with a regenerator.

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