A Simple Approach to Heat Engine Efficiency

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The Carnot cycle and the efficiency of heat engines remain staples of physical chemistry textbooks even in this age of decreasing emphasis on thermodynamics in chemistry. Many articles in this *Journal* during the last four decades examine various aspects of the Carnot cycle, from the true shape of the cycle on a *PV* diagram (*1*) to its historical impact on the derivation of Maxwell's relations (*2*). Recently Seidman and Michalik carried out a detailed analysis of the efficiency of reversible heat engines operating on cycles other than the Carnot cycle (*3*); they concluded that only the Carnot cycle has the efficiency given by the classic equation

$$\eta = \frac{T_H - T_C}{T_H}$$

and that reversible heat engines operating between the same two temperatures using other cycles must necessarily have a lower efficiency. Seidman and Michalik pointed out that this aspect of heat engine efficiency is not widely known; they noted that Atkins had published a textbook (*4*) stating that a Stirling cycle operating between the same two reservoirs would have the same efficiency as a Carnot cycle.[1] Their conclusion was challenged in a subsequent letter by Liley, who asserted that a reversible Stirling cycle employing a regenerator would have the Carnot efficiency (*5*). Liley's letter was printed without a rebuttal from Seidman and Michalik.

In this paper I hope to clear up the confusion created by this exchange. To do so I will employ a simple method of determining heat engine efficiency that appeared in this *Journal* nearly 40 years ago: temperature–entropy (*TS*) diagrams (*6*, *7*). The advantage of *TS* diagrams is that they immediately and graphically reveal the efficiency of a reversible cycle. (This is not true of *PV* diagrams.) *TS* diagrams will clearly show that Seidman and Michalik's careful analysis is correct: Stirling cycles and other reversible cycles cannot have an efficiency equaling the Carnot efficiency. Surprisingly, we will also see that Liley's statement about a Stirling cycle coupled with a regenerator is true (*8*); nevertheless, a careful analysis of this cycle will actually support the conclusion of Seidman and Michalik.

TS Diagrams

Figure 1 contains *TS* diagrams for three cycles that operate between 424 K and 300 K; the working substance is two moles of an ideal monatomic gas. The Stirling cycle (Fig. 1b) is defined as in Seidman and Michalik's paper. Figure 1a is a Carnot cycle that has the same low-temperature compression stage as the Stirling cycle. Figure 1c is a "hybrid" cycle that has a constant-volume heating like the Stirling cycle but an adiabatic cooling like the Carnot cycle; its high-temperature expansion matches that of the Stirling cycle. All three cycles are defined in the Appendix.

On a *TS* diagram isotherms are horizontal lines and adiabats are vertical lines; consequently the Carnot cycle becomes a rectangle. The Stirling cycle looks like a parallelogram; the constant-volume lines or isochores are slightly curved because they are exponential functions given by the equation

$$T_2 = T_1 \exp\left(\frac{\Delta S}{nC_{V,m}}\right)$$

(Isobaric processes are also exponential curves with $C_{P,m}$ replacing $C_{V,m}$.) The two isochores of a Stirling cycle are parallel to each other provided that $C_{V,m}$ is a function of T alone.

Just as areas on a *PV* diagram represent work ($w = \int P\, dV$), areas on a *TS* diagram represent heat ($q = \int T\, dS$). The area equals the amount of heat absorbed by the thermodynamic system during a process. To compute heat flow using this integral the thermodynamic temperature scale must be used, but absolute entropies (third-law entropies) are not needed.

Definition of Efficiency

A heat engine absorbs heat from the surroundings and converts some of the heat into work. Unconverted heat is released back to the surroundings. The efficiency of the heat engine measures how much heat is converted into work; thus efficiency is the work done in one cycle divided by the heat absorbed in one cycle.

$$\eta = \frac{w_{\text{cycle}}}{q_{\text{absorbed}}}$$

TS diagrams display both the numerator and denominator of this expression. The area bounded by the cycle represents the net heat absorbed by the engine, but by the first law this equals the work done by the engine. The area between the upper part of the cycle and the *S* axis equals the total heat (not the net heat!) absorbed in one cycle. The ratio of these two areas is the efficiency. A *PV* diagram cannot display total heat absorbed, so only a *TS* diagram can give a graphical indication of efficiency.

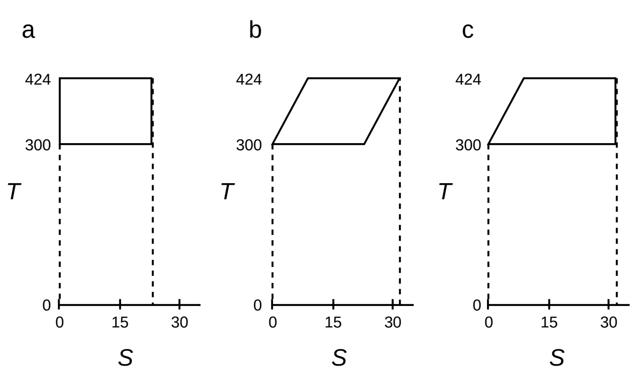

Figure 1. Temperature–entropy diagrams for matched cycles: (a) Carnot; (b) Stirling; (c) hybrid. Entropy units J/K, temperature units K. The dashed lines and upper curve of the cycle enclose the heat absorbed by the cycle.

Graphical Efficiency

In Figure 1a the Carnot cycle has $w_{cycle} = (T_H - T_C)\Delta S$ and $q_{absorbed} = T_H \Delta S$ (the rectangular area between the upper isotherm and the S axis), leading to the classic efficiency equation and an efficiency of 0.292. In Figure 1b the isochores are parallel, so the work equals that of the Carnot cycle; however, the Stirling cycle absorbs more heat than the Carnot cycle, so its efficiency is lower. The additional heat is absorbed during the isochoric heating; when this heat flow is included the equation for the efficiency of the Stirling cycle is obtained:

$$\eta = \frac{\Delta T \Delta S}{T_H \Delta S + nC_{V,m} \Delta T}$$

where $\Delta T = T_H - T_C$ and ΔS is the entropy change for the isothermal stages of the cycle. This equation reduces to the equation for the Carnot cycle when the isochores are replaced by adiabats ($C_{V,m}$ effectively zero). This equation yields 0.222 for the efficiency of the Stirling cycle shown in Figure 1b—the same efficiency computed by Seidman and Michalik.

Figure 1c shows that the hybrid cycle has exactly the same total heat input as the Stirling cycle, but it does more work. The diagram shows that the additional work equals $nC_{V,m}\Delta T - T_C \Delta S_{isochore}$. Adding this additional term to the numerator of the expression above yields the efficiency of the hybrid cycle, 0.261, which is better than the Stirling cycle but not as good as the Carnot cycle.

A simple geometric argument, illustrated in Figure 2a, shows that the TS diagrams can be used to determine the relative efficiencies of these cycles without any calculations. The Stirling cycle is "covered" by a Carnot cycle with the same T_H and T_C operating over the entire entropy range of the Stirling cycle. Labeled in the diagram are four areas that comprise the heat absorbed by the Carnot cycle: w is the work done by the Stirling cycle; x and y are regions of the Carnot cycle outside the Stirling cycle, but x is part of the heat absorbed by the Stirling cycle, y is not; q is the heat rejected by the Carnot cycle. The areas can be added to create expressions for the efficiency of the cycles

$$\eta_{stirling} = \frac{w}{w+x+q}; \quad \eta_{carnot} = \frac{w+x+y}{w+x+y+q}$$

leading to the following inequalities

$$\eta_{stirling} < \frac{w+x}{w+x+q} < \frac{w+x+y}{w+x+y+q} = \eta_{carnot}$$

The second inequality holds because the addition of y causes a larger proportional change in the numerator than in the denominator. Note that the first inequality shows that the hybrid cycle has an efficiency between that of the Stirling and Carnot cycles, because x is part of the work done by the hybrid cycle. As illustrated in Figure 2b, this geometric proof can be extended to any arbitrary cycle, proving that the Carnot cycle always has maximum efficiency for any given values of T_H and T_C.

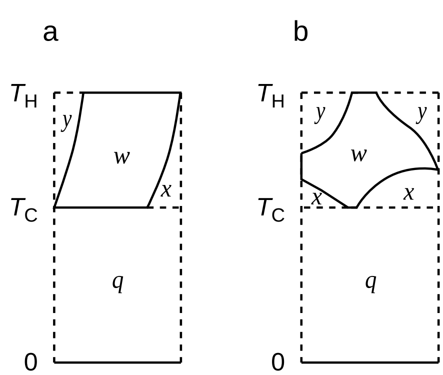

Figure 2. Geometric proof that the Carnot cycle is always more efficient than (a) the Stirling cycle and (b) any arbitrary cycle. Dashed lines bound the Carnot cycle; solid lines bound the other cycle; w is the work done by the arbitrary cycle; x is work done by the Carnot cycle below the arbitrary cycle; y is work done by the Carnot cycle above the arbitrary cycle; and q is the heat rejected by the Carnot cycle.

The Definition Revisited

The lower efficiency of the Stirling cycle results from the decision to define $q_{absorbed}$ as the *total* heat absorbed around the cycle. This is the definition used by Seidman and Michalik. Other articles in this *Journal* and some physical chemistry textbooks employ a different definition of efficiency: the ratio of work to *heat absorbed from the high-temperature reservoir* (*9–11*). The apparent justification for this definition is that the stage of the cycle involving the T_H reservoir is usually the power stroke, so this is the stage that is converting heat into work, and therefore its heat input is the "important" heat input. But in fact it is the cycle that converts heat into work; heat absorbed by the working fluid during other stages of the cycle can be converted to work.[2] This crude definition of heat input causes no problem for the Carnot cycle, where the T_H reservoir is the only heat source, but it is an oversimplification for other cycles and in particular leads to the conclusion that the Stirling cycle and the Carnot cycle have equal efficiencies. (See the derivation by Goldstein in ref *10*.)

What are the consequences of this definition? Consider the hybrid cycle in Figure 1c, which by our original definition has an efficiency less than the Carnot efficiency but greater than that of the Stirling cycle. The work done by this cycle is greater than the work done by the Carnot cycle (Fig. 1a), and the hybrid cycle absorbs the same amount of heat *from the high-temperature reservoir*. According to the crude definition of heat input the hybrid cycle is more efficient that the Carnot cycle! In computing the efficiency of any general cycle we must define the heat input as the heat absorbed by all stages around the cycle.

The Clausius Explanation

Seidman and Michalik point out that the isochoric stages of the Stirling cycle, to be reversible, require an infinite number of heat reservoirs, whereas the Carnot cycle requires only two. This they say is reason for the different efficiencies. But the real key is that these reservoirs are at intermediate temperatures. The Stirling cycle is less efficient than the Carnot cycle because some of its heat input comes from heat reservoirs at temperatures below T_H; also, the Stirling cycle is less efficient because some of its heat output is returned to heat reservoirs at temperatures above T_C. Both actions reduce efficiency; notice that the second action is not present in the hybrid cycle, so its efficiency is higher than that of the Stirling cycle.

The participation of even one intermediate reservoir, either as a heat source or a heat sink, will lower the efficiency of a cycle. This is a simple consequence of the Clausius idea that temperature is a measure of the availability of heat energy for work. Heat energy supplied from an intermediate reservoir is not as available for conversion to work as heat from the T_H reservoir. Conversely, if the intermediate reservoir serves as a heat sink, then less work has been obtained from some heat withdrawn from T_H. Either way the efficiency suffers. Figure 3a is a *TS* diagram of a cycle with one intermediate heat source; Figure 3b is a cycle with one intermediate heat sink. A Carnot cycle that covers these cycles will have greater efficiency.

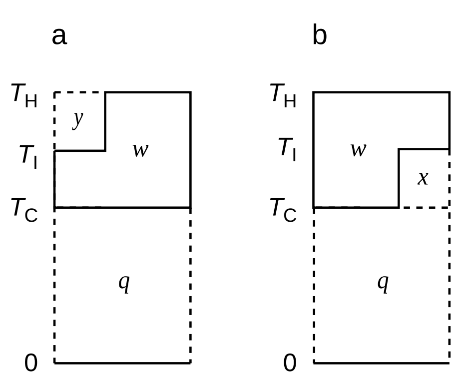

Figure 3. The efficiency of a heat engine is reduced when an intermediate temperature reservoir participates as (a) a heat source or (b) a heat sink. Areas defined as in Figure 2.

The Regenerator

Can the efficiency of the Stirling cycle be improved? Yes; a regenerator, which can be just a lump of metal mesh, is a device that improves the efficiency by permitting heat rejected during the isochoric cooling to be reused in the subsequent isochoric heating of the next stage of the cycle. (With a regenerator the Stirling cycle can be used to construct a practical heat engine; Cenco sells a Stirling engine for demonstrations. Analyses of the practical Stirling engine can be found in refs *4* and *12*.) The regenerator is, in effect, a reusable heat reservoir. In the usual analysis of thermodynamic processes, a heat reservoir is used once and then "thrown away". A perfect, reversible regenerator would capture all the heat from the cooling stage so that it could be reused in the heating stage; thus no intermediate heat reservoirs would be needed to drive the Stirling cycle. Since the only heat input is now the heat from T_H, and the only heat sink is the reservoir at T_C, the Stirling cycle with a reversible regenerator achieves the same efficiency as a Carnot cycle.

Does this mean that the Carnot cycle is not uniquely the most efficient heat engine? When the working fluid of the Stirling cycle undergoes isochoric heating and cooling, it does so solely by thermal contact with the regenerator; the intermediate reservoirs are no longer used. Thus the fluid and the regenerator are isolated from the surroundings. Taken together as a thermodynamic system, the "fluid/regenerator" system is undergoing an adiabatic process when the fluid undergoes an isochoric process. During the isothermal stages of the Stirling cycle the fluid and the regenerator absorb heat from T_H and release heat to T_C. From the standpoint of the fluid/regenerator system, the cycle is a pair of adiabatic stages linked by isothermal stages, which means that the Stirling cycle with a reversible regenerator is just a different way to implement a Carnot cycle. No wonder it has the same efficiency! The Carnot cycle is uniquely the most efficient heat engine that operates between two heat reservoirs because, as Seidman and Michalik pointed out, it is the only reversible heat engine that can operate between just two reservoirs. When the Stirling cycle is engineered so that it operates between just two reservoirs, it *becomes* a Carnot cycle. The Stirling cycle with a reversible regenerator is an excellent example of the principle that the inner workings of the heat engine are not important in determining efficiency, and its Carnot efficiency, properly understood, dramatically confirms the ideas of Seidman and Michalik.

Historical Footnote

As a physical chemistry student 20 years ago I was taught that all reversible heat engines obeyed the Carnot efficiency equation. This notion appears in current physical chemistry textbooks such as ref *11*. How did it start? My guess, from reviewing the literature, is that the efficiency of the Stirling cycle with a reversible regenerator became a source of confusion, and someone tried to remove the confusion with a careless definition of heat input. Together these two mutually supportive ideas spread like a virus throughout many articles and textbooks on thermodynamics. They spread because they sell an attractive idea: if all reversible heat engines are alike, then Nature is simple and parsimonious. It is an idea that other science professors are not likely to doubt, especially in an established field such as thermodynamics. I never doubted it. I therefore acknowledge my gratitude to Kurt Seidman and Thomas Michalik; their doubt inspired this work.

Notes

1. Atkins was actually referring to a Stirling engine using a regenerator, but Seidman and Michalik failed to mention the regenerator in their paper. Liley also did not point out their omission.

2. This is illustrated in Seidman and Michalik's paper: they analyze a three-stage cycle with no isothermal power stroke. By strict application of the crude definition, this cycle has an infinite efficiency.

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Appendix

The *TS* diagrams in Figure 1 are based on the following thermodynamic cycles for two moles of a monatomic ideal gas, $C_{V,m} = 1.5\ R$. The entropy of the gas is arbitrarily set at zero for the state T = 300 K, V = 6.96 L, P = 7.07 atm. For all three cycles the T_H isothermal stages are matched so that ΔS = 23.0 J/K and q = 9760 J. The isochores were plotted using four points to show the slight curvature.

Stirling Cycle

T_1 = 424 K V_1 = 6.96 L P_1 = 10.0 atm S_1 = 8.63 J/K	isothermal expansion →	T_2 = 424 K V_2 = 27.8 L P_2 = 2.50 atm S_2 = 31.7 J/K
↑ isochoric heating		↓ isochoric cooling
T_4 = 300 K V_4 = 6.96 L P_4 = 7.07 atm S_4 = 0.0 J/K	← isothermal compression	T_3 = 300 K V_3 = 27.8 L P_3 = 1.77 atm S_3 = 23.0 J/K

Carnot Cycle

T_1 = 424 K V_1 = 4.14 L P_1 = 16.8 atm S_1 = 0.0 J/K	isothermal expansion →	T_2 = 424 K V_2 = 16.5 L P_2 = 4.22 atm S_2 = 23.0 J/K
↑ adiabatic heating		↓ adiabatic cooling
T_4 = 300 K V_4 = 6.96 L P_4 = 7.07 atm S_4 = 0.0 J/K	← isothermal compression	T_3 = 300 K V_3 = 27.8 L P_3 = 1.77 atm S_3 = 23.0 J/K

Hybrid Cycle

T_1 = 424 K V_1 = 6.96 L P_1 = 10.0 atm S_1 = 8.63 J/K	isothermal expansion →	T_2 = 424 K V_2 = 27.8 L P_2 = 2.50 atm S_2 = 31.7 J/K
↑ isochoric heating		↓ adiabatic cooling
T_4 = 300 K V_4 = 6.96 L P_4 = 7.07 atm S_4 = 0.0 J/K	← isothermal compression	T_3 = 300 K V_3 = 46.7 L P_3 = 1.05 atm S_3 = 31.7 J/K