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

Bjarne Andresen, R. Stephen Berry, Abraham Nitzan, and Peter Salamon
Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 7 September 1976)

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. As Tisza points out, 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. Sometimes we expend energy on processes that could, in principle, return energy. One example is the conversion of copper sulfide ores to copper and SO₂. (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. 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,

\[ W = \int_{\lambda_1}^{\lambda_2} \mathcal{F}(\lambda, t) \cdot d\mathcal{S}(\lambda, t) \]  
(1)

or

\[ Q = \int_{\lambda_1}^{\lambda_2} C(\lambda, t) dT(\lambda, t), \]  
(2)

whose extremum we seek. The generalized force \( \mathcal{F} \) may be an exceedingly complicated quantity, dependent on a large set of internal variables \( \lambda \) 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. 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 Uhlenbeck 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

\[ W = \int_{V_1}^{V_2} P_i(t) \, dV \]

\[ = \int_{t_1}^{t_2} P_i(t) \, \frac{dV}{dt} \, dt. \]  
(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 \( P_i(t) \) 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. 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
the physics of each individual case will be in
dV/dt and in the constraints. For Q the heat-
capacity function also contains physical char-
acteristics of the system, so that it is often going
to be advantageous to recast (2) as
\[ Q = \int_{S_1}^{S_2} T(t) \, dS \]
\[ = \int_{t_1}^{t_2} T(t) \, \frac{dS}{dt} \, dt, \] (4)
where S denotes the entropy associated with the
heat flow into the system.

In some situations, we find that care is required
defining the constraints. Underconstrained mod-
els 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 thermo-
dynamics of irreversible processes.\textsuperscript{6-11} 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 ques-
tions; the integral, global approach is a comple-
ment 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 \( \text{discontinuously}, \) in
steps, in a manner controlled by a hypothetical
machine operator, with the steps always in-
volving an instantaneous change of \( P_e \) followed by
a change in the volume \( V \) and temperature \( T \)
of the working fluid, at constant \( P_e \) (not neces-
sarily \( P_e \)); and (c) the temperature, pressure,
and density within the working fluid are uniform
before each step; for those aspects dealing ex-
plitically with time this must be true for every in-
stant.

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.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{carnot_cycle}
\caption{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.}
\end{figure}

This is the essential difference between the ir-
reversible step-Carnot cycle and the reversible
Carnot cycle. Along the high-temperature "iso-
therm," 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 adi-
abatic 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 \( N_1, \ldots, N_4 \) among the four branches of the
cycle, so that \( N_1 + N_2 + N_3 + N_4 = N \), and of deter-
mining 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 \( W_I \) 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

\[ W_I = \sum_{i=1}^{N_I} P_n(V_n - V_{n-1}) \]

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

\[ W_I = nRT \sum_{n=1}^{N_I} P_n \left( \frac{1}{P_n} - \frac{1}{P_{n-1}} \right) \]

\[ = nRT \sum_{n=1}^{N_I} \left( 1 - \frac{P_n}{P_{n-1}} \right). \tag{5} \]

Maximum \( W_I \) is obtained for a fixed \( N_I \) when for any \( n \)

\[ \frac{dW_I}{dP_n} = -nRT \left( \frac{1}{P_{n-1}} - \frac{P_{n-1}}{P_n} \right) = 0 , \]

so

\[ P_{n-1}/P_n = P_{n-1}/P_n, \]

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

\[ \alpha_t = \frac{P_{n-1}}{P_n} = \left( \frac{P_{n-1}}{P_n} \right)^{1/N_I}. \tag{6} \]

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

\[ W_I = nRTN_I \left( 1 - \alpha_t \right). \tag{7} \]

As \( N_I \) increases it is reassuring to see that

\[ W_I = nRTN_I \left[ 1 - (P_{n-1}/P_n)^{1/N_I} \right] - nRT \ln(P_0/P_n), \]

which is the work obtained along the reversible isothermal.

V. ADIABATIC BRANCH

When no heat is exchanged with the surroundings, \( PdV = C_VdT \), so that the work extracted from one step is

\[ P_n(V_n - V_{n-1}) = nRT \left( \frac{T_n}{P_n} - \frac{T_{n-1}}{P_{n-1}} \right) \]

so

\[ T_n = T_{n-1} \gamma \left[ 1 + (P_{n-1}/P_n)(\gamma - 1) \right], \tag{8} \]

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

\[ P_n = P_{n-1}(\gamma - 1)^{-1}(T_n/T_{n-1} - 1) \tag{9} \]

Hence,

\[ V_n = nRT \gamma^{-1} \sum_{n=1}^{N_I} \left[ 1 + (P_n/(P_{n+1}))(\gamma - 1) \right]. \tag{10} \]

The total work

\[ W_A = \sum_{n=1}^{N_I} P_n(V_n - V_{n-1}) = -C_v(T_n - T_0) \tag{11} \]

is maximized when \( T_n \) is a minimum:

\[ T_n = T_0 \gamma^{-N_A} \prod_{n=1}^{N_A} \left[ 1 + (P_n/(P_{n+1}))(\gamma - 1) \right] \]

\[ \frac{d \ln T_n}{dP_n} = \gamma - 1 \left( \frac{1 + P_n}{P_{n+1}} \right)^{-1} - (\gamma - 1) \left( \frac{P_{n+1}}{P_n} \right)^{-1} \left( \frac{1 + P_n}{P_{n+1}} \right)^{-1} = 0 , \]

implying

\[ P_{n-1}/P_n = P_{n+1}/P_n, \]

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

\[ \alpha_A = P_{n-1}/P_n = (P_{n-1}/P_n)^{1/N_A}. \tag{12} \]

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

\[ P_n = P_0(P_{n-1}/P_n)^{N_A} = P_0 \alpha_A^n. \]

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

\[ \ln(P_n/v_n^2) = \ln(P_0/v_0^2) + \ln \left[ (1 + (\gamma - 1)/\gamma) \right] + \ln(P_0/v_0^2) + \ln(\alpha_A^n) + n \gamma \ln \left( \frac{\exp\left[-(n\alpha_A^n)/n\right] + \gamma - 1}{\gamma} \right) \]

\[ = \ln(P_0/v_0^2) + \ln(\alpha_A^n) + n \gamma \ln \left( 1 - \frac{\ln \alpha_A^n}{n\gamma} + \frac{(\ln \alpha_A^n)^2}{2n^2\gamma} - \cdots \right), \]
so that at constant pressure \((p/N_A)\) constant, 
\[ \lim_{N_A \to 0} (P_N V_N^2) = P_{N^*} V_{N^*}^2, \]
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 \(T = T_m\), 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 \(B_1\), 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 \((p^2/nR)(\partial B/\partial T)^p\), 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 \(P_1V_1T_1\) and \(P_2V_2T_2\) as the reversible Carnot cycle. These extremes satisfy the condition \(V_2/V_1 > (T_1/T_2)^1/(\nu-1)\) 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 \(P_2V_3\) must be chosen according to (9) and (10) so that

\[
\alpha_{N_1} = \frac{P_2}{P_1} = \frac{V_2}{V_1} = \frac{V_1}{V_3} \left( \frac{\nu - 1}{\nu - (\nu/T_1/T_2)^{1/(\nu-1)}} \right)^{\nu_2/\nu_3}.
\]

We can simplify by defining the ratios

\[
\delta = T_1/T_2 \quad \text{and} \quad \epsilon = V_1/V_3,
\]

so that

\[
\alpha_1 = \epsilon^{1/\nu_1} \left( \frac{\nu - 1}{\nu - \delta^{1/\nu_2}} \right)^{\nu_2/\nu_3}.
\]

Similarly,

\[
\alpha_3 = \epsilon^{1/\nu_3} \left( \frac{\nu - 1}{\nu - \delta^{1/\nu_4}} \right)^{\nu_4/\nu_3}.
\]

The total work extracted from the step-Carnot cycle is

\[
W = W_1 + W_3 = nRT_1N_1(1 - \alpha_1) + nRT_3N_3(1 - \alpha_3),
\]

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

\[
N = N_1 + N_2 + N_3 + N_4,
\]

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

\[
F = T_1N_1 \left[ 1 - \epsilon^{1/\nu_1} \left( \frac{\nu - 1}{\nu - \delta^{1/\nu_2}} \right)^{\nu_2/\nu_1} \right]
+ T_3N_3 \left[ 1 - \epsilon^{1/\nu_3} \left( \frac{\nu - 1}{\nu - \delta^{1/\nu_4}} \right)^{\nu_4/\nu_3} \right]
- \lambda \left( \sum_{i=1}^4 N_i - N \right),
\]

which leads to the conditions that four derivatives vanish:

\[
\frac{\partial F}{\partial N_1} = T_1T_1^{1/\nu_1} \left( \frac{\nu - 1}{\nu - \delta^{1/\nu_2}} \right)^{\nu_2/\nu_1} \times \left( \frac{N_1}{N_1} \ln \frac{\nu - 1}{\nu - \delta^{1/\nu_2}} - \lambda = 0 \right),
\]

\[
\frac{\partial F}{\partial N_2} = T_1T_1^{1/\nu_1} \left( \frac{\nu - 1}{\nu - \delta^{1/\nu_2}} \right)^{\nu_2/\nu_1} \times \left( \frac{1}{N_2} \ln \frac{\nu - 1}{\nu - \delta^{1/\nu_2}} - \lambda = 0 \right),
\]

plus a similar pair of equations with \((N_1, N_2, T_1, \delta, \epsilon)\) replaced by \((N_3, N_4, T_2, \delta, \epsilon)\). 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 \(1/N_1\) to second order, from which we obtain the expressions

\[
N_1 = \frac{N}{\eta} \sqrt{\delta} - \frac{1 - \gamma \ln \xi}{\sqrt{\gamma} \ln \delta},
\]

\[
N_2 = \frac{N}{\eta} \sqrt{\delta},
\]

\[
N_3 = \frac{N}{\eta} \sqrt{\delta} - \frac{1 - \gamma \ln \xi}{\sqrt{\gamma} \ln \delta},
\]

\[
N_4 = \frac{N}{\eta},
\]

where

\[
\xi = \epsilon^{\delta^{1/(\nu-1)}} \quad (0 < \xi < 1),
\]

and \(\eta\) is a normalization constant.
\[ \eta = \left(1 + \sqrt{\delta}\right) \left(1 - \frac{\gamma - 1}{\sqrt{\gamma}} \frac{\ln \xi}{\ln \delta} \right) \].

It is worth noting that \( N_i/N_3 = \sqrt{\delta} \), 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 \( P_2V_2 \). This is the effectiveness \( W/W_0 \) (also called second-law efficiency \(^3\)), the ratio of work done to the total change of availability. With

\[
P = \left(nRT_1/V_1\right) \delta^{1/\alpha}, \quad P_2 = \left(nRT_3/V_2\right) \delta^{1/\alpha},
\]

\[
W = nRT_1 \ln(P_1/P_2) + nRT_3 \ln(P_3/P_4)
\]

\[
= -nR(T_1 - T_3) \ln \xi,
\]

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

\[
\frac{W}{W_0} = 1 - \frac{\sqrt{\delta} + 1}{2N} \left(\frac{\sqrt{\gamma} \frac{\ln \xi}{\ln \delta}}{\gamma - 1} - \frac{\ln \xi}{\ln \delta}\right)^2 + \cdots
\]

\[
= 1 + \frac{1}{2N} T_1 + T_3 + 2\sqrt{T_1 T_3} \mu \ln \xi + \cdots,
\]

where

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

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 \( N \to \infty \).

**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:

\[
F = \frac{W}{Q_1} - \lambda \left( \sum_{i=1}^{N} N_i - N \right)
\]

\[
= 1 + \frac{W}{W_1} - \lambda \left( \sum_{i=1}^{N} N_i - N \right).
\]

Setting

\[
\frac{\partial F}{\partial N_i} = -W_i \frac{\partial W_i}{\partial N_i} - \lambda = 0,
\]

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

\[
\lambda = -\frac{\ln \xi}{2N \gamma} \left(1 - \frac{\ln \left(2N_i + 1\right)}{N_i}\right)
\]

\[
-\frac{\ln \delta}{2(\gamma - 1)^2} \frac{\gamma}{\ln \xi} \left(2N_i + 1\right),
\]

and a similar expression from the condition \( \partial F/\partial N_3 = 0 \). 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 \( \partial F/\partial N_4 = 0 \) that

\[
\lambda = -\frac{\ln \xi}{2N_4 \gamma} \left(1 + \frac{\ln \left(2N_4 + 1\right)}{N_4}\right)^2
\]

\[
-\frac{\ln \delta}{2(\gamma - 1)^2} \frac{\gamma}{\ln \xi} \left(2N_4 + 1\right)^2
\]

\[
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

\[
N_1 = \frac{N}{2\mu} - \frac{\mu}{4} \ln \xi,
\]

\[
N_2 = \frac{\mu - 1}{2\mu} N - \frac{\mu(\mu - 1)}{4} \ln \xi,
\]

\[
N_3 = \frac{N}{2\mu} + \frac{\mu}{4} \ln \xi,
\]

\[
N_4 = \frac{\mu - 1}{2\mu} N + \frac{\mu(\mu - 1)}{4} \ln \xi.
\]

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):

\[
\frac{W'}{W_0} = 1 + \frac{\mu^2}{N} T_1 + T_3 \ln \xi.
\]

The difference between the effectiveness of the two systems is

\[
\frac{W}{W_0} - \frac{W'}{W_0} = \frac{\mu^2}{2N} \ln \xi \left(2\sqrt{T_1 T_3} - T_1 - T_3\right)
\]

\[
= -\frac{\mu^2}{2N} \ln \xi \left(2\sqrt{T_1 T_3} - T_1 - T_3\right) > 0.
\]

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

\[
\frac{W}{Q_1} = 1 + \frac{W}{W_1} = \frac{T_1 - T_3}{T_1} \frac{\eta \mu}{2N \gamma - 1} \left(\frac{1}{\sqrt{\delta}} + 1\right) \ln \delta
\]

\[to order N^{-1}. For the cycle with maximized effi-\]
ciency ($Q'_1$ is the heat absorbed from the reservoir at $T_1$),
\[ \frac{W}{Q'_1} = \frac{T_1 - T_3}{T_1} + \frac{2 \mu^2}{3N} \ln \xi, \]  
again to order $N^{-1}$. The difference
\[ \frac{W}{Q'_1} - \frac{W}{Q_1} = -\frac{\mu}{3N} \left( \frac{\sqrt{\delta - 1}}{\sqrt{\gamma - 1}} \ln \delta - \ln \xi \right) > 0, \]  
\[ (31) \]

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 $\kappa$ 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 $T_L < T_1 < T_3 < T_H$. 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 branches 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
\[ W_0 = \kappa (T_1 - T_H) \xi_1^0 + \kappa (T_3 - T_L) \xi_3^0, \]
so one cycle is completed in time
\[ t_0 = t_1 + t_3 = -\frac{nR}{\kappa} \ln \xi \left( \frac{T_1}{T_1 - T_H} - \frac{T_3}{T_3 - T_L} \right); \]  
\[ (32) \]

$t_1^0$ 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 $T(l_s)$ where the gas is in equilibrium with the external pressure $P_s$, i.e., the time difference $t_s - t_e = 0$. The expansion from $V(l_s)$ to $V_s$ 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 $t_e$ to $t_s$
\[ P_s [V(l_s) - V_s] = nRT(l_s) - P_s V_s = -c[T(l_s) - T_1] \]
thus determines
\[ T(l_s) = \left( \frac{1}{\gamma} \frac{\gamma - 1}{\gamma} a_1 \right) T_1. \]  
\[ (33) \]
The energy balance equation
\[ \frac{dQ}{dt} = \kappa [T(t) - T_H] \]
\[ = c_p \frac{dT}{dt} + \frac{P}{dV} \frac{dV}{dt} \]
may be integrated to yield
\[ \frac{\kappa}{c_p} (t_s - t_e) = \ln \frac{T_1 - T_H}{T(l_s) - T_H}, \]
which upon substitution from (33), (14), and (19) gives the total time for expansion
\[ t_1 = N_1 (t_s - t_e) \]
\[ = -\frac{nR}{\kappa} \ln \xi \left( \frac{T_1}{T_1 - T_H} - \frac{T_3}{T_3 - T_L} \right) \times \left[ 1 - \frac{\eta \sqrt{\gamma} \ln \delta}{2N \sqrt{\delta} (\gamma - 1)} \left( 1 - \frac{\sqrt{\gamma} \ln \delta - \frac{T_1}{T_1 - T_H} \gamma - 1}{\xi} \right) \right] \]

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 $\kappa$.

FIG. 4. Enlargement of one step on the isothermal branch when thermal conductance from the heat reservoir is finite. Along the segment $t_e$ to $t_s$ work is done by adiabatic cooling of the gas. From $t_s$ to $t_0$ the gas is reheated to $T_1$, while in equilibrium with the external pressure $P_s$. 
for the maximum-effectiveness step-adiabatic expansion. Branch 3 gives a similar equation, whereas the step-adiabatic branches are not delayed by thermal resistance, so the total cycle time becomes

\[
t = t_4 + t_5 = t_0 + \frac{n R}{2 \pi} \ln \left( \frac{\sqrt{y} \ln \delta}{\alpha} \right) \left( \frac{T_1}{T_1 - T_H} - \frac{T_2}{T_2 - T_L} \right) \left( 1 - \frac{\sqrt{y} \ln \delta}{\gamma - 1} \right) - \left[ \frac{1}{\sqrt{\delta}} \left( \frac{T_1}{T_1 - T_H} \right)^2 + \left( \frac{T_2}{T_2 - T_L} \right)^2 \right] \frac{\gamma - 1}{\gamma}
\]

(34)

The step-cycle time \( t \) is for two reasons: Each step is speeded up by the instantaneous portion \( t_4 - t_2 \) as well as the larger temperature gradient from \( T_H \) to \( T_L \) than to \( T_1 \), and \( V_3 < V_2 \) (see Fig. 1), so the step isotherm is longer than the reversible isotherm. The first of the two reasons also holds for branch 3. However, \( V_4 < V_3 \) making the step isotherm longer than the reversible isotherm in this case. Therefore, \( t_4 \) can be either smaller or larger than \( t_2 \), and the whole cycle will run faster as a step process if the reservoirs are close to \( T_1 \) and \( T_2 \), 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,18 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

\[
t_{\text{max}} = -\frac{n R}{K} \left( \frac{T_H - T_L}{\sqrt{T_H - T_L}} \right) \left( \frac{1}{\gamma - 1} \ln \frac{T_L}{T_H} - 2 \ln \frac{V_4}{V_3} \right)
\]

so depends only on the reservoir temperatures, the mechanical parameter \( V_3/V_4 \), and the thermal conductance \( K \).

ACKNOWLEDGMENTS

This research was supported by a grant from the National Science Foundation. We would also like to thank Professor L. K. Nash and Professor Robert Socolow for pointing out the work of Curzon and Ahlborn to us.

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*Partially supported by a travel grant from the Danish Science Foundation.
†Permanent address: Department of Chemistry, University of Tel Aviv, Tel Aviv, Israel.