

Irreversibility, entropy production, and thermal efficiency

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The relationships between the entropy production per cycle and the thermal efficiency are investigated for a class of irreversible cyclic processes. Examples are given that pinpoint specific sources of irreversibility and their thermodynamic consequences. It is found that an increase (decrease) in an irreversible cycle's thermal efficiency does not necessarily lead to a decrease (increase) in its entropy production even if the work done per cycle is held constant. Only for the case of a reversible Carnot cycle is it guaranteed that a change (negative for this case) in the efficiency is met by an entropy production change of opposite algebraic sign. Sufficiency conditions are found for which the entropy production and the efficiency η are inversely related for more general cyclic processes. For a given set of heat reservoirs and specified values of the work output W , the absolute minimum and maximum entropy productions are determined and are shown to be monotonically decreasing functions of η for fixed W . It is shown also that, for an irreversible cycle with maximum and minimum temperatures T_+ and T_- , respectively, $\eta \leq (1 - T_-/T_+)(1 + T_- \Delta S/W)^{-1}$, where ΔS is the entropy production per cycle. The equality holds only for a cycle employing two reservoirs. The potential relevance of these results to environmental and technological problems is mentioned.

I. INTRODUCTION

The maximum amount of work produced by a cycle operating between two heat reservoirs has been a topic of considerable interest to physicists at least since the publication in 1824 of Carnot's book, *Reflections on the Motive Power of Fire and the Machines Fitted to Develop that Power*.¹ A major result in that book was Carnot's principle: "The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of caloric." Although his arguments employed the now-abandoned idea of the conservation of caloric, Carnot's principle remains to this day as a fundamental physical law. Its theoretical basis lies in

modifications of Carnot's work, utilizing subsequent developments in thermodynamics by a variety of people, especially Clapeyron, Thompson, and Clausius.¹

A modern-day statement of Carnot's principle is the following: Any reversible cyclic process operating between a maximum temperature T_+ and a minimum temperature T_- has a thermal efficiency which is less than or equal to $1 - T_-/T_+$. The equality holds only for a reversible Carnot cycle operating between two heat reservoirs, at T_+ and T_- .² A common generalization of this theorem to irreversible Carnot cycles is the following: The efficiency of an irreversible Carnot cycle operating between two heat reservoirs, at T_+ and T_- , is less than $1 - T_-/T_+$.³

Carnot's work itself preceded the introduction in 1865 of the concept of entropy by Clausius in connection with the second law of thermodynamics.⁴ Among its attributes, the concept of entropy provides a direct way to discuss irreversible processes. For example, completely reversible processes, by definition, produce zero entropy change for the universe. Indeed, it is this fact which allows the reversal of such processes without a violation of the second law of thermodynamics—that is, without a violation of the principle of entropy increase. Irreversible processes, on the other hand, are always accompanied by increases in the entropy of the universe. The magnitude of each increase can be viewed as a measure of the degree of irreversibility for the process under consideration.

Since irreversibility connotes wastefulness, one might expect a connection between the entropy produced by an irreversible cycle and the thermal efficiency of that cycle. To the authors' knowledge, the founders of thermodynamics did not address themselves to this point and few discussions of it appear in the existing literature on classical and irreversible thermodynamics.⁵ The most extensive discussion along these lines appears to be by Tolman and Fine.⁶ They pointed out that, "... a determination of the different irreversible processes that lead to the production of entropy inside a heat engine or other kind of industrial apparatus makes it possible to evaluate the relative contributions of these irreversible processes to the inefficiency of the overall process, in terms of useful work lost or made necessary by their occurrence." Tolman and Fine derived an equation relating the work done to the entropy produced per cycle for irreversible cyclic processes. Their emphasis was on an examination of the entropy produced by specific types of irreversible processes (e.g., viscous flow, chemical reactions, diffusion, shock waves), and no attempt was made to relate entropy production explicitly to the thermal efficiency for cyclic processes.

In a brief discussion of irreversible cycles, Fast has stated,⁷ "Thus, in the irreversible Carnot cycle, in order to obtain the same quantity of work as in the reversible operation, more heat must be extracted from the hot reservoir. A chance to obtain work from heat has here been missed. . . . This kind of loss of thermal efficiency is characteristic of the irreversible operation of a process." Again, however, the connection between entropy production and thermal efficiency was not pursued.

The connections between irreversibility, wastefulness, and entropy production are of particular relevance current-

ly. Large-scale thermodynamic systems such as electrical power-generating plants are under scrutiny because of their potential wastefulness of precious resources and also because of their capacity to create one or more forms of pollution. Certainly, an increase in the efficiency of a power-generating plant leads to a reduction in resource consumption for a given power output. Since it is tempting to relate the creation of pollution with the production of entropy,⁸ it is of interest also to know the effect, if any, that an efficiency change has on the net entropy production.

What is the relationship between irreversibility, entropy production, and thermal efficiency? In the present work, we study this question for cyclic processes. Specifically, the connections between thermal efficiency and entropy production are studied for a wide class of irreversible cyclic heat engines. The techniques used herein are simple extensions of those which are common in classical equilibrium thermodynamics. From a pedagogical point of view, the present treatment provides a bridge between classical thermodynamics and some of the elementary concepts in irreversible thermodynamics. Since it does so within a context which has overtones of technological and social relevance, it might serve as a useful topic for inclusion in classical thermodynamics courses.

The remainder of this paper is organized in the following way. In Sec. II, fundamental definitions and assumptions are stated and a system of mathematical notation is established. Section III consists of an analysis of irreversible Carnot cycles, including the examination of some simple examples which provide a view of the origin and effects of certain aspects of irreversibility. This is followed by a discussion of the relationship between the entropy production per cycle and the corresponding thermal efficiency for cycles with two heat reservoirs. In Sec. IV, irreversible cycles involving more than two heat reservoirs are discussed. This treatment reveals that irreversible cycles with only two heat reservoirs are special cases—a fact which parallels that for reversible cycles. Section IV also contains a discussion of upper and lower bounds on the entropy production for given values of the work output and the efficiency, as well as bounds on the efficiency for given values of the entropy production and work output. It includes the generalization of Carnot's principle (stated above) to irreversible cycles with more than two temperature reservoirs.

For precision, major results are stated in theorem form in Secs. III and IV. The proofs of some of the results of Sec. IV are in the Appendix. For the reader who is uninterested in the mathematical details, a general understanding of the results may be obtained by reading Sec. II, the statements (excluding proofs) of the theorems and corollaries, plus the discussion and conclusions in Sec. V.

II. DEFINITIONS AND ASSUMPTIONS

Consider a thermodynamic system which is taken from an initial equilibrium thermodynamic state, through an irreversible path, back to its initial state. The cycle is assumed to be carried out with the use of a sequence of reversible work and heat sources defined in the usual way.^{9,10}

A reversible work source is a system enclosed by adiabatic impermeable walls and characterized by relaxation times sufficiently short that all processes of interest

within it are essentially quasistatic. Its volume can change and it can do positive or negative work on another system. Throughout all such changes of interest its entropy is constant.

A reversible heat source (reservoir) is defined as a constant-volume, constant-temperature system enclosed by rigid impermeable walls. It can exchange heat with another system and is characterized by relaxation times sufficiently short that all processes of interest within it are essentially quasistatic. A gain of heat energy ($-Q$) gives the corresponding heat source entropy change $\Delta S = -Q/T$, where T is the constant temperature of the heat source.

Successive couplings of a system to such reversible work and heat sources enable the construction of a wide variety of reversible or irreversible cyclic processes.

If there are p reversible heat sources involved in the cycle, then the total entropy change of the universe in one cycle is

$$\Delta S = \Delta S_{\text{system}} + \sum_{i=1}^p \Delta S_i = \sum_{i=1}^p \Delta S_i. \quad (1)$$

Here, ΔS_{system} , the entropy change of the system itself, is zero since the initial and final states are identical. ΔS_i is the entropy change of the i th reversible heat source:

$$\Delta S_i = -Q_i/T_i. \quad (2)$$

In Eq. (2), Q_i is defined as the heat *gained* by the system (i.e., $-Q_i$ is the heat gained by the heat source). The second law of thermodynamics requires that

$$\Delta S = -\sum_{i=1}^p \frac{Q_i}{T_i} \geq 0 \quad (3)$$

with the equality holding if and only if the system's cycle is completely reversible.

For convenience, the reversible heat sources are labeled in such a way that

$$Q_i < 0 \quad \text{for } i = 1, \dots, n, \quad (4a)$$

$$Q_i > 0 \quad \text{for } i = n+1, \dots, p. \quad (4b)$$

Then the total heat *input* to the system during one cycle is

$$Q_{\text{in}} = \sum_{i=n+1}^p Q_i, \quad (5)$$

and the corresponding total heat *output* is

$$Q_{\text{out}} = \sum_{i=1}^n Q_i. \quad (6)$$

The first law of thermodynamics applied to one cycle gives the work W done by the system:

$$W = Q_{in} + Q_{out}. \quad (7)$$

The system's thermal efficiency is defined as

$$\eta = W/Q_{in} = 1 + Q_{out}/Q_{in}. \quad (8)$$

If W is positive, then

$$0 < |Q_{out}| < Q_{in}, \quad (9)$$

which implies that $0 < \eta < 1$. It is assumed that $W > 0$, unless specified otherwise.

Equations (3), (5), (6), and (8) allow one to relate the rate of entropy production ΔS (i.e., the entropy produced per cycle) to the thermal efficiency η . This relationship will be pursued in Secs. III and IV.

For a Carnot cycle which utilizes only two reversible heat sources with temperatures T_1 and T_2 ($T_2 > T_1$), one has $p = 2$ and $n = 1$. For this case Eqs. (5) and (6) reduce to $Q_{in} = Q_2$ and $Q_{out} = Q_1$. A reversible Carnot cycle is one which consists of two reversible isothermal paths (at T_1 and T_2) and two reversible adiabatic paths. For this special case the following notation is adopted: $Q_1 = Q_{1c}$, $Q_2 = Q_{2c}$ and $\eta = \eta_c$.

Since the cycle is reversible,

$$\Delta S = -(Q_{1c}/T_1 + Q_{2c}/T_2) = 0, \quad (10)$$

and therefore (10) and (8) imply the usual result,

$$\eta_c = 1 - T_1/T_2. \quad (11)$$

For a general irreversible Carnot cycle, (10) is replaced by

$$\Delta S = -(Q_1/T_1 + Q_2/T_2) \geq 0. \quad (12)$$

This implies that

$$\eta = 1 + Q_1/Q_2 \leq 1 - T_1/T_2 = \eta_c. \quad (13)$$

Expression (13) is the statement of Carnot's principle for irreversible Carnot cycles³ mentioned in Sec. I.

III. IRREVERSIBLE CARNOT CYCLES: SOURCES OF IRREVERSIBILITY

How can irreversibilities arise in a Carnot cycle? This can happen in a variety of ways,⁶ some of which are illustrated by the following, simple examples.¹¹ Consider first the cycle illustrated in Fig. 1. Paths BC and DA are the usual reversible adiabats along which the entropy of the system remains unchanged. Path CD is the usual reversible isotherm at temperature T_1 . However, path AB represents an irreversible process which connects the two equilibrium states, A and B, where the temperatures $T_A = T_B = T_2$. The irreversibility might result from a

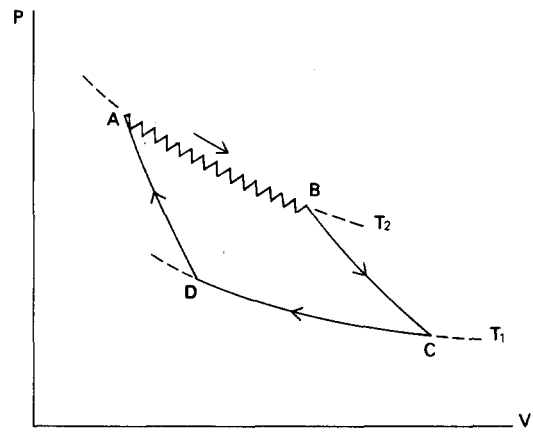


Fig. 1. Pressure-volume diagram for a Carnot cycle with an irreversible heat input AB, which is denoted by a sawtoothed line.

rapid expansion which drives the system into nonequilibrium states.

If states A and B were connected by a reversible isotherm at temperature T_2 , then the system's entropy change for path AB would be

$$S_B - S_A = Q_{2c}/T_2, \quad (14)$$

and the heat sources' entropy change would be the negative of this, namely, $-Q_{2c}/T_2$. However, for the irreversible path AB under consideration, the system's entropy change is given by

$$S_B - S_A = Q_2/T_2 + \sigma_2 \quad (15)$$

with

$$\sigma_2 \geq 0. \quad (16)$$

This follows from a generalized statement of the second law of thermodynamics which states that the entropy change of a system can be written as a portion related to the exchange of energy or matter with the environment, plus a nonnegative portion related to the system's internal entropy production.¹² The latter is σ_2 , which may be attributed to irreversible internal mass and/or energy flows that result from the existing deviations from equilibrium along the irreversible path.

If Eqs. (14) and (15) are combined, it becomes clear that

$$Q_2 = Q_{2c} - T_2\sigma_2 \leq Q_{2c}. \quad (17)$$

Notice that $Q_1 = Q_{1c} < 0$ and $0 < Q_2 \leq Q_{2c}$ imply, by using (8) and (11), that $\eta \leq \eta_c$ in agreement with (13). The present argument pinpoints the lower efficiency as being due to a decreased heat input Q_2 along path AB. Thus the irreversible cycle requires a lower heat energy input but is still less efficient than the corresponding reversible cycle.

It is clear from (12) and (13) that a decrease in Q_2 tends to increase ΔS and decrease η . Thus, ΔS decreases as η increases and vice versa. Formally, using (10) and

(13)–(17) in (12), one has

$$\Delta S = \sigma_2 = Q_{2c}/T_2 + (Q_{1c}/T_2)(1 - \eta)^{-1}. \quad (18)$$

Since states A, B, C, and D are fixed, as are temperatures T_1 and T_2 , η can be varied only by changing the degree of irreversibility along path AB. For such a change, one has

$$\frac{d}{d\eta} (\Delta S) = \frac{Q_{1c}}{T_2} (1 - \eta)^{-2} < 0, \quad (19)$$

which indicates the monotonicity of ΔS in η . It is straightforward to consider a similar example for which path CD rather than path AB is irreversible. Again, one finds that $d(\Delta S)/d\eta < 0$.

Suppose now that the reversible adiabatic path BC of the Carnot cycle is replaced by an irreversible adiabatic expansion BX as shown in Fig. 2. The expansion is to a volume sufficiently large to yield a final equilibrium temperature T_1 . Paths AB and DA are the usual reversible Carnot paths, while CD is replaced by an extended reversible isothermal path XD. The irreversibility of the path implies that

$$S_X - S_B = \sigma > 0, \quad (20)$$

where σ is the internal entropy produced along path BX. Since $S_X > S_C$ and $T_X = T_C$, V_X must exceed V_C (at least for "ordinary" substances with positive thermal expansion coefficients) as shown in Fig. 2. Notice that $Q_2 = Q_{2c}$ and $Q_1 = Q_{1c} + \Delta Q_1$, where $S_C - S_X = S_B - S_X = -\sigma = \Delta Q_1/T_1$. ΔQ_1 is the (negative) heat gained by the system over path XC. The entropy production ΔS again equals σ , and thus one has, using expression (13) together with the foregoing,

$$\Delta S = (Q_{1c} + Q_{2c} - \eta Q_{2c})/T_1 \quad (21)$$

and

$$\frac{d(\Delta S)}{d\eta} = -\frac{Q_{2c}}{T_1} < 0. \quad (22)$$

It is easy to repeat this type of analysis for an irreversible Carnot cycle which has an irreversibility only over the adiabatic portion leading from T_1 to T_2 , as depicted in Fig. 3. Again, one finds that $d(\Delta S)/d\eta < 0$.

In these examples, the effects of the irreversibility appear in changes of either Q_{in} or Q_{out} , but not both. These changes cause η and ΔS to change in opposite directions. There are, however, variations of both Q_{in} and Q_{out} that cause both η and ΔS to increase or both to decrease or one to remain constant and the other to increase so that, in general, there is no fixed relationship between changes in η and ΔS . One simple example of such a change is to double Q_{in} , Q_{out} , and W (this can be done by just defining a new cycle equal to two of the original cycles). This leaves η unchanged but doubles ΔS . This example suggests that ΔS might be normalized in some way to remove this essentially uninteresting change. This can be

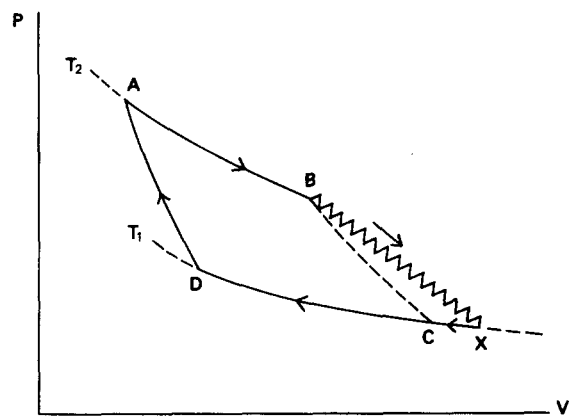


Fig. 2. Pressure-volume diagram for a Carnot cycle with an irreversible adiabatic expansion BX, which is denoted by a sawtoothed line. The adiabatic expansion BC of the corresponding reversible Carnot cycle is indicated by a dashed line.

done by considering, for example, the entropy production per unit work done. From Eqs. (8) and (12), one finds

$$\Delta S/W = -1/T_1 + (1/\eta)(1/T_1 - 1/T_2), \quad (23)$$

and therefore $\Delta S/W$ is a monotonically decreasing function of η . Any change of Q_{in} or Q_{out} that increases (decreases) η will decrease (increase) $\Delta S/W$. One can get a similar result by normalizing ΔS by the input or output heats. The point is that these normalized entropy productions are functions of η alone, so that no matter what variations are made in the Q 's the changes in the entropy production can be found from just the changes in efficiency.

These results can also be stated as follows: *The entropy production (rather than a normalized entropy production) is a monotonically decreasing function of η for all variations in the Q 's that leave W (or Q_{in} or Q_{out}) unchanged.*

Finally, it is clear that, if one starts with a reversible engine and introduces any irreversibility, η must decrease (since it is maximum for a reversible engine) and ΔS

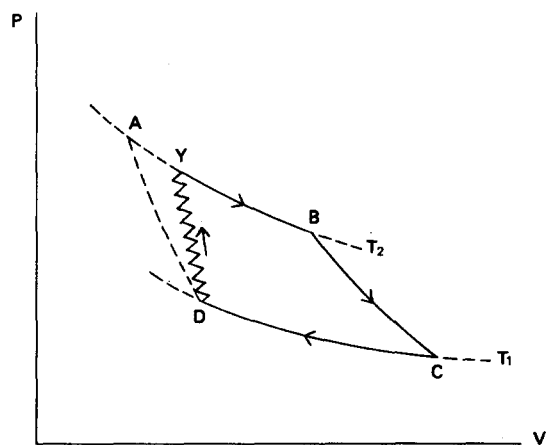


Fig. 3. Pressure-volume diagram for a Carnot cycle with an irreversible adiabatic contraction DY, which is denoted by a sawtoothed line. The adiabatic contraction DA of the corresponding reversible Carnot cycle is indicated by a dashed line.

must increase (since it is minimum for a reversible engine).

IV. GENERAL IRREVERSIBLE CYCLES WITH $p > 2$

Consider now the extent to which these considerations apply to engines with more than two heat reservoirs, that is, with $p > 2$. Recall that p is the number of reservoirs of different temperatures with which an engine exchanges heat [Eqs. (4a) and (4b)]. Suppose the heats $\{Q_i\}$ are varied infinitesimally. Do the algebraic signs of the corresponding changes in efficiency and entropy production have a fixed relationship? Specifically, is $d\eta d(\Delta S) \leq 0$? The answer to this question is *no*; in fact, none of the above results for $p = 2$ are true for $p > 2$.

The difficulty can be seen this way. Consider variations $\{dQ_i\}$ which leave both η and W unchanged. These variations also leave Q_{in} and Q_{out} fixed. For $p > 2$ the individual Q 's can be varied so that Q_{in} and Q_{out} remain fixed but $d(\Delta S)$ is either positive or negative; that is, variations exist for which $d\eta = 0$ and $d(\Delta S)$ is of either sign. This is because ΔS is a function of the individual Q 's, not just Q_{in} and Q_{out} , for $p > 2$. This means that for fixed W (or Q_{in} or Q_{out}) ΔS is not a function of η alone, so that there is in general no fixed relationship between $d\eta$ and $d(\Delta S)$. For each value of W and η there is a range of possible ΔS , and the end points of this range, ΔS_{min} , ΔS_{max} are functions of W and η alone. This suggests looking at the relationship between changes in η and the minimum and maximum entropy productions.

These points are addressed in more detail in the following theorems, the proofs of which will be found in the Appendix.

Theorem I. For any irreversible or reversible cycle with $p > 2$, there are variations $\{dQ_i\}$ for which $d(\Delta S) d\eta > 0$.

Remark. It is clear from this theorem that only for reversible ($\Delta S = 0$) two-heat reservoir cycles is one assured that $d(\Delta S) d\eta \leq 0$ for all $\{dQ_i\}$.

Theorem II. Define normalized entropy productions by $f_1 = \Delta S/Q_{out}$, $f_2 = \Delta S/Q_{in}$, and $f_3 = \Delta S/W$. Then for any engine with $p > 2$ there are, for each f_i , variations $\{dQ_i\}$ such that $df_i d\eta > 0$.

Remark. This shows that one cannot remove the difficulty by normalizing ΔS except for $p = 2$. Theorems I and II point to the unique nature of the two reservoir engines.

Theorem III. For irreversible cycles with $p \geq 2$, variations $\{dQ_i\}$ such that all $dQ_i \geq 0$ or all $dQ_i \leq 0$ yield $d(\Delta S) d\eta \leq 0$.

Remark. This theorem identifies a class of simple variations $\{dQ_i\}$ for which the inverse relationship between $d\eta$ and $d(\Delta S)$ holds. On the other hand, there seems to be nothing particularly important about this subclass of variations.

The following theorem (with the proof) and corollaries define the range of possible entropy production.

Theorem IV. For irreversible cycles with $p \geq 2$, let the reversible heat source temperatures be ordered as follows: $T_1 < T_2 < \dots < T_n$ (heat sinks) and $T_{n+1} < T_{n+2} < \dots < T_p$ (heat sources) with $T_p > T_1$. If the work done per cycle, $W = Q_{in} - |Q_{out}|$, and the efficiency, $\eta = W/Q_{in}$, are specified, then $\Delta S_{min} \leq \Delta S \leq \Delta S_{max}$, where

$$\Delta S_{max} = |Q_{out}|/T_1 - Q_{in}/T_p$$

and

$$\Delta S_{min} = |Q_{out}|/T_n - Q_{in}/T_{n+1} > 0 \quad \text{if } 0 < \eta < 1 - T_n/T_{n+1}$$

$$= 0 \quad \text{otherwise.}$$

When $\eta > 1 - T_n/T_{n+1}$ and $p \geq 4$, the set of heats $\{Q_i\}$ for which $\Delta S = 0$ is not unique.

Proof. ΔS_{max} follows directly from (3) and (4) since

$$\sum_{i=1}^n \frac{|Q_i|}{T_i} \leq \frac{|Q_{out}|}{T_1}$$

and

$$\sum_{j=n+1}^p \frac{Q_j}{T_j} \geq \frac{Q_{in}}{T_p}$$

The minimum value can be seen as follows. Starting with any set $|Q_1|, \dots, |Q_n|, Q_{n+1}, \dots, Q_p$, consider a differential transformation of this set which holds W and η fixed. This is equivalent to holding Q_{in} and Q_{out} fixed; therefore, $dQ_{in} = dQ_{out} = 0$, and one can set

$$d|Q_n| = -\sum_{i=1}^{n-1} d|Q_i| \quad \text{and} \quad dQ_{n+1} = -\sum_{j=n+2}^p dQ_j.$$

Then

$$d(\Delta S) = \sum_{i=1}^{n-1} \left(\frac{1}{T_i} - \frac{1}{T_n} \right) d|Q_i| + \sum_{j=n+2}^p \left(\frac{1}{T_{n+1}} - \frac{1}{T_j} \right) dQ_j.$$

If $d|Q_i| \leq 0$ for $i \leq n-1$ and $dQ_j \leq 0$ for $j \geq n+2$, then $d(\Delta S) \leq 0$. Therefore, ΔS can be decreased monotonically by decreasing one or more of the heats $|Q_1|, \dots, |Q_{n-1}|$, and Q_{n+2}, \dots, Q_p , holding $|Q_{out}|$ and Q_{in} fixed. As the individual heats are varied in this fashion, the absolute minimum is achieved for $Q_1 = Q_2 = \dots = Q_{n-1} = 0$, $Q_n = Q_{out}$, $Q_{n+1} = Q_{in}$, $Q_{n+2} = Q_{n+3} = \dots = Q_p = 0$. This minimum is $|Q_{out}|/T_n - Q_{in}/T_{n+1}$, which is nonnegative for $0 < \eta \leq 1 - T_n/T_{n+1}$. If the latter condition is not met, then $\Delta S = 0$ is the minimum since the entropy production can never be negative. This occurs if $T_n > T_{n+1}$ or if $T_n < T_{n+1}$ but $\eta > 1 - T_n/T_{n+1}$, that is, η sufficiently high. Suppose $\Delta S = 0$ occurs

for some set $\{Q_i\}$. For $p \geq 4$, this set is not unique since the three conditions, $Q_{in} = \text{const}$, $Q_{out} = \text{const}$, and $\Delta S = 0$, will not determine more than three of the $\{Q_i\}$ uniquely.

Corollary I. For fixed W and η , the maximum and minimum entropy productions are decreasing functions of η , except for the case $\Delta S_{min} = 0$. In fact,

$$(1/\eta)(1/T_n - 1/T_{n+1}) - 1/T_n \leq \Delta S/W \\ \leq (1/\eta)(1/T_1 - 1/T_p) - 1/T_1, \quad (24)$$

and if the lower bound is negative it can be replaced by zero.

Proof. Equation (24) follows from substituting $Q_{in} = W/\eta$ and $|Q_{out}| = W(1 - \eta)/\eta$ in Theorem IV. The property of decreasing in η follows from (24).

Corollary II. For fixed W and ΔS , the maximum and minimum efficiencies are decreasing functions of $\Delta S/W$ and

$$(1 - T_n/T_{n+1})(1 + T_n \Delta S/W)^{-1} \leq \eta \\ \leq (1 - T_1/T_p)(1 + T_1 \Delta S/W)^{-1}, \quad (25)$$

and if the lower bound is negative it can be replaced by zero.

Proof. Equation (25) is a rearrangement of (24). The property of decreasing in $\Delta S/W$ follows from (25).

Remarks. In the case $p = 2$, the upper and lower bounds in these corollaries coincide, so that (24) and (25) become equalities and we have the results already discussed in Sec. III for the $p = 2$ case. For $p > 2$, Eqs. (24) and (25) are generalizations of the $p = 2$ Carnot's principle mentioned in Sec. I.

V. DISCUSSION AND CONCLUSIONS

The main results of this paper are the following: (i) An increase in an irreversible cycle's thermal efficiency does not necessarily lead to a decrease in its entropy production. This is so even if the work done per cycle is held fixed. (ii) If an arbitrary infinitesimal irreversibility is introduced into a reversible cycle, then $d(\Delta S)/d\eta \leq 0$ is guaranteed if and only if the cycle employs two (not more) reversible heat sources—that is, one heat source and one heat sink (see Theorem I). (iii) Sufficiency conditions for $d(\Delta S)/d\eta \leq 0$ are that the infinitesimal variations in the individual heat input magnitudes and of the individual heat output magnitudes be of opposite algebraic signs or zero (see Theorem III). This condition is satisfied, in particular, if only one of the individual heats is altered, which was the case for the specific examples presented in Sec. III. (iv) Irreversible cycles with entropy production ΔS and work output W per cycle have efficiencies which are bounded according to Corollary II, and the bounds are decreasing functions of $\Delta S/W$. (v) Cycles of efficiency η and work W have entropy produc-

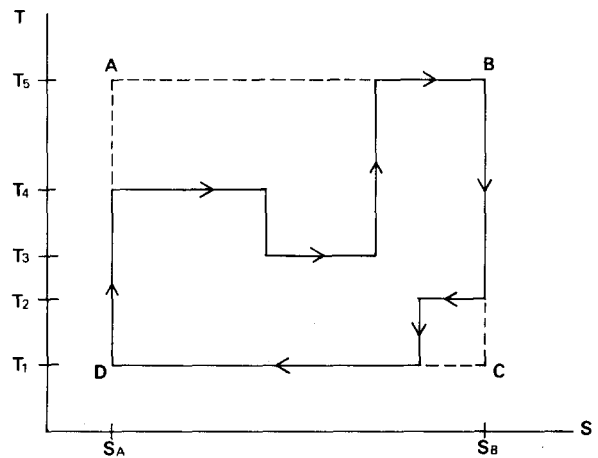


Fig. 4. Temperature-entropy diagram for a reversible cyclic process for which $p = 5$, $n = 2$, $T_n < T_{n+1}$. This cycle is bounded by the reversible Carnot cycle ABCD.

tions bounded according to Corollary I, and the bounds are decreasing functions of η . It follows from the lower bound that, if η is low enough and if no heat sink temperature exceeds the lowest heat source temperature, then the cycle cannot be reversible.

These results show that technological advances in the form of increased efficiencies, for fixed work output, need not lead to a lower rate of entropy production. This, in turn, suggests that increased efficiencies might not always lead to lower pollution production rates per unit work output.

When $\Delta S = 0$, the efficiency bounds given by Corollary II can be understood by using a temperature-entropy plot similar to that employed by Tobin and by Ehrenfest-Afanassejewa.² For convenience, suppose $p = 5$, $n = 2$, and $T_1 < T_2 < T_3 < T_4 < T_5$. Figure 4 illustrates such a cycle (solid lines). The corresponding Carnot cycle operating between T_1 and T_5 is indicated by the rectangle ABCD. For the solid curve $\eta = 1 - |Q_{out}|/Q_{in}$, where $|Q_{out}| < T_2(S_B - S_A)$ and $Q_{in} > T_3(S_B - S_A)$. It follows then that $\eta > 1 - T_2/T_3 > 0$. Since it is true also that $|Q_{out}| > T_1(S_B - S_A)$ and $Q_{in} < T_5(S_B - S_A)$, $\eta < 1 - T_1/T_5$. The last step parallels the arguments given

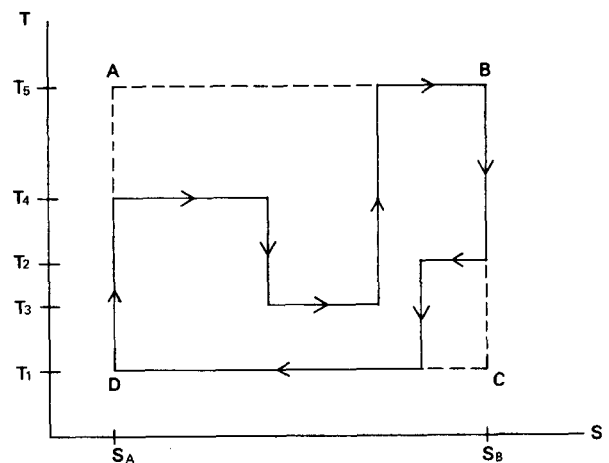


Fig. 5. Temperature-entropy diagram for a reversible cyclic process for which $p = 5$, $n = 2$, $T_n > T_{n+1}$. This cycle is bounded by the reversible Carnot cycle ABCD.

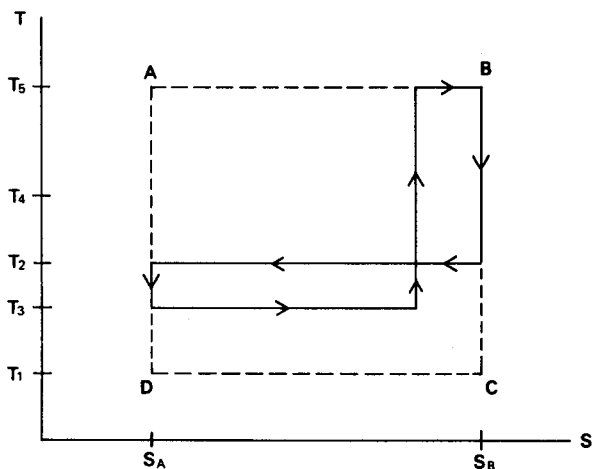


Fig. 6. Temperature-entropy diagram for a reversible cyclic process for which $p = 5$, $n = 2$, $T_n > T_{n+1}$, with $W = \eta = 0$.

by the authors cited in Ref. 2. Thus, $0 < 1 - T_2/T_3 < \eta < 1 - T_1/T_5$, which, in essence, is Corollary II for this special case—that is, $\Delta S = 0$, $p = 5$, $n = 2$, $T_n < T_{n+1}$. If, on the other hand, the solid curve is replaced by that in Fig. 5, for which $p = 5$, $n = 2$, but $T_2 > T_3$, the identical argument leads to $\eta > 1 - T_2/T_3 < 0$. Therefore, one must conclude that $\eta \geq 0$. $\eta = 0$ can occur by judiciously choosing the set $\{Q_i\}$ to give $W = 0$. This is possible only if at least one output heat temperature exceeds the lowest heat input temperature. For example, by choosing $Q_1 = Q_4 = 0$ and $Q_2 = -(Q_3 + Q_5) < 0$, the cycle appears as in Fig. 6, with $W = \eta = 0$.

APPENDIX

Lemma. Let $f(Q_1, \dots, Q_p)$ and $g(Q_1, \dots, Q_p)$ be functions whose partial derivatives $F_i = \partial f / \partial Q_i$ and $G_i = \partial g / \partial Q_i$, $1 \leq i \leq p$, exist. Let (Q_1, \dots, Q_p) be a point such that not all the F_i or all the G_i are zero. Let df and dg be the change in f and g caused by the differential variation (dQ_1, \dots, dQ_p) of the Q 's. Then $df dg \leq 0$ for all variations (dQ_1, \dots, dQ_p) if and only if $F_i = \alpha G_i$ for all $1 \leq i \leq p$, where α is negative and may depend on the point (Q_1, \dots, Q_p) .

Proof. The proof can be seen geometrically by considering F_i , G_i , and dQ_i as components of p -dimensional vectors. Then $df = \mathbf{F} \cdot d\mathbf{Q}$ and $dg = \mathbf{G} \cdot d\mathbf{Q}$, and the requirement that df and dg have opposite sign for an arbitrary $d\mathbf{Q}$ is that \mathbf{F} and \mathbf{G} be such that there is no vector $d\mathbf{Q}$ that has positive (or negative) projections on both \mathbf{F} and \mathbf{G} . This clearly is true only if \mathbf{F} is antiparallel to \mathbf{G} ; hence $\mathbf{F} = \alpha \mathbf{G}$, $\alpha < 0$.

For an algebraic proof, write

$$df dg = \sum_{i,j=1}^p \frac{1}{2} (F_i G_j + F_j G_i) dQ_i dQ_j. \quad (\text{A. 1})$$

For arbitrary variations $\{dQ_i\}$, $df dg \leq 0$ if and only if the matrix

$$A_{ij} = -\frac{1}{2} (F_i G_j + F_j G_i)$$

is positive semidefinite. This will be so if and only if all k -dimensional subdeterminants $||A_{ij}||_k$, $i, j = 1, 2, \dots, k$, are nonnegative for $k = 1, 2, \dots, p$.¹³ For $k = 1$ and $k = 2$, this condition reduces to

$$F_1 G_1 \leq 0$$

and

$$-\frac{1}{4} (F_1 G_2 - F_2 G_1)^2 \geq 0,$$

respectively. By reordering the terms in (A.1), it is clear also that, for example,

$$F_2 G_2 \leq 0 \quad \text{and} \quad -\frac{1}{4} (F_1 G_2 - F_2 G_1)^2 \geq 0.$$

An extension of this argument shows that

$$F_i G_i \leq 0 \quad (\text{A. 2})$$

and

$$-\frac{1}{4} (F_i G_j - F_j G_i)^2 \geq 0 \quad (\text{A. 3})$$

for $1 \leq i, j \leq p$. Equation (A.3) implies that

$$F_i / G_i = F_j / G_j = \alpha \quad (\text{A. 4})$$

for all i and j ; that is, $F_i = \alpha G_i$ for all i . Then (A.2) implies that $\alpha \leq 0$ or $\mathbf{F} = \alpha \mathbf{G}$ (\mathbf{F} antiparallel to \mathbf{G}).

Proof of Theorem I. Write $d(\Delta S) = \delta \cdot d\mathbf{Q}$ and $d\eta = \mathbf{N} \cdot d\mathbf{Q}$, where $\delta_i = -1/T_i$ and $N_i = 1/Q_{in}$ if $i \leq n$, $N_i = -Q_{out}/Q_{in}^2$ if $i > n$. If $\Delta S > 0$, then any infinitesimal $d\mathbf{Q}$ will not drive ΔS negative, so any $d\mathbf{Q}$ gives a possible heat engine. Suppose $d(\Delta S) d\eta \leq 0$ for all $d\mathbf{Q}$. Then by the Lemma $N_i = \alpha \delta_i$ or $-1/T_i = \alpha/Q_{in}$ for $i \leq n$ and $+1/T_i = \alpha Q_{out}/Q_{in}^2$ for $i > n$. These conditions imply that $T_i = T_-$ if $i \leq n$ and $T_i = T_+$ if $i > n$, with $Q_{in}/T_+ - Q_{out}/T_- = 0$. This contradicts the hypothesis $p > 2$ (and also $\Delta S > 0$). Therefore, there must be some $d\mathbf{Q}$ for which $d(\Delta S) d\eta > 0$.

If $\Delta S = 0$, then not all $d\mathbf{Q}$ are possible since in this case $d(\Delta S) = \delta \cdot d\mathbf{Q} \geq 0$ in order that $d\mathbf{Q}$ generate an allowable engine. It is clear, however, from the geometric proof of the previous Lemma that the Lemma is true even if the allowed $d\mathbf{Q}$ are restricted to have positive projections on one of the vectors. Hence, the proof of Theorem I follows even if $\Delta S = 0$.

Proof of Theorem II. The proof is given for f_3 . The arguments for f_1 and f_2 are similar. Since $f_3 = \Delta S/W$, one can write $df_3 = \mathbf{F} \cdot d\mathbf{Q}$ with $F_i = -(1/W)(1/T_i + \Delta S/W)$. Since $W > 0$ and $\Delta S \geq 0$, $F_i \neq 0$ for any i . The remaining part of the proof is the same as that of Theorem I.

Proof of Theorem III. If $dQ_i \geq 0$ for $1 \leq i \leq p$, then $d(\Delta S) = -\sum_{i=1}^p dQ_i/T_i \leq 0$ and $d\eta = dQ_{out}/Q_{in} - (Q_{out}/Q_{in}^2) dQ_{in} \geq 0$ since $Q_{in} > 0$ and $Q_{out} < 0$. If $dQ_i \leq 0$ for $1 \leq i \leq p$, the same argument gives $d(\Delta S) \geq 0$ and $d\eta \leq 0$.

- ¹A review of Carnot's work, including relevant references, may be found in M. J. Klein, *Phys. Today* **27** (8), 23 (1974).
- ²A particularly elegant proof may be found in M. C. Tobin, *Am. J. Phys.* **37**, 1115 (1969); see also T. Ehrenfest-Afanassejewa, *Die Grundlagen Der Thermodynamik* (Brill, Leiden, 1956), p. 74.
- ³A common method of demonstrating this is to couple reversible and irreversible Carnot cycles and to invoke the second law of thermodynamics. See, for example, D. ter Haar and H. N. S. Wergeland, *Elements of Thermodynamics* (Addison-Wesley, Reading, MA, 1966), p. 20. An approach which is more in the spirit of the present work may be found in H. Reiss, *Methods of Thermodynamics* (Ginn-Blaisdell, Waltham, MA, 1965), p. 66.
- ⁴An account of Clausius's contributions to thermodynamics, especially as reviewed by J. W. Gibbs, along with numerous references is given by M. J. Klein, *Hist. Stud. Phys. Sci.* **1**, 127 (1969). An analysis of the thread of ideas leading from Clausius's initial thermodynamic statement of the second law to its basis as a statistical law may be found in M. J. Klein, *Am. Sci.* **58**, 84 (1970).
- ⁵Typically, books on irreversible thermodynamics do not treat cyclic processes at all. See, for example, S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962); A. Katchalsky, *Nonequilibrium Thermodynamics in Biophysics* (Harvard University, Cambridge, MA, 1965); W. Yourgrau, A. Vander Merwe, and G. Raw, *Treatise on Irreversible and Statistical Thermophysics* (Macmillan, New York, 1966); P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley, New York, 1971).
- ⁶R. C. Tolman and P. C. Fine, *Rev. Mod. Phys.* **20**, 51 (1948).
- ⁷J. D. Fast, *Entropy* (Macmillan, London, 1970; distributed by Crane, Russack, New York), pp. 36, 89.
- ⁸This association is a natural one for thermal pollution and is suggested also by the concept of "entropy of mixing" for some forms of air and water pollution.
- ⁹H. Callen, *Thermodynamics* (Wiley, New York, 1960), p. 65.
- ¹⁰The use of reversible heat and work sources is commonplace in classical thermodynamics. It assumes the existence, at least in principle, of work and heat sources which have relaxation times that are considerably smaller than those for the system itself. These enable one to consider processes which produce irreversibilities within the system itself but not within the work and heat sources. This idealization makes possible the study of entropy production which emanates from irreversible processes that occur within the system and not in its environment. Of course, since $\Delta S_{\text{system}} = 0$ for one cycle, the entropy increase ultimately always manifests itself in the environment even though that is not where it originated.
- ¹¹A simple way of introducing irreversibility is contained in G. Weirich, *Fundamental Thermodynamics* (Addison-Wesley, Reading, MA, 1968), Chap. 8. That treatment allows a heat leak between T_2 and T_1 . Although this does cause ΔS to be positive, it is quite independent of the cycling system itself and therefore is not of interest in the present context.
- ¹²See any of the textbooks cited in Ref. 5; see also Ref. 6.
- ¹³R. Bellman, *Introduction to Matrix Analysis* (McGraw-Hill, New York, 1968), p. 74.

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