

Thermodynamics in finite time. I. The step-Carnot cycle

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The object of this paper is the beginning of a formulation of a method to find bounds to process functions, such as work and heat, for processes occurring in finite time. A general variational statement of the problem is given. Then model problems are solved, all but one of which are based on the "step-Carnot" cycle. This is similar to the reversible Carnot cycle but with the external pressure varying in finite steps. Such a system only needs to go through a finite number of equilibrium states during its cycle. The problems are the maximization of effectiveness of the step-Carnot cycle, the maximization of efficiency of the same cycle, the determination of optimal period for a step-Carnot cycle whose contact with the external reservoirs has finite heat conductance, and the determination of the maximum power and the rate at which maximum power is obtained, for a continuous Carnot cycle with finite heat conductance between system and thermostats.

I. INTRODUCTION

Thermodynamics gives us many insights. One of the most important of them, since the earliest years of the subject, has been the capacity of this discipline to furnish natural limits on the effectiveness with which we can carry out real processes. Much of the first strong motivation for the creation of a science of heat was the desire to make steam engines as effective as possible.¹ As Tisza points out,² the emphasis from the time of Carnot, and the tradition that was carried on by Clausius and Kelvin and made rigorous by Caratheodory, was on using thermodynamics as a tool to find limits on work, heat transfer, and efficiency. But with Gibbs, the focal point of the subject moved away from the *process* variables of heat and work, toward the *state* variables, particularly among scientists, perhaps less so among engineers. The Gibbsian view only became possible with the recognition of the existence of the state variables energy E and entropy S . The approach we take here, as the discussion following will show, is far more in the spirit of the Carnot, Clausius, and Kelvin view than of Gibbs.

The Carnot-Clausius-Kelvin view emphasizes the interaction of the thermodynamic system with its surroundings, while the Gibbsian view makes the properties of the system, the state variables themselves, dominant. Thus the Carnot-Clausius-Kelvin formulation is the one in which the impossibility of perpetual motion machines is an important physical postulate. Most important for us, this is the formulation in which the role of the thermodynamic potentials becomes one of setting natural limits: The thermodynamic potentials are the state variables whose changes are the natural limits on the process variables of heat

and work. Traditionally, thermodynamic potentials are defined without regard to time, and thus achieve their roles as limits when the corresponding limiting processes proceed reversibly and therefore infinitely slowly. In the Carnot-Clausius-Kelvin approach, it is these limits on process variables that we really want to know.

In the real world, we find that the actual changes in enthalpy and free energy in a process rarely approach the ideal thermodynamic enthalpy and free energy changes for that process. Typically, the actual expenditure of enthalpy and free energy as fuel and other inputs is ten to a hundred times the ideal thermodynamic limit.³ Sometimes we expend energy on processes that could, in principle, return energy. One example is the conversion of copper sulfide ores to copper and SO_2 . (A few processes are exceptions to this general picture; the generation of electric power from fossil fuel and the manufacture of ammonia are two examples of relatively efficient real thermodynamic systems.) We would obviously like to understand the origin of this large disparity and do what we can to reduce it.

It is tempting to use the difference of actual and ideal requirements for energy, enthalpy, free energy, or availability as an index of how much a process could be improved.³⁻⁵ Any realistic thermodynamicist challenges this position on the grounds that nobody wants to operate a factory reversibly. This and subsequent discussions are intended to meet this challenge by providing an extension of conventional thermodynamics that will give limits on process variables for processes carried out in *finite* time intervals.

The goal of our present line of thinking is the creation of a means to evaluate the ideal limits of heat and work for processes operating at finite

rates. One approach is to require processes to take place in an arbitrary but fixed time intervals. Given a set of constraints sufficient to define the possible paths, we find the path which makes the work done or the heat exchanged in the process an extremum, and evaluate the work or heat along that path. We then carry the analysis one step further, to determine the *optimum time interval* in which a process should be carried out, in order to optimize power, output, or whatever else one chooses as an index of optimality.

In the following sections, we give a rather quick picture of our broad overview and then turn to a detailed treatment of the simplest system we have been able to analyze, which we call the step-Carnot cycle. In much of our treatment of this particular problem, we can eliminate all explicit considerations of time; only in a later section do we examine the problem in a way that makes its time-dependence explicit.

This presentation is not meant to explore in depth the general principles of natural constraints on processes conducted in finite time. We want now to provide examples of solvable systems, upon which we shall build.

II. FORMULATION OF THE PROBLEM

One way to take the first step in finite-time thermodynamics is to set up the (Stieltjes) path integral for work or heat,

$$W = \int_{\lambda_1 t_1}^{\lambda_2 t_2} \vec{F}(\lambda, t) \cdot d\vec{S}(\lambda, t) \quad (1)$$

or

$$Q = \int_{\lambda_1 t_1}^{\lambda_2 t_2} C(\lambda, t) dT(\lambda, t), \quad (2)$$

whose extremum we seek. The generalized force \vec{F} may be an exceedingly complicated quantity, dependent on a large set of internal variables λ as well as the time t ; so may the generalized heat-capacity function C . However, we shall see that the integrals can, in several interesting and perhaps even useful cases, be put in simple, tractable form.

In conventional thermodynamics, the only system parameters are masses, volumes, and heat capacities. To do finite-time thermodynamics, one must expand one's set of parameters to include relaxation-rate parameters, such as diffusion coefficients, heat-transfer coefficients, friction constants, and relaxation times among different degrees of freedom. The most general problems, involving a nonuniform working fluid and many interacting degrees of freedom, are clearly too

difficult to solve now, if ever. By making suitable assumptions about the time scale of our process, relative to the time scales set by the relaxation parameters, we can set up simpler problems. For one, we assume throughout this discussion that the working fluid is always uniform, so that its internal pressure, density, and temperature are always well-defined and independent of position within the fluid. This assumption is equivalent to supposing that the processes we are now examining occur slowly with respect to the internal transport and relaxation times of the working fluid, at least for all those internal degrees of freedom that participate in energy exchange in the process.⁶ Thus the heat capacity of the system must be treated as a function of the characteristic time of the process. Here we shall not consider processes occurring on time scales comparable to internal relaxation times of the system. (Such situations have been examined many times in the past; in fact the approach of Wang Chang and Uhlenbeck⁷ on relaxation in shock waves was influential in our thinking about the finite-time problem.) In the step processes equilibrium with the surroundings is required only at a finite number of points, viz., after each step change in the external pressure. The time spent on each step is composed of a period in which the gas moves toward a new internal equilibrium at the new pressure, and a subsequent period when the system is quasistatic, while it regains equilibrium with the surroundings. The latter, quasistatic period vanishes for adiabatic steps, but not for any other kind of step. Our assumption of fast internal relaxation amounts to assuming the former time period is instantaneous.

Let us now specialize (1) to the case of an ideal gas acting as a working fluid on a piston, subject to the condition that the internal pressure P_i and temperature T_i will always be well-defined and uniform within the gas, so that

$$\begin{aligned} W &= \int_{V_1}^{V_2} P_e(t) dV \\ &= \int_{t_1}^{t_2} P_e(t) \frac{dV}{dt} dt. \end{aligned} \quad (3)$$

The time interval $t_2 - t_1$ is fixed, dV/dt must be obtained from the properties of the system, and the external pressure $P_e(t)$ is the control variable whose path we want to find, in order to make W an extremum.

Our language already indicates our mathematical tools, the variational methods of optimal control theory.⁸ The work W is the objective function. We need only specify the constraints that make the

problem well-defined, and we are on our way. For W the physics of each individual case will be in dV/dt and in the constraints. For Q the heat-capacity function also contains physical characteristics of the system, so that it is often going to be advantageous to recast (2) as

$$\begin{aligned} Q &= \int_{s_1}^{s_2} T(t) dS \\ &= \int_{t_1}^{t_2} T(t) \frac{dS}{dt} dt, \end{aligned} \quad (4)$$

where S denotes the entropy associated with the heat flow into the system.

In some situations, we find that care is required in defining the constraints. Underconstrained models lead to trivial solutions and overconstrained systems are either redundant or inconsistent. However, the example of the step-Carnot cycle which we are about to analyze is straightforward, in that necessary and sufficient constraints can be stated easily from the onset.

A word is in order about the relationship of the optimal control or variational approach of finite-time thermodynamics and the conventional thermodynamics of irreversible processes.⁹⁻¹¹ Both obviously deal with irreversible systems. The two approaches can be thought of, in some regards, as integral and differential approaches to the same problem. As such, they ask different questions; the integral, global approach is a complement to the differential, microscopic approach, not in any sense a replacement for it.

III. DEFINITION OF THE STEP-CARNOT CYCLE

The step-Carnot cycle is a simple modification of Carnot's original reversible cycle as follows. We suppose that (a) the working fluid is an ideal gas; (b) the system operates against an external pressure $P_e(t)$ that varies *discontinuously*, in steps, in a manner controlled by a hypothetical machine operator, with the steps always involving an instantaneous change of P_e followed by a change in the volume V and temperature T of the working fluid, at constant P_e (but not necessarily P_i); and (c) the temperature, pressure, and density within the working fluid are uniform before each step; for those aspects dealing explicitly with time this must be true for every instant.

The system goes through a cycle shown by the stepwise path inscribed in the reversible Carnot cycle of Fig. 1. Note that although (c) implies that the system follows a quasistatic path insofar as internal relaxation times are short compared with the time of any step, the path is only required to contain a finite number of points of equilibrium.

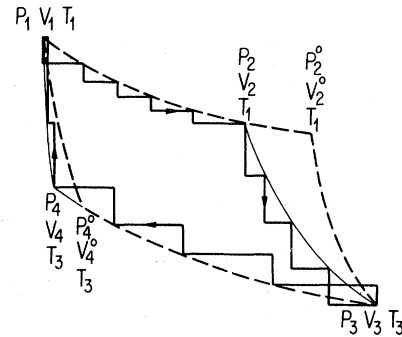


FIG. 1. PV diagram of the step-Carnot cycle (—) with its envelope (—) and the reversible Carnot cycle (---) operating between the same extreme states. The indicated pressure for the step-Carnot cycle is the external pressure P_e , not the internal pressure.

This is the essential difference between the irreversible step-Carnot cycle and the reversible Carnot cycle. Along the high-temperature "isotherm," the system, in contact with a reservoir at temperature T_H , expands irreversibly, working against a constant external pressure P_e until it returns to equilibrium. Similarly, along the low-temperature "isotherm," the system, in contact with a reservoir at temperature T_L , is compressed by subjection to an instantaneous increase in P_e , until equilibrium is attained. Along the adiabatic expansion branch of the cycle, in each step the volume of the system increases until equilibrium is reached with the external pressure. We shall see that this occurs at a volume greater than that of a reversible adiabat, or at a temperature higher than that of a reversible adiabat. In other words the stepwise adiabatic expansion has an outer envelope that is flatter than a continuous, reversible adiabat. Likewise, the stepwise adiabatic compression, branch 4, has an outer (left) envelope steeper than the curve of a reversible adiabatic compression.

To complete the specification of the system for the first part of our analysis, we now fix the total number of steps N . The first large stage of the problem is thus one of allocating the number of steps N_1, \dots, N_4 among the four branches of the cycle, so that $N_1 + N_2 + N_3 + N_4 = N$, and of determining that pressure and final volume for each step that maximizes the work done per cycle. To carry this out, we now examine the "isothermal" and "adiabatic" branches individually, and then optimize the entire process.

IV. ISOTHERMAL BRANCH

The work W_n done in step n is done against the constant external pressure $P_e = P_n$ over the volume

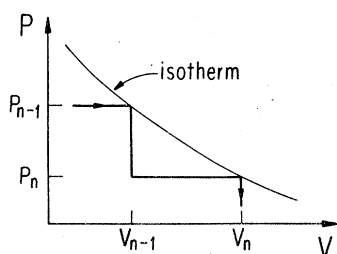


FIG. 2. Enlargement of one step on the isothermal branch showing work being done by the gas against the external pressure P_n from V_{n-1} to V_n .

$V_n - V_{n-1}$ (see Fig. 2), so it is $W_n = P_n(V_n - V_{n-1})$, and the total work obtained along the isothermal branch is

$$W_I = \sum_{n=1}^{N_I} P_n (V_n - V_{n-1}).$$

Note that for each step, the initial and final points (P_{n-1}, V_{n-1}) and (P_n, V_n) of the step-isothermal process are state points on the reversible isothermal curve, since the gas has reached the reservoir temperature at the end of each step. The working fluid is an ideal gas, $PV = nRT$, so

$$\begin{aligned} W_I &= nRT \sum_{n=1}^{N_I} P_n \left(\frac{1}{P_n} - \frac{1}{P_{n-1}} \right) \\ &= nRT \sum_{n=1}^{N_I} \left(1 - \frac{P_n}{P_{n-1}} \right). \end{aligned} \quad (5)$$

Maximum W_I is obtained for a fixed N_I when for any n

$$\frac{dW_I}{dP_n} = -nRT \left(\frac{1}{P_{n-1}} - \frac{P_{n+1}}{P_n^2} \right) = 0,$$

so

$$P_n/P_{n-1} = P_{n+1}/P_n,$$

i.e., all the steps must change the pressure by the same factor α_I and all N_I steps must give the total pressure change from P_0 to P_{N_I} . Hence

$$\alpha_I = P_n/P_{n-1} = (P_N/P_0)^{1/N_I}. \quad (6)$$

Combining (5) and (6) the total work obtained along the isothermal branch is

$$W_I = nRTN_I(1 - \alpha_I). \quad (7)$$

As N_I increases it is reassuring to see that

$W_I = nRTN_I[1 - (P_N/P_0)^{1/N_I}] \rightarrow nRT \ln(P_0/P_N)$, which is the work obtained along the reversible isotherm.

V. ADIABATIC BRANCH

When no heat is exchanged with the surroundings, $PdV = -C_v dT$, so that the work extracted from one step is

$$\begin{aligned} P_n(V_n - V_{n-1}) &= nRP_n \left(\frac{T_n}{P_n} - \frac{T_{n-1}}{P_{n-1}} \right) \\ &= -C_v(T_n - T_{n-1}), \end{aligned}$$

so

$$T_n = T_{n-1} \gamma^{-1} [1 + (P_n/P_{n-1})(\gamma - 1)], \quad (8)$$

where as usual $\gamma = C_p/C_v$. Solving instead for P_n gives

$$P_n = P_{n-1}(\gamma - 1)^{-1} (\gamma T_n/T_{n-1} - 1). \quad (9)$$

Hence,

$$V_n = nRT_n/P_n = V_{n-1} \gamma^{-1} [P_{n-1}/P_n + (\gamma - 1)]. \quad (10)$$

The total work

$$W_A = \sum_{n=1}^{N_A} P_n(V_n - V_{n-1}) = -C_v(T_N - T_0) \quad (11)$$

is maximized when T_N is a minimum:

$$T_N = T_0 \gamma^{-N_A} \prod_{n=1}^{N_A} [1 + (P_n/P_{n-1})(\gamma - 1)],$$

$$\begin{aligned} \frac{d \ln T_N}{dP_n} &= \frac{\gamma - 1}{P_{n-1}} \left(1 + \frac{P_n}{P_{n-1}}(\gamma - 1) \right)^{-1} \\ &\quad - (\gamma - 1) \frac{P_{n+1}}{P_n^2} \left(1 + \frac{P_{n+1}}{P_n}(\gamma - 1) \right)^{-1} = 0, \end{aligned}$$

implying

$$P_n/P_{n-1} = P_{n+1}/P_n,$$

so that again the pressure must change in steps by a constant factor α_A (although different from α_I), and

$$\alpha_A = P_n/P_{n-1} = (P_N/P_0)^{1/N_A}. \quad (12)$$

Now let us examine the system when N_A becomes large. The pressure of the n th point is

$$P_n = P_0 (P_N/P_0)^{n/N_A} = P_0 \alpha_A^n.$$

Hence, to fix our reference to a specific pressure, we require that n/N_A (and thus α_A^n) be constant. From (10)–(12) we obtain

$$\begin{aligned} \ln(P_n V_n^n) &= \ln(P_0 V_0^n) + \ln \left[\alpha_A^n \left(\frac{1}{\gamma \alpha_A} + \frac{\gamma - 1}{\gamma} \right)^{n\gamma} \right] = \ln(P_0 V_0^n) + \ln(\alpha_A^n) + n\gamma \ln \left(\frac{\exp[-(\ln \alpha_A^n)/n] + \gamma - 1}{\gamma} \right) \\ &= \ln(P_0 V_0^n) + \ln(\alpha_A^n) + n\gamma \ln \left(1 - \frac{\ln \alpha_A^n}{n\gamma} + \frac{(\ln \alpha_A^n)^2}{2n^2\gamma} - \dots \right), \end{aligned}$$

so that at constant pressure (n/N_A constant), $\lim_{n \rightarrow \infty} (P_n V_n^\gamma) = P_0 V_0^\gamma$, the equation of the reversible adiabatic process for an ideal gas. Note however, that for finite N_A , once this branch leaves the initial point at which $T = T_H$, the step adiabat does not touch the reversible adiabat again. This is because the irreversible adiabatic expansion converts less internal energy to work than the reversible process does and therefore achieves a higher temperature for a given final volume or a larger volume for a given final temperature. The envelope of the step-adiabatic expansion will therefore be flatter and that of the compression steeper than the corresponding reversible branches (see Fig. 1).

For real gases the derivation of the behavior on an isothermal branch is the same, through the order of the second virial coefficient B , as it is for the ideal gas. However, the behavior of real gases differs from that of ideal gases on the adiabatic branches. The difference sets in with terms of the form $(p^2/nR)(\partial B/\partial T)_v$, and complicates the expressions from (8) onward.

VI. CLOSING THE CYCLE

We are now in a position to combine two step isotherms and two step adiabats into a step-Carnot cycle as shown in Fig. 1. We want this cycle to operate between the same extreme states $P_1 V_1 T_1$ and $P_3 V_3 T_3$ as the reversible Carnot cycle. These extremes satisfy the condition $V_3/V_1 > (T_1/T_3)^{1/(\gamma-1)}$ so that positive work is achieved in going from 1 to 3 in a reversible process. For the present case of finite-step processes the onset of the adiabatic branch $P_2 V_2$ must be chosen according to (9) and (10) so that

$$\alpha_1^{N_1} = \frac{P_2}{P_1} = \frac{V_1}{V_3} \frac{V_3}{V_2} = \frac{V_1}{V_3} \left(\frac{\gamma-1}{\gamma - (T_1/T_3)^{1/N_2}} \right)^{N_2}$$

We can simplify by defining the ratios

$$\delta \equiv T_1/T_3 \text{ and } \epsilon \equiv V_1/V_3, \quad (13)$$

so that

$$\alpha_1 = \epsilon^{1/N_1} \left(\frac{\gamma-1}{\gamma - \delta^{1/N_2}} \right)^{N_2/N_1} \quad (14)$$

Similarly,

$$\alpha_3 = \epsilon^{-1/N_3} \left(\frac{\gamma-1}{\gamma - \delta^{-1/N_4}} \right)^{N_4/N_3} \quad (15)$$

The total work extracted from the step-Carnot cycle is

$$W = W_1 + W_3 = nRT_1 N_1 (1 - \alpha_1) + nRT_3 N_3 (1 - \alpha_3), \quad (16)$$

since the contributions from the adiabatic branches cancel according to (11). Although only N_1 and N_3 enter explicitly in (16), W still depends on N_2 and N_4 through (14) and (15).

VII. MAXIMIZING WORK AND EFFECTIVENESS

For a given total number of steps

$$N = N_1 + N_2 + N_3 + N_4. \quad (17)$$

The distribution of the steps which produces maximum work per cycle may be found as the maximum of

$$F = T_1 N_1 \left[1 - \epsilon^{1/N_1} \left(\frac{\gamma-1}{\gamma - \delta^{1/N_2}} \right)^{N_2/N_1} \right] + T_3 N_3 \left[1 - \epsilon^{-1/N_3} \left(\frac{\gamma-1}{\gamma - \delta^{-1/N_4}} \right)^{N_4/N_3} \right] - \lambda \left(\sum_{i=1}^4 N_i - N \right),$$

which leads to the conditions that four derivatives vanish:

$$\frac{\partial F}{\partial N_1} = T_1 + T_1 \epsilon^{1/N_1} \left(\frac{\gamma-1}{\gamma - \delta^{1/N_2}} \right)^{N_2/N_1} \times \left(\frac{N_2}{N_1} \ln \frac{\gamma-1}{\gamma - \delta^{1/N_2}} + \frac{1}{N_1} \ln \epsilon - 1 \right) - \lambda = 0, \quad (18)$$

$$\frac{\partial F}{\partial N_2} = T_1 \epsilon^{1/N_1} \left(\frac{\gamma-1}{\gamma - \delta^{1/N_2}} \right)^{N_2/N_1} \times \left(\frac{1}{N_2} \frac{\delta^{1/N_2}}{\gamma - \delta^{1/N_2}} \ln \delta - \ln \frac{\gamma-1}{\gamma - \delta^{1/N_2}} \right) - \lambda = 0,$$

plus a similar pair of equations with $(N_1, N_2, T_1, \delta, \epsilon)$ replaced by $(N_3, N_4, T_3, \delta^{-1}, \epsilon^{-1})$. We have not been able to solve (18) for arbitrary N . However, for large N_1, N_2, N_3, N_4 , as the step cycle approaches the reversible Carnot cycle, we can use expansions in $1/N_i$ to second order, from which we obtain the expressions

$$N_1 = \frac{N}{\eta} \sqrt{\delta} \frac{1 - \gamma \ln \xi}{\sqrt{\gamma} \ln \delta}, \quad (19a)$$

$$N_2 = \frac{N}{\eta} \sqrt{\delta}, \quad (19b)$$

$$N_3 = \frac{N}{\eta} \frac{1 - \gamma \ln \xi}{\sqrt{\gamma} \ln \delta}, \quad (19c)$$

$$N_4 = \frac{N}{\eta}, \quad (19d)$$

where

$$\xi \equiv \epsilon \delta^{1/(\gamma-1)} \quad (0 < \xi < 1), \quad (20)$$

and η is a normalization constant

$$\eta = (1 + \sqrt{\delta}) \left(1 - \frac{\gamma - 1}{\sqrt{\gamma}} \frac{\ln \xi}{\ln \delta} \right).$$

It is worth noting that $N_1/N_3 = \sqrt{\delta}$, which in physical terms says that the optimal path takes more steps along the upper isothermal branch than along the lower one. This reflects what we see when we compare the actual work, Eq. (16), with the work for the ideal Carnot engine, Eq. (21), below: The irreversible losses are weighted in proportion to their thermostat temperatures, so that the optimal path allocates more and smaller steps to the high-temperature branch.

We find it informative to look at W relative to the work done by an ideal reference system, a reversible Carnot cycle operating between the same two heat reservoirs, and between P_1V_1 and P_3V_3 . This is the effectiveness¹² W/W_0 (also called second-law efficiency⁵), the ratio of work done to the total change of availability. With

$$\begin{aligned} P_2 &= (nRT_1/V_3)\delta^{1/\gamma-1}, & P_4 &= (nRT_3/V_1)\delta^{-1/\gamma-1}, \\ W_0 &= nRT_1 \ln(P_1/P_2) + nRT_3 \ln(P_3/P_4) \\ &= -nR(T_1 - T_3) \ln \xi, \end{aligned} \quad (21)$$

which, combined with (14)–(16), and (19), gives the effectiveness

$$\begin{aligned} \frac{W}{W_0} &= 1 - \frac{1}{2N} \frac{\sqrt{\delta} + 1}{\sqrt{\delta} - 1} \left(\sqrt{-\ln \xi} + \frac{\sqrt{\gamma}}{\gamma - 1} \frac{\ln \delta}{\sqrt{-\ln \xi}} \right)^2 + \dots \\ &= 1 + \frac{1}{2N} \frac{T_1 + T_3 + 2\sqrt{T_1 T_3}}{T_1 - T_3} \mu^2 \ln \xi + \dots, \end{aligned} \quad (22)$$

where

$$\mu = 1 - \frac{\sqrt{\gamma} \ln \delta}{\gamma - 1 \ln \xi}.$$

The expressions (22) are correct to first order in N^{-1} for the optimal distribution of steps. The second term in (22) is negative for all initial and final states, so $W < W_0$ as it should but approaches the reversible limit from below as $N \rightarrow \infty$.

VIII. MAXIMIZING EFFICIENCY

As an alternative to maximizing the total work per cycle and the effectiveness, we can find that program of steps which maximizes the efficiency of the step-Carnot cycle. We now maximize W/Q_1 , the ratio of net work, per cycle, to the heat absorbed from the hot reservoir, again subject to (17), the constant number of steps:

$$\begin{aligned} F &= \frac{W}{Q_1} - \lambda \left(\sum_{i=1}^4 N_i - N \right) \\ &= 1 + \frac{W_3}{W_1} - \lambda \left(\sum_{i=1}^4 N_i - N \right). \end{aligned} \quad (23)$$

Setting

$$\frac{\partial F}{\partial N_1} = -\frac{W_3}{W_1^2} \frac{\partial W_1}{\partial N_1} - \lambda = 0,$$

we find, to first order in N^{-1} ,

$$\begin{aligned} \lambda &= -\frac{\ln \xi}{2\delta N_1^2} \left[1 - \frac{\ln \xi}{2} \left(\frac{2}{N_1} + \frac{1}{N_3} \right) \right. \\ &\quad \left. - \frac{\ln^2 \delta}{\ln \xi} \frac{\gamma}{2(\gamma-1)^2} \left(\frac{2}{N_2} + \frac{1}{N_4} \right) \right], \end{aligned} \quad (24)$$

and a similar expression from the condition $\partial F/\partial N_2 = 0$. In this example, the expressions for the other two branches are not of the same form as (24), in contrast to the case of maximum work. We find from $\partial F/\partial N_3 = 0$ that

$$\lambda = -\frac{\ln \xi}{2\delta N_3^2} \left(1 + \frac{\ln \xi}{2N_1} + \frac{\ln^2 \delta}{\ln \xi} \frac{1}{2N_2} \frac{\gamma}{(\gamma-1)^2} \right)^{-1} \quad (25)$$

to order N^{-1} . A similar expression comes from the condition $\partial F/\partial N_4 = 0$. We solve the four equations for $N_1, N_2, N_3,$ and N_4 to find (again to first order in N^{-1}) that

$$N_1 = \frac{N}{2\mu} - \frac{\mu}{4} \ln \xi, \quad (26a)$$

$$N_2 = \frac{\mu-1}{2\mu} N - \frac{\mu(\mu-1)}{4} \ln \xi, \quad (26b)$$

$$N_3 = \frac{N}{2\mu} + \frac{\mu}{4} \ln \xi, \quad (26c)$$

$$N_4 = \frac{\mu-1}{2\mu} N + \frac{\mu(\mu-1)}{4} \ln \xi. \quad (26d)$$

Let us call the work per cycle W' , when the efficiency is a maximum. The effectiveness W'/W_0 for the most efficient cycle is less than W/W_0 , the effectiveness of the most effective cycle, Eq. (22):

$$\frac{W'}{W_0} = 1 + \frac{\mu^2}{N} \frac{T_1 + T_3}{T_1 - T_3} \ln \xi. \quad (27)$$

The difference between the effectiveness of the two systems is

$$\begin{aligned} \frac{W}{W_0} - \frac{W'}{W_0} &= \frac{\mu^2}{2N} \frac{\ln \xi}{T_1 - T_3} (2\sqrt{T_1 T_3} - T_1 - T_3) \\ &= -\frac{\mu^2}{2N} \frac{\ln \xi}{T_1 - T_3} (\sqrt{T_1} - \sqrt{T_3})^2 > 0. \end{aligned} \quad (28)$$

We can also compare the efficiencies of the two kinds of optimized step cycles. First, for the cycle with maximized work per cycle, the efficiency

$$\begin{aligned} \frac{W}{Q_1} &= 1 + \frac{W_3}{W_1} \\ &= \frac{T_1 - T_3}{T_1} - \frac{\eta \mu}{2\delta N} \frac{\sqrt{\gamma}}{\gamma - 1} \left(\frac{1}{\sqrt{\delta}} + 1 \right) \ln \delta \end{aligned} \quad (29)$$

to order N^{-1} . For the cycle with maximized effi-

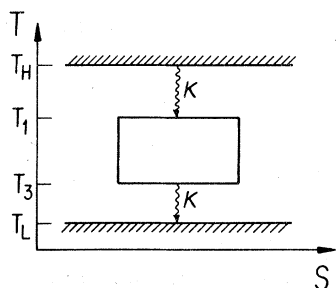


FIG. 3. TS diagram of Carnot cycle operating between T_1 and T_3 with heat exchanged with the reservoirs at T_H and T_L through the thermal conductances κ .

ciency (Q'_1 is the heat absorbed from the reservoir at T_1),

$$\frac{W'}{Q'_1} = \frac{T_1 - T_3}{T_1} + \frac{2\mu^2}{\delta N} \ln \xi, \quad (30)$$

again to order N^{-1} . The difference

$$\frac{W'}{Q'_1} - \frac{W}{Q_1} = \frac{\mu}{\delta N} \frac{(\sqrt{\delta} - 1)^2}{2\sqrt{\delta}} \left(\frac{\sqrt{\gamma}}{\gamma - 1} \ln \delta - \ln \xi \right) > 0. \quad (31)$$

IX. OPTIMAL PERIOD

So far time has not entered our analysis, because we have assumed that the gas adjusts instantaneously to changing conditions, and that there is perfect thermal conductance to the reservoirs T_1 and T_3 . Now we will relax the last assumption and introduce a (finite) thermal conductance κ between the reservoirs at temperatures T_H and T_L and the system, so that the system has isothermal steps at the temperatures T_1 and T_3 , respectively, between which the cycle actually runs, and $T_L < T_3 < T_1 < T_H$. This is illustrated in Fig. 3. The differences between T_1 and T_H and between T_3 and T_L allow a finite-time operation of the isothermal branches, while the adiabatic steps may be assumed to occur instantaneously on the time scale associated with thermal conduction.

Again we take the reversible cycle as our yardstick. It follows from (21) and the heat-flow equation $dQ/dt = \kappa \Delta T$, that

$$W_0 = \kappa(T_1 - T_H)t_1^0 + \kappa(T_3 - T_L)t_3^0,$$

so one cycle is completed in time

$$t_0 = t_1^0 + t_3^0 = -\frac{nR}{\kappa} \ln \xi \left(\frac{T_1}{T_1 - T_H} - \frac{T_3}{T_3 - T_L} \right); \quad (32)$$

t_1^0 and t_3^0 are the times associated with the upper and lower isothermal branches. We assume that the adiabatic branches transpire in time intervals

negligible compared with t_1^0 and t_3^0 , since the system exchanges no heat with the surroundings along these branches.

Let us examine in detail each step along the step-isothermal branch. The first part, drawn with a heavy line in Fig. 4, is effectively instantaneous in that no heat is transferred. Work is done by adiabatic cooling from T_1 to $T(t_a)$ where the gas is in equilibrium with the external pressure P_b , i.e., the time difference $t_a - t_c = 0$. The expansion from $V(t_a)$ to V_b is done while the gas remains in equilibrium with the external pressure and at a rate determined by the rate at which heat leaks into the gas and heats it to T_1 . The work done from t_c to t_a

$$P_b[V(t_a) - V_a] = nRT(t_a) - P_bV_a = -c_v[T(t_a) - T_1]$$

thus determines

$$T(t_a) = \left(\frac{1}{\gamma} + \frac{\gamma - 1}{\gamma} \alpha_1 \right) T_1. \quad (33)$$

The energy balance equation

$$\begin{aligned} \frac{dQ}{dt} &= \kappa[T(t) - T_H] \\ &= c_v \frac{dT}{dt} + P_b \frac{dV}{dt} = c_p \frac{dT}{dt} \end{aligned}$$

may be integrated to yield

$$\frac{\kappa}{c_p} (t_b - t_a) = \ln \frac{T_1 - T_H}{T(t_a) - T_H},$$

which upon substitution from (33), (14), and (19) gives the total time for expansion

$$\begin{aligned} t_1 &= N_1(t_b - t_a) \\ &= -\frac{nR}{\kappa} \ln \xi \frac{T_1}{T_1 - T_H} \\ &\times \left[1 - \frac{\eta \sqrt{\gamma} \ln \delta}{2N \sqrt{\delta} (\gamma - 1)} \left(1 - \frac{\sqrt{\gamma}}{\gamma - 1} \frac{\ln \delta}{\ln \xi} - \frac{T_1}{T_1 - T_H} \frac{\gamma - 1}{\gamma} \right) \right] \end{aligned}$$

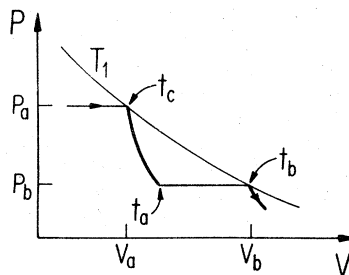


FIG. 4. Enlargement of one step on the isothermal branch when thermal conductance to the heat reservoir is finite. Along the segment t_c to t_a work is done by adiabatic cooling of the gas. From t_a to t_b the gas is reheated to T_1 while in equilibrium with the external pressure P_b .

for the maximum-effectiveness step-isothermal expansion. Branch 3 gives a similar equation, whereas the step-adiabatic branches are not delayed by thermal resistance, so the total cycle time becomes

$$t = t_1 + t_3 = t_0 + \frac{1}{2N} \frac{nR}{K} \ln \xi \frac{\eta \sqrt{\gamma} \ln \delta}{\gamma - 1} \left\{ \left(\frac{1}{\sqrt{\delta}} \frac{T_1}{T_1 - T_H} - \frac{T_3}{T_3 - T_L} \right) \left(1 - \frac{\sqrt{\gamma} \ln \delta}{\gamma - 1 \ln \xi} \right) - \left[\frac{1}{\sqrt{\delta}} \left(\frac{T_1}{T_1 - T_H} \right)^2 + \left(\frac{T_3}{T_3 - T_L} \right)^2 \right] \frac{\gamma - 1}{\gamma} \right\}. \quad (34)$$

The step-cycle time $t_1 < t_1^0$ for two reasons: Each step is speeded up by the instantaneous portion $t_c - t_a$ as well as the larger temperature gradient from T_H to $T(t_a)$ than to T_1 , and $V_2 < V_2^0$ (see Fig. 1), so the step isotherm is shorter than the reversible isotherm. The first of the two reasons also holds for branch 3. However, $V_4 < V_4^0$ making the step isotherm longer than the reversible isotherm in this case. Therefore, t_3 can be either smaller or larger than t_3^0 , and the whole cycle will run faster as a step process if the reservoirs are close to T_1 and T_3 , slower if there is already a considerable temperature gradient. The precise dividing point, where $t = t_0$, is determined implicitly by the transcendental condition that the quantity in braces in Eq. (34) be zero.

The irreversibility introduced in this section has been purely thermal. Mechanical irreversibility (friction) could also be added, but that will be treated in a more general framework in a subsequent paper.

Other approaches can be taken to optimize thermodynamic systems by variational methods. For

example one can maximize the power output of a Carnot engine with finite heat conductance to its thermostats. This analysis was carried out by Curzon and Ahlborn,¹³ who showed that the maximum power of this engine depends only on the heat conductance and the reservoir temperatures, and that its efficiency is $1 - (T_L/T_H)^{1/2}$, rather than $1 - (T_L/T_H)$. This efficiency is independent of heat conductance. The period for maximum power of such an engine is

$$t^{\max} = - \frac{nR}{K} \frac{\sqrt{T_H} + \sqrt{T_L}}{\sqrt{T_H} - \sqrt{T_L}} \left(\frac{1}{\gamma - 1} \ln \frac{T_L}{T_H} - 2 \ln \frac{V_1}{V_3} \right),$$

so depends only on the reservoir temperatures, the mechanical parameter V_1/V_3 , and the thermal conductance K .

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