

FINITE-TIME THERMODYNAMICS

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Physics Laboratory II
University of Copenhagen
1983

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ISBN 87-88318-02-8

JJ tryktechnik a-s, København

Denne afhandling er af Det naturvidenskabelige Fakultet ved Københavns Universitet antaget til offentligt at forsvares for den naturvidenskabelige doktorgrad.

København, den 25. april 1984
Henning E. Jørgensen
h. a. dec.

Forsvaret finder sted
fredag den 16. november 1984 kl. 14 præcis
i auditorium 3, H. C. Ørsted Institutet.

PREFACE

*Taking fun as simply fun
and earnestness in earnest
shows how thoroughly thou none
of the two discernest.*

(Piet Hein: Grooks I)

The field of finite-time thermodynamics was started in 1975 by professor R. Stephen Berry, Peter Salamon, and myself as a result of the increased awareness of the limitations of the earth's resources. The oil crisis of 1973 made it clear to everybody that energy sources are neither inexhaustible nor free, and later on the same realization emerged with regard to our environment, clean air and water, as well as a number of minerals such as several strategic metals. The criteria of merit provided by traditional reversible thermodynamics were, with few exceptions, far too unrealistic for evaluating the potential for conservation in real processes. Irreversible thermodynamics could, in principle, evaluate the losses in rate processes, but it requires extensive knowledge of the microscopic mechanism of the process, something which is usually not available, and relies on rather severe assumptions far from equilibrium. So we decided to try to formulate a macroscopic theory of lossy processes in the tradition of reversible thermodynamics, and requiring as little additional information about the system as possible. The result is finite-time thermodynamics. Other researchers soon became interested in the topic and decisively influenced its development, notably Morton H. Rubin, Yehuda Band, and Luigi Sertorio.

The present booklet summarizes the most important results obtained so far, obviously with a bias toward work in which I have participated myself, but not to the exclusion of other contributions. The main text gives a qualitative overview without derivations, but emphasizing the general procedures and the continuity which is easily lost in the wealth of formal research papers, and might not even have been realized at the time of writing. The eleven papers reprinted in the appendices may be consulted for the detailed results.

Much of the work has been carried out while the collaborators visited each other, in Chicago, Copenhagen, Tel Aviv, Torino, and, not to forget, Aspen. The financial support for these visits, as well as for participation in meetings, from the Danish Natural Science Research Council (Statens Naturvidenskabelige Forskningsråd), the Danish Technical Science Research Council (Statens Tekniskvidenskabelige Forskningsråd), NATO Scientific Affairs Division, the National Science Foundation, and

Exxon is much appreciated. I also wish to thank Inge Teisen for her expert composition of this booklet and my wife Karin for taking such good care of me while it was being written as well as carefully proofreading the final product.

I am greatly indebted to my colleagues and collaborators, Yehuda Band, Michael Mozurkewich, Abraham Nitzan, Mary Ondrechen, Morton Rubin, Peter Salamon, Luigi Sertorio, and Bert de Vries for numerous discussions, some quiet some agitated, some in university offices some on mountain trails, but all inspiring. I also want to express my sincere gratitude to professor Thor A. Bak for his uninterrupted guidance, encouragement, and interest in my work since before I became a student. Fond memories go to all my friends from Chicago who have made life there so pleasant. But above all I wish to thank professor R. Stephen Berry for being such an inspiring and optimistic collaborator and terrific host. I have enjoyed immensely raising this 'baby' of ours with him, helping it develop and become strong, showing it around, and seeking friends for it. I hope to be able to continue this joint task.

Copenhagen, April 1983.

Bjarne Andresen

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1. EXTENSION OF THERMODYNAMICS TO FINITE-TIME PROCESSES

*Put up in a place
where it's easy to see
the cryptic admonishment
T. T. T.*

*When you feel how depressingly
slowly you climb,
it's well to remember that
Things Take Time.*

(Piet Hein: Grooks I)

1.1. Motivation

From its infancy, over 150 years ago, thermodynamics has provided limits on work or heat exchanged during real processes. The first problem treated in a systematic way was how much work a steam engine can produce from the burning of one ton of coal. With true scientific generalization Sadi Carnot concluded that *any* engine taking in heat from a hot reservoir at temperature T_H has to deposit some of that heat in a cold reservoir (e.g. the surroundings), whose temperature we call T_L ; the largest fraction of the heat which can be converted into work is

$$\eta_C = 1 - \frac{T_L}{T_H}, \quad (1)$$

traditionally known as the Carnot efficiency. This expression contains the two basic ingredients of a thermodynamic limit: a) it applies to *any* process converting heat into work; and b) it is an *absolute* limit, i.e. no process, however ingenious, can do better.

As thermodynamic theory developed, emphasis changed from process variables like work or heat exchanged to state variables like entropy and chemical potential. A bridge between the two are the thermodynamic work potentials, such as the Helmholtz free energy H for isothermal, isochoric processes or the Gibbs free energy G for isothermal, isobaric processes. They were defined such that their changes provide upper bounds on the work a process can supply or lower bounds on the work required

to drive a process. Gibbs introduced the concept of ‘available work’ as the maximum work that can be extracted from a system allowed to go from a constrained, internally equilibrated state to a state in equilibrium with its surroundings. This quantity is used more and more frequently in engineering contexts^{1,2} under the names ‘availability’ in the U.S. and ‘exergy’ in Europe. For a system relaxing to an ambient temperature T_0 , pressure P_0 , and chemical potentials μ_{0i} it is given by

$$A = U + P_0V - T_0S - \sum_i \mu_{0i}N_i \quad (2)$$

and is thus not a state function in the usual sense of depending only on variables of the system; the availability depends on the intensive variables of the environment as well. (The availability should not be confused with the true state function, the generalized Gibbs potential

$$G = U + PV - TS - \sum_i \mu_i N_i, \quad (3)$$

which transforms all extensive variables into conjugate intensive variables.) Related criteria of performance emerged, such as the effectiveness ϵ , the ratio of the actual work supplied by a work source to the change in availability of the system. The effectiveness ϵ has the advantage that its upper bound is always unity, compared to the efficiency η whose upper bound η_c depends on system parameters.

All these criteria have long been common currency for thermodynamic studies in physics, chemistry, and engineering. They all share one characteristic: The ideal to which any real process is compared is a *reversible process*. Stated in a different way, *traditional thermodynamics is a theory about equilibrium states and about limits on process variables for transformations from one equilibrium state to another*. Nowhere does time enter the formulation, so these limits must be the lossless, reversible processes which proceed infinitely slowly and thus take an infinite length of time to complete. However, referring back to the original question addressed by Carnot, who is interested in an engine which operates infinitely slowly (and thus produces zero power) — or any other process with zero rate of operation, for that matter? Consequently one must ask whether reversible limits are close enough to real performances to be useful comparisons and criteria. For some processes they are — large steam turbines, and the industrial fusion of hydrogen and nitrogen to form ammonia are two examples — but in most cases one is rather encouraged to seek more realistic limits to the performance of real processes. Is it possible to find general bounds for the costs of operating those processes in finite time, and can one use such bounds to find better criteria of merit for real processes?

1.2. Formulation

Finite-time thermodynamics is the extension of traditional thermodynamics to deal with processes which have explicit time or rate dependences. These constraints, of course, imply a certain amount of loss, or entropy production, which is at the heart of the questions posed at the end of the previous section. As our various results emerged, the theory seemed to crystallize around the following logical sequence of questions:

- What are the necessary and sufficient *conditions for the existence* of quantities — extensions of conventional thermodynamic potentials — whose changes give the extremal values of the process variables of heat or work that may be exchanged during a process, when the constraints on that process include constraints on the rate or the duration of the process? Naturally those generalized thermodynamic potentials should be functions of conventional thermodynamic variables of state, and necessarily depend on the constitutive parameters and the rate or duration. In addition they must depend on one or more time response parameters (relaxation coefficients) of the system. After all, if we are going to squeeze more physics out, we have to expect to put more physics into the problem.
- Are there *algorithms for evaluating* these generalized thermodynamic potentials or their changes, given the conditions for their existence? When we do evaluate them, what do we learn about the price we have to pay for operating processes faster or slower?
- Can we find the idealized but finite-time *pathways* that will yield the extremal work or heat exchange given by the generalized potentials? And how can we use these results to improve real processes?
- What are the operational differences among processes of the same kind but operating so as to *optimize different quantities*?

Complexity increases from one question to the next, so in short, question a) concerns just the existence of generalized potentials, question b) provides a single optimal value, question c) an entire optimal time path, and question d) compares time paths.

The processes for which the generalized thermodynamic potentials and time paths are to be constructed are not supposed to be extremely detailed descriptions of a specific real system, including all interconnections and losses — that would be duplicating the highly accurate, but far from general, simulations of the practicing engineer. Rather, finite-time thermodynamic systems and processes are idealized models which contain what is typical of a certain class of real systems. The construction of such *generic models* to represent broad classes of processes is central to finite-time thermodynamics. Each generic model should contain all the important qualities of the type of real systems studied, but not the individual details which would obscure the physical content and make calculations very difficult or impossible. We are already used to such models in traditional thermodynamics: The Carnot engine is, for example, the highly idealized reversible representation of all heat engines. Other standard reversible cycles, such as the air-standard Stirling, Brayton, Otto, Diesel, etc.

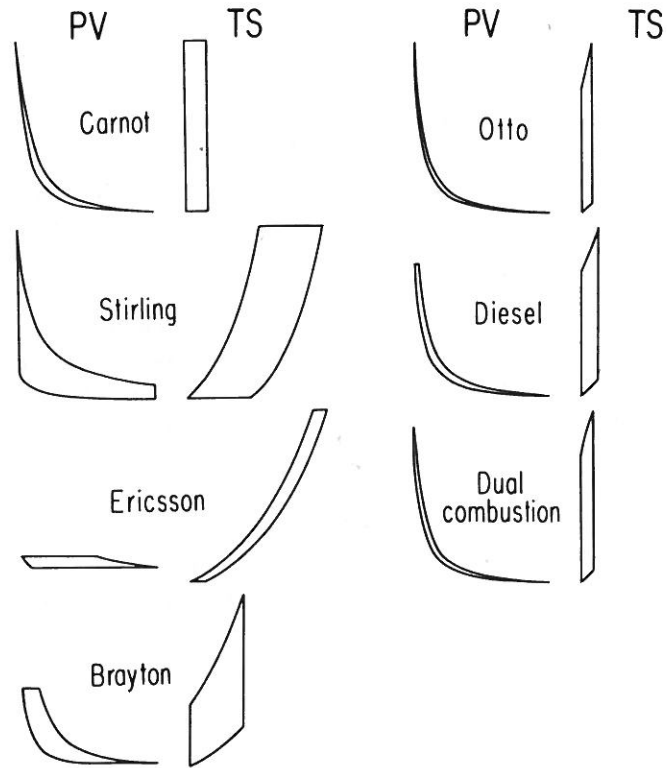


Figure 1. PV and TS diagrams on common scales for several standard heat engine cycles using ideal gas working fluid. The volume ratio $V_{max}:V_{min}$ is 10:1 for all the cycles, and the temperature ratio $T_{max}:T_{min}$ is 6:1 for all cycles except the Carnot cycle which has 3:1. (It cannot operate at 6:1 with a volume ratio of 10:1.) The branches of the cycles are listed in Table 1. The areas enclosed by the PV or the TS diagrams are proportional to the work produced in each cycle.

Table 1. Branches employed in several heat engine cycles.

Cycle	Adiabats	Isotherms	Isochors	Isobars
Carnot	2	2		
Stirling		2	2	
Ericsson		2		2
Brayton	2			2
Otto			2	
Diesel	2		1	1
Dual Combustion	2		2	1

cycles, have been useful for describing the limiting behavior of real heat engines. A selection of these is shown in Fig. 1 with their branches summarized in Table 1. Finite-time thermodynamics retains the same philosophy of model construction, but makes them somewhat more realistic. The first 'improvement' of the Carnot engine is the endoreversible engine shown in Fig. 2 (*endoreversible* means that all irreversibilities are located in the coupling of the system (engine) to its surroundings, there are no internal irreversibilities) of which Curzon and Ahlborn's engine³, mentioned below, is a special case.

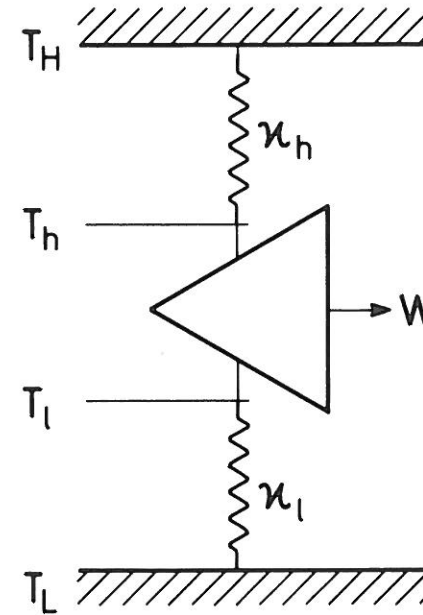


Figure 2. An endoreversible engine has all its losses associated with its coupling to the environment, there are no internal irreversibilities. This is illustrated here as resistances in the flows of heat to and from the working device indicated by a triangle. These unavoidable resistances cause the engine proper to work across a smaller temperature interval, $[T_h;T_l]$, than that between the reservoirs, $[T_H;T_L]$, one which depends on the rate of operation.

In the course of developing finite-time thermodynamics we discovered that a few isolated papers already had considered different aspects of processes operating at nonzero rates. The first of these was the important work of Tolman and Fine⁴ who put the Second Law of thermodynamics into equality form,

$$W = -\Delta A - T_0 \int_{t_i}^{t_f} \dot{S}_{tot} dt \tag{4}$$

by subtracting the work equivalent of the total entropy produced during the process from the reversible work, i.e. the decrease of system availability, as defined in eq. (2). The superscript dot indicates rate, and the integral limits are the initial and final times of the process. These authors used eq. (4) in a number of examples to derive more realistic bounds on work output from some physical and chemical systems, but they

did not develop the theory further, and in particular they did not search for an optimal process within the duration $\tau = t_f - t_i$. We will use eq. (4) as the starting point for defining a finite-time availability in Sec. 2.2.

Almost twenty years later the three-level laser was treated as a thermodynamic system by Geusic, Schulz-DuBois, and Scovil⁵ in a formalism that looks amazingly like one we later devised independently for macroscopic systems with heat leaks, friction, and finite rates of heat transfer⁶ (see Sec. 2.3). The laser analysis maximized the work that can be produced as light energy when the ratios of level populations define the reservoir temperatures.

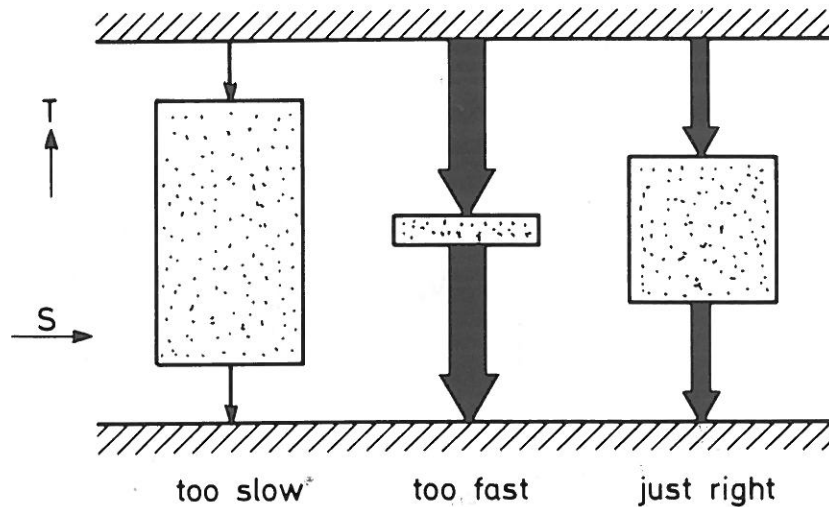


Figure 3. In this pseudo temperature-entropy plot for a heat engine operating between a hot and a cold reservoir, the area of each rectangle is proportional to the amount of work produced in each cycle. For slow operation, losses associated with heat transfer to and from the engine are small, but there are only a few cycles per second. Rapid operation achieves many cycles per second, but each one delivers little work. Maximum power is obtained at a compromise between rate and losses, and is therefore necessarily accompanied by a loss of efficiency compared with reversible operation.

Another model has evolved into almost a classic paradigm of systems operating in finite time. This is the model of Curzon and Ahlborn³, a Carnot engine with the simple constraint that it be linked to its reservoirs through *finite* heat conductances. Fig. 2 illustrates the slightly more general endoreversible system with the triangle signifying any reversible engine. It turns out that the results derived by Curzon and Ahlborn explicitly for an interior Carnot engine are equally valid for a general endoreversible system. The maximum efficiency of their engine is of course $\eta_c = 1 - T_L/T_H$, obtained

at zero rate so that losses across the resistors vanish, but these authors showed that, when the system operates to produce *maximum power*, the efficiency of the engine is only

$$\eta_w = 1 - \sqrt{\frac{T_L}{T_H}}. \quad (5)$$

Fig. 3 illustrates why there is a maximum to the power produced, and why this causes a drop in efficiency. Based on the numbers reproduced in Table 2, the paper also points out that typical power plants are properly so named, because their actual efficiencies indicate that they operate much nearer the point of maximum power than the point of maximum efficiency. In a recent paper⁷ Howe introduces additional loss terms in the central engine of Fig. 2 to make the system reflect reality a bit more. The efficiency at maximum power then loses the simplicity of eq. (5).

Table 2. Observed performance of real heat engines (power plants).
[From Ref. 3]

Power source	T_H [°C]	T_L [°C]	η_c [eq. (1)]	η_w [eq. (5)]	η [observed]
Coal fired steam plant	565	25	64.1%	40%	36%
PHW nuclear reactor	300	25	48.0%	28%	30%
Geothermal steam plant	250	80	32.3%	17.5%	16%

1.3. Other approaches

Originally thermodynamics was restricted to reversible reference processes to the degree that time-dependent, lossy processes only were treated in the form of inequalities, as for example for the Second Law

$$W \leq -\Delta A \quad (6)$$

rather than the exact equality form of eq. (4), i.e. as deviations from a reversible, infinitely slow process. The first to break away from this pattern and develop a theory of irreversible thermodynamics was Onsager⁸. His starting point was that the deviation ΔS of the entropy of the universe from its equilibrium value is a quadratic form in the deviations ΔB_i of the variables of the system from their equilibrium values,

$$\Delta S = -\frac{1}{2} \sum_{i,j} g_{ij} \Delta B_i \Delta B_j. \quad (7)$$

Further he assumed that the rate of return of the system variables toward their equilibrium values can be described by linear phenomenological equations,

$$\frac{d \Delta B_i}{dt} = - \sum_j M_{ij} \Delta B_j, \quad (8)$$

where the M_{ij} are the phenomenological coefficients. Defining conjugate thermodynamic forces

$$X_i \equiv \frac{\partial \Delta S}{\partial \Delta B_i} = - \sum_j g_{ij} \Delta B_j \quad (9a)$$

and fluxes

$$J_i \equiv \frac{d \Delta B_i}{dt}, \quad (9b)$$

such that the rate of entropy production is a bilinear expression in the forces and fluxes,

$$\frac{dS}{dt} = \sum_i J_i X_i, \quad (10)$$

and transforming the phenomenological coefficients M_{ij} to these new variables,

$$L_{ij} = \sum_k g_{kj}^{-1} M_{ik}, \quad (11)$$

he arrived at the celebrated Onsager reciprocal relations,

$$L_{ij} = L_{ji}, \quad (12)$$

which reduce the number of independent coefficients from n^2 to $n(n+1)/2$. In his very thorough analysis of the minimum entropy production principle⁹, Jaynes distills the assumptions necessary to obtain the reciprocal relations generally into the following three:

- the phenomenological equations are linear and have no memory;
 - fluctuations around a point away from equilibrium decay in the same manner as fluctuations around equilibrium;
 - correlations of fluctuations evolve forward and backward in time in the same way, i.e. they follow a sort of 'microscopic reversibility' at small but not atomic levels.
- Since in particular assumption b) is very restrictive, this means that the validity of the reciprocal relations for realistic models is usually restricted to the vicinity of equilibrium.

All the subsequent work in 'irreversible thermodynamics', as represented e.g. by the books by Prigogine¹⁰, de Groot and Mazur¹¹, Tykodi¹², and Truesdell¹³, rests on Onsager's approach. The central point is to *write down a set of dynamical equations*

for the thermodynamic state variables of the system and subsequently solve them — under various assumptions. By contrast, finite-time thermodynamics is based on the four basic questions of Sec. 1.2, which amount to a search for the *effects of time or rate constraints on the process variables and hence the performance of a process*. The focus of irreversible thermodynamics on dynamical equations leads naturally to a formulation in terms of differential equations and to examination of the local, differential behavior of systems. The focus of finite-time thermodynamics on the net changes of process variables leads to integral equations, variational principles, and global descriptions of systems. There are, of course, many points of contact between the two approaches, but as yet only the simplest relationships between the two have been explored. As some of the examples will show, the viewpoint of finite-time thermodynamics sometimes makes it easier to address questions generally. For example, the global view may help to expose the extent to which assumptions of linear behavior, such as the assumption of linear phenomenological equations (8), limit the applicability of an analysis and may even lead to more general approaches¹⁴.

The approach of finite-time thermodynamics also differs in two ways from that of the practicing engineer. The engineer optimizes a model which is as detailed a representation as possible of the particular system he wants to build or use. This typically leads to an elaborate and specific simulation. Our approach, by contrast, aims to isolate how the dominant temporal characteristics of each broad class of processes set limits on the performance of that class. Secondly, the engineer typically optimizes the values of key *parameters* of the apparatus, whereas finite-time thermodynamic optimizations, in their most elaborate form, find the temporal *path* that maximizes the performance of a process (Chapter 3). When it suffices to know the extremal work or heat for a process, the more elaborate optimal control treatment can be avoided by constructing a suitable generalized potential (Chapter 2).

An entirely different approach for finding the optimal value of thermodynamic variables relies on the information-theoretic 'maximum entropy' formalism¹⁵. The essence of the method is to find that partition function for the system which maximizes our ignorance (the entropy) subject only to the few macroscopic constraints, so that the number of free parameters is still of the order of Avogadro's number. Specifically, if P_i is the probable fractional population of the i th level, then one postulates that the distribution over all the quantum states of the system takes on that form which maximizes the quantity $-k \sum_i P_i \ln P_i$, subject to whatever constraints are given. This maximized sum is then identified as the entropy S . The relation between the maximum entropy approach and thermodynamic availability was established by Schlögl and later repeated by Procaccia and Levine¹⁶. It has proven very successful also in other areas, such as spectral analysis¹⁷ and atomic and molecular collision theory¹⁸.

2. PERFORMANCE BOUND WITHOUT PATH

*To start in a hurry
and finish in haste
will minimize worry
and maximize waste.*

(Piet Hein: Grooks V)

The smallest amount of information one can ask for concerning the performance of a system is a single number, e.g. the work or heat exchanged during the process, its efficiency, or any other figure of merit. In most cases this can be calculated without knowledge of the path followed and is then computationally much simpler to obtain. This amounts to the second of our basic questions in Sec. 1.2 (implicitly expecting question one, the existence conditions, to be fulfilled).

2.1. Generalized potentials

In traditional thermodynamics potentials are used to describe the ability of a system to perform some kind of work under given constraints. These constraints are usually the constancy of some state variables, like pressure, volume, temperature, entropy, chemical potential, particle number, etc. Under such conditions the decrease in thermodynamic potential P from state i to state f is equal to the amount of work that is produced when a reversible process carries out the transition, and hence is the upper bound to the amount of work produced by any other process,

$$W \leq W_{\text{rev}} = P_i - P_f. \quad (13)$$

In this section¹⁹ we will show that the constraints need not simply be the constancy of some state variable, and that the potentials may be generalized to contain constraints involving time. The procedure will be a straight forward extension of the Legendre transformations²⁰ used in traditional thermodynamics^{21,22}, and we will start with such an example.

In a reversible process heat and work can be expressed as inexact differentials,

$$dQ = TdS, \quad dW = PdV, \quad (14)$$

i.e. they cannot by themselves be integrated, further constraints defining the integration path are required. Such a constraint could be that the process is isobaric, $dP=0$. One can then add a suitable integrating zero-term $x dP$ to make dW an exact differential. The obvious choice is $x=V$,

$$dW = PdV = PdV + VdP = d(PV), \quad (15)$$

such that the isobaric work potential becomes $P=PV$. Similarly the isobaric heat potential $U+PV$ is obtained from

$$dQ = TdS = dU + PdV = dU + PdV + VdP = d(U+PV), \quad (16)$$

where the First Law of thermodynamics

$$dU = TdS - PdV \quad (17)$$

has been used. Table 3 shows the results of this procedure for the classical examples.

Table 3. The classical thermodynamic potentials for the process variables of work $dW = PdV$ and heat $dQ = TdS$.

Process type	Zero along process	Integrating term	Work potential	Heat potential
Isobaric	dP	VdP	PV	$U+PV$
Isothermal	dT	SdT	$TS-U$	TS
Isochoric	dV	$-PdV$	0	U
Isentropic	dS	$-TdS$	$-U$	0

Now, the constraint need not be the constancy of one of the state variables. Consider a balloon with constant surface tension α . In equilibrium with an external pressure P_{ex} such a sphere of radius r has an internal pressure

$$P = P_{\text{ex}} + \frac{2\alpha}{r}, \quad (18)$$

which can be rearranged into

$$(P - P_{\text{ex}})V^{1/3} = 2\alpha \left(\frac{4\pi}{3}\right)^{1/3}. \quad (19)$$

Since the right hand side of this equation is a constant, this means that $(P - P_{ex})V^{1/3}$ is an integral of motion for the fluid inside the balloon. We can then add a suitable amount of $d[(P - P_{ex})V^{1/3}] (= 0)$ to dW to make it exact,

$$dW = PdV = PdV + \frac{1}{2}V^{2/3}d[(P - P_{ex})V^{1/3}] = d[\frac{1}{2}V(3P - P_{ex})]. \quad (20)$$

Thus the work done by the coupled system surface + fluid is given by the decrease in the potential $P = \frac{1}{2}V(3P - P_{ex})$, regardless of path followed.

In its most general form the Legendre transformation can be used to calculate a potential P for the arbitrary process variable B , expressible as a path integral in terms of generalized forces and displacements,

$$B = \int \mathbf{f} \cdot d\mathbf{x}; \quad (21)$$

B will usually be work. To find P , one adds to $\mathbf{f} \cdot d\mathbf{x}$ an integrating term $\mathbf{g} \cdot d\mathbf{y}$, where $d\mathbf{y}$ is necessarily zero as a result of the constraints defining the process. Note that $d\mathbf{y} = \mathbf{0}$ may involve time and could come from a condition in the form of a differential equation as well as from the more familiar thermodynamic condition of a constant variable, as used in the example above. Hence the differential form $d\mathbf{y} = \mathbf{0}$ is used rather than the integrated form $\mathbf{y} = \text{constant}$, since \mathbf{y} itself may not exist. The mathematical problem of finding P has two steps, finding a function \mathbf{g} which makes $d\omega = \mathbf{f} \cdot d\mathbf{x} + \mathbf{g} \cdot d\mathbf{y}$ an exact differential dP , and then finding P itself. The first step involves the Cauchy-Riemann condition that $d\omega$ has equal cross derivatives with respect to the free state variables, e.g. a and b :

$$\frac{\partial}{\partial b} [\mathbf{f} \cdot (\frac{\partial \mathbf{x}}{\partial a})_b + \mathbf{g} \cdot (\frac{\partial \mathbf{y}}{\partial a})_b] = \frac{\partial}{\partial a} [\mathbf{f} \cdot (\frac{\partial \mathbf{x}}{\partial b})_a + \mathbf{g} \cdot (\frac{\partial \mathbf{y}}{\partial b})_a] \quad (22)$$

or

$$(\frac{\partial \mathbf{g}}{\partial a})_b \cdot (\frac{\partial \mathbf{y}}{\partial b})_a - (\frac{\partial \mathbf{g}}{\partial b})_a \cdot (\frac{\partial \mathbf{y}}{\partial a})_b = (\frac{\partial \mathbf{f}}{\partial b})_a \cdot (\frac{\partial \mathbf{x}}{\partial a})_b - (\frac{\partial \mathbf{f}}{\partial a})_b \cdot (\frac{\partial \mathbf{x}}{\partial b})_a. \quad (23)$$

With \mathbf{f} , $d\mathbf{x}$, and $d\mathbf{y}$ known, this is the equation from which \mathbf{g} may be obtained. In the usual case of $\mathbf{f} = P$, $d\mathbf{x} = dV$, $a = V$, and $b = P$, the right hand side of eq. (23) simplifies to 1. The second step in finding P , the integration of dP , is, of course, only unique within a constant of the motion; i.e. two methods of integration may yield two different potentials P and P' , but their variations will always be the same, $\Delta P = \Delta P'$.

Whereas for reversible processes there is no question that thermodynamic potentials exist, because the process can always be reversed or go by way of an arbitrary third state, this is not obvious for generalized potentials with built-in time dependence and possible loss terms. In generalizing the Legendre transformation above, we have implicitly assumed the existence of a potential or, equivalently, a solution to eq. (23). The conditions for existence are¹⁹:

- a) the process is quasistatic, and
- b) the process variable can be expressed as a path integral [eq. (21)].

The quasistaticity is equivalent to saying that the relaxation times of the system are negligible compared to the time scale of the process. In other words, the system is not required to be in equilibrium with its surroundings at all times, but all state variables must be defined (make sense) at a countable pointset along the path. The second condition is similar in content, because this seemingly trivial condition is violated when one tries to describe the extraction of work from a system at a rate faster than that system can equilibrate internally (think of a combustion process). In such a case thermodynamic variables lose their meaning, and one must go to a definition of work in terms of energy transfer at the microscopic level, which sometimes can be too complex to be useful. Nevertheless, work and availability can be defined for some systems, such as simple lasers whose operation depends on changes in populations of specific quantum states⁵. Another approach relies on the information-theoretic 'maximum entropy' formalism described in Sec. 1.3.

2.2. Finite-time availability

Probably the most powerful result in finite-time thermodynamics obtained so far is the definition of a finite-time availability²³. As mentioned in Sec. 1.1, the traditional availability A of a system in contact with given surroundings is a state function with the quality that the decrease in its value in going from state i to state f is the maximum (and hence reversible) work that can be extracted during that process. The finite-time availability A retains this property and simply adds that the process is restricted to operate (go to completion) during time $\tau = t_f - t_i$. Then

$$A = W_{\max}(\tau) = \max [A(t_i) - A(t_f) - T_0 \int_{t_i}^{t_f} \dot{S}_{\text{tot}} dt], \quad (24)$$

where the last equality uses the Tolman-Fine form⁴ of the Second Law of thermodynamics, eq. (4).

The extension may seem trivial, but the principal content lies in the way the maximization is carried out, or rather restricted. It must be carried out within the constraints imposed on the process, temporal or otherwise. These constraints in effect define a generic model (cf. Sec. 1.2) which constitutes the confines within which we expect to be able to modify our real system in order to improve its performance. As mentioned when we introduced the notion of a generic model, these constraints should not be excessively detailed, but only contain the essential loss terms and limiting factors in the process, otherwise the calculations will become unwieldy. Of course, if one is going to use the finite-time availability to compare the performance of two different processes, they must be represented by the same generic model. Otherwise a path allowed in one may not be available to the other process, and such a restriction

always costs performance. An example of this is the apparent paradox of Ben-Shaul and Levine's²⁴ lasing system, that introducing a relaxation, i.e. a loss process, will increase the light output. As stated the comparison is not allowed, because the first system lacks a connection available in the second. Thus losses are not always detrimental to the performance of a system if they open up new pathways — actually some processes depend on irreversibilities for their very existence²⁵. We are currently investigating the effects of varying the parameters of a system in general.

In addition to the above considerations, the maximum search in eq. (24) can either be constrained to exactly reach a given final state at time t_f (the initial state is always considered known), in which case ΔA is fixed, and the optimization becomes one of minimizing the entropy production, or also the final state may be included in the optimization, in which case A must be evaluated by optimal control. If the final state is specified, a solution may not exist if τ is too short, since only a certain set of states can be reached from a given initial state in time τ . In addition, the finite-time availability does not necessarily have ΔA as its limit for very long times, because the system may contain internal relaxation processes which remain irreversible even for very slow operation. If there is a direct heat leak from the system reservoir to the surroundings, then a long process time may even reduce A to zero.

As defined, the finite-time availability is as general as the traditional availability, i.e. it can be applied to *any* thermodynamic process. Sec. 3.1 describes an optimal control calculation²³ of the finite-time availability for a work-producing system with competing internal relaxation which can be interpreted as heat engines, internal molecular degrees of freedom, a hydraulic system, or a chemical reaction, simply by changing nomenclature.

2.3. The tricycle formalism

An entirely different way to assess the cost of finite-time operation is through the 'tricycle' formalism⁶, a construction based on conservation equations for the process in question. A heat exchange system is represented pictorially in Fig. 4 by a triangle with heat flows q_1 , q_2 , q_3 into reservoirs with temperatures T_1 , T_2 , T_3 . A conventional heat engine or refrigerator is a special case with one of the temperatures, e.g. T_1 , infinite, such that no entropy flow is associated with this energy flow, and q_1 is identifiable as work. Any such process can then be divided into its reversible part with zero entropy production, $s=0$, and a totally irreversible component (see Fig. 4). Nothing new, of course, is learned from such a decomposition per se, but by putting in specific loss mechanisms like heat resistance, friction, and heat leak, the rate dependencies of such irreversibilities can be deduced. It may seem that these three loss mechanisms should be treated individually, but they are in fact interdependent and can be solved simultaneously.

A convenient way to represent the results is a contour diagram or a three

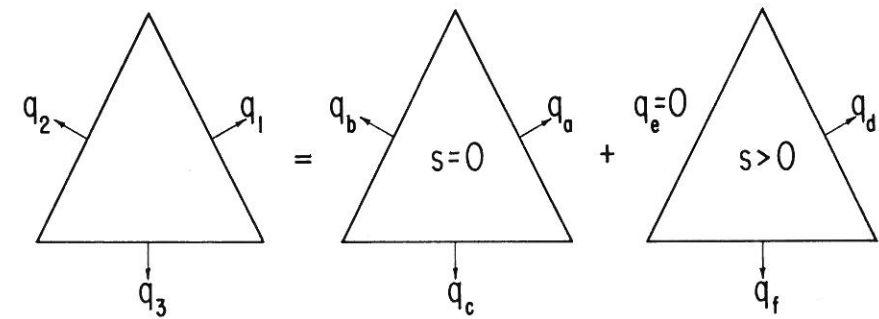


Figure 4. Tricycle decomposition of the general heat flows q_1 , q_2 , q_3 of a process into reservoirs with temperatures T_1 , T_2 , T_3 in terms of a reversible component and a totally irreversible component.

dimensional plot like Fig. 5, where the height represents power output for a heat engine/heat pump. Reduced variables are used such that the ordinate is a measure of rate, and the abscissa has friction, relative to thermal resistance, increasing to the right (for details see Ref. 6). First of all one observes that the rate coordinate is divided into three distinct regions. The system operates as a heat pump for all negative values and as a heat engine for positive rates, but only up to a certain limit. The region above that limit (9 with the parameters used in Fig. 5) is inaccessible because such large rates would require negative temperatures to overcome the resistances. The loci of maximum power are indicated by heavy line, and for negligible friction (to the far left) there is indeed one such maximum, as discussed for the endoreversible engine in Sec. 1.2. This remains unchanged as friction increases until a point where a classical bifurcation splits the locus of maximum power into two with a minimum in between. Thus in this region there are two quite different heat rates which yield (actually identical) maxima in the power production, obviously at vastly different thermal efficiencies. The friction parameter divides the space into distinct heat resistance- and friction-dominated regions. No such structure exists in the heat pump region, not even a single maximum, since there is no limit to how much power can be put in to speed up the pump.

The advantage of such diagrams over a single optimum-performance number is that one can also read the penalty for off-optimum operation — in the low-friction region of Fig. 5 it is, for example, very slight. Similar diagrams can of course be drawn for the efficiency⁶ or any other objective function.

The tricycle formalism with the reversible contributions separated off enables one to focus on the losses and calculate which are the most serious ones. Certain processes, like ordinary distillation, have unavoidable irreversibilities built into them. It will then be convenient to divide the loss-tricycle further into one for unavoidable losses and

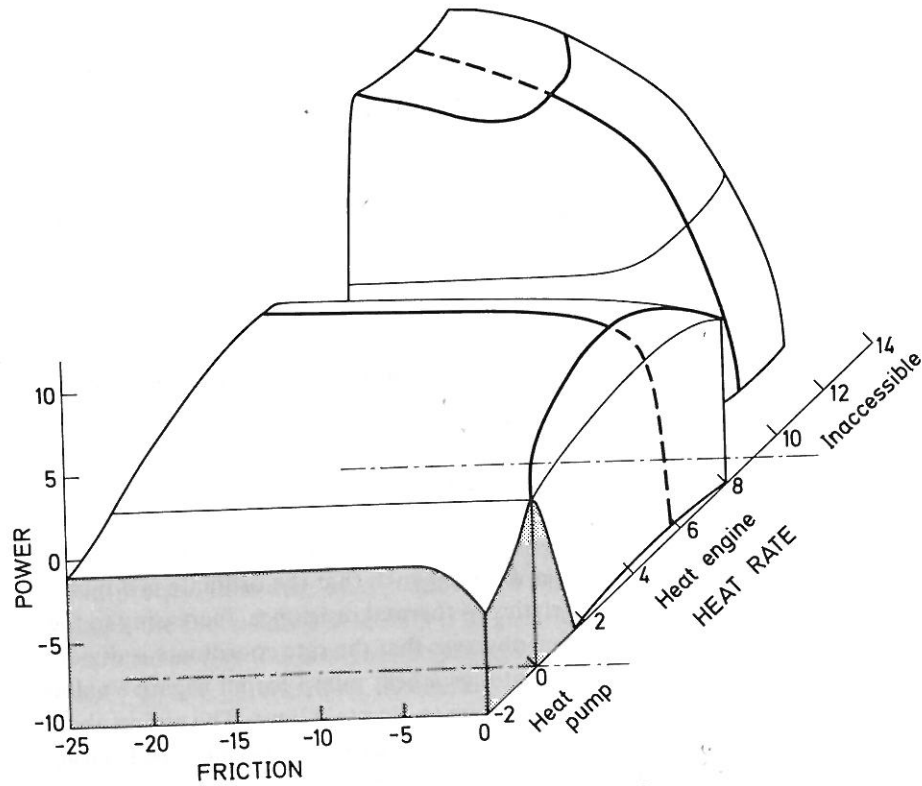


Figure 5. The power output for an endoreversible engine/heat pump with heat resistances to its reservoirs and friction as function of its rate of operation and frictional coefficient (increasing to the right); everything is scaled with the heat resistances. The heat rate divides the mode of operation into three regions: acting as a heat pump, acting as a heat engine, and an inaccessible region where heat transfers exceed the physically possible. Extrema are indicated by heavy line. Thus the mode of operation of the heat engine is also divided into a heat resistance dominated region with one maximum (to the left) and a friction dominated region with two maxima (to the right).

one for the excess losses, as shown in Fig. 6. Comparing different (e.g. separation) processes, the latter then tells how much room there is for improvement of this particular process, and the former how much energy can be saved by developing an entirely new, more nearly reversible process.

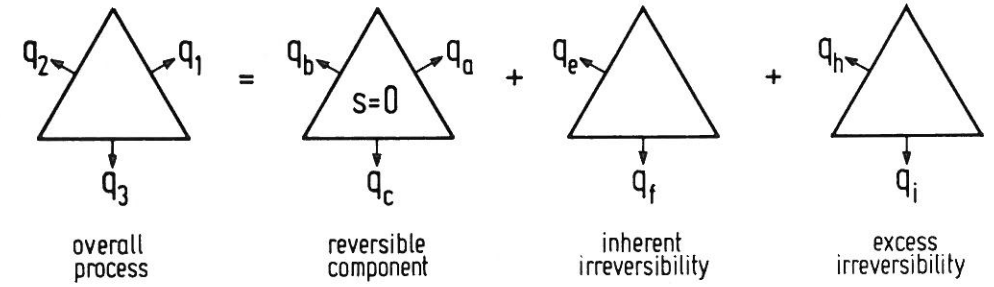


Figure 6. Tricycle decomposition of the general heat flows q_1, q_2, q_3 of a process into the reservoirs with temperatures T_1, T_2, T_3 in terms of reversible, inherent irreversible, and excess irreversible components. Part one is the payload, part two characterizes the process used, and part three the equipment for this process. Such a decomposition is particularly useful for comparing intrinsically irreversible processes such as separation.

2.4. Geometric formulation

The heat rates q_1, q_2, q_3 of the tricycle formalism lend themselves readily to a geometric representation⁶ as the independent coordinates in a three-dimensional heat-rate space. In this space energy conservation $\sum_i q_i = 0$ defines a plane. Similarly, the Second Law of thermodynamics $\sum_i q_i/T_i \geq 0$ defines a half-space of spontaneous processes with the limiting plane containing all isentropic processes. The intersection of the two planes, then, is the line of reversible processes, bounding the physical half-plane where all real processes $\mathbf{q} = (q_1, q_2, q_3)$ must lie. The situation is pictured in Fig. 7. In this framework the decomposition of Fig. 4 becomes

$$\mathbf{q} = \mathbf{q}_r + \mathbf{q}_r^\perp, \tag{25}$$

where \mathbf{q}_r is a vector along the reversible line, and \mathbf{q}_r^\perp is the irreversible component 'perpendicular' to \mathbf{q}_r . Unfortunately thermodynamics does not define a unique irreversible process — in Fig. 4 it was taken to be the degradation of heat from temperature T_1 to T_3 (or vice versa), but it could just as well have been from T_2 to T_3 (or vice versa) or any combination — so there is considerable freedom to define a metric which yields convenient formulas; Ref. 6 contains two choices. Geometrically the ambiguity amounts to the question of what is 'perpendicular', apart from scale factors.

Regardless of choice of metric we define the *drive*

$$\delta \equiv q_r^\perp/q \tag{26}$$

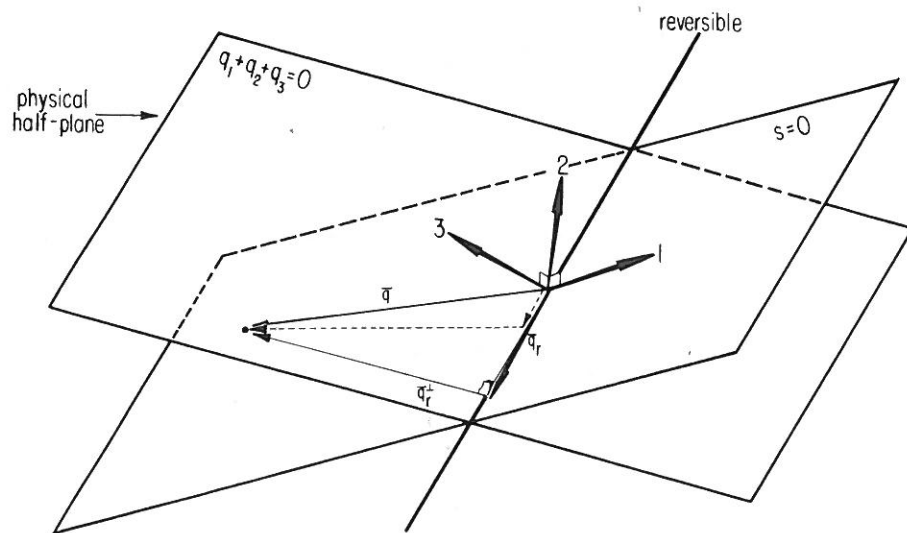


Figure 7. Tricycle space with the planes defined by conservation of energy and by zero entropy production. Real processes lie on the 'physical half-plane' indicated, with the reversible limit given by the intersection of the two planes. Two decompositions of a general tricycle $\mathbf{q} = (q_1, q_2, q_3)$ into its reversible and irreversible components (cf. Fig. 4) are shown. The *drive* is defined as the ratio of the length of the irreversible component q_r^+ to the total length of \mathbf{q} , the vector representing the real process.

as a useful dimensionless measure of the irreversibility of the process. It is zero for a reversible process and unity for a process containing no reversible component q_r . The drive thus is a convenient generalization of the efficiency η which is only defined for processes involving work.

About the same time, Weinhold identified²⁶ the quantities $\partial^2 U / \partial X_i \partial X_j$, where U is the internal energy, and X_i and X_j are extensive variables, as a metric on the abstract space of equilibrium states of a system. He proposed using the corresponding vector quantities as a more direct and transparent way of calculating all the well known partial derivatives in traditional thermodynamics. However, second derivatives are usually identified as curvatures and, as such, should be interpreted as availabilities in Gibbs space (U as a function of all the extensive variables). This lead us to seek another interpretation of pathlengths calculated with Weinhold's metric, and we found²⁷ that they always are changes in some molecular velocities, depending, of course, on the constraints of the process (isobaric, isochoric, etc.).

Subsequently Salamon and Berry²⁸ found a connection between the Weinhold length along a process path and the (reversible) availability lost in the process. Specifically, if the system moves via states of local thermodynamic equilibrium from an initial

equilibrium state i to a final equilibrium state f in time τ , then the dissipated availability $-\Delta A$ is bounded by the square of the distance (i.e. length of the shortest path) from i to f times ϵ/τ , where ϵ is a mean relaxation time of the system. If the process is endoreversible, the bound can be strengthened to

$$-\Delta A \geq L^2 \epsilon / \tau, \quad (27)$$

where L is the length of the *traversed* path from i to f . The geometry is illustrated in Fig. 8.

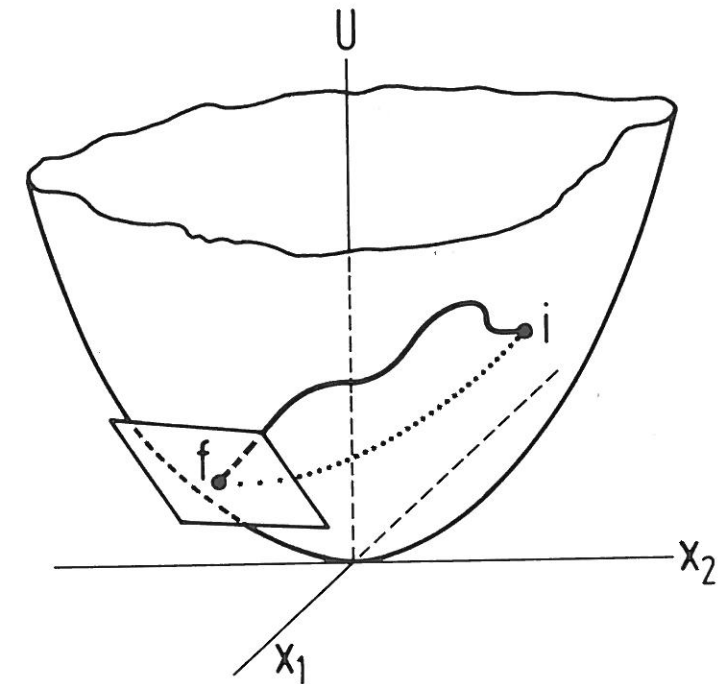


Figure 8. In this thermodynamic state space picture the internal energy U is plotted as a function of the extensive variables X_1 and X_2 . The paraboloid represents equilibrium states of the system. A system initially in state i can move toward equilibrium with the environment at point f , represented by the tangent plane, along an infinite number of internal equilibrium paths. The length of the shortest of these (dotted) is determined by the Weinhold metric, but the actually traversed path (solid) may be longer. The availability dissipated in the process is related to the square of this distance divided by the duration of the process.

The complete group of coordinate transformations which preserves the Weinhold length has been derived by Salamon, Ihrig, and Berry²⁹. Rather surprisingly, of the

large number of Legendre transformations implied in Sec. 2.1, only that which changes the free coordinates from all extensive to all intensive (and vice versa) is included in this group. Consequently, the internal energy U and the Gibbs free energy G share the same Weinhold length, but that is different from the one for, say, the Helmholtz free energy H .

2.5. Finite-time thermodynamics in economics

Let us close this chapter by pointing out that finite-time effects also have a bearing on economic theory³⁰. In economics one usually assumes that energy (-consumption) and capital are substitutable quantities: If one builds expensive machinery one can reduce the energy consumption in the process, and vice versa. This is illustrated by the so-called production function in Fig. 9; each of the 'hyperbolas' is an isoquant, the locus of tradeoff between energy and capital for a certain production rate of one's product. The slope of the diagonal line represents the price of energy relative to that of capital, such that the most economical point of operation is the point of tangency between one of these parallel lines and the required isoquant. Now, conventional economic theory assumes complete substitutability between energy and capital (dashed curves), whereas finite-time thermodynamics tells us that the energy consumption depends on the rate of production, requiring more energy the higher the rate (solid curves). This implies that the economically optimal consumption of energy is larger than that calculated from conventional production functions. If, on the other hand, one wishes to operate 'within ϵ ' of the energy asymptote P , this is only advantageous if the price of energy exceeds $-dK/dE$.

The thermodynamic constraints from finite-time operation can be used in economic analysis in two different ways:

- One can calculate the total cost C of producing the quantity Q of product in a given time, consisting of the capital cost for a plant of a certain size plus the operating cost for optimal operation at a rate r necessary to produce Q . Obviously, there is a tradeoff between a larger plant operating at a lower rate (and therefore usually at higher efficiency) and the capital cost of that plant, so one can find the economic optimum by either minimizing C for fixed Q or maximizing Q for fixed C .
- One can add information about the operating and capital costs as functions of rate to the definition of the extremal equations and solve them with constrained product quantity Q .

Both procedures will arrive at the same optimum, so it is a matter of taste whether one prefers the black-box approach of b) or is interested in the intermediate physical information of a).

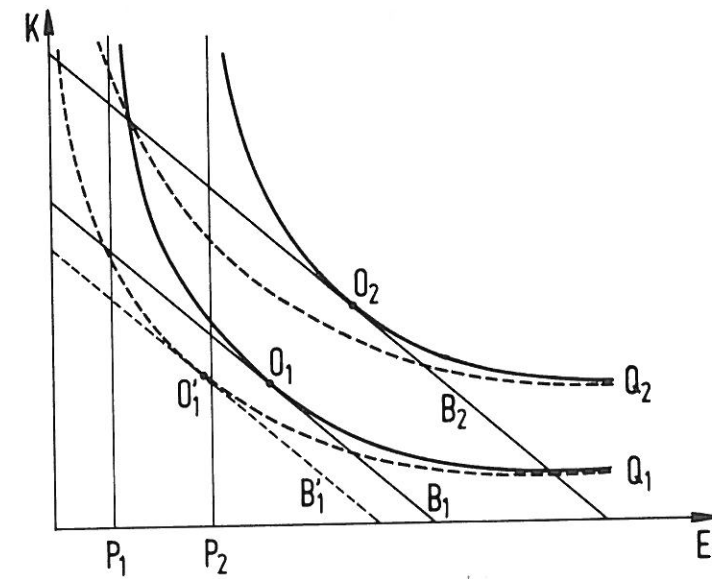


Figure 9. Production isoquants Q_1 and Q_2 ($Q_1 < Q_2$) with two substitutable input factors E (energy) and K (capital). Finite-time thermodynamics predicts energy asymptotes P_1 and P_2 for the production rates Q_1 and Q_2 , respectively, while traditional economic theory assumes complete substitutability of the input factors (dashed curves). The relative prices of E and K determine the slope of the budget lines B and thus the optimum operating points O .

3. OPTIMAL PATH

*Does time exist?
I gravely doubt it.
But gosh, what should we do
without it?*

(Piet Hein: Grooms III)

3.1. Optimal path calculation

A knowledge of the maximal work that can be extracted during a given process, e.g. calculated by one of the procedures described in the previous chapter, may not itself be sufficient. One may also want to know *how* this maximum work can be extracted, i.e. to specify the time path of the thermodynamic variables of the system. The tool for obtaining this path is optimal control theory.

This is not the place to repeat the mechanics of optimal control calculations; Ref. 31 contains a few standard texts on the method. Let it suffice to point out that in order to set up the optimal control problem one must specify

- the controls, i.e. the variables that can be manipulated by the operator (they may be a volume, rate, voltage, heat conductance, etc.);
- limits on the controls and on the state variables, if any (in order to avoid unphysical situations such as negative temperatures and infinite speeds);
- the equations that govern the time evolution of the system (they will usually be differential equations describing heat transfer rates, chemical reaction rates, friction, and other loss mechanisms);
- the constraints that are imposed on the system (e.g. the conserved quantities, the quantities held constant, or any requirements of reversibility. The constraints may either be differential, instantaneous i.e. algebraic, or integral i.e. not obeyed at each point but over the entire interval);
- the desired quantity to be maximized, called the objective function (usually expressed as an integral); and finally
- whether the duration of the process is fixed or part of the optimization.

Typical manipulation usually leads to a set of coupled, non-linear differential equations for which a qualitative analysis and a numerical solution are the only hope. Thus answering the more demanding question about the optimal time path rather than the standard question about maximum performance requires a considerably larger computational effort. On the other hand, once the time path is calculated, all other

thermodynamic quantities may be calculated from it, much like the wave function is the basis of all information in quantum mechanics.

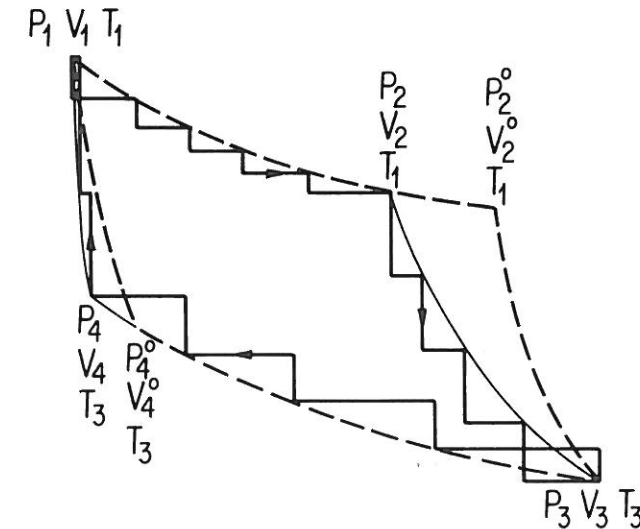


Figure 10. PV diagram of the step-Carnot cycle (heavy line) with its envelope (light line) and the reversible Carnot cycle (dashed) operating between the same extreme states. The indicated pressure for the step-Carnot cycle is the external pressure, not the internal pressure which may be undefined except at the points touching the envelope.

Our first attempt³² to calculate an optimal time path considered a sufficiently simple system that it could be solved without the use of optimal control theory. It was the 'step-Carnot' cycle, a model of a heat engine which strives to follow a Carnot cycle, but where the unlubricated stick-slip motion of the piston produces discontinuous changes in the external pressure, as shown on Fig. 10. Thus the working fluid comes into equilibrium with the surroundings only at a finite number of points around the cycle (cf. the requirement of quasistaticity as one of the conditions for the existence of a generalized potential, Sec. 2.1). The objective is to distribute the fixed number of equilibrium points in such a way as to maximize either the efficiency (work output divided by heat input), the effectiveness (work output divided by theoretically possible reversible work output), or the produced work; the two latter are equivalent. Because of the finite number of equilibrium points this system can be treated by ordinary calculus. Nevertheless, it already contains some of the features found in all finite-time processes: The optimal solution depends on what is optimized (see Sec. 3.2), and the performance degrades with decreasing duration (here: number of steps). The exact form of the solution is unimportant at this point.

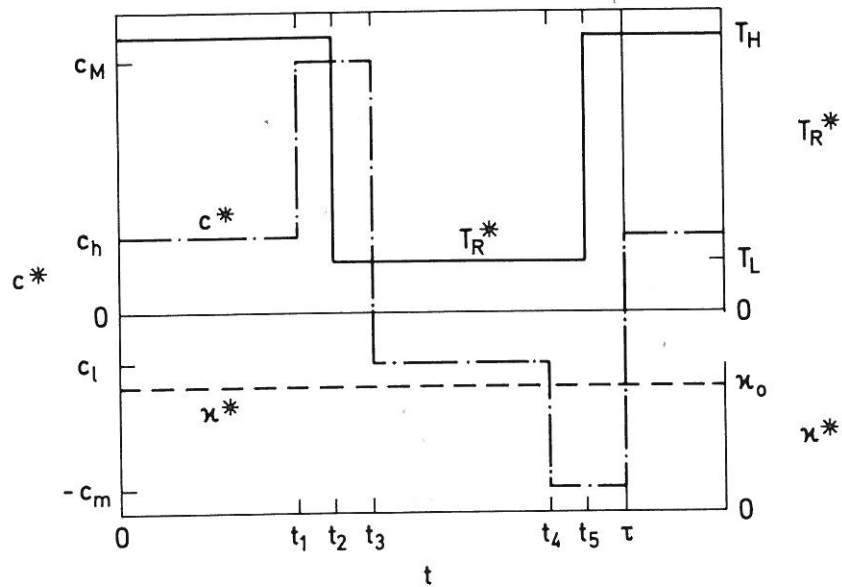


Figure 11. The optimal controls over a period τ for an unrestricted optimization of the endoreversible engine (Fig. 2). $c^*(t) = \dot{V}/V$ is the relative rate of change of volume, and $\kappa^*(t)$ is the heat conductance to the reservoir with temperature $T_R^*(t)$. Note that, except for the rate of change of volume on the isothermal branches $[0; t_1]$ and $[t_3; t_4]$, only the extreme values of the controls are required.

Gutkowicz-Krusin, Procaccia, and Ross made the first attempt³³ to calculate the best time path for the endoreversible engine, but the first full-fledged application of optimal control theory to a finite-time system is due to Rubin³⁴. He calculated the optimal time path for the general endoreversible engine of Fig. 2 which maximizes its power output. Without any restrictions as to type of branches, but only limiting the reservoir temperatures, heat conductances, and rate of change of volume, he found the optimal cycle to consist of six branches: two isotherms and four maximum-power branches, but no adiabats. The optimal controls (reservoir temperature, heat conductance, and relative rate of volume change) are shown in Fig. 11, and the optimal state variables (temperature and pressure) in Fig. 12. Note that only the extreme available temperatures, T_H and T_L , are required, as is the maximum conductance to the reservoirs. The adiabats of a Carnot cycle are replaced by the maximum-power branches along which the volume changes at its maximum permissible rate while the working fluid is still in contact with one or the other heat reservoir. Thus the optimal cycle is never isolated from both its reservoirs. If the limitation on the rate of volume change is lifted, these new branches proceed instantaneously and in effect become adiabats. This

optimal cycle is the finite-time equivalent of the Carnot cycle in reversible thermodynamics and serves the same purpose, viz. as an idealized reference process for evaluation of real cycles. Curzon and Ahlborn's assumption of an interior Carnot cycle in their system³ (see Sec. 1.2) is now justified by this optimization. Another important property of the Carnot cycle, its staging, is explored for endoreversible engines in Sec. 4.1.

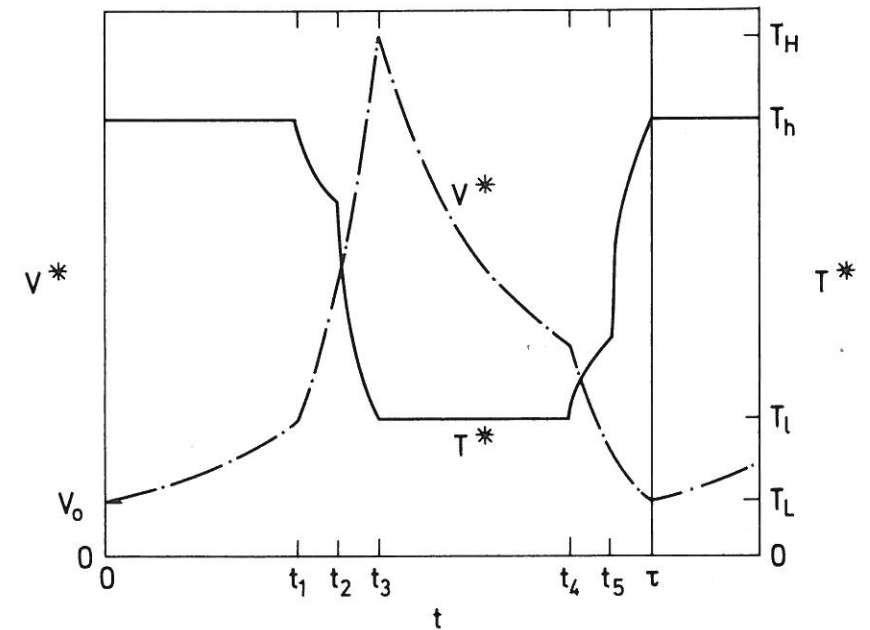


Figure 12. The optimal trajectories associated with the controls in Fig. 11. $V^*(t)$ and $T^*(t)$ are the volume and temperature of the working fluid, respectively.

In a subsequent study³⁵ Rubin made his system more realistic by restricting the compression ratio, i.e. the ratio between the largest and the smallest volume, to a fixed value. With this constraint the number of branches in the optimal cycle increases to eight: Two fixed-volume branches enter where each pair of maximum-power branches meet. These branches allow the working fluid to heat up or cool at its volume limits.

About the same time we analyzed¹⁴ the performance of endoreversible heat engines in terms of their entropy production. Minimizing that is equivalent to minimizing the loss of availability, but not to maximizing efficiency or power, as most other studies have done. The system exchanges generalized fluxes with the surroundings at a rate which depends on the generalized forces in a completely arbitrary way, but not on time or any time-derivative of the forces. Then, regardless of whether the internal or the

external temperature can be controlled by the operator, minimum total entropy production always implies constant rate of entropy production on each branch of the cycle. If the fluxes are linear in the forces, this constant entropy production rate must be the same on all branches of the cycle. If the class of systems is further restricted to admit only Fourier heat flow through a conductance κ to the reservoir, one finds that the total entropy produced in a cycle with period τ is bounded by

$$\Delta S \geq \left(\sum_i |\sigma_i| \right)^2 / \kappa \tau, \quad (28)$$

where σ_i is the entropy change of the working fluid on branch i . Combining this expression with the equality form of the Second Law, eq.(4), the work W produced by such an engine is bounded by

$$W \leq W_{\text{rev}} - T_0 \left(\sum_i |\sigma_i| \right)^2 / \kappa \tau, \quad (29)$$

where T_0 is the temperature of the environment with respect to which availability is defined. This expression is a particularly clear exposition of one kind of cost of finite-time operation.

The main result of this paper¹⁴, that the ‘best process’ is associated with a constant rate of entropy production, is reminiscent of Prigogine’s theorem of irreversible thermodynamics which states³⁶ that the entropy production rate is minimum at near-equilibrium steady states. Both results are derived from variational principles. However, the approach of Prigogine (‘irreversible thermodynamics’) involves instantaneous quantities while our formalism (‘finite-time thermodynamics’) investigates the extrema of integrals over time — a nice illustration of a point made in Sec. 1.3.

As an illustration of finite-time availability (Sec. 2.2) we have found²³ that time path for the system in Fig. 13 which produces the most work in time τ , starting from a given initial state. The system, as drawn, consists of two finite-size heat reservoirs, each drained by an endoreversible heat engine, and interconnected. Thus it illustrates the extraction of work in competition with internal relaxation. This situation is very common, and, just by a change of nomenclature, the entire calculation of Ref. 23 can represent a chemical reaction with diffusion resistance to and from a catalytic surface, a hydraulic system with viscous resistance, or a molecular system with e.g. rotational and vibrational degrees of freedom pumped separately combined with internal energy transfer (cf. the lasing system of Ref. 24). Either way, the finite-time availability increases monotonically with process duration to the asymptotic limit A_∞ . This limit is less than A_{rev} , the total (reversible) availability of the initial state and hence the maximum work that could be extracted reversibly with the environment at T_0 , because the finite conductance κ always permits the two reservoirs to come to thermal equilibrium, whether or not the engines run infinitely slowly. The true limit A_∞ is only the same as A_{rev} when the initial constrained state of the system is in internal equilibrium. In most situations, when all five conductances are of the same order of magnitude,

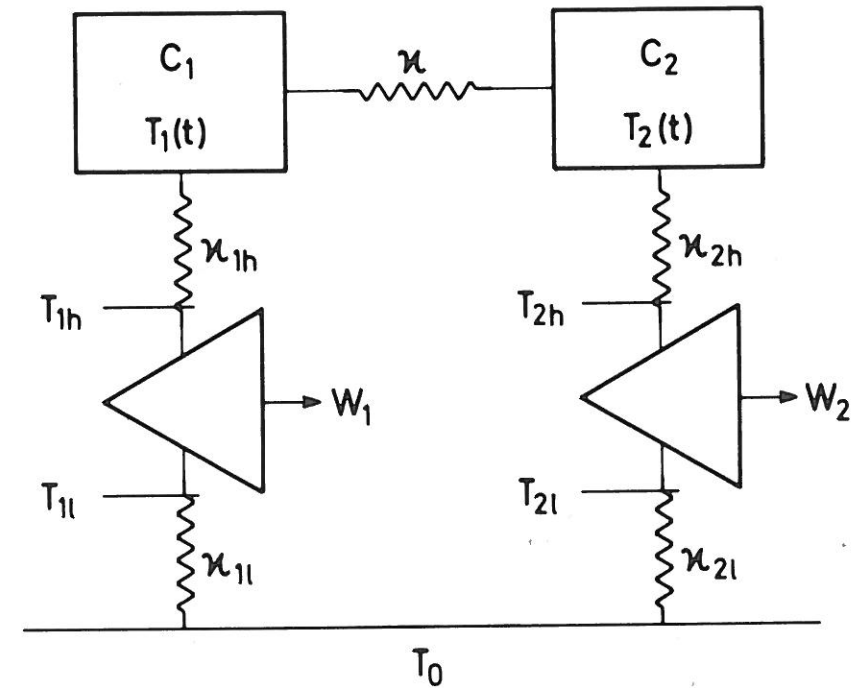


Figure 13. A model system consisting of two finite reservoirs at temperatures $T_1(t)$ and $T_2(t)$ and the environment at temperature T_0 . The reservoirs produce work through their respective engines in competition with internal relaxation through the conductance κ .

roughly only half of the drop in availability of the two reservoirs is captured as work, compared to an effectiveness of unity for reversible operation. This effectiveness of one half has actually been proposed as a general conjecture for all systems producing maximum power³⁷, and it is certainly well known in electronics in connection with impedance matching. Fig. 14 shows the optimal temperature development of the two reservoirs when the same initial system is required to produce the most work possible during different lengths of time. It is quite apparent that the entire time path is changed by varying the duration of the process, so it is essential for optimal performance to know the available time from the outset.

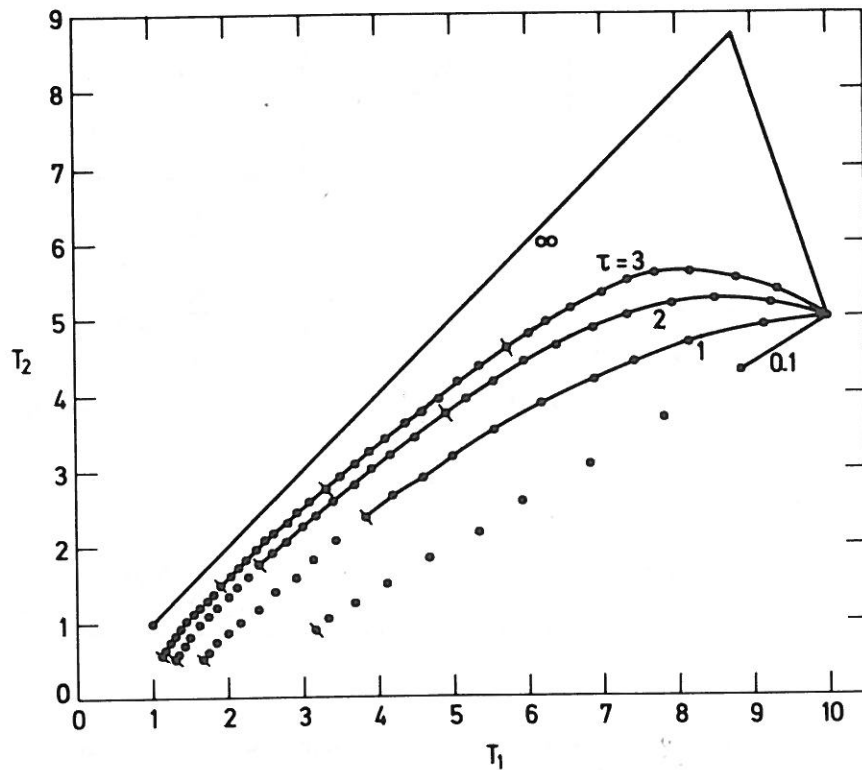


Figure 14. Two finite heat reservoirs of temperatures T_1 and T_2 relax and produce work by coupling to an environment at $T_0=1$ through endoreversible engines (see Fig. 13). Starting from the same initial state, $T_1=10$ and $T_2=5$, the optimal temperature time paths for producing work in periods $\tau=0.1, 1, 2, 3$, and ∞ time units are shown with marks for every 0.1 unit. The curves are continued for 1 unit of operation past the assumed stopping time to emphasize the importance of knowing the duration of a process from the outset.

3.2. Criteria of performance

Efficiency, the earliest criterion of performance for engines, measured how much water could be pumped out of a mine by burning a ton of coal. Other familiar criteria include effectiveness, change of thermodynamic potential, and loss of availability, all of which are measures of work. Potentials for heat can also be defined¹⁹ (see Sec. 2.1) but are less common, and we have used the minimization of entropy production¹⁴ in Sec. 3.1. Rubin has compared³⁸ some of these criteria of performance for the Atwood machine.

The Curzon-Ahlborn analysis³ and most of our own analyses use a quite different criterion, that of *power*. This quantity is of course zero for any reversible system, and maximizing power forces us to deal with systems operating at finite rates. Other criteria of performance are the rate of entropy production and the rate of loss of availability. Entropy production was a function introduced in the earliest thinking about irreversible thermodynamics^{8,10,36}, but more from the differential, local, instantaneous viewpoint than from the global, integral view of entire optimized processes (see the discussions in Sec. 1.3 and 3.1). Under some circumstances, optimizing one of these quantities is equivalent to optimizing another. For example, minimizing the entropy production is equivalent to minimizing the loss of availability, at least in those cases in which the irreversibilities can be represented as spontaneous heat flows¹⁴.

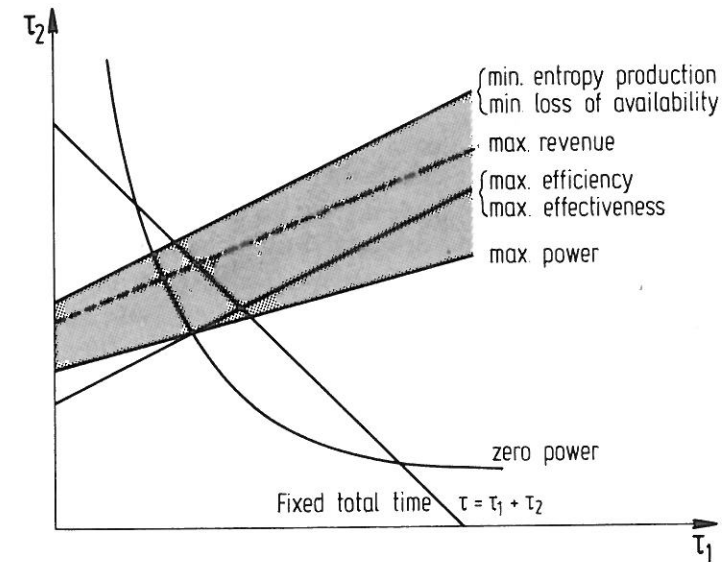


Figure 15. If an endoreversible engine (Fig. 2) spends time τ_1 in contact with the hot reservoir and τ_2 in contact with the cold reservoir, the optimal proportioning between τ_1 and τ_2 depends on what one chooses to optimize, as indicated. The locus of maximum revenue for a power producing system falls in the shaded area for any choice of prices, as described in the text. Only contact times above the hyperbola marked 'zero power' actually correspond to positive power production.

Salamon and Nitzan have optimized³⁹ the Curzon-Ahlborn engine for a number of these objective functions. Assuming the working fluid to be in contact with the hot reservoir for the period τ_1 and the cold reservoir for the period τ_2 , the optimal time distributions are shown in Fig. 15. The diagonal $\tau=\tau_1+\tau_2$ indicates fixed total cycle

time, and only processes above the curve labeled 'zero power' produce positive power. It is quite obvious that different criteria of merit dictate different operating conditions for the process. Even when not knowing the precise objective function but only that it belongs to a specified class, one can sometimes say a good deal about the possible optimal behavior of a system. If one considers the Curzon-Ahlborn engine to be a model of a power plant which buys heat (coal) at the unit price α and sells work (electricity) at the unit price β , its net revenue is $\Pi = \beta w - \alpha q_1$. All solutions to the problem of maximizing this revenue are bounded on one side by the solutions to the maximum power problem (when α is insignificant compared with β) and on the other side by the solutions corresponding to minimum loss of availability (when coal and electricity are priced according to their availability content). While this is a very simple example, this approach has far reaching possibilities for describing biological, ecological, and economic systems.

3.3. Field description

Whereas the main stream of finite-time thermodynamics considers lumped systems, i.e. consisting of individual resistors, engines, etc., Sertorio and coworkers in a series of papers⁴⁰⁻⁴² has developed a field description in which all these components are distributed in space. Thus temperature becomes a field, $T(\mathbf{x}, t)$, and the Fourier heat flow equation

$$\mathbf{q} = -\kappa(\mathbf{T} - \mathbf{T}') \quad (30)$$

is replaced by

$$\mathbf{q} = -\kappa \nabla T. \quad (31)$$

Conservation of energy in this dissipative flow yields

$$c\varrho \frac{\partial T}{\partial t} = \kappa \nabla^2 T \quad (32)$$

with the associated entropy equation

$$\varrho \frac{\partial s}{\partial t} = \kappa \frac{\nabla^2 T}{T}; \quad (33)$$

ϱ is the density of the system, and c the specific heat capacity. If distributed Carnot engines are inserted to capture the availability of the temperature field, their efficiency

$$\eta_c = 1 - \frac{T + dT/dr}{T} = -\frac{1}{T} \frac{dT}{dr} \quad (34)$$

results in the produced power density

$$w = \kappa \frac{(\nabla T)^2}{T}, \quad (35)$$

such that the energy and entropy equations (32) and (33) are replaced by

$$c\varrho \frac{\partial T}{\partial t} = \kappa \nabla^2 T - \kappa \frac{(\nabla T)^2}{T} \quad (36)$$

and

$$\varrho \frac{\partial s}{\partial t} = \kappa \frac{\nabla^2 T}{T} - \kappa \frac{(\nabla T)^2}{T^2} = \kappa \nabla \cdot \left(\frac{\nabla T}{T} \right), \quad (37)$$

respectively. Eqs. (32) and (37) are conservation equations based on the heat flux density vector \mathbf{q} , eq. (31) for purely dissipative flow and the entropy flux density vector

$$\mathbf{s} = \kappa \frac{\nabla T}{T} \quad (38)$$

for a reversible flow. A real system will, of course, be somewhere between these two extremes.

In applications of this formalism eqs. (36) and (37) will be augmented by specific loss and source terms and must then be solved in the appropriate space with given boundary conditions. The task will usually be formidable without serious approximations. Even though no continuously distributed energy capture processes are known, the method is useful for finding upper bounds to the work content of temperature gradients in the atmosphere or the oceans⁴⁰, or limits to the passive temperature control possible simply by varying the heat conductance to a certain area of space over time⁴¹.

4. SOME SPECIFIC SYSTEMS

*Solutions to problems
are easy to find:
the problem's a great
contribution.
What is truly an art
is to bring from your mind
a problem to fit
a solution.*

(Piet Hein: Grooks III)

The previous two chapters have presented the general methods of finite-time thermodynamics for determining performance bounds, either by themselves or in connection with the optimal paths that yield them, illustrated with a number of examples. In this chapter we will mention some additional optimizations which either inspired the general methods or elaborate on the conclusions.

4.1. Theorems for endoreversible engines

Since it is the building block of finite-time thermodynamics, just like the Carnot engine is in reversible thermodynamics, most analyses so far have focused on the endoreversible engine, as a unit, with different objective functions, branch by branch, connected to other units, without and with knowledge of the optimal path, etc. etc. We will here summarize some of the theorems proven.

- a) The efficiency at maximum power is $1 - \sqrt{T_L/T_H}$ (Sec. 1.2).
 b) The maximum power for any cycle is³² $\kappa(\sqrt{T_H} - \sqrt{T_L})^2$. This result has been generalized by Salamon, Band, and Kafri⁴³ to a model engine driven by a time-dependent source supplying heat at a rate $f(t)$ and connected to a reservoir with an arbitrary temperature variation through the conductance κ . This thermal energy source simulates the supplying of energy to the working fluid either from internal degrees of freedom, such as a chemical reaction, or from an external source, such as in laser-driven engines. If the pumping f and the reservoir temperature T_{res} are given periodic functions of time, then the maximum average power delivered by the model is equal to the variance of $\sqrt{f + \kappa T_{res}}$. The form of $f(t)$ giving maximum power is a delta function, dumping all the heat into the working fluid at an instant when its tempera-

ture is high, so as to minimize the concomitant addition of entropy.

- c) Any extremum of the form $\beta(\text{output}) - \alpha(\text{input})$, such as revenue, lies between the thermodynamic limits of maximum power and minimum loss of availability (Sec. 3.2).
 d) The entropy production is bounded by $\Delta S \geq (\Sigma_i |\sigma_i|)^2 / \kappa \tau$ (Sec. 3.1).
 e) The loss of availability is bounded by $-\Delta A \geq L^2 \epsilon / \tau$ (Sec. 2.4).
 f) The optimal cycle consists of two isotherms and four maximum-power branches (Sec. 3.1).
 g) Endoreversible engines have the same staging property as Carnot engines: If one puts two or more engines of the same kind in sequence, then the whole system behaves as a single engine of the same kind⁴⁴. In this unconstrained optimization the interface between the two stages, which for the present model is the intermediate temperature and the relative timing of the two engines, is arbitrary and can be used to satisfy other, non-thermodynamic constraints. A possible constraint which could be added to make the problem more realistic concerns the volume swept by the two engines, e.g. the total volume or the sum of the compression ratios. However, if we want to go into such detail, we must also specify the amount of working fluid in each engine and its equation of state, and those new parameters precisely balance the added constraints, so the interface is still arbitrary. This conclusion implies that one of the stages could shrink to zero without it being detected from the outside. There is thus no *thermodynamic* reason for the usual practice of dividing turbines, compressors, refrigerators, and the like into stages. This staging property of endoreversible engines makes it a unique building block for constructing and analyzing more complex finite-time thermodynamic systems — much like the Carnot engine is in reversible thermodynamics.
 h) The possible branches of the optimal cycle have been determined⁴⁵ for a more realistic extension of the bare endoreversible engine. The addition is a finite-size 'slave reservoir' connected to the working fluid through a conductance κ_s , but otherwise insulated and uncontrollable (see Fig. 16). In reality the slave reservoir could be the heat capacity of the innermost layer of the cylinder wall in an internal combustion engine, or it could represent the coupling of the thermal motion of the working fluid to other degrees of freedom, e.g. rotation, vibration, or a chemical reaction. The slave reservoir, of course, does not contribute to the overall energy flow, but its effect is to phase delay the temperature of the working fluid, such that it absorbs heat when the working fluid is hot (and could have produced work) and returns it when the working fluid is cold. However, this model has the standard endoreversible engine (see Sec. 3.1) as its limit when either $\kappa_s \rightarrow 0$ (the slave reservoir is decoupled from the working fluid) or $\kappa_s \rightarrow \infty$ (the slave reservoir becomes an integral part of the working fluid); in both limits no additional entropy is generated due to κ_s . The complexity of the optimal control problem has increased considerably, and all combinations of the optimal branches have not been tested and compared yet. The control variables and state variables of the most likely candidate for the optimal cycle are shown in Figs. 17 and 18, respectively (cf. Figs. 11 and 12).

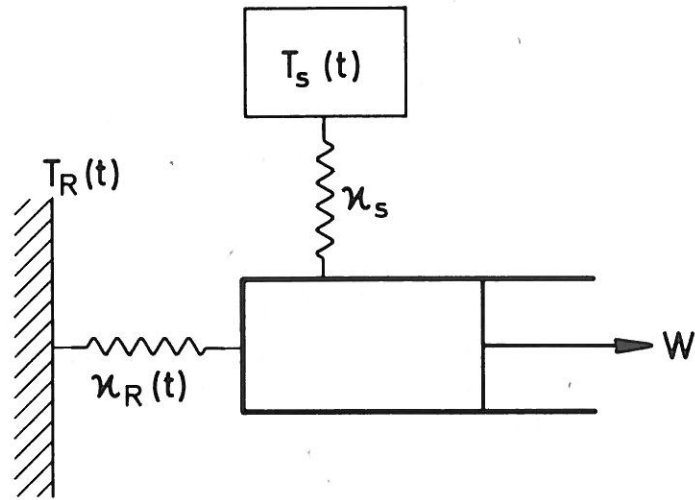


Figure 16. The endoreversible engine, consisting of a power producing cylinder and piston connected to its variable heat reservoir $T_R(t)$ through the conductance $\kappa_R(t)$, is augmented with a passive slave reservoir $T_s(t)$ coupled to the working fluid through the fixed conductance κ_s .

4.2. The Otto cycle

About the most realistic optimization carried out so far is the analysis by Mozurkewich and Berry⁴⁶ of a somewhat idealized Otto cycle (ordinary gasoline engine). The system was chosen to be an engine with friction and a finite heat leak proportional to the exposed cylinder area, operating at constant period and constant fuel consumption per cycle. The optimization, carried out with several sets of engine parameters, was done to find the time path of the piston that would yield the maximum work per cycle. The cycle was approximated as a four stroke cycle of intake, compression, power, and exhaust. The intake, compression, and exhaust strokes have minimum losses when they are run at constant velocity for as long as possible, preceded and followed by acceleration (or deceleration) at the maximum possible rate to the optimum velocity. Like the solutions of Rubin's models^{34,35}, these are 'turnpike' solutions in the terminology of optimal control theory.

The most interesting part of the cycle is the power stroke. For parameters corresponding to real automobile engines, heat leakage, especially during the hottest portion of the power stroke, is the most important source of inefficiency. The consequence of this is that the optimum path has the piston accelerating as fast as possible to a high expansion velocity. If the acceleration can be infinite, the optimum velocity at the beginning of the power stroke is about twice the maximum velocity of the piston in a corresponding conventional engine. Fig. 19 shows the velocity and

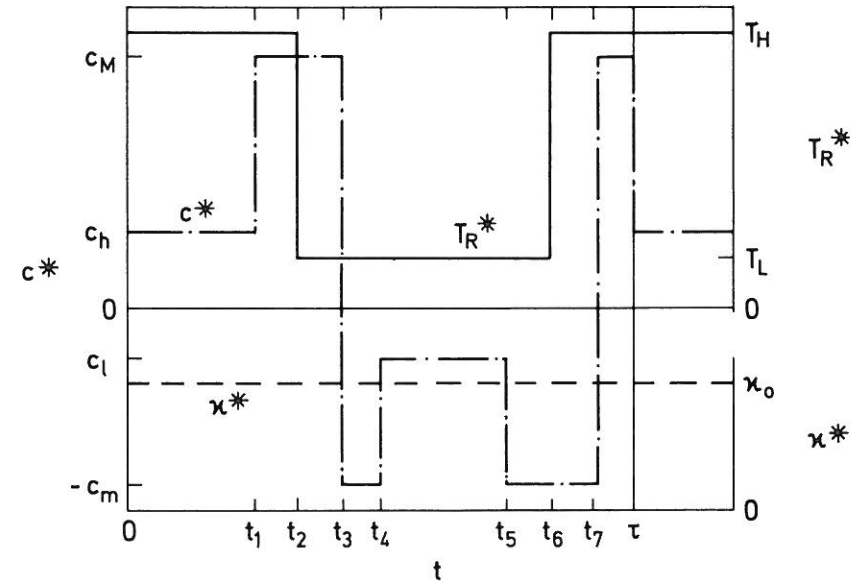


Figure 17. The optimal controls over a period τ for the cycle which most likely maximizes the power output of the engine in Fig. 16. $c^*(t) = \dot{V}/V$ is the relative rate of change of volume, and $\kappa_R^*(t)$ is the heat conductance to the reservoir with temperature $T_R^*(t)$. Note that, again, except for the rate of change of volume on the isothermal branches $[0; t_1]$ and $[t_4; t_5]$, only the extreme values of the controls are required.

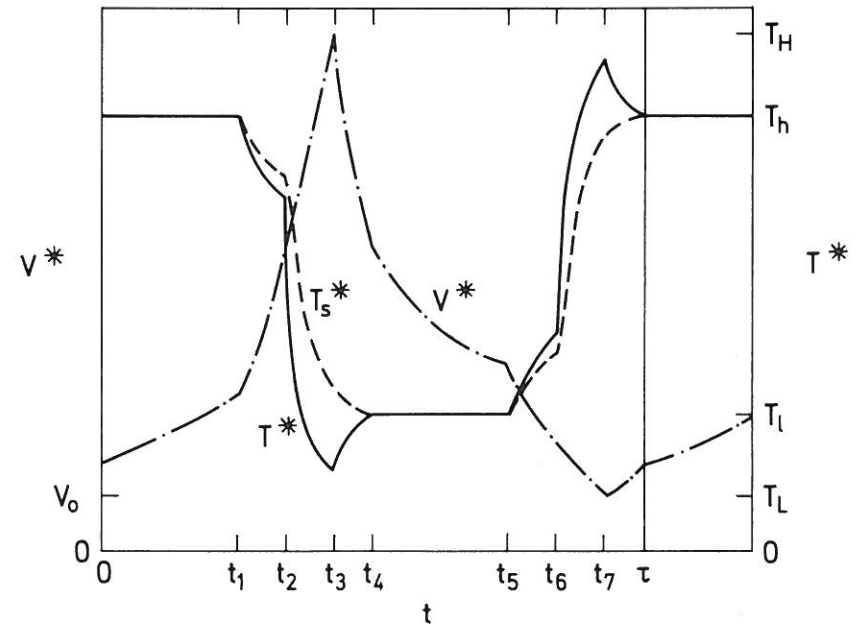


Figure 18. The optimal trajectories associated with the controls in Fig. 17. $V^*(t)$ and $T^*(t)$ are the volume and temperature of the working fluid, respectively. The slave reservoir temperature $T_s^*(t)$ is drawn dashed. Cf. Fig. 12.

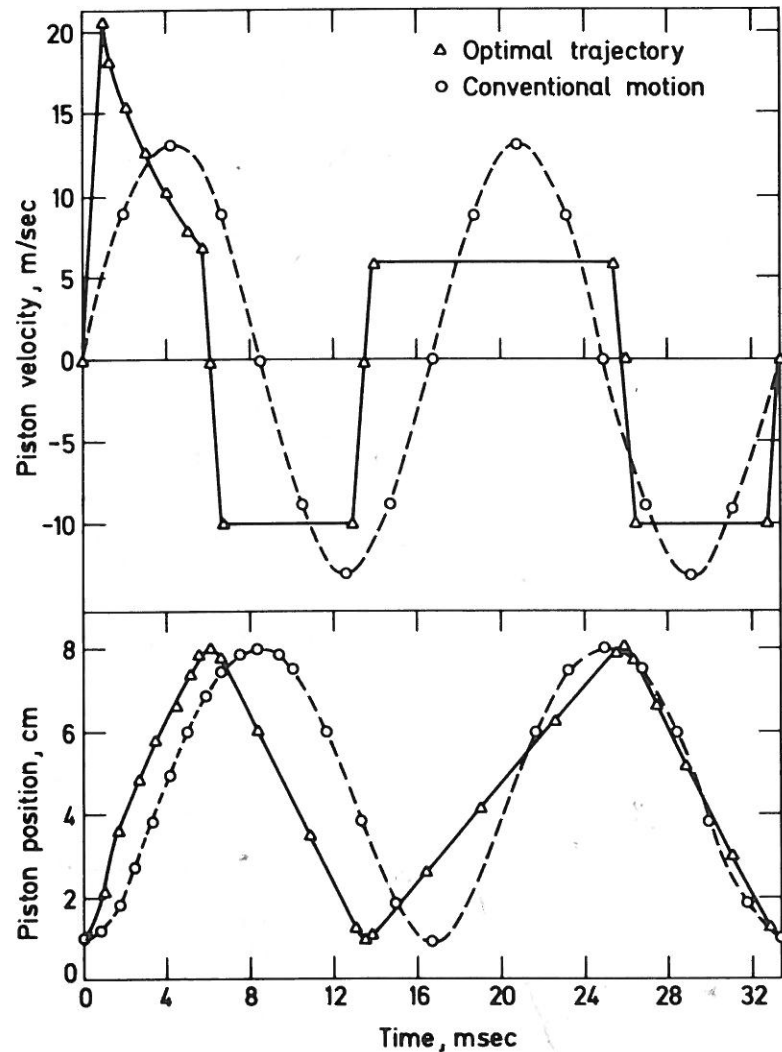


Figure 19. The time path of the Otto cycle has been optimized for maximum work output with all parameters fixed at values representative of a real car engine. By extracting work rapidly before the hot combustion gases cool too much on the cylinder wall, and by reducing friction in the remaining three strokes through constant piston speed, the power output can be increased by 8 to 15%.

position of the piston for an optimized cycle with a finite maximum acceleration of $5 \cdot 10^4$ m/s², about ten times the maximum acceleration of the piston in a corresponding conventional engine, along with the conventional time path.

For a range of engine parameters, the net work delivered to the piston and its work reservoir is between 8 and 15% greater than that from a conventional engine with the well-known connecting rod-crank-flywheel linkage that moves the piston in a nearly-sinusoidal path in time.

4.3. Oscillating systems

The systems treated by our group have all had a monotonic time evolution or have been cycles composed of monotonic branches. However, in certain situations oscillating processes give rise to less dissipation. John Ross' group has done most of the work on this topic⁴⁷, for mechanical as well as chemical systems. The oscillations are always driven from the outside and will for most frequencies increase the dissipation, but in a narrow interval around some frequencies — resonances or limit cycles — dissipation drops below its steady-state value. In these intervals dissipation and process rate depend critically on the phase of the applied oscillation; this is expected to be one of the regulatory mechanisms of the biochemical reactions for which such oscillations are actually observed *in vivo*. It has also been claimed⁴⁸ that the efficiency of a distillation column can be improved considerably by operating it in a pulsating manner.

4.4. Finite-size effects

In most real heat engines the heat sources are not infinite⁴⁹. The combustion products in gasoline and diesel engines have finite heat capacities and, as with all combustion heat sources, the exhaust gases should ideally be cooled to the surrounding temperature while doing work. If instead an engine with fixed-temperature heat intake, e.g. a Carnot engine, is used, the combustion products must be exhausted at that fixed temperature, and the best possible efficiency falls far short of η_C (see Fig. 20 for $N=1$). The remaining heat may be recovered by adding bottoming cycles ($N>1$ in Fig. 20), increasing the efficiency to the limit

$$\eta(\infty) = 1 - \frac{T_L}{T_H - T_L} \ln \left(\frac{T_H}{T_L} \right), \quad (39)$$

but a far better solution is to construct new cycles with the heat accepting (and possibly discharging) branches designed to match the heat capacity of the exhaust gas. The new polytropic branch needed is

$$P V^{\gamma} + \frac{R}{c_v - c} = \text{constant}, \quad (40)$$

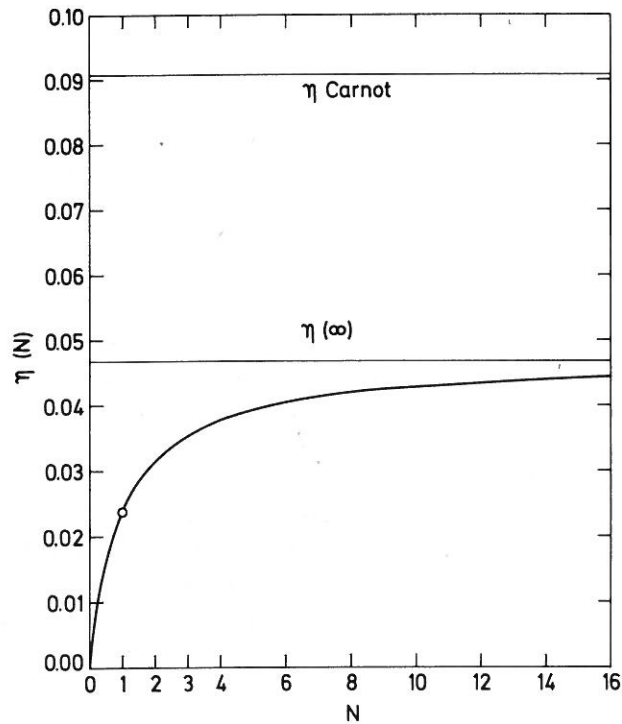


Figure 20. A finite hot reservoir is drained by a Carnot engine followed by $N - 1$ bottoming engines, to make a total of N sequential Carnot engines with an optimal distribution of intermediate temperatures. The resulting thermal efficiency $\eta(N)$ is plotted for the initial ratio of reservoir temperatures $T_H/T_L = 1.1$; the heat capacity of the hot reservoir is immaterial. The limit $\eta(\infty)$ for reversible conversion of heat from the finite reservoir, and η_{Carnot} for an infinite heat source at the initial temperature are also shown.

where C is the heat capacity of the reservoir and C_v that of the working fluid. The special cases $C = 0, \infty, C_v,$ and C_p reproduce the usual adiabat, isotherm, isochor, and isobar, respectively. Assuming that only the high-temperature reservoir is finite, whereas the low-temperature reservoir is infinite, e.g. the environment, a reversible cycle that completely drains the heat source can be constructed from the polytrope, eq. (39), an isotherm, and an adiabat (see Fig. 21). Finite-size effects are frequently emphasized by finite-time operation because of the time it takes to drain a reservoir through a finite conductance, and the optimal cycles depend critically on that heat capacity^{23,50}.

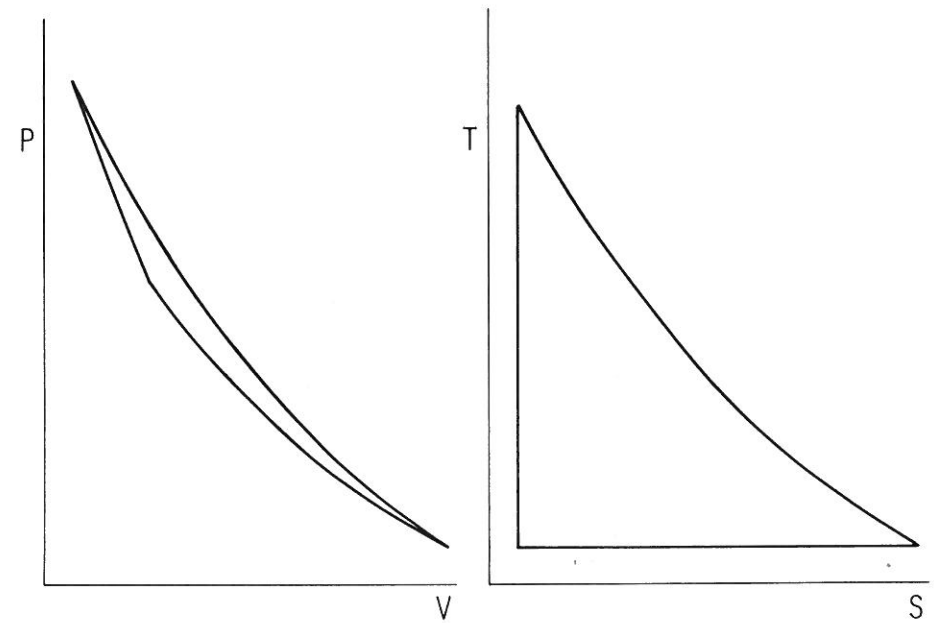


Figure 21. PV and TS diagrams for the ideal gas reversible polycycle which extracts the maximum possible work from a finite-heat-capacity reservoir. The left branch is the adiabat, the bottom one the isotherm, and the upper-right branch the polytrope defined by eq. (40).

4.5. Systems doing chemical work

Separation processes are a bridge between the thermo-mechanical systems first analyzed by finite-time thermodynamics and chemical or completely general systems. In conventional binary distillation there is a, largely economic, tradeoff between the number of plates in the column, i.e. basically capital, and the heat load required to perform a certain separation, i.e. operating costs. Even when pushing its heat requirement to the minimum, the effectiveness of separating a mixture of similar compounds into pure products by distillation — expressed as the reversible work of separation divided by the work equivalent of the heat used in the distillation process — is only approximately

$$\epsilon = -[x_F \ln x_F + (1 - x_F) \ln (1 - x_F)], \quad (41)$$

where x_F is the feed composition as mole fraction of light component. The expression in eq. (41) has a maximum of 70% for an even mixture, $x_F = 0.5$. The remaining 30% are lost due to the inherent mechanics of the process and cannot be avoided without

altering the distillation process itself. In the extended tricycle decomposition of Fig. 6 (Sec. 2.3) these are the unavoidable losses.

In an unpublished study we introduced two simple models for the losses resulting from the vapor and liquid flows and incomplete mixing and optimized the throughput with respect to heat load and reflux ratio. These results by themselves were not very realistic, but they did point out a risk that the usual dynamic computer regulation of large distillation columns may lock in on a local performance maximum rather than the global one. The study also inspired our definition of finite-time availability²³ as well as an extensive analysis by Mullins and Berry⁵¹ of entropy production in distillation and how to reduce it by adding intermediate reboilers and condensers.

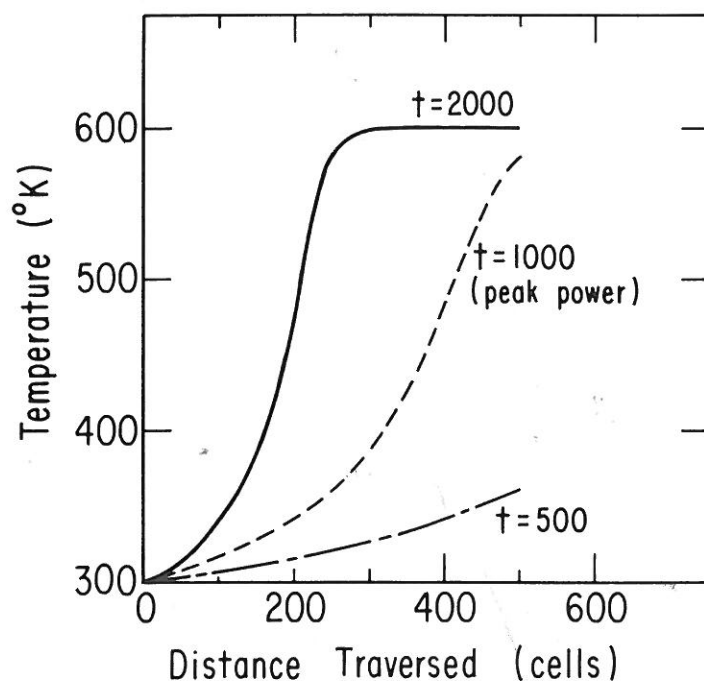


Figure 22. The reactants of an exothermic first-order Arrhenius-law reaction are mixed at distance 0. The resulting temperature profile along the reaction tube is shown for different traversal times t . Maximum engine power, at $t = 1000$, is obtained when the rapid increase in temperature, the 'combustion zone', occurs just before the end of the reactor.

An exothermic chemical reaction may be used to drive a power-producing tricycle⁵². Expressions were derived for the power production from first and second order processes as a function of the rate at which the reactants are sent through the flow reactor. They all exhibit a single maximum at a fairly rapid rate at which roughly half

the heat of reaction is lost. Introducing rate constants with a temperature dependence given by an Arrhenius expression⁵³ results in a sharpening of this power peak. Expressed as the temperature of the reaction mixture down the flow reactor (Fig. 22) the release of energy is observed to occur in a fairly narrow 'combustion' zone, and peak power is obtained when that is situated just before the end of the reactor.

Other chemical reactions have been analyzed for possible resonances when they are driven harmonically⁴⁷, as mentioned in Sec. 4.3.

Related to our own work on competing processes (cf. Fig. 13, Sec. 3.1) is that of Robert T. Ross and coworkers⁵⁴ on the efficiency of solar energy converters, be they made of silicon or chlorophyll. They analyze a model in which solar energy is absorbed by a quantum system under less than reversible conditions and where some of the absorbed energy is lost by retransmission and by nonradiative recombination, much like in photosynthesis. The analysis yields the optimal spectral absorbance of the device for a range of decay rates and the associated conversion efficiency. The most spectacular result is that the efficiency can be made to exceed the ideal thermal efficiency by rapid equilibration among the electronically excited states, which reduces reradiation and actually leaves the chemical potential of the excited electronic band below that of the ground band. This result is akin to the previously discussed observation by Ben-Shaul and Levine for a lasing system²⁴.

5. FUTURE DIRECTIONS

*The height of technical felicity
is to combine sublime simplicity
with just sufficient ingenuities
to show how difficult to do it is.*

(Piet Hein: Grooms IV)

The previous chapters have laid the groundwork for an all encompassing theory of finite-time thermodynamics. Chapter 1 gave the motivation why such an extension of traditional reversible thermodynamics is desired, and stated the general approach. The following two chapters proceeded to present the basic avenues for calculating finite-time thermodynamic quantities — chapter 3 in their most general form which yields a complete description of the optimal process, chapter 2 in the simpler version when only the value of the optimized quantity is desired — illustrated by a number of examples, and with additional examples in chapter 4.

The introductory sentence of this chapter may seem to be the result of an attack of hubris. I don't believe so. Traditional thermodynamics has long been accepted as probably the most general theory in science (with strong competition from quantum mechanics for this title), because *all* systems with more than a few particles must obey it, be they microscopic or astrophysical, dead or living. Finite-time thermodynamics is based on the same ideas, calculates the same types of quantities, etc., the only difference is the additional constraint of finite duration. Thus all the well known results of reversible thermodynamics should, in principle, be extendable to finite time. That sounds quite straight forward and could be taken as a statement of policy for future work in finite-time thermodynamics. However, it sidesteps the great wealth of new insight — basic physics, if you prefer — and hence complexity in derivation associated with this simple time constraint, so a more realistic outlook for the future will probably be to follow the approach which historically led to the present state of the theory, that of working through a number of models of increasing complexity (and thus reality) and then base a general formulation on the experience gained. Specifically, I envision some of the topics to be treated in the near future to be:

a) Explicit application of the theory to chemical systems; within reach are also systems in e.g. biology, population analysis, and economics. Such applications are, of course, in principle already covered by the heat engine examples because of the beautiful general nature of thermodynamics, but they are essential to explore the effects of time or rate constraints in these fields. Oscillating and self-regulating

systems of reactions are particularly interesting.

- b) Rules for combining optimized finite-time systems into larger units. It is a wide spread practice in engineering and reversible thermodynamics to analyze large, complicated systems in terms of their components. Although an optimization is inherently global, finite-time thermodynamics needs the same capability to reduce the calculational burden and increase its usefulness.
- c) Further development of geometric methods to calculate (realistic) bounds on process variables (cf. Sec. 2.4).
- d) An analysis of processes which have no reversible counterparts, i.e. processes which rely on irreversibilities for their very existence (see e.g. Ref. 25).
- e) Establishment of formal ties with the other theories of irreversible thermodynamics, notably with the bulk of work by the Prigogine school, with statistical mechanics, and with the maximum entropy formalism.

Finite-time thermodynamics is useful in at least the following four situations:

- a) to calculate realistic bounds on process variables and thus provide an estimate of the cost (in the widest possible sense) of finite-time operation;
- b) to pinpoint bottlenecks in processes, where improvement would be particularly beneficial;
- c) to suggest more efficient ways of operating existing equipment, i.e. to provide the optimal path for the process;
- d) as an aid in the design phase of a system to compare losses and possibly suggest new and more efficient processes (cf. Fig. 6).

6. DANISH SUMMARY

*Vil du med rette
ha ry som lærd,
så tag det lette
og gør det svært.*

(Piet Hein: Korte Gruk I)

Denne afhandling søger at give status over det øjeblikkelige stade af den nye disciplin endelig-tids termodynamik, såvel hvad angår mine egne som andres bidrag — de første dog, af naturlige årsager, noget mere udførligt. Afhandlingen er kun en oversigt, og der henvises til originalartiklerne, bl.a. i Appendices, for de detaljerede udledninger.

Kapitel 1 giver en begrundelse for, hvorfor en udvidelse af den traditionelle reversible termodynamik er ønskværdig, og hvorledes vi griber den an. Baggrunden er, at det store flertal af termodynamiske processer i det virkelige liv drives meget langt fra reversibilitet, simpelt hen fordi vi er utålmodige: hvem kunne vente på, at man lavede en bil — eller noget som helst andet — reversibelt og dermed uendelig langsomt? Faktisk er vore daglige processer normalt så irreversible, at sammenligning med de reversible ydelseskriterier ikke har megen mening. De to væsentligste undtagelser til dette er fremstillingen af elektricitet og af ammoniak. Endelig-tids termodynamik indkorporerer en endelig procestid samt de vigtigste tabsmekanismer i den traditionelle termodynamiks fremgangsmåde og opnår dermed et mere realistisk sammenligningsgrundlag for virkelige processer.

Logisk er teorien bygget over følgende sekvens af spørgsmål:

- a) Eksisterer der — eller rettere, hvad er *betingelserne for eksistensen* af — generaliserede termodynamiske potentialer, således at disses ændring er grænsen for det udvekslede arbejde eller varme i den berørte proces, når den er pålagt bånd med hensyn til sin hastighed eller varighed?
- b) Hvorledes udregnes disse *potentialer* eller deres ændringer, og hvad lærer man derigennem om prisen (i bred betydning) for den ønskede hastighed?
- c) Hvilken *procesvej* giver den maksimale ydelse, og hvorledes kan den bruges til at forbedre eksisterende processer?
- d) Hvad er forskellene i optimal drift af et system, når *forskellige størrelser ønskes optimeret*?

Kapitel 2 besvarer spørgsmål a) og b) med en række fremgangsmåder, der bl.a. generaliserer konstruktionen af de kendte termodynamiske potentialer, som f.eks. Gibbs fri energi for isoterme og isobare processer. En anden metode udvider begrebet

exergi.

Kapitel 3 omhandler spørgsmål c) og d). Det beskrives, hvorledes den optimale procesvej beregnes med optimal kontrolteori, og hvordan denne vej afhænger af det »kvalitetskriterium«, der er valgt.

Alle beskrivelser er illustreret med eksempler, og *kapitel 4* indeholder yderligere eksempler på optimerede systemer.

Noget mere udførlige gennemgange på dansk af endelig-tids termodynamik, end der er plads til i dette resume, findes i Ref. 45 og 55.

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*My adversary's argument
is not alone malevolent
but ignorant to boot.
He hasn't even got the sense
to state his so-called evidence
in terms I can refute.*

(Piet Hein: Grooks II)

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8. APPENDICES

*If no thought
your mind does visit,
make your speech
not too explicit.*

(Piet Hein: Grooms I)

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

Phys. Rev. A 15, 2086 (1977)

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

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(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.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 Carathéodory, 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

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

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

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

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.

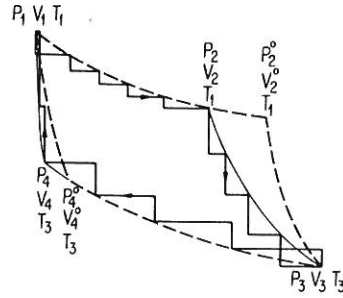


FIG. 1. PV diagram of the step-Carnot cycle (—) with its envelope (—) and the reversible Carnot cycle (---) operating between the same extreme states. The indicated pressure for the step-Carnot cycle is the external pressure P_e , not the internal pressure.

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

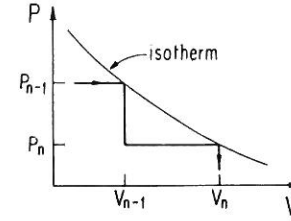


FIG. 2. Enlargement of one step on the isothermal branch showing work being done by the gas against the external pressure P_n from V_{n-1} to V_n .

$V_n - V_{n-1}$ (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

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

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

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

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

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

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

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

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

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:

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

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

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

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

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

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

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

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

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

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 $P_1 V_1$ and $P_3 V_3$. This is the effectiveness¹² W/W_0 (also called second-law efficiency⁵), the ratio of work done to the total change of availability. With

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

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

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

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:

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

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} ,

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

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

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

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

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

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

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

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

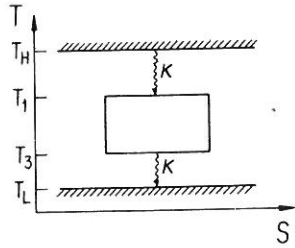


FIG. 3. TS diagram of Carnot cycle operating between T_1 and T_3 with heat exchanged with the reservoirs at T_H and T_L through the thermal conductances κ .

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

$$\frac{dQ}{dt} = \kappa[T(t) - T_H]$$

$$= c_v \frac{dT}{dt} + P_b \frac{dV}{dt} = c_p \frac{dT}{dt}$$

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

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

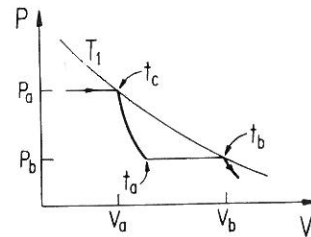


FIG. 4. Enlargement of one step on the isothermal branch when thermal conductance to the heat reservoir is finite. Along the segment t_c to t_a work is done by adiabatic cooling of the gas. From t_a to t_b the gas is reheated to T_1 while in equilibrium with the external pressure P_b .

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

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

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 .

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.

*Partially supported by a travel grant from the Danish Science Foundation.

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8.2. Thermodynamics in finite time. II. Potentials for finite-time processes

Phys. Rev. A 15, 2094 (1977)

Thermodynamics in finite time. II. Potentials for finite-time processes

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(Received 7 September 1976)

Within the context of conventional time-independent thermodynamics, an algorithm is developed to construct potentials Φ that define the extremal values of work for processes with arbitrary constraints. An existence theorem is proved that demonstrates that such potentials Φ can be given for any quasistatic process. This theorem extends the capability of thermodynamics from reversible processes to one class of time-dependent processes. A corollary shows how such potentials can be constructed for systems whose time dependence is first order. A final theorem shows the equivalence of the extremal work derived by solution of an optimal control problem with the work derived as a change in the generalized potentials, $\Delta\Phi$. Examples are given to illustrate the constructions.

I. INTRODUCTION

The three laws of thermodynamics were conceived about irreversible processes. The subsequent development of the subject however turned away from irreversible processes and focused on equilibrium systems. This happened even though many questions which gave the subject its original impetus remained unanswered. Examples of such questions are, as follows: (1) What is the least energy ΔE required by a given machine, to produce a given work W in time t ? (2) What is the most work W that can be produced by a given machine in time t , utilizing a given energy ΔE ? (3) What is the most efficient way to run a given thermodynamic process in finite time?

Classical thermodynamics does not try to answer these questions, although it does give a fairly complete description of equilibrium states and reversible processes. The only facts it tells us about real processes is that they always produce less work and more entropy than the corresponding reversible processes.¹ Reversible processes, however, are possible only in the limit of infinite time. But no one wants to run a factory infinitely slowly, and in practice engines seldom attain more than 30–40% of the reversible efficiency.¹

We should be capable of extending the classical theory to at least quasistatic processes. (We take a process to be quasistatic if the internal relaxation times of the system are much shorter than times characterizing interactions between system and surroundings.¹) This would be a significant extension, since quasistatic processes happen in finite time, produce entropy, and provide an excellent approximation to many real processes. Conventional irreversible thermodynamics^{2,3,4} has become increasingly powerful but its micro, dif-

ferential viewpoint does not lend itself to global questions such as those stated above.

The methods of optimum control theory⁵ provide a natural way to attack the above questions for quasistatic processes. We can express the work as an integral and use the calculus of variations to find the process which optimizes that integral. This approach, although very useful in a precise formulation of problems, almost always results in cumbersome nonlinear differential equations. Analytic solutions have been found only for the simplest examples.^{5,6} For this reason, we have examined several other approaches,^{5,7} and results to date seem to indicate that much can be accomplished in the field.

Below, we present one such approach toward a theory of processes: the construction of thermodynamic potentials for finite-time processes. The word "potential" will be used to mean a function of state whose changes give (or bound) the value of a process variable such as heat or work.

In Sec. II we review the classical theory in the context of processes. We then proceed (in Sec. III) to examine the classical Legendre transform, and we extend it to the general reversibly coupled system. In Sec. IV we present an original theorem about the existence and uniqueness of potentials for quasistatic processes. We go on (Sec. V) to present the algorithm for the construction of potentials in some time dependent examples and conclude (Sec. VI) with the connection of the theory to a variational approach.

II. REVIEW OF THE CONCEPTUAL HISTORY (REF.8)

Thermodynamics started as a subject dealing with practical energy conversion, especially in the operation of steam engines.⁹ The first law asserts that the process variables heat and work

can have identical effects on a system.¹⁰ The second law asserts that heat flows spontaneously only from a body at a higher temperature to a body at a lower temperature. These two laws were used to construct two functions of state: the internal energy E and the entropy S . We will see in Sec. IV how the technique of using process variables to construct functions of state can be extended to a more general setting.

Gibbs used the state variables E and S to characterize equilibrium states.¹¹ The success of the equilibrium theory soon led to the development of statistical mechanics and a microscopic theory of equilibrium states. This evolution of the focus of the theory left the questions of optimality for irreversible processes to the engineers. The engineers in turn responded with the traditional techniques of experimental design,^{12,13} specific to each device or process.

The one mathematical technique that the Gibbsian formalism provides for processes is the Legendre transform. This is a way of constructing thermodynamic potentials (free energies) for certain reversibly coupled processes. In the following sections, we discuss this classical construction and proceed to extend it to progressively larger classes of processes.

Process type	Zero along process	Integrating form	Process variable	Potential
Isobaric	dP	$V dP$	$P dV$ $T dS$	PV $E + PV$
Isothermal	dT	$S dT$	$P dV$ $T dS$	$TS - E$ TS
Isochoric	dV	$-P dV$	$P dV$ $T dS$	0 E
Isentropic	dS	$-T dS$	$P dV$ $T dS$	$-E$ 0

The construction as described above can be readily generalized.¹⁵ For example, we could calculate the work potential for an ideal gas in an adiabatic process by using the integral of motion $PV^\gamma = \text{const}$:

$$dW = P dV = P dV + V^{1-\gamma}/(1-\gamma) d(PV^\gamma) \\ = d[PV/(1-\gamma)]. \quad (2)$$

This calculation yields the work potential $PV/(1-\gamma)$ whose differential is of course the same as dE , the previously calculated potential for an isentropic process, since in this case

III. LEGENDRE TRANSFORM FOR REVERSIBLY COUPLED SYSTEMS

A. Classical Legendre transforms

Recall that the work for a reversible process bounds the work for all irreversible processes between the same states and with the same integrals of motion, e.g., the isobaric irreversible work done by a system is always less than the isobaric reversible work done by the same system. In a reversible process heat and work can be expressed as differential forms on the space of functions of state,¹⁴ e.g.,

$$dQ = T dS, \quad dW = P dV. \quad (1)$$

Now given an integral of motion (e.g., constant pressure) we can make these differential forms exact by adding a zero. In the constant pressure case, this "zero" is the differential form $V dP$. If we add this form to dW and dQ , we get (using the first law of thermodynamics in the form $dE = T dS - P dV$)

$$dW = P dV = P dV + V dP = d(PV),$$

$$dQ = T dS = dE + P dV = dE + P dV + V dP = d(E + PV).$$

The table below shows the results of this procedure for the classical examples.

$$dE = P dV - T dS = P dV.$$

The technique above does more than provide different ways to re-derive the classical potentials. It can calculate *new* potentials as well.

B. Nonclassical examples

1. Example 1. Spherical system with constant surface tension

Consider a spherical system in equilibrium with its elastic surface of constant surface tension. The actual system inside the surface can be any fluid. Even the amount of fluid inside the surface

can vary. Recall the well-known expression¹⁶ for the increase in pressure inside a spherical system with radius r and surface tension $\hat{\gamma}$,

$$P = P_{\text{ex}} + 2\hat{\gamma}/r. \quad (3)$$

When rearranged, this becomes an equation in pressure and volume,

$$V^{1/3}(P - P_{\text{ex}}) = (16\pi/3)^{1/3}\hat{\gamma}. \quad (4)$$

This equation says that $V^{1/3}(P - P_{\text{ex}})$ is an integral of motion for the fluid inside the surface. Using this integral of motion, we find a work potential for a fluid in equilibrium with the surface,

$$\begin{aligned} dW &= P dV = P dV + \frac{3}{2}V^{2/3}d[V^{1/3}(P - P_{\text{ex}})] \\ &= d[(V/2)(3P - P_{\text{ex}})]. \end{aligned} \quad (5)$$

The method of finding the zero form to be added is described in Part C of this section. The work potential for the coupled system: surface + fluid is $\phi = \frac{1}{2}V(3P - P_{\text{ex}})$. This means that the work done by such a coupled system is given by the change in the potential function ϕ .

2. Example 2: Cylinder with a spring-loaded piston

Consider a fluid in a cylinder equipped with a spring-loaded piston. (Again the amount of fluid need not stay constant.) We examine the work done by the fluid-spring system maintained in internal equilibrium, i.e., the pressure of the fluid always balancing the force of the spring. If k is the force constant of the spring and A is the surface area of the piston, then in order to maintain zero net force F_{net} on the piston during a change in the pressure of the fluid, the spring must respond. This response of the spring can be used to give a zero along the path, and therefore an integral of motion:

$$F_{\text{net}} = A dP - (k/A) dV = d(AP - kV/A) = 0, \quad (6)$$

therefore

$$AP - kV/A = \text{const.}$$

We can then use this integral of motion to find a potential for work done by the fluid-spring system.

$$\begin{aligned} dW &= P dV = P dV + (A/k)Pd(AP - kV/A) \\ &= d(A^2P^2/2k) = d\phi. \end{aligned} \quad (7)$$

The general algorithm for finding the factor A/k is given in the next section. Once again the work done by the coupled system is bounded by the change in the potential function $\phi = A^2P^2/2k$.

C. General reversible coupling

We now examine the above construction of potential functions for reversibly coupled systems in

general. It is a tool for calculating the work or heat extracted from a composite system in internal equilibrium. This composite system, for the classical examples, is made up of the thermodynamic system of interest, and one or more of the following: constant pressure reservoir, constant temperature reservoir, ideal rigid vessel (constant volume reservoir), or ideal insulated vessel (constant entropy reservoir). The two examples above show how we can consider more generally coupled systems, when equilibrium between the coupled systems exists. The potential function is obtained by using the condition that equilibrium be maintained to find an integral of motion for one of the coupled systems. This integral of motion can then be used to integrate the inexact differential forms dW and dQ to give potentials for these flows. We thus get the work (or heat) extracted from a coupled system expressed as a change in a function of state of one of the coupled systems.

The actual construction is as follows. Given the integral of motion $g(P, V) = \text{constant}$, we look for a function $f(P, V)$ such that $P dV + f dg$ is an exact differential. To this end we can expand and get

$$\begin{aligned} P dV + f dg &= P dV + f \left(\frac{\partial g}{\partial P} dP + \frac{\partial g}{\partial V} dV \right) \\ &= \left(P + f \frac{\partial g}{\partial V} \right) dV + \left(f \frac{\partial g}{\partial P} \right) dP. \end{aligned} \quad (8)$$

We then equate cross derivatives giving

$$\begin{aligned} \frac{\partial(P + f \partial g / \partial V)}{\partial P} &= 1 + \frac{\partial f}{\partial P} \frac{\partial g}{\partial V} + f \frac{\partial^2 g}{\partial P \partial V} = \frac{\partial(f \partial g / \partial P)}{\partial V} \\ &= \frac{\partial f}{\partial V} \frac{\partial g}{\partial P} + f \frac{\partial^2 g}{\partial V \partial P}. \end{aligned} \quad (9)$$

Rearrangement yields the partial differential equation

$$\left(\frac{\partial f}{\partial V} \right)_P \left(\frac{\partial g}{\partial P} \right)_V - \left(\frac{\partial f}{\partial P} \right)_V \left(\frac{\partial g}{\partial V} \right)_P = \{f, g\}_{P, V} = 1, \quad (10)$$

where $\{\cdot, \cdot\}$ denotes the Poisson bracket. Given a solution f , we form the exact differential $P dV + f dg = d\phi$ and obtain a potential function ϕ . We shall refer to the construction of an exact differential for a reversible process by this technique as a Legendre construction. The existence and uniqueness of solutions is discussed in Theorem 1 below. We consider an example of the nonuniqueness of solutions for the cylinder with a spring-loaded piston before stating and proving the results in general.

3. Example 3: Nonuniqueness of solutions

We re-examine the cylinder with a spring-loaded piston example. For this example we have the integral of motion $g = AP - kV/A$. Substituting this g into Eq. (1) gives

$$A \left(\frac{\partial f}{\partial V} \right)_P + \frac{k}{A} \left(\frac{\partial f}{\partial P} \right)_V = 1. \quad (11)$$

Recall that we are interested in any solution f of this equation and can therefore choose $\partial f / \partial V = 0$, giving $f = AP/k$. This was the f used in the solution of example 2 that give $\phi = A^2P^2/2k$. We could as well have chosen $\partial f / \partial P = 0$, giving $f = V/A$. We now find

$$\begin{aligned} dW &= P dV = P dV + (V/A)d(AP - kV/A) \\ &= d(PV - kV^2/2A^2) = d\phi' \end{aligned}$$

and a "different" potential $\phi' = PV - kV^2/2A^2$. Note however that the two potentials ϕ and ϕ' in this example have the property

$$\begin{aligned} \Delta(\phi - \phi') &= \Delta\phi - \Delta\phi' = \Delta(A^2P^2/2k) - \Delta(PV - kV^2/2A^2) \\ &= (1/2k)\Delta(AP - kV/A)^2 = (1/2k)\Delta g^2 = 0 \end{aligned} \quad (12)$$

that their difference is an integral of motion, so that the derived process variable remains the same. The fact that this is always the case is proved in Theorem 1 below.

Theorem 1

Suppose we are given a function $g(P, V)$, continuously differentiable on an open set U in P, V space. If the vector ∇g is zero on at most a finite number of points in U , then there exist continuously differentiable functions $f(P, V)$ and $\phi(P, V)$ such that $d\phi = P dV + f dg$. Furthermore if f, ϕ and f', ϕ' are any two pairs of functions with the above property, then $f - f'$ and $\phi - \phi'$ can be expressed as functions of g .

We pause before the proof of the theorem for a brief discussion of its assumptions. In stating this theorem, we deal with only two variables, for convenience only, because the argument can be made without recourse to techniques of differential geometry. The general case is covered in Corollary 3, below. The smoothness conditions on g are present so standard existence theorems from the theory of partial differential equations may be applied. The condition that the gradient be non-zero has an easy physical interpretation. We will be interested in a process for which g is a constant of motion. In that case the directional derivative of g along the process trajectory is zero. This condition assures that the gradient of g is locally

orthogonal to the trajectory of the process. We can think of this relation as the information content of the constraint $g = \text{constant}$ on the trajectory. Whenever $\nabla g = 0$, the directional derivative of g is zero for every direction, not only in the direction of the process. Hence, if $\nabla g = 0$ at more than a finite number of points along the path, there is a region in which g cannot give information about the process.

Proof. If $\nabla g \neq 0$ then either $\partial g / \partial V \neq 0$ or $\partial g / \partial P \neq 0$. Recall that in order for $d\phi$ to equal $P dV + f dg$, we must have $\{f, g\} = 1$. If g satisfies our hypotheses, then this equation is a linear partial differential equation with continuous function coefficients not all of which vanish, and we can invoke the standard existence theorem from the theory of partial differential equations¹⁷ to insure that f exists on the entire domain U .

As for uniqueness, consider any two solutions f, ϕ and f', ϕ' . We first show that the function $\phi - \phi'$ can be expressed as a function of g . We have

$$\begin{aligned} d(\phi - \phi') &= d\phi - d\phi' = (P dV + f dg) - (P dV + f' dg) \\ &= (f - f') dg. \end{aligned} \quad (13)$$

Since g is not a constant function either we can express $\phi - \phi'$ as a function of g , or the difference $\phi - \phi'$ and g form (at least locally) a coordinate system in P, V space. To show that the latter is not the case we show that the Jacobian of the coordinate transformation (P, V) into $(g, \phi - \phi')$ equals zero, which means that the two functions considered are not a good coordinate system. The Jacobian of the coordinate transformation is

$$\begin{aligned} \frac{\partial(\phi - \phi', g)}{\partial(P, V)} &= \begin{vmatrix} \partial(\phi - \phi')/\partial P & \partial g/\partial P \\ \partial(\phi - \phi')/\partial V & \partial g/\partial V \end{vmatrix} \\ &= \frac{\partial(\phi - \phi')}{\partial P} \frac{\partial g}{\partial V} - \frac{\partial(\phi - \phi')}{\partial V} \frac{\partial g}{\partial P}. \end{aligned} \quad (14)$$

This is the determinant of the matrix whose columns are the components of the vectors dg and $d(\phi - \phi')$. Since a determinant is an anti-symmetric function of its column vectors, this Jacobian vanishes since by Eq. (13) dg and $d(\phi - \phi')$ are multiples of each other. Therefore $\phi - \phi'$ can be expressed as some function $F(g)$. Now we get using (13)

$$f - f' = d(\phi - \phi')/dg = dF(g)/dg = G(g) \quad (15)$$

for some function $G(g)$, which is not dependent on any other variables, and the theorem is proved.

In the event that g is an integral of motion, we call f its conjugate¹⁸ and ϕ its potential. We can then express the result of the theorem above as follows.

Corollary 1

Given an integral of motion, any two conjugates, as well as any two potentials, of the integral of motion differ by some integral of motion.

Process type	Zero along process	Integrating form	Process variable	Potential
Constant g	dg	$f dg$	$P dV$	$\Phi = \int (P dV + f dg)$
			$T dS$	$\Phi^* = E + \Phi$

where the integral in the table is independent of path.

IV. EXISTENCE THEOREM FOR POTENTIALS OF QUASISTATIC PROCESSES

We proceed to extend the construction of potential functions to quasistatic processes. Since some variation exists in the usage of the term "quasistatic" we begin with a careful examination of the meaning of the term.

Description of most real processes is complicated by the fact that the uniformity of the system is disrupted during the process. Variables such as temperature and pressure cannot be assigned a single real value. The nonuniformity makes the number of degrees of freedom (independent observables) infinite. There are however real processes with only a finite number of degrees of freedom. A very important subset of the finite degree of freedom processes are quasistatic. Recall¹ that a process Π is quasistatic for a system Σ if and only if the relaxation times of the system Σ are negligibly short compared to the time scale of the process Π . A small displacement from equilibrium causes a spontaneous process to occur in Σ , in zero time compared with times of interaction with the outside. Hence Σ is in *internal* equilibrium after each displacement so that every state of Σ during the process Π is a state of internal equilibrium. We can consider the process Π as a time-parametrized sequence of equilibrium states of Σ . If we ignore what happens outside the system, then this time-parametrized curve in the space of equilibrium states is a complete description of the process. If we wish to distinguish between a quasistatic process that goes completely dissipatively and the "same" process proceeding with some nondissipative work exchange, we have to look outside Σ and specify more than just the sequence of its equilibrium states. We can, for example, insist that in order for two processes to be the same they must both produce the same amount of work (or power, entropy, etc.) as a function of time. We show below that such func-

Before we proceed to the irreversible constructions, note that we can now extend the table of Legendre transforms by adding the reversibly coupled case.

tions of time can be expressed (represented by) functions of the equilibrium states. For example, we can find a function of state whose changes are the values of the useful work delivered by the process. We again call such free energy-like functions *potentials*.

We emphasize that quasistatic processes provide a far more realistic model of real processes than do reversible ones, for which equilibrium between Σ and surroundings is required. In order to reverse a quasistatic process, we have to convert work to heat. Quasistatic processes also produce entropy and proceed in finite time.

Theorem 2

Suppose given a system Σ a quasistatic noncyclic process Π of Σ . (For cyclic processes, each branch must be treated separately.) The process Π is given by the time-parametrized curve $\sigma(t)$ of states of Σ and a function $W(t)$ of time that specifies (say) the work output of the system during the process. Then there exists a function of state $\Phi[\sigma]$ such that $\Delta\Phi[\sigma(t)] = W(t)$ for all t along the process Π . Φ is unique up to an integral of motion.

Proof. For the existence part of the theorem, we need to find a function of state $\Phi[\sigma]$ such that

$$\Phi[\sigma(t)] - \Phi[\sigma(0)] = W(t). \quad (16)$$

If we take $\Phi[\sigma(0)] = 0$, then we can let Eq. (16) define Φ on the equilibrium states of Σ that lie on the curve representing the process Π . This definition can be extended to all equilibrium states of Σ by Tietze's extension theorem.¹⁹ This theorem guarantees that any continuous function on a compact set in a manifold has a continuous extension to the entire manifold. Since the time-parametrized curve of equilibrium states is a compact set, our proof of existence is complete.

To show uniqueness, suppose we have two functions Φ and Φ' with the above property. Then

$$\Delta(\Phi - \Phi') = \Delta\Phi - \Delta\Phi' = W(t) - W(t) = 0.$$

Therefore, $\Phi - \Phi'$ is constant on all states along Π .

V. POTENTIALS FOR SOME QUASISTATIC PROCESSES

In the preceding section we showed the existence and uniqueness of potentials for quasistatic processes. The next step is to show how these potential functions can be computed. Below we present a computational scheme for a class of quasistatic processes. The technique as presented is limited, particularly by assumption 2, but other approaches permit one to extend the calculation to more general cases.⁷

Our knowledge of a process is frequently stated in the form of a system of differential equations. For example we might know that heat is flowing between systems Σ_1 and Σ_2 due to conduction through a wall with heat conductance κ . Newton's law of heat conduction implies that

$$-T_1 dS_1 = T_2 dS_2 = \kappa(T_1 - T_2) dt, \quad (17)$$

where T_i and S_i refer to the temperature and the entropy of systems Σ_i on either side of the wall, and the boundary conditions are the initial states of Σ_i . This example points out quite clearly the difficulties in integrating such differential equations. The equation itself involves variables of both systems and of the wall that connects them. We now make two simplifying assumptions which serve to eliminate such difficulties and allow the computation of potential functions.

Assumption 1. All variables appearing in the differential equations describing the process are either constant or expressible in terms of state function of Σ_1 and time. Note that if any intensities appear, the process is quasistatic in that degree of freedom.

Assumption 2. The differential equations describing the process are first order. This means that no second derivatives appear in the equations. This does not imply that the second derivatives are zero or that the equations are linear.

We now present an example to show the utility of these assumptions.

Example 4: Quasistatic expansion

Consider a gas inside a cylinder equipped with a piston. We denote the usual state functions of the gas by P , V , T , and S . The temperature of the environment is denoted by T_{ex} . For the boundary variables we use α for the coefficient of friction against the walls and κ for the heat conductance of the wall.

It is assumed that all the heat created by friction is absorbed by the environment. We also assume that the system obeys Newton's law of heat conduction to the environment and that the gas is expanding according to the equations

$$dS/dt = \kappa(T - T_{ex})/T, \quad dV/dt = aV. \quad (18)$$

Volume-dependent rates are typical of many engines.²⁰ The above equations satisfy our assumptions 1 and 2 only if T_{ex} and κ are constant. We now combine the equations to eliminate time and get

$$dS/dV = (\kappa/a)(T - T_{ex})/TV, \quad (19)$$

$$(TV) dS - (\kappa/a)(T - T_{ex}) dV = 0 = d\Phi. \quad (20)$$

The differential $d\Phi$ of Eq. (20) generates an integral of motion in the sense of Cartan.^{21,22} If we reexamine Sec. III, we notice that state function integrals of motion are not necessary for the construction of potential functions. It is sufficient to have differential forms that vanish during the process. The useful work is given by

$$dW = P dV - \alpha(dV/dt) dV = (P - \alpha aV) dV, \quad (21)$$

and we look for a state function f such that the differential form

$$(P - \alpha aV) dV + f[(TV) dS - (\kappa/a)(T - T_{ex}) dV] = d\Phi \quad (22)$$

is exact.

Applying the ideal gas law, with C_v the molar heat capacity at constant volume and n the number of moles of gas, we have

$$d\Phi = [nRTV^{-1} - \alpha aV + nRTf - a^{-1}\kappa(T - T_{ex})f] dV + nfVC_v dT. \quad (23)$$

The condition that cross-partial derivatives be equal gives

$$nfC_v + nVC_v \frac{\partial f}{\partial V} = nRV^{-1} + nRTf + nRT \frac{\partial f}{\partial T} - a^{-1}\kappa f - a^{-1}\kappa(T - T_{ex}) \frac{\partial f}{\partial T}. \quad (24)$$

Using one arbitrary condition, we set $\partial f/\partial T = 0$ to obtain

$$f = \frac{nR}{V} \frac{1}{(a^{-1}\kappa - nR)}. \quad (25)$$

When (25) is substituted into (23), the exact differential becomes

$$d\Phi = A dT - 2BV dV + CV^{-1} dV, \quad (26)$$

where

$$A = \frac{n^2 R C_v}{a^{-1} \kappa - nR}, \quad B = \frac{1}{2} \alpha a,$$

and

$$C = T_{ex} \left(\frac{1}{nR} - \frac{a}{\kappa} \right)^{-1} = \frac{T_{ex} \kappa}{nC_v a} A.$$

By integrating (26), we obtain the potential

$$\begin{aligned}\phi &= AT - BV^2 + C \ln V. \\ &= A \left(\frac{T_{\text{ex}}}{nC_v} \ln V + T \right) - BV^2.\end{aligned}\quad (27)$$

This potential ϕ has the property that $\Delta\phi$ is the value of the useful work delivered in a quasistatic process which proceeds according to Eq. (18).

The calculation involved in the above example is considerably easier than actual integration of the equations of motion. It requires finding any solution of a partial differential equation in which one can choose some terms equal to zero.

The technique in the example above can be used only when it is possible to eliminate explicit time dependence from the equations of motion. Otherwise we must resign ourselves to including time in the set of thermodynamic variables. This yields a potential explicitly dependent on time. We can extend the construction of Theorem 1 to deal with processes that satisfy Assumptions 1 and 2.

Corollary 2

If a process satisfies assumptions 1 and 2, and the pressure P and volume V are described by the differential equations²³

$$dP/dt = F(P, V, t) \text{ and } dV/dt = G(P, V, t), \quad (28)$$

then a time-dependent potential $\phi(t)$ can be constructed for the process, such that ϕ is a potential for the work done in the process.

Proof. We construct the invariant differential forms

$$d\theta_1 = dP - F dt \text{ and } d\theta_2 = dV - G dt, \quad (29)$$

and make the work form exact by adding functional multiples of these Cartan integrals of motion:

$$d\phi = dW + f_1 d\theta_1 + f_2 d\theta_2. \quad (30)$$

The resulting potential ϕ is a function of state and time whose changes are the work done during a process proceeding according to the differential equations

$$d\theta_1/dt = 0, \quad d\theta_2/dt = 0. \quad (31)$$

We now extend Corollary 2 to an arbitrary number of coordinates.

Corollary 3

Suppose a given process satisfying Assumption 1 and 2, and a complete set of coordinate X_i , $i = 1 \dots n$, where n is the number of degrees of freedom of a system. If the time evolution of the X_i 's is described by the differential equations

$$\frac{dX_i}{dt} = F^i(X_1, \dots, X_n, t),$$

then a potential $\phi(X_1, \dots, X_n, t)$ can be constructed for the process.

Again we choose f_i 's such that

$$dW + f_i(F^i dt - dX_i)$$

is exact. We have now completed the extension of the development of a potential ϕ by the Legendre transform method to all processes satisfying assumptions 1 and 2. We shall refer to this generalization of the Legendre construction to time-dependent processes as the Legendre-Cartan construction.

We have in mind for Eqs. (28), Euler-Lagrange equations as well as equations of external constraint.

VI. CONNECTION TO A VARIATIONAL APPROACH

We now examine the connection of the potential formalism developed above to the optimal control theory mentioned in the introduction.^{5,6} The optimal control theory approach proceeds briefly as follows. We have part of the process determined, and we adjust the remaining "free part" of the process to optimize a given process variable. Consider for example a slight variant of example 4 above in which we retain the equation for heat conduction through the walls, and adjust the rate of motion of the piston to maximize work output. In terms of the mathematical formalism employed, the determined part of the process is an incomplete system of differential equations. Since the process must satisfy these equations, they are called the constraint equations. The process variable to be optimized is expressed as an integral. The Euler-Lagrange equations that result from the requirement that this integral be stationary, complete our system of differential equations. Then together with the initial and final states of the process we have the optimal process completely determined.

As mentioned in the Introduction, the explicit solution of the equations of motion for such optimal processes is possible only for the simplest examples.²⁴ We can however settle for less information and ask only for the value of the optimized process variable for the optimally running process.

Theorem 3

If we can construct a potential for a process variable by using the Legendre-Cartan construction based on constraint equations and Euler-

Lagrange differential equations, then changes in this potential tell us the value of the process variable for that process satisfying the condition of optimal control. The process variable plays the role of object function, and the variations leading to the Euler-Lagrange equations are taken with respect to the control variables.

Proof. The potential is constructed by making an exact differential from the integrand that gives rise to the process variable. To the integrand we add precisely those differential forms that vanish along the path for the process. The path is either completely fixed by external constraints (and thus trivially optimal) or is nontrivially optimal because it is required to satisfy a variational condition. Since these forms are zero along the optimal path, they do not alter the value of the integral on that path. We thereby evaluate the optimized process variable without having to solve the Euler-Lagrange equations and find the path explicitly.

The Legendre-Cartan differential forms must be found from either the constraint or the Euler-Lagrange equations. Unfortunately the computation schemes discussed in the previous sections

apply only if the equations of motion for the process satisfy the stringent conditions of Assumptions 1 and 2 of Sec. V. Further work is needed to extend the construction to less restrictive assumptions.²⁵ Potentials for realistic processes ought to provide a valuable tool for thermodynamic design.

VII. CONCLUSION

The above results show a step-by-step extension of the thermodynamic Legendre transform—the assignment of state functions to limiting values of process variables—to progressively larger classes of processes. Similar work on extending the other standard constructions of classical thermodynamics to encompass real time processes is needed. We will discuss these other extensions in forthcoming articles.

ACKNOWLEDGMENTS

This research was supported by a Grant from the National Science Foundation. One of us (B. A.) would like to acknowledge a Travel Grant from the Danish Science Foundation.

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¹⁸"Conjugate" is defined here by $\{f, g\} = 1$ as in classical mechanics, and not by $(\partial E/\partial g)_V = f$, as is customarily done in thermodynamics.

¹⁹See for example C. T. C. Wall, *A Geometric Introduction to Topology* (Addison-Wesley, Reading, Mass. 1972), p. 79; or I. Singer and A. Thorpe, *Lecture Notes on Elementary Topology and Geometry* (Scott Foresman, Glenview, Ill., 1967). The space of internal equilibrium states defines a manifold, which therefore guarantees the T_1 topology necessary for Tietze's theorem.

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²⁴The Euler-Lagrange equation for the presently available examples are very nonlinear and often include non-constant parameters from the environment. Even the

formulation of these variational problems required great care as they are very easily over or under determined.

²⁵A weaker form of this restriction is possible. If the

relaxation time to some degrees of freedom is so long compared to the time scale of the process that the corresponding degrees of freedom is frozen out, the active system can be defined to exclude these modes.

8.3. Thermodynamics in finite time: Extremals for imperfect heat engines

J. Chem. Phys. 66, 1571 (1977)

Thermodynamics in finite time: extremals for imperfect heat engines

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(Received 8 September 1976)

A general description is developed for processes involving work and two heat reservoirs or three heat reservoirs in terms of rates for continuous processes or of cycle averages for periodic processes. The description is applied to heat engines having friction, thermal resistance, and heat losses in order to determine the maximum power and maximum efficiency of such engines. By use of a geometric representation the reversible and irreversible parts of a process are separated as the components of a vector. This leads to the definition of a dimensionless quantity that measures irreversibility and is related in a complementary way to the traditional concept of efficiency. The new quantity appears to be useful in cases where efficiency has no well-defined meaning.

I. INTRODUCTION

The first goal of traditional thermodynamics was evaluating how well heat engines perform and how well they might perform in an idealized limit. The idealized limit became the reversible Carnot engine. The corresponding criteria of merit are the capacity of this engine to convert heat at a high temperature into work (the efficiency η) and the ratio of actual work performed to the work that a reversible Carnot engine could perform with the same heat input (the effectiveness). This approach served many useful purposes, but the high degree of idealization of the reversible Carnot engine puts a serious limit on what it can tell us about how well real engines might perform. We would like to have general methods for finding the maximum efficiency and maximum effectiveness for realistic engines operating at finite rates. This series of papers directs itself to finding such extrema.

We previously investigated the optimal operation of a simple model¹ and extended the use of thermodynamic potentials to quasistatic processes.² The first approach¹ involved finding the detailed time dependence of the various thermodynamic quantities using optimal control theory. This, of course, is the most complete analysis, but the resulting differential equations are frequently too difficult to solve and in many cases such detailed information is not needed. Thermodynamic potentials² offer a more economical way of determining the maximum work that can be extracted from a given process without describing how it is to be carried out.

Still, however, one has to solve a differential equation for each particular process.

In the present paper we develop a formalism which focuses on processes of energy conversion, treating the energy conversion system itself as a black box. The approach we use begins much like the method given by Keenan³ for describing energy availability and work in real and ideal steady-flow systems. Keenan's prescription in its simplest form takes the energy conservation equation for a working fluid, which, with neglect of heat losses and the change of kinetic energy of the fluid, becomes an equation relating the specific enthalpy of the fluid at the entrance to the sum of the specific work and specific enthalpy at the exit. With inclusion of kinetic energy changes and real losses, the formulation permits one to evaluate the work done by real steady-flow and reciprocating systems, their changes in availability, and their effectivenesses and engine efficiencies.

We seek a description of a general heat/work process based, not on the enthalpies of a working fluid at different points as Keenan does, but on the heat flows obtained by the interaction of three heat reservoirs at three different temperatures T_1 , T_2 , and T_3 . This includes the possibility that one is a work reservoir for which $T = \infty$. The process can be represented by a triangular diagram as shown in Fig. 1, which we cavalierly call tricycles. (The choice of the name is discussed below.) The basic idea is that a tricycle cannot itself consume or produce energy, so that conservation

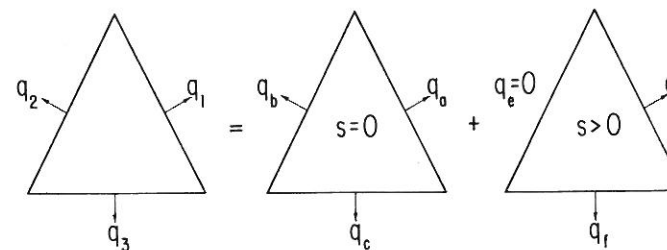


FIG. 1. Decomposition of tricycle (q_1, q_2, q_3) into a reversible part (with zero entropy production) and an irreversible part consisting of heat flow between reservoirs 1 and 3 uncoupled from reservoir 2.

laws govern the heat flows. These laws, applied to certain classes of tricycles, are used to find the maximum power output and efficiency for realistic engines. The triangular pictures have been helpful in clarifying the decomposition of processes into reversible and irreversible parts. In a later section, a geometric interpretation of the tricycle concept is developed to help quantify the degree of irreversibility of a process.

II. DEFINITION OF A TRICYCLE

A tricycle represents the interaction of three heat reservoirs at temperatures T_1 , T_2 , and T_3 with the corresponding heat flows q_1 , q_2 , and q_3 all taken to be positive for heat leaving the system. The rate of heat exchange q_i may either be thought of as an instantaneous value $q_i = dQ_i/dt$ or as an average over a cycle $q_i = Q_i/\Delta t$. The differential form is appropriate to continuous systems such as turbines, and the difference form, to systems that cycle mechanically so that Δt is the period and Q_i is the i th heat flow per cycle. In either case the system returns to its original state, so that

$$q_1 + q_2 + q_3 = 0. \quad (1)$$

In this sense, the energy conversion system, whether continuous or periodic, is cyclic; and therefore its representation as a triangle is given the name "tricycle." The rate of entropy production in the process is, like heat flow, either $s = dS_{\text{prod}}/dt$ or $\Delta S_{\text{prod}}/\Delta t$; and the rate of entropy production—continuous or cycle-averaged—is:

$$s = q_1\tau_1 + q_2\tau_2 + q_3\tau_3 \geq 0, \quad (2)$$

where we define $\tau_i = T_i^{-1}$. A work reservoir has $\tau = 0$ and thus produces no entropy. Most systems of interest will correspond to one τ equal to zero; however, the absorption refrigerator is an example for which all three τ 's are nonzero.

Any tricycle fulfilling Eqs. (1) and (2) represents a physically possible process. To further analyze the interaction we want to decompose it into its reversible and (totally) irreversible components. The former is unambiguously defined by $s=0$, but there is a degree of choice about the meaning of "the amount of irreversibility." One such choice is presented in Fig. 1, where q_1 , q_2 , and q_3 is decomposed into the reversible q_a , q_b , and q_c , and the irreversible heat flow from τ_1 to τ_3 ($q_e=0$). Others, in particular one totally symmetric in the three reservoirs, are presented in section 4. Although the temperatures are free to vary within the bounds of Eq. (2), it may be useful to visualize the tricycles with $\tau_1 < \tau_2 < \tau_3$ or equivalently $T_1 > T_2 > T_3$. In that case a tricycle with $q_2 > 0$ is a refrigerator or heat pump, one with $q_2 < 0$ and $\tau_1 = 0$ is a conventional heat engine.

With the decomposition of Fig. 1 it is easy to derive:

$$q_a/(\tau_3 - \tau_2) = q_b/(\tau_1 - \tau_3) = q_c/(\tau_2 - \tau_1), \quad (3)$$

$$q_d = -q_f = q_1 + q_2(\tau_3 - \tau_2)/(\tau_3 - \tau_1),$$

and

$$s = q_1(\tau_1 - \tau_3) + q_2(\tau_2 - \tau_3). \quad (4)$$

III. EXAMPLES OF WORK-HEAT-HEAT TRICYCLES

Of the three originally independent variables q_1 , q_2 , and q_3 , one may be fixed through Eq. (1), another one by defining a functional form for the losses q_f , and the last degree of freedom will then specify the extent of the process. In this section we look at tricycles where side 1 is a work reservoir, so that $\tau_1 = 0$, and we re-label $q_1 = w$. We will apply different expressions for q_f representing friction, heat leak, and thermal resistance, and derive the maximum power w and efficiency $\eta = w/(-q_2)$ that can be obtained from these tricycles.

A. Friction and heat leak

We define the losses to be

$$q_f = \alpha q_a^2 + q_0, \quad (5)$$

where the coefficient of friction $\alpha > 0$, and q_0 is a rate-independent heat leak from τ_1 to τ_3 which tends to speed up the most efficient operation of the tricycle. The quadratic friction term corresponds to a thick layer of fluid lubricant between sliding surfaces.⁴ Other forms apply for thin lubricant layers and for dry surfaces. The power is $w = q_a - q_f$. We set its derivative with respect to q_2 equal to zero to find the maximum power:

$$w = (1/4\alpha) - q_0, \quad (6)$$

obtained for:

$$q_2 = \frac{-1}{2\alpha} \frac{\tau_3}{\tau_3 - \tau_2}. \quad (7)$$

Maximizing the efficiency gives two solutions:

$$\eta = \frac{\tau_3 - \tau_2}{\tau_3} (1 \pm 2\sqrt{\alpha q_0}), \quad (8)$$

for

$$q_2 = \pm \frac{\tau_3}{\tau_3 - \tau_2} \sqrt{\frac{q_0}{\alpha}},$$

and

$$w = -2q_0 \mp \sqrt{\frac{q_0}{\alpha}}, \quad (9)$$

with the upper signs for a heat pump and the lower signs for a heat engine.

B. Thermal resistance

Let us for a moment drop the black box restriction of the tricycle and look inside it. We assume that it is composed of another tricycle—dashed in Fig. 2—connected to the outer reservoirs at τ_2 and τ_3 through thermal resistances ρ_2 and ρ_3 , so that its actual operating temperatures are:

$$\begin{aligned} T_1^i &= T_1 (= \infty), \\ T_2^i &= T_2 - q_2\rho_2, \\ T_3^i &= T_3 - q_3\rho_3. \end{aligned} \quad (10)$$

We now decompose the tricycle into reversible and irreversible *internal* tricycles as in Fig. 2 to find the reversible parts:

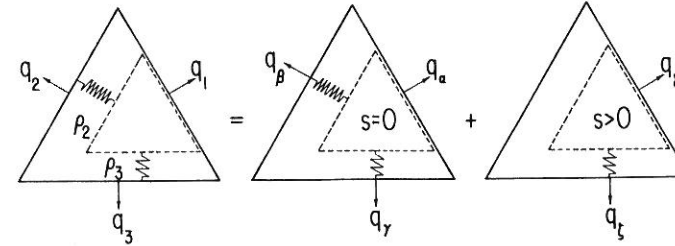


FIG. 2. Tricycle with thermal resistances ρ_2 and ρ_3 between reservoirs 2 and 3 and an interior tricycle (dashed). The interior tricycle is decomposed into its reversible and irreversible parts in analogy to Fig. 1.

$$\begin{aligned} q_a &= -q_2 + T_3 q_2 / (T_2 - q_2 \rho), \\ q_b &= q_2 = q_b, \end{aligned} \quad (11)$$

and

$$q_f = -T_3 q_2 / (T_2 - q_2 \rho);$$

and the irreversible parts:

$$\begin{aligned} q_b &= -q_c = q_1 + q_2 - T_3 q_2 / (T_2 - q_2 \rho), \\ \text{where,} \\ \rho &= \rho_2 + \rho_3. \end{aligned} \quad (12)$$

Decomposition of the same outer tricycle according to Fig. 1 and Eq. (3) yields:

$$q_3 = q_c + q_f = q_f + q_c,$$

or

$$q_f = q_c + (q_a - q_b),$$

which means that the "uncaptured work" arising from the thermal resistance is:

$$q_a - q_b = -\frac{T_3}{T_2} \frac{q_2^2 \rho}{T_2 - q_2 \rho}. \quad (13)$$

This quantity must be positive to have physical significance, which requires that:

$$\Delta T = q_2 \rho < T_2. \quad (14)$$

Using the expression (13) for the loss term q_f gives a maximum power output of:

$$w = -\rho^{-1} (\sqrt{T_2} - \sqrt{T_3})^2, \quad (15)$$

for

$$\Delta T = T_2 - \sqrt{T_2 T_3}. \quad (16)$$

These results are identical to the ones obtained in an analysis⁵ of a Carnot engine with finite heat conductance to its reservoirs. However, some care must be exercised in the comparison, since the Carnot engine described by Curzon and Ahlborn only absorbs and discharges heat through the thermal resistances in the respective half-periods of its cycle, whereas Eqs. (10) imply that the coarse-grained tricycle assumes constant heat flow, or that ρ_1 and ρ_2 are *effective* values of the conductances that permit the actual heat flows to be represented by an equivalent constant flow. Consequently the values of ρ_2 and ρ_3 must be twice those used in Ref. 3 in order to produce the same losses.

Maximum efficiency is obtained for the value of q_2

for which

$$d\eta/dq_2 = -\rho T_3 / (T_2 - q_2 \rho)^2$$

equals zero. No such finite, nonzero q_2 exists. The efficiency increases monotonically, as $q_2 \rightarrow 0$, just as intuition suggests.

C. Friction, heat leak and thermal resistance

Combining the terms (5) and (13) which together represent the difference between ideal and real work, we obtain an accurate description of real heat machines with their frictional losses, constant heat losses, and resistance to heat transfer. The power, continuous or average depending on the system, is

$$w = -\alpha \left(\frac{T_2 - T_3 - q_2 \rho}{T_2 - q_2 \rho} \right)^2 q_2^2 - \frac{T_2 - T_3}{T_2} q_2 + \frac{T_3}{T_2} \frac{q_2^2 \rho}{T_2 - q_2 \rho} - q_0. \quad (17)$$

The extrema of Eq. (17) are located at:

$$\begin{aligned} \Delta T &= T_2 \pm \sqrt{T_2 T_3}, \text{ and} \\ \frac{1}{2} [-\nu + T_2 - T_3 \mp \sqrt{(\nu + T_2 + T_3)^2 - 4T_2 T_3}], \end{aligned} \quad (18)$$

where

$$\nu = \rho/2\alpha, \quad (19)$$

as substitution of (18) in (17) shows. (Direct derivation of the extrema of (17) is a rather lengthy exercise, not recommended for the casual reader.)

A contour diagram of $-\rho u(\nu, \Delta T)$ for $T_2 = 9$, $T_3 = 1$ and $\Delta T_0 = q_0 \rho = 0$ is shown in Fig. 3 with the curves of maxima and minima drawn in heavy solid and dashed lines respectively. The physical region, $\Delta T < T_2$, is divided into a frictionally dominated region for $\nu > (\sqrt{T_2} - \sqrt{T_3})^2$ with two maxima and a minimum, and a resistively dominated region for $\nu < (\sqrt{T_2} - \sqrt{T_3})^2$ with one maximum. Furthermore, the two maxima have the same value. Calling the four roots (18) $\Delta T_{a,b,c,d}$ we have ΔT_a always nonphysical, and

$$-\rho u(\Delta T_c) = -\rho u(\Delta T_d) = \Delta T_0 - \frac{1}{2}\nu, \quad (20)$$

so the same extremal power output may be obtained with two different expenditures of heat input and thus at different efficiencies. The extremum $-\rho u(\Delta T_b)$ (and thus w) is a monotonically decreasing function of ν , so no global maximum of w exists for finite α .

The region around the point where the three roots $\Delta T_{b,c,d}$ coalesce is very flat, viz., to second order in

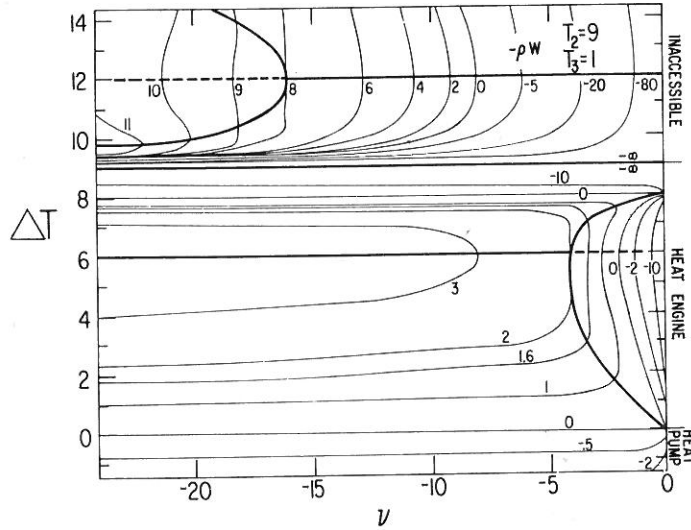


FIG. 3. Contour map of $-\rho w$ of (17) as a function of relative friction ($\nu = \rho/2\alpha$) and heat exchange rate with reservoir 2 ($\Delta T = \rho q_2$) for a work-heat-heat tricycle with friction and thermal resistance. The figure is drawn for reservoir temperatures $T_2 = 9$ and $T_3 = 1$, in arbitrary units. The heavy lines indicate singularities and maxima (full line) and minima (broken line), Eq. (18). The region of ν near zero is the frictionally-dominated region with two real and equal maxima, and the region of larger negative ν is the resistance-dominated region with only a single maximum.

variations around the bifurcation point $(\nu, \Delta T)_* = [-(\sqrt{T_2} - \sqrt{T_3})^2, T_2 - \sqrt{T_2 T_3}]$,

$$-\rho w = \frac{z^2}{2} \left(1 + \frac{\nu}{z^2} - \frac{\nu^2}{z^4} \right) + \Delta T_0 - \frac{u^2}{\sqrt{T_2 T_3}} \frac{\nu}{z^2} \left(1 - \frac{\nu}{z^2} \right), \quad (21)$$

with

$$(\nu, \Delta T) = (\nu, \Delta T)_* + (v, u),$$

and

$$z = \sqrt{T_2} - \sqrt{T_3}.$$

In order to give the dimensionless quantities in Fig. 3 more physical meaning let us make each temperature "unit" equal to 300°K, so $T_2 = 2700$ °K and $T_3 = 300$ °K. At the point $(\nu, \Delta T)_*$ a thermal resistance of $-1^\circ/\text{kW}$, a reasonable value for heat machines of the 100 kW class like car engines, and frictional coefficient $\alpha = 4.167 \times 10^{-4} \text{ kW}^{-1}$ produces a power output $w = 600$ kW at a heat consumption of $q_2 = -1800$ kW, and therefore at the efficiency $\eta = 0.33$. Twice as large friction, $\alpha = 8.333 \times 10^{-4} \text{ kW}^{-1}$, makes the machine operate in the frictionally dominated region where the maximum power output $w = 300$ kW can be obtained at either of the heat consumptions $q_2 = -706$ kW or $q_2 = -2294$ kW with corresponding efficiencies $\eta = 0.42$ and 0.13. In the thermal resistance dominated region where only one maximum exists, a frictional coefficient $\alpha = 2.083 \times 10^{-4} \text{ kW}^{-1}$ allows a maximum $w = 1200$ kW at $q_2 = -1800$ kW and $\eta = 0.67$.

Whereas finding the extrema (18) of the power output involves solving a quartic equation, the extrema of the efficiency are located at the roots of the quintic:

$$\Delta T^5 - 3T_2 \Delta T^4 - [2\nu(T_3 + \Delta T_0) - (3T_2^2 - 2T_2 T_3 - \Delta T_0^2)] \Delta T^3 + T_2 [2\nu(T_3 + 3\Delta T_0) - (T_2 - T_3)^2] \Delta T^2 - 6\nu T_2^2 \Delta T_0 \Delta T$$

$$+ 2\nu T_2^3 \Delta T_0 = 0, \quad (22)$$

which we have been unable to solve analytically. Instead contour diagrams of $\eta(\nu, \Delta T) = w/(-q_2)$ are plotted in Fig. 4 for $T_2 = 9$, $T_3 = 1$, and $\Delta T_0 = 0$ and -1 . For heat engines ($\Delta T > 0$), small losses correspond to large η ($\eta \rightarrow 1$) and for heat pumps ($\Delta T < 0$), to numerically small η ($\eta \rightarrow 0$). (The coefficient of refrigerator performance⁹ is $q_3/q_1 = \eta^{-1} - 1$.) When $\Delta T_0 = 0$, there are no losses which encourage a fast process, and the best efficiency is $\eta = \eta^{rev} = 0.89$ for an infinitely slow process at $\Delta T = 0$. When there are heat leaks, $\Delta T_0 \neq 0$ creates a singularity at $\Delta T = 0$, and the heat engine region of the contour map is very similar to what was found in the power contour plot with two maxima and a minimum discernible in the frictionally dominated region $\nu \geq -4$ and only one maximum in the resistive region $\nu \leq -4$. Heat pumps display only one minimum over the entire interval, which makes $(\eta^{-1} - 1)$ a maximum.

IV. GEOMETRIC INTERPRETATION

Mathematically, a tricycle is an ordered triple of real numbers $q = (q_1, q_2, q_3)$, satisfying the equations

$$\sum q_i = 0, \text{ and } \sum \tau_i q_i \geq 0.$$

Such ordered triples lend themselves naturally to geometric interpretation in which each point of a 3-dimensional q -space corresponds to a process. The geometric picture in turn suggests new ways to examine the physics it describes. One of these is a way to describe the irreversibility of a process, as we shall see, which requires that we examine the concept of distance in q -space. Moreover geometrization is suggestive of ways to treat systems with several reservoirs or even a continuously varying heat bath temperature, such as Rankine or Otto cycles, which we hope to

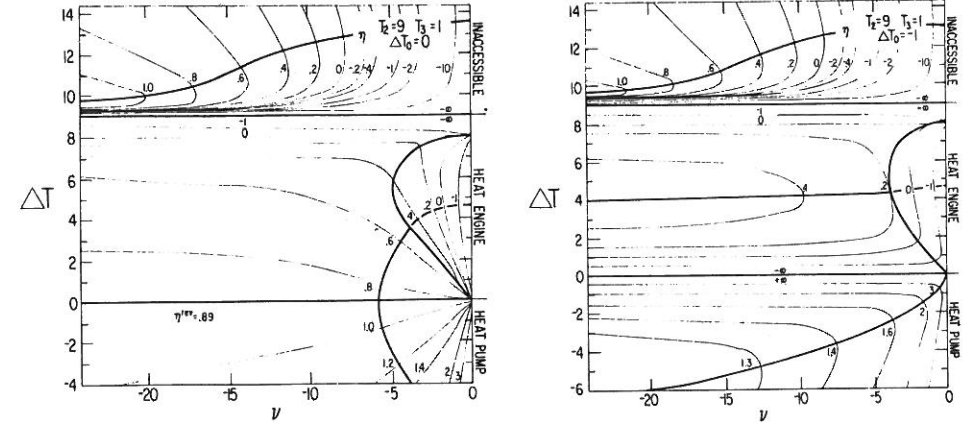


FIG. 4. Contour maps of the efficiency η as a function of relative friction ($\nu = \rho/2\alpha$) and heat exchange rate with reservoir 2 ($\Delta T = \rho q_2$) for a work-heat-heat tricycle with friction, thermal resistance, and constant heat leak $q_0 = \Delta T_0/\rho$: (a) $\Delta T_0 = 0$, so the maximum efficiency is that of the reversible Carnot engine; (b) $\Delta T_0 = -1$, which yields contours much like those of Fig. 3. However, unlike the extremal work, the extremal efficiency has a fifth root in the heat pump region of ΔT . The heavy lines indicate singularities and maxima (full line) and minima (broken line). The extrema drawn are estimated solutions of Eq. (22). The reservoir temperatures are the same as for Fig. 3, $T_2 = 9$, $T_3 = 1$.

examine in the future. Meanwhile, we concentrate on the 3-dimensional (q_1, q_2, q_3) space and 2-reservoir heat/work or 3-reservoir heat processes.

In order to define distance in this space, one must first adopt a metric.⁷ Nothing in the mathematics of this space defines a natural metric, but the physics makes some choices particularly useful. In general, the metric c , restricted here to be diagonal, appears in the scalar product of vectors a and b , thus:

$$\mathbf{a} \cdot \mathbf{b} = \sum_i \frac{a_i b_i}{c_i}, \quad (23)$$

where c is undetermined for the time being. The length of a vector is as usual:

$$a = |\mathbf{a}| = (\mathbf{a} \cdot \mathbf{a})^{1/2}, \quad (24)$$

and \perp denotes an orthogonal vector $\mathbf{a}^\perp \perp \mathbf{a}$.

The energy conservation Eq. (1) defines a plane which, for convenience, we call the q -plane. Similarly, the locus of zero entropy production is the s -plane for which Eq. (2) is an equality. The representative point of a reversible process must satisfy both $\sum q_i = 0$ and $s = \sum \tau_i q_i = 0$, and thus lie on the intersection of the two planes which define a reversible line r with unit direction vector:

$$\mathbf{d}_r = \theta / \theta, \quad (25)$$

where:

$$\theta = (\tau_3 - \tau_2, \tau_1 - \tau_3, \tau_2 - \tau_1), \quad (26)$$

with components equal to differences of inverse temperatures. Since a spontaneous process has a positive entropy production, all physical tricycles will be represented by points on that half of the q -plane lying above the s -plane (see Fig. 5).

Decomposition of q into its reversible and irreversible components:

$$\mathbf{q} = \mathbf{q}_r + \mathbf{q}_i^+, \quad (27)$$

gives:

$$\mathbf{q}_r = (\mathbf{q}_r \cdot \mathbf{d}_r) \mathbf{d}_r = \sum_{i=1}^3 \left(\frac{q_i \theta_i}{\theta_i} \right) \theta^{-2} \theta, \quad (28a)$$

$$\mathbf{q}_i^+ = \mathbf{q} - \left[\sum \left(\frac{q_i \theta_i}{c_i} \right) \right] \theta^{-2} \theta, \quad (28b)$$

which, of course, depend on the metric chosen. A useful dimensionless measure of the irreversibility of the process is the quantity we call the *drive*:

$$\delta = \frac{q_i^+}{q} = [1 - (\mathbf{q} \cdot \theta)^2 / q^2 \theta^2]^{1/2}, \\ = \left[1 - \frac{(\sum q_i \theta_i / c_i)^2}{(\sum q_i^2 / c_i) (\sum \theta_i^2 / c_i)} \right]^{1/2}, \quad (29)$$

which is the length of the irreversible part of q , relative to the total length of q . The drive is zero for a reversible process, and unity for a process containing no reversible component \mathbf{q}_r . The length of \mathbf{q} and its components depend on the metric, so the vector \mathbf{q}_i^+ does also. Hence there is no invariant (metric-independent) meaning to "totally irreversible." However, we shall see that the extrema of δ for the friction-heat leak-resistance problem occur at the values of ΔT that solve (22), which themselves are invariant.

Any metric of the form:

$$\theta_i / c_i = \theta_3 / c_3 \neq \theta_2 / c_2, \quad (30)$$

yields:

$$\mathbf{q}_i^+ = \mathbf{q} - (q_2 / \theta_2) \theta = \left(q_1 - q_2 \frac{\theta_1}{\theta_2}, 0, q_3 - q_2 \frac{\theta_3}{\theta_2} \right), \quad (31)$$

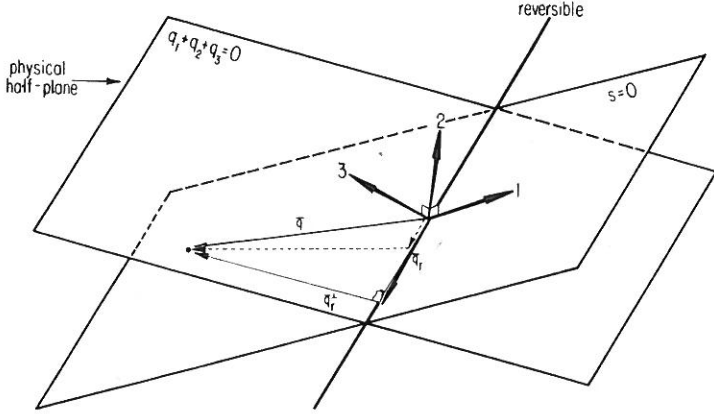


FIG. 5. The (q_1, q_2, q_3) space, with the planes defined by conservation of energy and zero entropy production. Real processes lie on the "physical half-plane" indicated, with the reversible limit given by the intersection of the two planes. Two decompositions of a general tricycle \mathbf{q} into its reversible and irreversible components are shown. The drive is defined as the ratio of the length of the irreversible component q_i to the total length of \mathbf{q} , the vector representing the real process.

which is identical to the decomposition arbitrarily chosen in Fig. 1. This is shown as the dotted vectors in Fig. 5. The inequality of θ_2/c_2 in Eq. (30) is necessary to keep q_r from vanishing. A more desirable decomposition would be one that does not single out one component, such as q_2 above, but treats all heat exchanges on an equal footing. One such metric is:

$$\mathbf{c} = C(\theta_1^2, \theta_2^2, \theta_3^2), \quad (32)$$

with:

$$C = \left(\sum \theta_i^2 \right) / 3\pi\theta_i^2. \quad (33)$$

In this metric the reversible part of the vector \mathbf{q} has length

$$q_r = \frac{|\mathbf{q}| \theta_i}{\sum \theta_i} \sum (q_i / \theta_i), \quad (34a)$$

while the irreversible part and the drive take on the simple forms:

$$q_i = s, \quad (34b)$$

and

$$\delta = s/q. \quad (34c)$$

This metric measures distance in entropy units.

This 3-dimensional representation (actually 2-dimensional since \mathbf{q} must be on the physical half plane) of any tricycle is a convenient way of visualizing a heat process, with the drive as a generalized inefficiency.

V. APPLICATION OF METRIC

The analysis of power and efficiency for work-heat-heat tricycles in section 2 was independent of metric. In this section we will use the geometric representation to elaborate on these examples. We include an unspecified uncaptured work f so that:

$$W = -\frac{\tau_3 - \tau_2}{\tau_3} q_2 - f, \quad s = f\tau_3. \quad (35)$$

Going back to the general metric for a moment we find from Eq. (28) that:

$$q_r = s / \left[\sum \tau_i^2 c_i - \frac{(\sum \tau_i c_i)^2}{\sum c_i} \right]^{1/2}, \quad (36a)$$

$$q_r = \frac{-1}{\theta \tau_3} \left[q_2 \left(\sum \frac{\theta_i^2}{c_i} \right) + s \left(\frac{\theta_1}{c_1} - \frac{\theta_3}{c_3} \right) \right], \quad (36b)$$

which says that for all metrics q_r is proportional to s and q_r is linear in s , so for increasing f the point \mathbf{q} will describe a straight half-line from the reversible line back towards the heat pump region. Metric (32) is seen to be exactly the one which simplifies Eqs. (36) to:

$$q_r = s, \quad (37a)$$

$$q_r = -\frac{\text{sign}(\tau_3 - \tau_2)}{\sqrt{\sum \theta_i^2}} [3q_2\tau_2(\tau_3 - \tau_2) + s(\tau_3 - 2\tau_2)], \quad (37b)$$

$$q^2 = \frac{3}{\theta_1^2 + \tau_2^2} \left\{ \left[\sum \theta_i^2 \right]^{-1} [q_2\theta_1\tau_2(\tau_3 - 2\tau_2) - s(\theta_1^2 + \tau_2^2)]^2 + q_2^2\theta_1^2\tau_2^2 \right\}. \quad (37c)$$

Here, as well as in Eqs. (36), the loss term enters only through its accompanying entropy production.

The most nearly reversible process is obtained when the drive δ , Eq. (29), is at its minimum which happens when:

$$\frac{d\delta}{dq_2} = \frac{(\sum \theta_i^2/c_i)^2}{q^3\theta^2\tau_3^2[\sum \tau_i^2 c_i - (\sum \tau_i c_i)^2/\sum c_i]^{1/2}} \left(\frac{ds}{dq_2} q_2 - s \right) \times \left[q_2 \sum \theta_i^2/c_i + s \left(\frac{\theta_1}{c_1} - \frac{\theta_3}{c_3} \right) \right] = 0, \quad (38)$$

which is satisfied when:

$$\frac{s}{q_2} = \frac{ds}{dq_2}, \quad (39a)$$

or

$$\frac{s}{q_2} = -\frac{\theta_1^2/c_1 + \tau_3^2/c_2 + \tau_2^2/c_3}{\theta_1/c_1 - \tau_2/c_3}. \quad (39b)$$

Introducing the full friction, heat leak and thermal resistance losses from Eq. (17), Eq. (39a) becomes identical to Eq. (22), the quintic equation defining the optimal efficiency in section C. Minimization of the

drive is thus equivalent to maximizing the efficiency η , irrespective of metric. The relation between δ and η for an arbitrary metric is:

$$1 - \delta^2 = \frac{\{\eta[c_1^{-1}\tau_3 - \tau_2(c_1^{-1} + c_3^{-1})] + c_2^{-1}\tau_3 + c_3^{-1}\tau_2\}^2}{[c_1^{-1}\eta^2 + c_2^{-1} + c_3^{-1}(1 - \eta)^2][c_1^{-1}(\tau_3 - \tau_2)^2 + c_2^{-1}\tau_3^2 + c_3^{-1}\tau_2^2]}. \quad (40)$$

For metric of Eq. (32), this simplifies somewhat to:

$$1 - \delta^2 = \frac{\{\eta[\tau_3 - \tau_2]^{-1} - \tau_2^{-1}\} + \tau_2^{-1} + \tau_3^{-1}\}^2}{3[\eta^2(\tau_3 - \tau_2)^{-2} + \tau_3^{-2} + (1 - \eta)^2\tau_2^{-2}]}. \quad (41)$$

When $\eta = \eta^{\text{rev}}$, $\delta = 0$ independent of metric, but when $\eta = 0$, δ approaches a value that depends on the metric.

As has been shown in this section, the geometric representation of tricycles is a powerful tool for obtaining information about a general class of heat processes, especially when the equations are not simplified by the presence of a work reservoir. In that case the drive offers a natural way to extend the traditional concept of efficiency in a complementary way closely related to the entropy production.

ACKNOWLEDGMENTS

This research was supported by a grant from the National Science Foundation. One of us (B.A.) would like to acknowledge a travel grant from the Danish Science Foundation. We would also like to thank the Aspen Center for Physics for its hospitality.

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8.4. Thermodynamics in finite time: A chemically driven engine

J. Chem. Phys. **72**, 5118 (1980)

Thermodynamics in finite time: A chemically driven engine

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(Received 5 September 1979; accepted 23 January 1980)

The methods of finite-time thermodynamics are applied to processes whose relaxation parameters are chemical rate coefficients within the working fluid. The direct optimization formalism used previously for heat engines with friction and finite heat transfer rates—termed the tricycle method—is extended to heat engines driven by exothermic reactions. The model is a flow reactor coupled by a heat exchanger to an engine. Conditions are established for the achievement of maximum power from such a system. Emphasis is on how the chemical kinetics control the finite-time thermodynamic extrema; first order, first order reversible, and second order reaction kinetics are analyzed. For the types of reactions considered here, there is always a finite positive flow rate in the reactor that yields maximum engine power. Maximum fuel efficiency is always attained in these systems at the uninteresting limit of zero flow rate.

I. INTRODUCTION

The Carnot–Clausius–Kelvin approach toward thermodynamics emphasizes the process variables of work and heat, in contrast with the Gibbsian view that emphasizes the state variables.¹ From the former standpoint, the importance of the thermodynamic potentials lies largely in their roles as bounds on process variables, for processes limited but not completely determined by constraints. Traditional thermodynamics admits constraints on state variables, such as constancy of temperature, pressure, or volume, or on process variables, such as adiabaticity, but has no place for constraints on time or rate. For a significant class of processes, one can extend the concept of thermodynamic potential to functions that bound the process variables of work and heat where the constraints include constraints on time or rate.² Two ways have been developed to evaluate these bounds, one by means of Legendre–Cartan transformations which yield absolute but not unique potentials,² and the other by direct determination of the extremal values of the process variables.³ Until now, these methods have been applied only to mechanical processes and simple heat engines. In these processes, the time constraints originate in heat transfer and friction.

Here, we present the first application of finite-time thermodynamics to a system in which chemical change is part of the process and the time constraints enter through the rate coefficients of the chemical reactions. The system adopted is a continuous flow reactor that converts reactants to products in an exothermic process and supplies heat to an engine. The simplifying assumption is made that the rate coefficients of the chemical reactions are independent of temperature. This provides a simple model of the boiler section of a power plant. The reaction supplying heat will not, in general, go to completion and the temperature of the heat going to the engine may be lower than that of the reactor. The formalism used to analyze the problem is the direct maximization based on the “tricycle” representation of a thermal process,³ which is reviewed briefly in the next section.

One has several reasonable options when one chooses

the variable whose extremum is to be determined.

Curzon and Ahlborn⁴ compared the efficiencies of two kinds of idealized electric power generating systems—Carnot engines with finite thermal conductances to their heat reservoirs: engines operating at maximum efficiency and engines yielding maximum power. The time path of optimal cycles depends markedly on what quantity is optimized: Optimizing efficiency, effectiveness, and entropy production all give quite different paths.⁵ Here we examine the functional dependence of objective functions, particularly fuel efficiency and power output from the driven engine, upon the flow rate within the flow reactor.

While one can draw parallels between our model and real processes, we make no claim that the specific system analyzed here has immediate applications, particularly because of the simplifying assumptions regarding the temperature dependence of reactions. However, it serves very well indeed as an illuminating model problem for the extension of finite-time thermodynamics to chemical processes. For the systems studied previously,^{2,3,6,7} it was assumed that any working fluids attained hydrodynamic and chemical equilibrium rapidly relative to the rates associated with heat transfer and frictional heat generation. In the system examined here, we assume again that the hydrodynamic degrees of freedom come to equilibrium quickly but the rate of chemical equilibration is comparable to or slower than the rates of heat transfer. No frictional effects are considered for this system.

In the next section, we review the tricycle representation and describe how a heat engine driven by an exothermic chemical process may be visualized as two coupled tricycles. In subsequent sections, the model is analyzed for commonly encountered systems following first and second order kinetics.

II. TWO COUPLED TRICYCLE MODELS FOR A HEAT ENGINE DRIVEN BY CHEMICAL WORK

A tricycle is a point in three-space representing the interactions between three heat reservoirs at temperatures T_1 , T_2 , and T_3 .³ The three dimensions of the space correspond to the three rates of heat flow into each of the respective reservoirs. They are designated

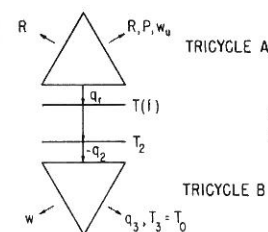


FIG. 1. A chemically driven engine as two coupled tricycles.

q_1 , q_2 , and q_3 . One may be a work reservoir, such as a weight that may be lifted; the corresponding temperature is infinite. We use $q_1 = w$ conventionally to represent power or average power produced.

There are two constraints upon the tricycle: Energy must be conserved over time

$$q_1 + q_2 + q_3 = 0; \quad (1)$$

and the rate of entropy production cannot be negative

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} + \frac{q_3}{T_3} \geq 0. \quad (2)$$

Using the conventions established in Ref. 3, we shall designate reservoir 1 of our heat engine as the work reservoir, reservoir 2 as the high-temperature reservoir from which heat flows into the engine, and reservoir 3 as the low-temperature reservoir into which the unconverted heat flows. Reference 3 discusses the role of irreversibilities such as friction, heat leak, and thermal resistance in determining the maximum power output or maximum efficiency of such an engine. We shall now focus upon the rate at which the heat which drives the engine (q_2) is produced of q_2 is generated by an exothermic chemical process.

Consider the exothermic process



which releases an amount of heat per unit time q_r . Suppose that this process, represented in Fig. 1, occurs in Tricycle A (with initial reactant concentration R_0), and supplies q units of heat per unit time to Tricycle B, a heat engine. In Tricycle A, w is the chemical work which is not released as heat. In Tricycle B, w is the power produced and q_3 is the unconverted heat released per unit time.

Tricycle A differs from a heat engine tricycle in that some of the energy flow is in the form of chemical work. A common feature of Tricycles A and B is the incomplete conversion of energy; unreacted starting material R is lost in A and waste heat q_3 is lost in B. In both cases, some of the loss results from second-law restrictions. Additional losses occur because of the finite-time nature of the problem; this constraint may appear as a finite rate of reaction in Tricycle A or as friction in a heat engine.

$T(f)$ is the “flame” temperature at which q_r is released from the chemical reaction and T_2 is the temperature of the hot reservoir of the engine. Suppose further that the chemical reaction $R - P$ occurs in a flow tube,

so that the time τ during which the reaction is allowed to proceed is inversely proportional to the flow rate f . (Obviously, in this model the flow rate, the reactor length, or the dwell time in the reactor could be treated as the independent variable.) If we define the extent of the reaction $\epsilon(\tau)$ as

$$\epsilon(\tau) = P(\tau)/R_0, \quad (4)$$

then we may express q_r as

$$q_r = Q_m \epsilon(\tau) f, \quad (5)$$

where Q_m is the molar exothermicity of the reaction and f is the flow rate in moles per unit time. Since τ and f may be expressed in terms of each other by simple relations such as

$$f = \frac{(A \cdot l)(\rho_m)}{\tau}, \quad (6)$$

with $(A \cdot l)$ the volume of the flow tube and ρ_m the density of reaction mixture (moles/unit volume), q_r may be written as a function of the flow rate

$$q_r(f) = Q_m f \epsilon(f). \quad (7)$$

Of course, the functional dependence of $\epsilon(f)$ on f will be determined by the reaction kinetics.

The temperature at which the heat q_r is released will depend upon the extent of the reaction, and therefore on the flow rate. Since one generally solves for flame temperatures self-consistently,⁸ one cannot write a general analytic expression for $T(f)$. We shall see that simplifying assumptions are necessary for some of the cases treated here. For all our cases, we assume that the mixture of product gases is homogeneous and that any relaxation within the translations, vibrations, and rotations of the gas itself occurs very rapidly with respect to the time scale of the chemical reaction. In the first case we assume that the heat capacity C of the reacting mixture remains constant through the temperature range T_0 (the inlet temperature) to $T(f)$ (the flame temperature). The temperature at which the heat of reaction is released is then given by

$$T(f) = \frac{Q_m \epsilon(f)}{C} + T_0. \quad (8)$$

The constant heat capacity restriction will be lifted in the second case.

In order to produce work, q_r may be utilized over a temperature range beginning with $T(f)$, or, alternatively, the heat from the product mixture may be transferred to maintain a reservoir at a lower temperature T_2 .

Case I: Consider first Case I, where the heat of reaction q_r is extracted from the products emerging at the flame temperature $T(f)$, so that $T(f)$ is the highest temperature at which heat is supplied to do work. Note that the hot products, in this case, constitute a hot reservoir with finite heat capacity. The maximum amount of work recoverable from a substance with finite, constant heat capacity C at $T(f)$ in contact with a reservoir at a constant lower temperature T_0 is given by a reversible process

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$$W_{\max} = C \int_{T_0}^{T(f)} \left(1 - \frac{T_0}{T}\right) dT \quad (9)$$

$$= C \left\{ [T(f) - T_0] - T_0 \ln \left(\frac{T(f)}{T_0} \right) \right\},$$

with corresponding maximal efficiency

$$\eta = 1 + \frac{T_0}{T(f) - T_0} \ln [T_0/T(f)]. \quad (10)$$

Combining Eqs. (7) and (10), we obtain an expression for the power production for Case I:

$$w(f) = Q_m f \epsilon(f) \left[1 + \frac{T_0}{T(f) - T_0} \ln \left(\frac{T_0}{T(f)} \right) \right], \quad (11)$$

so long as the engine converts the heat of reaction into work with the maximal efficiency. For convenience, we have taken the low temperature of the engine T_0 to be the same as the inlet temperature of the reaction mixture. When C is independent of T , Eq. (11) becomes

$$w(f) = Q_m f \epsilon(f) - CT_0 f \ln \left[\frac{Q_m \epsilon(f)}{CT_0} + 1 \right]. \quad (12)$$

To find the values for the flow rate f where the power production (12) is maximized, the first derivative is set equal to zero:

$$\frac{dw}{df} = Q_m f \frac{d\epsilon(f)}{df} + Q_m \epsilon(f) - CT_0 \ln \left[\frac{Q_m \epsilon(f)}{CT_0} + 1 \right] - CT_0 f \left[\frac{Q_m \epsilon(f)}{CT_0} + 1 \right]^{-1} \frac{Q_m}{CT_0} \frac{d\epsilon(f)}{df} = 0. \quad (13)$$

Case II: Another way in which a chemical process might drive a tricycle would have the product mixture transfer heat to the high-temperature reservoir of Tricycle B, maintaining its temperature at T_2 , as in a steam generator. The product mixture escapes at T_2 , carrying with it some of the energy produced by the combustion process. In this case, termed Case II, T_2 is independent of the flow rate and is presumably fixed by external factors. If the rate of heat transfer to the engine is $-q_2$, then the rate at which heat is thrown away with the product mixture is given by $(q_r + q_2)$. Such a system may be represented by the diagram of Fig. 2. The only restriction on the engine in Case II is that the efficiency be independent of the reaction mixture flow rate f ; the engine need not be a Carnot engine.

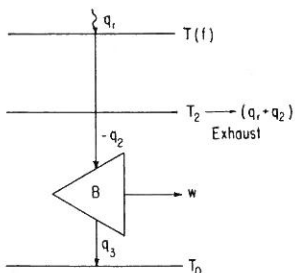


FIG. 2. A schematic diagram of a product mixture, initially at $T(f)$, transferring heat to the hot (T_2) reservoir of a tricycle.

The rate at which heat is transferred to Tricycle B (a heat engine) is given by

$$q_2 = -f \int_{T_2}^{T(f)} C(T) dT, \quad (14)$$

where $C(T)$ is the general, temperature-dependent heat capacity of the product mixture. We shall assume that the heat capacity of the mixture is independent of the extent of the reaction $\epsilon(f)$. This assumption is valid if $\epsilon(f)$ is near to unity, or if $C(T)$ is roughly the same for reactants and products. In Sec. VI we show how to remove this restriction for reactions of any order. Since

$$Q_m \epsilon(f) = \int_{T_0}^{T(f)} C(T) dT, \quad (15)$$

q_2 may be rewritten as

$$q_2 = -f Q_m \epsilon(f) + f \int_{T_0}^{T_2} C(T) dT. \quad (16)$$

III. FIRST ORDER KINETICS

For the case where the reaction R-P is first order in R with first order rate constant k_1 :

$$\frac{-dR}{dt} = k_1 R, \quad (17)$$

the extent of the reaction is given by

$$\epsilon(\tau) = 1 - e^{-k_1 \tau}. \quad (18)$$

Combining Eqs. (18) and (6), we obtain

$$\epsilon(f) = 1 - e^{-k' f}, \quad (19)$$

with $k' = A l \rho_m k_1$. Therefore, the rate at which heat is produced is given by

$$q_r(f) = Q_m f (1 - e^{-k' f}). \quad (20)$$

As one might expect for a simple first order process, there is no ideal flow rate at which the rate of heat production is maximized. In fact, q_r is a strictly increasing function of f , and has the upper bound $Q_m k'$: $\lim_{f \rightarrow \infty} q_r(f) = Q_m k'$. One further notes that heat is produced at a zero rate if $f=0$: $q_r(f=0)=0$. Likewise, there is no optimum value for f (in the domain $f > 0$) at which the heat released per unit amount of fuel spent $q_r(f)/f$ is maximized. The fuel efficiency is improved as f decreases, approaching an upper bound Q_m as $f \rightarrow 0$. In practice, however, it is often the power produced (or the power produced per unit amount of fuel) and not the heat of reaction which one might wish to maximize.

Case I, represented by Eq. (12), with first order kinetics, gives the power

$$w = Q_m f \left\{ 1 - e^{-k' f} - u^{-1} \ln [1 + u(1 - e^{-k' f})] \right\}, \quad (21)$$

where

$$u = Q_m / CT_0 \quad (22)$$

is the molar heat of reaction in reduced units. Equation (21) has no analytic solution, but can be solved numerically. Figure 3 shows the power produced, in units of $CT_0 f$, as a function of $k' f$, essentially the traversal time through the reaction chamber, for $u=1$. The fuel efficiency w/f is highest for $f=0$ (infinite reaction time) and we shall assume that the heat capacity of the mixture

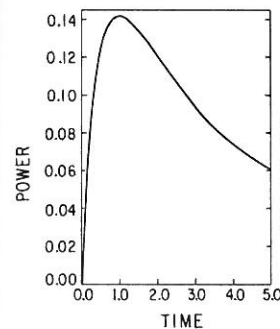


FIG. 3. The power produced (in units of $CT_0 f$) as a function of $k' f$, which is proportional to the traversal time through the reactor, for Case I with first order kinetics, with $u=1$.

$$\lim_{f \rightarrow 0} (w/f) = Q_m \left[1 - \frac{\ln(1+u)}{u} \right]. \quad (23)$$

Turning to Case II with first order kinetics, we find the heat input [Eq. (16)]

$$-q_2 = f Q_m (1 - e^{-k' f}) - f \int_{T_0}^{T_2} C(T) dT. \quad (24)$$

Setting the first derivative dq_2/df equal to zero, one obtains

$$-\frac{dq_2}{df} = Q_m (1 - e^{-k' f}) - \frac{k'}{f} Q_m e^{-k' f} - \int_{T_0}^{T_2} C(T) dT = 0. \quad (25)$$

Equation (24) always has a maximum at some positive f , corresponding to a positive, real solution to Eq. (25) (provided $\int_{T_0}^{T_2} C(T) dT < Q_m$, which is always true). While graphically exact solutions to Eq. (25) may be obtained, an approximate solution is given by

$$f_{\max} \approx k' Q_m^{1/2} \left[2 \int_{T_0}^{T_2} C(T) dT \right]^{-1/2}, \quad (26)$$

which is valid when $Q_m \gg 2 \int_{T_0}^{T_2} C(T) dT$. Under any conditions, the maximum power for Case II is

$$w_{\max} = \eta \cdot \left[f_{\max} Q_m (1 - e^{-k' f_{\max}}) - f_{\max} \int_{T_0}^{T_2} C(T) dT \right], \quad (27)$$

where η is the engine efficiency. Thus, for simple first order systems with the product mixture cooled to T_2 (Case II), there is a finite, positive f at which the power is maximized. Such an optimum does not exist for the fuel efficiency; w/f is always improved as f decreases.

IV. REVERSIBLE FIRST ORDER PROCESSES

The results for a first order process may be easily generalized to take into account the reverse reaction. Consider the same reaction as above, with forward and backward first order rate constants k_f and k_b :

$$R \xrightleftharpoons[k_b]{k_f} P. \quad (28)$$

The rate of buildup of products is then given by

$$\frac{dP(t)}{dt} = k_f R_0 - (k_f + k_b) P. \quad (29)$$

Solving Eq. (29) in the usual way, we obtain an expression for the extent of the reaction $\epsilon(t)$:

$$\epsilon(t) = \frac{P(t)}{R_0} = [k_f / (k_f + k_b)] (1 - e^{-(k_f + k_b)t}) \quad (30)$$

or

$$\epsilon(f) = [k_f / (k_f + k_b)] (1 - e^{-k'' f}), \quad (31)$$

with $k'' = A l \cdot \rho_m (k_f + k_b)$. Equation (31) will then lead to the same optima as for the simple first order reactions for both cases, if the prefactor $k_f / (k_f + k_b)$ is subsumed in Q_m , and if k'' is used instead of k' .

V. SECOND ORDER PROCESSES

A. Reactions second order in a single component

If the process R-P is second order in R, the solution to the differential equation

$$\frac{-dR}{dt} = k_2 R^2 \quad (32)$$

yields an expression for the extent of the reaction

$$\epsilon(t) = \frac{P(t)}{R_0} = \frac{k_2 R_0 t}{k_2 R_0 t + 1}. \quad (33)$$

Note that this system is equivalent to a process with two reactants R_1 and R_2 , which is first order in R_1 , first order in R_2 , and second overall, provided that R_1 and R_2 are in stoichiometric amounts.

As in the first order case, ϵ may be expressed as a function of the flow rate

$$\epsilon(f) = \frac{k_2 R_0 c'}{k_2 R_0 c' + f}, \quad (34)$$

where $c' = A \cdot l \cdot \rho_m$. The flame temperature is given by

$$T(f) = \frac{Q_m}{C} \left(\frac{k_2 R_0 c'}{k_2 R_0 c' + f} \right) + T_0 \quad (35)$$

(assuming constant heat capacity); the rate of heat released from the reaction is

$$q_r(f) = Q_m f \left(\frac{k_2 R_0 c'}{k_2 R_0 c' + f} \right). \quad (36)$$

Again we look at two possible methods for converting q_r into work. Firstly, q_r may be used by reversible cooling from the flame temperature $T(f)$ to the ambient temperature T_0 (Case I). Recalling Eq. (12), the expression for the power produced by such an engine, we obtain for this second order case

$$w = Q_m f \left[\left(\frac{k_2 R_0 c'}{k_2 R_0 c' + f} \right) - u^{-1} \ln \left(1 + \frac{u k_2 R_0 c'}{k_2 R_0 c' + f} \right) \right]. \quad (37)$$

Case I with second order kinetics is illustrated in Fig. 4 for $u=1$. Time is in units of $k_2 R_0 c' / f$ and power is again in units of $CT_0 f$.

Also of interest is the type of engine where the product mixture is cooled to a fixed T_2 , as described for first order processes. The heat transferred to Tricycle B in Case II is given by Eq. (16), which upon substitution for $\epsilon(f)$ becomes

$$-q_2 = f \left[Q_m \left(\frac{k_2 R_0 c'}{k_2 R_0 c' + f} \right) - \int_{T_0}^{T_2} C(T) dT \right]. \quad (38)$$

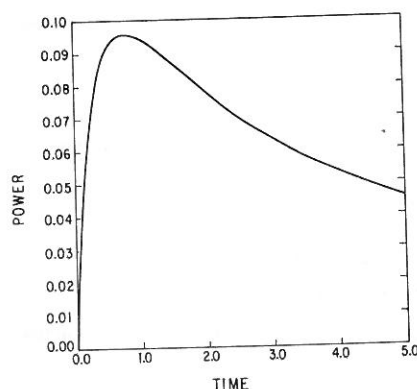


FIG. 4. The power produced (in units of CT_0f) as a function of k_2R_0c'/f (proportional to the traversal time through the reactor) for Case I with second order kinetics, for $u=1$.

Again, setting dq_2/df equal to zero, an expression for the optimum flow rate is obtained:

$$f_{\max} = (k_2R_0c') \cdot \left[\left(\frac{Q_m}{\int_{T_0}^{T_2} C(T)dT} \right)^{1/2} - 1 \right] \quad (39)$$

We note that the expression in Eq. (39) is always positive, and corresponds to a maximum $-q_2$ (and hence a maximum power) with no restrictions on the size of $u\epsilon$.

B. Reactions first order in two different components

Another kinetic system of practical interest is that which is second order overall, but first order in each of two components, where one component is in excess and the other is limiting. Let X be the limiting reagent, and let Y be the reagent in excess. Using the conservation equations for $X+Y \rightarrow P$:

$$X_0 - X = Y_0 - Y = P, \quad (40)$$

the differential equation

$$-\frac{dX}{dt} = kX^2 + k(Y_0 - X_0)X \quad (41)$$

is obtained. The corresponding expression for $\epsilon(t)$ is then

$$\epsilon(t) = \frac{\exp[(Y_0 - X_0)kt] - 1}{\exp[(Y_0 - X_0)kt] - \frac{X_0}{Y_0}} \quad (42)$$

For this situation, where the rate of reaction depends upon the concentrations of both X and Y, the heat released from the reaction is now given in terms of Q'_m , the exothermicity per mole of limiting reagent, and f , the flow rate in total moles of starting material (X and Y) per unit time:

$$q_r(f) = Q'_m f \left(\frac{X_0}{X_0 + Y_0} \right) \epsilon(f). \quad (43)$$

q_r may be recast as a function of $y \equiv (Y_0 - X_0)kt$:

$$q_r(y) = Q'_m k c' X_0 \left[\frac{(Y_0/X_0) - 1}{(Y_0/X_0) + 1} \right] \epsilon(y) y^{-1}. \quad (44)$$

As an illustration of the dependence of the power upon f for systems obeying Eq. (41), we have calculated the power as a function of time for Case I. When the rate of reaction is bilinear in X and Y, the power production will depend both upon $u' \equiv CT_0/Q'_m$ and upon the ratio X_0/Y_0 .

Figure 5 shows an example of the power as a function of traversal time through the reaction chamber for $u'=1$ and $X_0/Y_0=1/2$, with power in units of $Q'_m c' k X_0 y^{-1}$ and time in units of y .

VI. DEPENDENCE OF HEAT CAPACITY ON EXTENT OF REACTION

In the preceding discussion, we have assumed that the heat capacity is independent of the extent of reaction $\epsilon(f)$. Of course, since the product mixture contains both products and unreacted starting material, the heat capacity of this mixture will, in general, depend on the extent of the reaction. However, the functional form of the power is not changed when the above restriction is lifted.

For Case II, this dependence of C on $\epsilon(f)$ may be incorporated into the above treatment very simply. At each point, the heat capacity of the reacting mixture is the average of the heat capacities of reactants and products C_r and C_p , respectively, as

$$C(T, f) = \epsilon(f)C_p(T) + [1 - \epsilon(f)]C_r(T). \quad (45)$$

Substituting $C(T, f)$ for $C(T)$ in Eq. (15), one obtains

$$Q_m \epsilon(f) = \epsilon(f) \int_{T_0}^{T(f)} (C_p - C_r) dT + \int_{T_0}^{T(f)} C_r dT. \quad (46)$$

Thus, for Case II, where the product mixture transfers heat to the reservoir at T_2 , the rate of heat transfer to the reservoir is given by

$$-q_2 = f \epsilon(f) \left[Q_m - \int_{T_0}^{T_2} (C_p - C_r) dT \right] - f \int_{T_0}^{T_2} C_r dT. \quad (47)$$

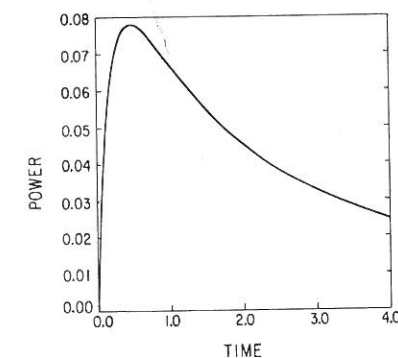


FIG. 5. The power produced (in units of $Q'_m c' k X_0 y^{-1}$) as a function of reaction time (in units of y) for a Case I system driven by a process which is first order in each of two reactants (X and Y) and second order overall, with $u'=1$ and $X_0/Y_0=1/2$.

Equation (47) is virtually identical to Eq. (16), except that C_r replaces C in the last term and there is one new term, the integral of $(C_p - C_r)$. Hence, relaxation of the assumption that C is independent of $\epsilon(f)$ does not alter the functional form of the power $w(f)$. The expressions for $w(f)$ and w_{\max} may be corrected in Case II, by substituting $[Q_m - \int_{T_0}^{T_2} (C_p - C_r) dT]$ for Q_m and $\int_{T_0}^{T_2} C_r dT$ for $\int_{T_0}^{T_2} C(T) dT$.

In case I, the expression for the high temperature of the engine is

$$T(f) = \frac{Q_m \epsilon(f)}{\epsilon(f)(C_p - C_r) + C_r} + T_0. \quad (48)$$

Substitution of Eq. (48) into the equations for the power production results in additional terms. While this does not correspond to a simple substitution of parameters as it does in Case II, $w(f)$ remains qualitatively the same.

VII. DISCUSSION AND CONCLUSIONS

For all of the kinetic systems (first and second order) considered, there is an optimum value for the flow rate at which the power produced by an engine which has maximal efficiency and is driven by an exothermic chemical reaction is maximized. This is true for Case I, where the heat of reaction is transferred reversibly to the engine starting at the reaction temperature $T(f)$, and also for Case II, where the reaction products transfer heat to a reservoir at T_2 and then escape at T_2 . For all these situations, $T(f)$ is a strictly decreasing function of the flow rate f . Therefore, the fuel efficiency w/f is also a strictly decreasing function of f within the framework of our present model.

The flow rate at which maximum power production is attained corresponds to fuel efficiency less than maximal, i. e., $\epsilon(f) < 1$ and therefore small w/f . Hence, in our hypothetical system, one would want to have some means of recovery of unreacted starting material. Such an extension would add another work-consuming process that would be coupled to our system. Since the present treatment does not deal with coupled sets of reactions, including a recovery process would go beyond the scope of this paper.

Let us explore this example a bit further by comparing the results just obtained by maximizing power and fuel efficiency with the behavior of the same system optimized to give minimum entropy production. Systems generating minimum entropy have been discussed recently⁵ and it has been shown that at least one class of systems optimized to correspond to minimum cost will fall between systems giving maximum power and systems giving minimum entropy production.⁹

If the reaction $R \rightarrow P$ were carried out isothermally at temperature T_0 with molar entropy of reaction ΔS_r , the rate of entropy production would be

$$s(f) = \epsilon f \Delta S_r. \quad (49)$$

With the heat of reaction being used reversibly from $T(f)$ down to T_0 (Case I), an extra term enters

$$s(f) = \epsilon f \Delta S_r + f C_p \ln [T(f)/T_0]. \quad (50)$$

Possible solutions with minimum entropy production for first order kinetics are then

$$\begin{aligned} f=0 &: s=0, \\ f=\infty &: s = k' \left(\Delta S_r + \frac{Q_m}{T_0} \right). \end{aligned} \quad (51)$$

When the second equation is rewritten as $s = k' \Delta G/T_0$, where ΔG is the change in free energy for the combustion process, it becomes obvious that $s=0$ is the absolute minimum. The result is analogous for second order kinetics:

$$\begin{aligned} f=0 &: s=0, \\ f=\infty &: s = k_2 R_0 c' \left(\Delta S_r + \frac{Q_m}{T_0} \right). \end{aligned} \quad (52)$$

In Case II the irreversible cooling of the product mixture from $T(f)$ to T_2 and (in the exhaust) to T_0 adds further terms to Eq. (50):

$$\begin{aligned} s(f) &= \epsilon f \Delta S_r + (\epsilon f Q_m - w)/T_0 \\ &= \epsilon f \Delta S_r + f C [(T(f) - T_0) - (T(f) - T_2) \eta]/T_0. \end{aligned} \quad (53)$$

In this expression η is the efficiency with which the engine converts heat at temperature T_2 to work [cf. Eq. (14)]. Finding the minima of Eq. (53) is a bit more involved than for Case I, but for both first and second order kinetics it turns out that there are no interior extrema in the possible flow range from $f=0$ to $T(f) = T_2$. The boundary solutions are for first order kinetics

$$\begin{aligned} f=0 &: s=0, \\ T(f)=T_2 &: s = k' \left(\frac{\Delta S_r}{u} + C \right) \left(\frac{T_2}{T_0} - 1 \right) / \ln \left(\frac{u}{1+u-T_2/T_0} \right) \end{aligned} \quad (54)$$

and for second order kinetics

$$\begin{aligned} f=0 &: s=0, \\ T(f)=T_2 &: s = k_2 R_0 c' \left(\frac{\Delta S_r}{u} + C \right) \left(1 + u - \frac{T_2}{T_0} \right). \end{aligned} \quad (55)$$

Both expressions for $T(f)=T_2$ are positive, so the minimum rate of entropy is again produced at zero flow rate.

For the chemically driven engine we thus find that maximum fuel efficiency and minimum entropy production are obtained in the uninteresting limit $f=0$, whereas any nonvanishing power production, in particular the maximum power sought in the previous sections, is accompanied by a sacrifice of efficiency just as in mechanical systems.^{3-7,10}

While Case II was treated for a product mixture with general heat capacity $C(T)$ and for an engine with general efficiency $\eta(T_2, T_0)$, constant heat capacity was assumed in Case I. It is straightforward to extend the calculations to at least some other systems. For example, we have analyzed the case in which T_1 is a linear function of $\epsilon(f)$, the extent of reaction, but in which the heat capacities and rate coefficients are temperature independent. More realistic situations appear to be a bit more challenging, but demand examination.

Indeed, we recognize that our model should be extended to include the following:

(1) a temperature-dependent heat capacity in Case I,
 (2) nonequilibrium conditions in the internal degrees of freedom or density of the working substances, and, finally,

(3) most important, temperature-dependent reaction rate coefficients.

Inclusion of a T -dependent rate constant, even with simplifying assumptions (Arrhenius temperature dependence, constant heat capacity, and zeroth order kinetics), entails rather cumbersome numerical analysis. The extension of the analysis to include temperature-dependent rates is currently in progress.

In addition, we have not mentioned how engines operating with a finite-heat-capacity heat source might be set up to give the efficiency of Eq. (10). This will be discussed in a forthcoming paper.¹¹

Even with its idealizations, the present work demonstrates the importance of the finite rate of chemical processes in setting thermodynamic extrema for energy conversion processes operating in finite time.

ACKNOWLEDGMENTS

We would like to thank the Shell Companies Foundation and Exxon, USA for support of this research, and acknowledge a NATO travel grant. We thank Natalia

Meshkov and H. Bert de Vries for helpful comments and discussion. We are particularly grateful to Michael Mozurkewich and C. H. Barkeley for their criticisms of a preliminary draft of this work. The final stages of the work were performed at the Aspen Center for Physics.

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8.5. Minimum entropy production and the optimization of heat engines

Phys. Rev. A **21**, 2115 (1980)

Minimum entropy production and the optimization of heat engines

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(Received 16 February 1979; revised manuscript received 2 November 1979)

We consider the problem of minimum entropy production in a heat engine subject only to thermal-resistance losses. For such engines, minimizing the total entropy production is equivalent to minimizing the loss of availability. We show for any engine operating with a given cycle time that minimum total entropy production is achieved in a heat engine by operating it so as to keep the entropy production rate constant along each branch. For the limit of slow engine operation, the entropy production rate should be the same constant for all branches of the cycle. We obtain an expression for the minimum total entropy production and use this to give a bound on the maximum work which can be produced by such engines. This bound is significantly more realistic than the reversible one. Analogous results are derived for a working fluid which carries arbitrary flows from one potential to another.

I. INTRODUCTION

Considerable research effort has been expended recently¹⁻⁸ on finding more realistic limits on the optimal operation of heat engines in finite time. This effort was spurred by the economic importance⁹ of such limits in connection with decisions concerning the possible benefits which might result from research on various energy consuming or producing processes. Below we present a general framework, which is one step better than the reversible formalism, for finding limits on the operation of heat-engine processes.

Consider a working fluid that absorbs heat from a reservoir at one temperature T_1 and transfers some of the heat to a second reservoir at a lower temperature T_2 while converting the rest of the heat to work (see Fig. 1). Classical thermodynamics analyzes this process under the assumptions:

- (1) no friction;
- (2) ideal working fluid in internal equilibrium;
- (3) heat flows between substances at equal temperatures.

These assumptions give rise to the reversible formalism whose crucial component is the existence of an extra conserved observable called entropy S . The equation expressing the conservation of S completes our otherwise incomplete set of equations and allows us to calculate everything related to the operation of our heat engine. For instance, we can compute the fraction of heat which can be converted to work

$$W/Q_1 = 1 - T_2/T_1. \quad (1)$$

This result, due to Carnot, provides a limit on the optimal operation of heat engines.

This limit, however, is frequently of little practical importance, because it is achieved only if the heat engine runs reversibly. For real machinery, assumptions (1)–(3) are fulfilled only in the limit that the process is infinitely slow, thus produces zero power. Machinery producing nonzero power must operate in finite time, necessitating losses. Some engines, such as steam turbines driving electric generators, do operate near enough to the reversible limit for the thermodynamic bound to be significant; for others, such as the Otto cycle automobile engine, the reversible thermodynamic

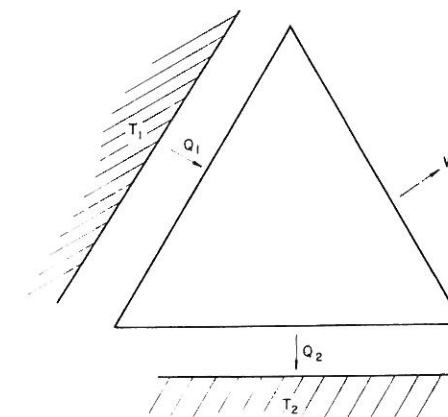


FIG. 1. The flow of heat from reservoir 1 to reservoir 2 while producing work W .

bound has little relevance.

Deviations from ideality in real heat engines may result from many causes, which fall into the following categories³:

(i) *heat resistance* of the surfaces which couple the working fluid to the heat reservoirs;

(ii) *friction* of the mechanical linkage which couples the working fluid to the work reservoir;

(iii) *internal losses* in the working fluid such as turbulence, slow chemical reactions, and other unequilibrated degrees of freedom;

(iv) *heat leak* due to imperfect insulation of the two heat reservoirs.

In the present paper, we treat the optimal operation of heat engines under the influence of loss mechanism (i) only. We include this loss mechanism by relaxing assumptions (3) above and replacing it by Newton's law of heat conduction across a boundary. We also assume that

(3') heat flows between substances in contact through a wall with conductance κ at a rate given by

$$q = \frac{dQ}{dt} = \kappa(T^{ex} - T), \quad (2)$$

where dQ/dt is the heat flux across the boundary separating the temperatures T and T^{ex} . In addition to assumptions (1)–(3') above, we make the further assumption:

(4) The time involved in the purely mechanical coupling branches is very short and may be disregarded relative to the total cycle time. Mathematically we assume that these processes proceed in zero time. Physically this implies the absence of inertial effects, e.g., when a mechanical branch involves the motion of a piston we assume a piston of zero mass. Assumptions that the mechanical steps involve no losses or zero time have been made also in some previous works on the subject,^{6,7} but cannot be used when frictional (type-ii) losses are significant.³

The resulting theoretical framework retains the advantage of allowing explicit calculation of all quantities related to the operation of the heat engine, and adds time to the list of variables of the system, thereby making it a thermodynamic system, rather than a thermostatic system. This gives more realistic bounds on work production or consumption. Obviously these bounds depend on the prescribed cycle time.

In previous papers concerning model engines with these loss mechanisms, we have determined the rates at which they operate to optimize efficiency, effectiveness, or power. In this paper we focus on entropy production, taking it as an objective function to determine criteria for optimal operation of heat engines. The main results are stated in Sec.

V. These are derived in Secs. VI–VIII for heat engines and generalized in Sec. IX to general flows.

II. HEAT ENGINES

Heat engines may be conveniently classified by the type of cycle undergone by the working fluid. For all the conventionally treated examples, such cycles are made up of branches of the following types: *adiabatic*: $q=0$, the working fluid does not exchange heat with its surroundings; *isothermal*: T^{ex} is a constant, the working fluid is allowed to exchange heat with a constant temperature environment; *isometric*: V is a constant, the working fluid is maintained at constant volume; *isobaric*: pressure P is a constant, the working fluid is maintained at constant pressure; *polytropic*: the working fluid satisfies the relation $PV^n = \text{const}$.

Note that when a heat resistance is inserted between the reservoirs and the working fluid, the external and internal temperatures are no longer the same along isothermal branches; we have chosen to define "isothermal" to mean the external temperature (the reservoir temperature) is kept constant. Below we derive two theorems concerning any heat engine in which the working fluid goes through a cycle made up of branches of the above five types. More generally these theorems apply to any cycle during which we can control the ratio of outside to inside temperatures (T^{ex}/T) on each non-adiabatic branch of the cycle.

Table I shows the kinds of branches that make up the commonly used heat cycles employing gaseous working fluids. Diagrams of these cycles on common scales in the PV and TS planes are shown in Fig. 2. The Carnot cycle is used almost exclusively as a theoretical model, because its excessively high compression and expansion make it impractical. The other cycles serve as conceptual prototypes for the design of real engines. The Stirling and Ericsson cycles are the basis of hot air external combustion engines, which have received considerable attention of late.^{10,11} The Brayton cycle has been used mainly for refrigeration, while the Otto, Diesel, and dual combustion cycles are used for internal combustion engines. (Sometimes these cycles are altered so as to use one or more polytropic branches.)

III. THE WORKING FLUID

The Carnot treatment of the operation of a heat engine makes liberal use of the analogy between the extraction of work from the spontaneous flow of water from one height to another and of entropy from one temperature to another. The maximum work extractable is^{12,13}

TABLE I. Branches employed in several heat engine cycles.

Cycle	Adiabats	Isotherms	Isometrics	Isobars	Polytropes
Carnot	2	2			
Stirling		2	2		
Ericsson		2		2	
Brayton	2			2	
Otto	2		2		(1-2) ^a
Diesel	2		1	1	(1-2) ^a
Dual combustion	2		2	1	(1-2) ^a

^a Sometimes polytropes may be used instead of isometrics and isobars.

$$W_{\text{max}} = \sigma(T_1 - T_2), \quad (3)$$

where σ is the amount of entropy carried from T_1 to T_2 . Graphically, σ is the total width of the TS diagram for any cycle, as shown, e.g., in Fig. 2. For example, if the working fluid is an ideal gas undergoing a Carnot cycle, then

$$\begin{aligned} \sigma &= S(V_1, T_1) - S(V_2, T_2) \\ &= R \ln(V_2/V_1) + C_V \ln(T_2/T_1), \end{aligned} \quad (4)$$

where V_1 and V_2 are the smallest and largest volumes of the gas, and T_1 and T_2 are the highest and lowest temperatures. We make further use of this analogy and view our working fluid as a carrier of entropy. However, our situation is more complicated than Carnot's, because entropy is not only carried, but also created. Nevertheless, the en-

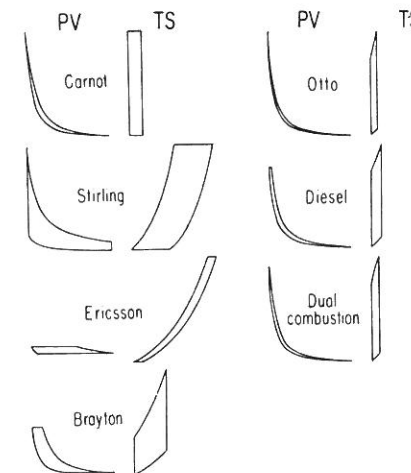


FIG. 2. PV and TS diagrams on common scales for several heat-engine cycles using ideal-gas working fluid. The volume ratio $v^{\text{min}}:v^{\text{max}}$ is 1:10 for all the cycles, and the temperature ratio $T_1:T_2$ is 6:1 for all cycles except the Carnot cycle which has 3:1. (It cannot operate at 6:1 with a volume ratio of 1:10.)

gine in which entropy creation is due only to Newtonian heat-flow constraints turns out to be a fully solvable model of very general applicability. The results follow very simply if we choose the entropy content of the working fluid as the basic parameter and express all other quantities in terms of it.

IV. CONTROL PARAMETERS

It might seem that the most natural choices of control variables for operating a heat engine would be the load on the piston and the external or reservoir temperature T^{ex} . These may be used, provided that we know the equation of state of the working fluid. However there is another choice of control variable that is just as practical as the piston load and that makes the analysis much easier, namely the internal temperature T of the working fluid. This quantity can be controlled at any point in a process by introducing a fast (effectively instantaneous) adiabatic compression or expansion to produce the desired change. We may equally well consider such adiabatic steps as controls on the difference between internal and external temperatures, i.e., on the thermal force between the working fluid and the reservoir. We choose to express the optimal control problem in terms of functions $F(T^{ex}, T)$; we are free to do so, just as long as these functions are single-valued where we use them. We shall pick the F for each branch of a process to suit the constraints of that branch. For example on "isothermal" branches—strictly, branches with constant T^{ex} — F is controlled by adjusting T ; on branches with fixed mechanical coupling,¹⁴ the function F is controlled by adjusting T^{ex} . We shall show how the optimal variation of a properly chosen function $F(T^{ex}, T)$ can be obtained so as to give the extremal entropy, without any explicit use of an equation of state.

To end this section we note that throughout our discussion we implicitly assume that the control process requires no time. For the control of internal temperature by mechanical coupling this is already implied by our assumption (4), Sec. I.

V. MAIN RESULTS

Although one can use many different objective functions to define what one means by the "optimal operation" of a heat engine (efficiency, power, entropy production, cost, etc.), we will be concerned with optimal only in the sense of minimizing the total entropy production. This is equivalent to minimizing the loss of availability (see Appendix A), but not to maximizing efficiency or power which were used as objective functions in other works.^{1,3-7}

We derive the main theorem below.

Theorem 1. Minimum total entropy production implies constant rate of entropy production on each branch of the process¹⁵:

$$\min(\Delta S) - dS_i/dt = \text{constant for branch } i. \quad (5)$$

These constants depend on the heat conductances along the different branches.

Corollary 1. In the slow-process limit (to be defined in Sec. VII A) dependence of the constants in Eq. (5) on heat conductances disappears, and the optimal operation then implies the same constant rate of entropy production along all branches.

The theorem and its corollary are equally valid for a working fluid carrying any number of fluxes operating in a cycle between any number of reservoirs. The derivations leading to Theorem 1 have a useful byproduct.

Theorem 2. The entropy produced by a heat engine in which the working fluid interacts with heat reservoirs through conductances $\kappa_1, \dots, \kappa_N$ for a total cycle time $\tau \gg |\sum_i \sigma_i / \kappa_i|$ is bounded by

$$\Delta S \geq \left(\sum_i |\sigma_i| \right)^2 / \kappa \tau, \quad (6)$$

where ΔS is the entropy produced,

$$\kappa = \max[\kappa_1, \dots, \kappa_N],$$

and σ_i denotes the entropy change of the working fluid (i.e., entropy flow into the working fluid) along branch i . This theorem has the immediate corollary¹³:

Corollary 2. The work produced by a heat engine in finite time and subject to heat conduction losses is bounded by

$$W \leq W_{\text{rev}} - T_0 \left(\sum_i |\sigma_i| \right)^2 / \kappa \tau, \quad (7)$$

where T_0 is the temperature of the environment which defines the proportionality between loss of availability and entropy production (see Appendix A), and where $W_{\text{rev}} = W_{\text{rev}}(T_0)$ is the work available from a reversible process connecting the same initial and final states of the heat sources and sinks.¹⁶

This section has been worded for heat engines

with emphasis on heat conduction. Generalizations to other flows are derived in Sec. IX.

VI. OUTLINE OF METHOD

We use the calculus of variations with the entropy production as the objective function and the fixed cycle time τ as the main constraint for the minimization. The procedure is composed of the following steps:

(1) Divide the total cycle time τ into $\tau_1 + \dots + \tau_N = \tau$, where τ_i is the time spent on the i th branch with the working fluid in contact with the reservoir at temperature T_i^{ex} through conductance κ_i . [By assumption (4), Sec. IV, branches on which only mechanical energy is exchanged are assumed to proceed in zero time.]

(2) Optimize the time behavior of the working fluid so as to minimize the entropy production on each branch i subject to fixed τ_i and fixed initial and final states of the working fluid.

(3) Given a set of times $\{\tau_i\}$, the results from step (2), and the characteristic limitations of the engine (e.g., compression ratio, temperature, and pressure ranges, etc.) solve for the (unique) consistent set of initial and final states on each branch.

(4) Optimize the allocation of the total time τ among the different branches, that is, determine the values of τ_i , ($\sum_i \tau_i = \tau$) which minimize the total entropy production per cycle.

The optimization uses two types of variations required by steps (2) and (4). A simple argument shows that this procedure indeed gives the correct optimal cycle. If only one branch of the optimal cycle is varied, the resulting cycle can perform no better. The Euler equations from the one branch optimizations in step (2) express this fact in mathematical terms. These equations are necessary conditions on the optimal cycle but are not by themselves sufficient to determine the optimal cycle uniquely. However, when we carry out step (3) (Sec. VIII) we shall see that these necessary conditions do define a unique optimal path for each specific time allocation τ_i . It remains to determine the optimal times [step (4)]. We do this by finding a second set of necessary conditions which follow from altering the optimal cycle to one with different τ_i but which still satisfies the Euler equations from step (2). The fact that the optimal cycle is extremal with respect to variations in τ_i as well gives us this second set of conditions and completely determines the optimal cycle.

This argument can be expressed as a sequence of inequalities, thus,

$$\Delta S = \sum_i \Delta S_i(\tau_i) \geq \sum_i \Delta S_i^{\text{opt}}(\tau_i) \geq \sum_i \Delta S_i^{\text{opt}}(\tau_i^{\text{opt}}) = \Delta S^{\text{opt}}. \quad (8)$$

In words, the entropy production associated with the cycle is the sum of contributions (all positive) along each branch. Each of these contributions is at least as large as the entropy produced for the optimal behavior along that branch in the same time τ_i . Further, optimizing the allocation of the fixed total time τ among the τ_i can only decrease (or leave unchanged) the sum.

We now focus our attention on step (2): Optimization along a branch. Here we minimize the value of an integral over a path subject to certain constraints. Though the technique is standard,¹⁷ we reproduce the general formulas here for easy reference.

We start with the control variables $X = (X_1, X_2, \dots, X_k)$, the time interval $(0, \tau)$ the objective function

$$\Phi = \int_0^\tau \mathcal{L}(X, \dot{X}, \ddot{X}, \dots) dt, \quad (9)$$

and the constraints

$$\int_0^\tau F_i(X, \dot{X}, \ddot{X}, \dots) dt = \text{const}, \quad (10)$$

$$G_j(X, \dot{X}, \ddot{X}, \dots) = 0.$$

The path yielding the extremum of Φ subject to the constraints (10), is given by the solution of the Euler-Lagrange equations

$$\frac{\partial L}{\partial X_l} - \frac{d}{dt} \frac{\partial L}{\partial \dot{X}_l} + \frac{d^2}{dt^2} \frac{\partial L}{\partial \ddot{X}_l} - \dots = 0, \quad l=1, \dots, k, \quad (11)$$

where L is the modified Lagrangian,

$$L = \mathcal{L} - \sum_i \lambda_i F_i - \sum_j \lambda_j(t) G_j, \quad (12)$$

$\{\lambda_i\}$ are constant undetermined multipliers, and the $\{\lambda_j(t)\}$ are undetermined multiplier functions of time. This framework will give the same results, of course, in any system of coordinates. When we use the entropy content of the working fluid as a state parameter, the Euler-Lagrange equations reduce to simple algebraic equations, because the Lagrangian does not depend on time or on any time derivative.

The optimization in step (4) is done by standard N -variable calculus techniques, solving the set of algebraic equations

$$d\Phi^{\text{opt}}/d\tau_i - \lambda = 0, \quad (13)$$

where the Lagrange multiplier λ comes from the constraint $\sum_i \tau_i = \tau$. The details of these optimization procedures are provided in the following sections.

VII. DERIVATION FOR THERMAL PROCESSES

A. One branch, internal temperature as control variable

On branch i , the system at temperature $T_i(t)$ is in contact with a heat reservoir at constant temperature T_i^{ex} through a conductance κ_i so that the heat flux is

$$\frac{dQ_i}{dt} = \kappa_i [T_i^{\text{ex}} - T_i(t)]. \quad (2')$$

Then for the given duration τ_i on the i th branch, the heat flow into the system is

$$Q_i = \int_0^{\tau_i} dQ_i = \int_0^{\tau_i} \kappa_i [T_i^{\text{ex}} - T_i(t)] dt, \quad (14)$$

where $T_i(t)$ is as yet undetermined. The entropy change of the system (the flow of entropy into the system) is

$$\sigma_i = \int_0^{\tau_i} \frac{dQ_i}{T_i(t)} = \int_0^{\tau_i} \kappa_i \frac{T_i^{\text{ex}} - T_i(t)}{T_i(t)} dt, \quad (15)$$

and the total entropy change is

$$\Delta S_i = \int_0^{\tau_i} \left(\frac{dQ_i}{T_i(t)} - \frac{dQ_i}{T_i^{\text{ex}}} \right) = \int_0^{\tau_i} \kappa_i [T_i^{\text{ex}} - T_i(t)] \left(\frac{1}{T_i(t)} - \frac{1}{T_i^{\text{ex}}} \right) dt. \quad (16)$$

Recall that our approach divides the optimization into steps. In step (2), carried out here, the "corners" of the process are fixed with regard to thermodynamic states and time, and we solve for the optimal paths which connect these corners. In step (4), (Sec. VIII), we find the optimal permissible locations of these corners. Fixed corners (i.e., given initial and final states of the working fluid) for each branch i , constrain the values of σ_i , Eq. (15). We are free to include in our optimal path infinitely fast reversible adiabatic segments. These do not enter into the Euler equation. Rather, they serve to connect the optimized segments determined by the Euler equations with the initial and final states, as shown in Fig. 3. Thus the values of the σ_i 's are the only constraints that enter into the Euler equations. We take ΔS_i as our objective function and, with T_i^{ex} constant, $T_i(t)$ becomes our control variable. The Lagrangian for the optimization is

$$L = \kappa_i [T_i^{\text{ex}} - T_i(t)] \left(\frac{1}{T_i(t)} - \frac{1}{T_i^{\text{ex}}} \right) - \lambda \left(\kappa_i \frac{[T_i^{\text{ex}} - T_i(t)]}{T_i(t)} \right), \quad (17)$$

where λ is a constant Lagrange multiplier. The Euler equation is

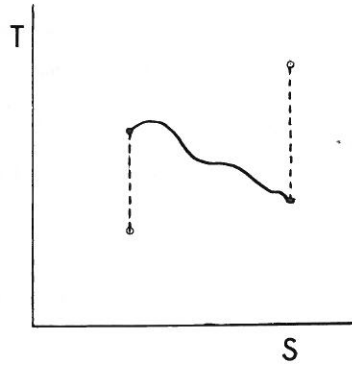


FIG. 3. Arbitrary curve (solid line) spliced to given initial and final states by adiabats (dashed lines).

$$\frac{\partial L}{\partial T_i} = -\kappa_i \left(\frac{1}{T_i(t)} - \frac{1}{T_i^{ex}} \right) - \kappa_i \left(\frac{T_i^{ex} - T_i(t)}{T_i(t)^2} \right) + \lambda \kappa_i \frac{T_i^{ex}}{T_i(t)^2} = 0, \quad (18)$$

because L depends only on T_i and not on any of its time derivatives. Thus $T_i(t)$ is obtained from an algebraic, not a differential, equation, which implies that the solution has no arbitrary constants, and neither the initial nor final values of the control function $T_i(t)$ can be specified arbitrarily. As illustrated in Fig. 3, we are free to include infinitely fast reversible adiabats, and hence we need not be concerned that the solution to the Euler equation will, in general, not fall at $T_i(0)$ and $T_i(\tau_i)$ when $t=0$ and τ_i . Without this freedom, the calculus of variations problem between given initial and final states does not have a solution. This is due to the openness of the set of trajectories over which one optimizes. However, there is a least upper bound to our objective function on this set of trajectories. We can come arbitrarily close to achieving this upper bound by compressing (or expanding) as fast as we can to get to the appropriate Euler solution and, after staying on it as long as possible, expanding (compressing) as fast as possible to get the required final state. Examples of such systems have been worked out recently. This kind of solution is well known in many subjects where optimization methods are used; in economics, they are known as "turnpike" solutions, for example.^{9f,18}

We note that, since the only time dependence in Eq. (18) is in $T_i(t)$, this function must be constant, and the optimal trajectory is of the form shown in Fig. 4. Thus heat should be transferred with system and reservoir remaining isothermal at their own temperatures. The internal temperature is

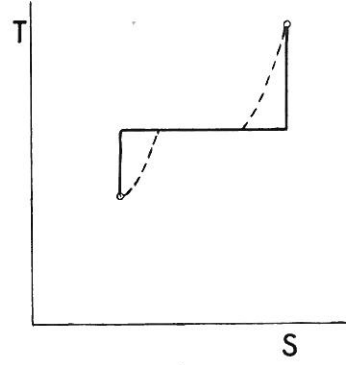


FIG. 4. The form of the optimal branch required by the Euler equation (18). The vertical solid lines correspond to the case in which the adiabats may occur infinitely fast. If there is a constraint limiting the velocity, the system will follow the dashed curves to and from the isotherm (turnpike theorem Refs. 23 and 24); the exact forms of the dashed curves depend on the form of the constraint.

most easily determined from the constraint

$$\sigma_i = \int_0^{\tau_i} \kappa_i [(T_i^{ex} - T_i)/T_i] dt = \kappa_i \tau_i (T_i^{ex}/T_i - 1), \quad (19)$$

$$T_i = T_i^{ex} / (1 + \sigma_i / \kappa_i \tau_i),$$

so that

$$\Delta S_i = \frac{\sigma_i^2 / \kappa_i \tau_i}{1 + \sigma_i / \kappa_i \tau_i}, \quad (20)$$

and

$$\frac{dS_i}{dt} = \frac{\Delta S_i}{\tau_i} = \frac{\sigma_i^2 / \kappa_i \tau_i^2}{1 + \sigma_i / \kappa_i \tau_i} = \text{const.} \quad (21)$$

The value of T_i is thus that value compatible with the entropy change σ_i , the fixed time τ_i , and the requirement that $T_i(t) = \text{const}$.

In the limit in which other processes are slow with respect to heat transfer, i.e., when $\tau_i \gg |\sigma_i| / \kappa_i$, these expressions reduce to

$$\Delta S_i = \sigma_i^2 / \kappa_i \tau_i \quad (20')$$

and

$$dS_i/dt = \sigma_i^2 / \kappa_i \tau_i^2. \quad (21')$$

We call such processes for which $\tau_i \gg |\sigma_i| / \kappa_i$ *slow processes*. For heat engines producing power on the order of 100 kW, realistic values for heat conductance and entropy flows are¹⁹ $\kappa \sim 200$ J/K sec and $\sigma \sim 10$ J/K implying $\sigma_i / \kappa_i \sim 0.05$ sec. (See Appendix B.)

We note in passing that the same conclusion, constant dS_i/dt , is obtained starting from any other

pair of functions chosen from Eqs. (14)–(16) as constraint and objective functions. In particular we may use the heat exchanged and the total entropy produced along the branch as constraint and objective functions, respectively. Here we seek to minimize the total entropy produced for a specified amount of heat exchanged. The role of these functions may also be interchanged: For a prescribed amount of entropy produced, we may determine the extremal heat exchange. In all these cases we obtain in general a Lagrangian which does not depend on time or on any time derivative. The Euler equation for the optimal evolution of the control variable is therefore an algebraic equation involving constants only, thus yielding a constant solution.

B. One branch, external temperature as control variable

We now consider branches on which the working fluid is subjected to some (prespecified) nonthermal coupling. In particular, this category includes isometric, isobaric, and polytropic branches. We can still optimize the thermal interaction by controlling the temperature $T_i^{ex}(t)$ of the reservoir.

As in the previous section we want to minimize the entropy production, ΔS_i , for a given transfer of entropy σ_i . In the spirit of Sec. IV, we define a new control variable $x_i(t) \equiv T_i^{ex}(t)/T_i(t)$. The Lagrangian for the system becomes

$$L = \kappa_i (T_i^{ex} - T_i) \left(\frac{1}{T_i} - \frac{1}{T_i^{ex}} \right) - \lambda \kappa_i (T_i^{ex} - T_i) / T_i = \kappa_i (x_i - 1) (1 - x_i^{-1}) - \lambda \kappa_i (x_i - 1), \quad (22)$$

and the solution of the Euler equation

$$\partial L / \partial x_i = \kappa_i (1 - x_i^{-2}) - \lambda \kappa_i = 0 \quad (23)$$

is a constant $x_i = 1 + \sigma_i / \kappa_i \tau_i$, so that again the rate of entropy production is constant:

$$\frac{dS_i}{dt} = \kappa_i (x_i - 2 + x_i^{-1}) = \frac{\sigma_i^2 / \kappa_i \tau_i^2}{1 + \sigma_i / \kappa_i \tau_i} \quad (24)$$

and the reservoir temperature should be varied so that

$$T_i^{ex}(t) = T_i(t) (1 + \sigma_i / \kappa_i \tau_i). \quad (25)$$

Note that again our solution has no arbitrary constants, and an optimal path exists only between $T_i^{ex}(0)$ and $T_i^{ex}(\tau_i)$ which satisfy Eq. (25). This is why we introduced the assumption of noninertial controls, thereby freeing us from any initial or final conditions on the control functions. For T_i^{ex} this is true by fiat, although for $T_i(t)$ in Sec. VII A it was true because of the freedom to include adiabatic jumps. We have lost this freedom for the present optimizations since we assume that the

mechanical coupling is specified, e.g., constant volume.

Note that these expressions for T_i^{ex}/T_i and dS_i/dt are identical to Eqs. (19) and (21) of Sec. VII A, which are obtained with the internal temperature as the control parameter. This is not surprising. We can always perform the optimization in terms of $x_i(t)$; the result $x_i = \text{const}$ is obtained independently of the nature of the branch. The results (19) and (21) are obtained by putting $T_i^{ex} = \text{const}$.

C. Consecutive branches

We are now in a position to allocate the total time among N branches of a process which has been optimized along each branch by the techniques of Secs. VII A and VII B. In doing so we assume that the engine constraints are such that the σ_i 's are predetermined independently of the τ_i 's for each branch i , making step (3) of our procedure (Sec. VI) unnecessary. Optimization over time allocation is therefore performed taking the σ_i 's to be constants. For more general constraints, the σ_i 's may be functions of the τ_i 's. This point is taken up more fully in Sec. VIII where we show that in the long cycle time limit the σ_i 's may always be regarded as constants for the present optimization. For short times the optimization depends on the equations of state of the working fluid and becomes analytically intractable even for the example of an ideal gas in a cylinder. Numerical solutions for this example are given in Appendix B.

If along each branch i the working fluid absorbs σ_i units of entropy in time τ_i through heat conductance κ_i , we want to minimize the total entropy production

$$\Delta S = \sum_i \Delta S_i = \sum_i \frac{\sigma_i^2 / \kappa_i \tau_i}{1 + \sigma_i / \kappa_i \tau_i}, \quad (26)$$

for constant total time

$$\tau = \sum_i \tau_i, \quad (27)$$

by varying the individual τ_i (σ_i and κ_i are fixed). We make the substitution

$$\tau'_i = \tau_i + \sigma_i / \kappa_i, \quad (28)$$

so that

$$\Delta S = \sum_i \sigma_i^2 / \kappa_i \tau'_i, \quad (29)$$

and

$$\tau' = \sum_i \tau'_i = \tau + \sum_i \sigma_i / \kappa_i. \quad (30)$$

Optimizing gives

$$\frac{\partial \Delta S}{\partial \tau'_i} = \frac{\sigma_i^2}{\kappa_i \tau_i'^2} = \lambda \frac{\partial \tau'_i}{\partial \tau'_i} = \lambda, \quad (31)$$

where λ is a Lagrange multiplier. Solving for τ'_i and evaluating λ by the constraint (27) gives

$$\tau'_i = C |\sigma_i| / \sqrt{\kappa_i}, \quad (32)$$

or

$$\tau_i = C |\sigma_i| / \sqrt{\kappa_i} - \sigma_i / \kappa_i, \quad (33)$$

with

$$C = \tau' / \left(\sum_i |\sigma_i| / \sqrt{\kappa_i} \right) = \left(\tau + \sum_i \frac{\sigma_i}{\kappa_i} \right) / \left(\sum_i \frac{|\sigma_i|}{\sqrt{\kappa_i}} \right). \quad (34)$$

Note that C depends symmetrically on the parameters of all the branches. The entropy change is

$$\Delta S = C^{-1} \sum_i \frac{|\sigma_i|}{\sqrt{\kappa_i}}, \quad (35)$$

so we obtain:

Theorem 3. The optimal rate of entropy production along branch i is the constant

$$dS_i/dt = [C(C - \text{sgn} \sigma_i / \sqrt{\kappa_i})]^{-1}. \quad (36)$$

As mentioned in Sec. IV, this constant depends on the best conductance κ_i .

In the slow-process limit $\tau_i \gg |\sigma_i| / \kappa_i$ (cf. Sec. VII A), $\Delta S = \sum_i \sigma_i^2 / \kappa_i \tau_i$, so we obtain the primed equations above without the substitution defined in Eq. (28). Thus in this limit

$$\tau_i = C |\sigma_i| / \sqrt{\kappa_i}, \quad (33')$$

and we get

Corollary 3.

$$dS_i/dt = C^{-2}; \quad (36')$$

i.e., the optimal rate of entropy production is in the slow-process limit the same for all branches of the cycle.

By comparing Eqs. (33), (36), with (33'), (36'), one sees that if the processes are driven faster than the "natural thermal transfer times," $|\sigma_i| / \kappa_i$, the optimal rate of entropy production will vary from branch to branch, unless heat is transferred in the same direction ($\text{sgn} \sigma_i = \text{sgn} \sigma_j$) through the same heat conductances ($\kappa_i = \kappa_j$). Equation (33) implies that the system spends most time on branches with large entropy flows or small heat conductances.

The expression for ΔS assumes a nice form for long times $\tau \gg |\sum_i \sigma_i / \kappa_i|$. Then we get from Eqs. (33)–(35), the following:

Theorem 4.

$$\Delta S = \left(\sum_i \frac{|\sigma_i|}{\sqrt{\kappa_i}} \right)^2 / \tau \geq \left(\sum_i |\sigma_i| \right)^2 / \kappa \tau, \quad (37)$$

where $\kappa = \max(\kappa_1, \dots, \kappa_N)$. Note that this quantity depends only on the variation in the entropy of the working fluid $\sum_i |\sigma_i|$, or in other words, the total amount of entropy transferred in the cycle.

Tolman and Fine¹³ have proven that the upper bound on the work produced by a process which generates entropy ΔS at discharge temperature T_0 is

$$W \leq W_{\text{rev}} - T_0 \Delta S, \quad (38)$$

where W_{rev} is the theoretical work output for the corresponding lossless process.¹⁶ Combining this with Eq. (37) we find the upper bound for our process.

Corollary 4.

$$W \leq W_{\text{rev}} - T_0 \left(\sum_i |\sigma_i| \right)^2 / \kappa \tau. \quad (39)$$

VIII. REAL ENGINE CONSTRAINTS

The results obtained in Sec. VII and summarized in Sec. V are based on a picture of a heat engine as a system operating in a cycle which is made of distinct branches. Each branch is characterized by the change in the entropy of the system. Real engines are of course subjected to different constraints, e.g., the volume of the cylinder, the permissible working temperature and pressure ranges, etc. Such constraints can usually be specified in terms of the state of the working fluid in the extreme corners of the cycle. For example, a Carnot cycle can be characterized by the high and low temperatures and volumes, which define the state of the working gas at the starting point of each isotherm. We shall refer to such constraints as *corner constraints*.

Consider now a cycle which is supposedly optimized under some given real engine constraints. Focusing on a particular branch, we consider altering the path on this branch alone, while keeping the rest of the cycle fixed. In particular, this implies that the initial and final states of the working fluid on the special branch are constrained, as is the time to be spent on this branch. Suppose that by such a change the total entropy produced along this branch is lowered. This would obviously imply that the total entropy produced during the cycle operation is lowered and thus contradict our assumption that we started with the optimal cycle. Thus each branch of a cycle optimized (with respect to total entropy production) under any corner constraints has to satisfy Theorem 1 (Sec. V): The optimal path is that on which entropy is produced at a constant rate.

Next, consider the cycle as a whole. In the study of heat engines, enough information is usually provided to enable us to construct the corresponding reversible cycle (which has traditionally served as a basis for comparison with the actual work produced). The indicator diagram (the path of the working fluid in state space) of this reversible cycle also defines the state of the environment, which is in equilibrium with the working fluid at each point. Restrictions which define the indicator diagram may be specified either in terms of the working fluid or in terms of the environment.

For finite time cycles, we should distinguish between constraints imposed on the working fluid and constraints imposed on the environment. If the set of constraints used to define a reversible cycle is imposed on the working fluid alone, the indicator diagram of the latter (and therefore the set $\{\sigma_i\}$) is completely specified. In such cases the procedure described in Sec. VII is sufficient and the results provide the necessary conditions for minimum total entropy production. These conditions give the time-dependent behavior of the working fluid and of the environment (temperature of a reservoir, load on a piston, etc.).

In the more general case where engine limitations are given in part or in full in terms of the environment (e.g., temperature of a reservoir) the problem becomes more difficult. Now the set $\{\sigma_i\}$ is no longer given. We can obtain the σ_i 's in terms of the τ_i 's from the given restrictions, the optimal operation conditions [Eq. (25)], and the equations of state of the working fluid.

Example: Consider a Carnot-type cycle composed of two isothermal branches (characterized by temperatures T_1^{ex} and T_3^{ex} of the external reservoirs) and two adiabatic branches. We assume that the working fluid is an ideal gas with constant heat capacity C_v . Equation (25) implies for the isothermal branches

$$T_1 = T_1^{\text{ex}} / (1 + \sigma_1 / \kappa_1 \tau_1), \quad (40)$$

$$T_3 = T_3^{\text{ex}} / (1 + \sigma_3 / \kappa_3 \tau_3). \quad (41)$$

On the adiabatic branches $\sigma_2 = \sigma_4 = \tau_2 = \tau_4 = 0$. The closure condition for the cycle $\sum_i \sigma_i = 0$ implies

$$\sigma_1 = -\sigma_3 \equiv \sigma. \quad (42)$$

Finally, the ideal-gas equations of state lead to

$$\sigma = R \ln(V^{\text{max}}/V^{\text{min}}) + C_v \ln(T_3/T_1), \quad (43)$$

where V^{max} and V^{min} are the largest and smallest volumes of the cylinder. From Eqs. (40), (41), and (43), we get

$$\sigma = \sigma_{\text{rev}} + C_v \ln \left(\frac{1 + \sigma / \kappa_1 \tau_1}{1 - \sigma / \kappa_3 \tau_3} \right), \quad (44)$$

where

$$\sigma_{\text{rev}} = R \ln(V^{\text{max}}/V^{\text{min}}) + C_v \ln(T_3^{\text{ex}}/T_1^{\text{ex}}). \quad (45)$$

If the compression ratio $V^{\text{max}}/V^{\text{min}}$ is given as an additional constraint, Eq. (44) provides an expression for σ as a function of τ_1 and τ_3 . Alternatively, if the maximum pressure P^{max} and the maximum volume are given as constraints rather than the compression ratio, Eq. (44) is replaced by (using $P^{\text{max}} V^{\text{min}} = nRT_1$)

$$\sigma = \sigma_{\text{rev}} + C_p \ln(1 + \sigma / \kappa_1 \tau_1) - C_v \ln(1 - \sigma / \kappa_3 \tau_3), \quad (46)$$

where

$$\sigma_{\text{rev}} = R \ln \left(\frac{V^{\text{max}} P^{\text{min}}}{nR} \right) + C_v \ln T_3^{\text{ex}} - C_p \ln T_1^{\text{ex}} \quad (47)$$

is a constant.

In general the σ_i 's are complicated functions of the τ_i 's. To minimize the total entropy production

$$\Delta S = \sum_{i=1}^N \frac{\sigma_i^2 / \kappa_i \tau_i}{1 + \sigma_i / \kappa_i \tau_i}, \quad (48)$$

subject to $\sum_i \tau_i = \tau$, we must use

$$\frac{\partial \Delta S}{\partial \tau_i} + \sum_j \frac{\partial \Delta S}{\partial \sigma_j} \frac{\partial \sigma_j}{\partial \tau_i} = \lambda, \quad (49)$$

for the Lagrange multiplier λ , rather than

$$\partial \Delta S / \partial \tau_i = \lambda \quad (50)$$

as was done in Sec. VIII C.

For infinitely slow operation, the σ_i 's are given as properties of the corresponding reversible cycle. Assuming that $\{\sigma_i(\tau_1, \dots, \tau_N)\}$ ($i=1, \dots, N$) are continuously differentiable functions of the variables $\{1/\tau_i\}$, we can write

$$\sigma_i = \sigma_i^{\text{rev}} + \sum_{j=1}^N b_{ij} \frac{1}{\tau_j} + \dots \quad (51)$$

This leads to

$$\partial \sigma_i / \partial \tau_j = -b_{ij} / \tau_j^2 + \dots \quad (52)$$

Also, in the slow-process limit Eq. (26) in the form $\Delta S = \sum_i \sigma_i^2 / \kappa_i \tau_i + \dots$ implies

$$\left(\frac{\partial \Delta S}{\partial \tau_j} \right)_{\{\sigma_i\}} = -\frac{\sigma_j^2}{\kappa_j \tau_j^2} + \dots \quad (53)$$

and

$$\left(\frac{\partial \Delta S}{\partial \sigma_j} \right)_{\{\tau_i\}} = \frac{2\sigma_j}{\kappa_j \tau_j} + \dots \quad (54)$$

The terms omitted in Eqs. (51)–(54) are of higher order in the $(1/\tau_j)$'s. To the lowest order in these variables we have

$$\sum_j \frac{\partial \Delta S}{\partial \sigma_j} \frac{\partial \sigma_j}{\partial \tau_j} = -\sum_j 2b_{ji} \frac{\sigma_i}{\kappa_j} \frac{1}{\tau_j \tau_i^2}, \quad (55)$$

which for large τ_i 's may be disregarded relative

to the right-hand side of Eq. (53). This is possible provided

$$\tau_j \gg \frac{2b_{ij}\sigma_i}{\sigma_i^2} \frac{\kappa_i}{\kappa_j} \sim \frac{b_{ij}}{\sigma_j}. \quad (56)$$

For the Carnot cycle where $\sigma_1 = -\sigma_3 = \sigma_{rev}$, we obtain from Eqs. (44) and (51),

$$b_j = \sigma_{rev} C_v / \kappa_j, \quad (57)$$

so that the long-time condition (56) takes the form

$$\tau_j \gg C_v / \kappa_j. \quad (58)$$

Subject to this condition, we may keep the σ_i 's constant while taking derivatives of ΔS with respect to the τ_i 's and to the same approximation, the optimization procedure of Sec. VII C is valid.

To end this section, we stress again that there exist reasonable constraints (e.g., for the Otto or the Diesel cycle) which imply constant σ_i and thus justify the analysis of Sec. VII C even for short times.

IX. DERIVATION FOR GENERAL FLOWS

A. One branch

Consider the exchange of the generalized fluxes $\vec{j} = (j_1, j_2, \dots, j_n, \dots)$ driven by the forces $\vec{X} = (X_1, X_2, \dots, X_n, \dots)$ between the appropriate reservoirs and the system. By our assumptions, there is no internal entropy production, so all irreversibility resides at the boundary. We assume that the fluxes have a phenomenological relationship $j_k(\vec{X})$ to the forces. These relationships are not necessarily linear as in traditional irreversible thermodynamics close to equilibrium. We take the forces at the boundary as control variables and assume that the fluxes are functions only of the forces X_k , not of time or of any time derivatives of the forces. Thus we want to minimize the entropy produced.

$$\Delta S = \int_0^\tau \sum_k j_k X_k dt = \int_0^\tau \vec{j} \cdot \vec{X} dt, \quad (59)$$

for given integrated flows,

$$J_k = \int_0^\tau j_k dt. \quad (60)$$

This gives the Lagrangian

$$L = \sum_k j_k(\vec{X}) X_k - \sum_k \lambda_k j_k(\vec{X}) \quad (61)$$

and Euler equations

$$\frac{\partial L}{\partial X_i} = j_i(\vec{X}) + \sum_k (X_k - \lambda_k) \frac{\partial j_k(\vec{X})}{\partial X_i} = 0. \quad (62)$$

The phenomenological relationships $j_k(\vec{X})$ can now be used to calculate $\partial j_k(\vec{X})/\partial X_i$ and solve Eq. (62)

for the forces X_i . Again the Euler equations are (coupled) algebraic equations so that the solutions, however complicated they may be, will be independent of time. This implies that also $dS/dt = \vec{j}(\vec{X}) \cdot \vec{X}$ is a constant. Thus we deduce in general the following:

Theorem 1': Minimum total entropy production for a process with given net fluxes implies constant entropy production rate along any one branch.

This is the general version of Theorem 1. If the j_k are independent and linear in \vec{X} , the solution of Eq. (62) comes from solving the determinantal (secular) equation for the X_i , whereas if the j_k are independent but nonlinear, the solution of Eq. (62) is the point set of intersections of the surfaces defined by (62).

B. Consecutive branches

We have from Eq. (60) for consecutive branches

$$\Delta S = \sum_i \Delta S_i = \sum_i (\vec{j}_i \cdot \vec{X}_i) \tau_i = \sum_i \vec{J}_i \cdot \vec{X}_i, \quad (63)$$

since the fluxes and forces along each branch are constant. Unless we know the functional form of $\vec{X}_i(\vec{J}_i/\tau_i)$, we cannot optimize Eq. (63) with respect to the τ_i , so let us at this point assume the relationship to be linear

$$\vec{j} = \underline{L} \vec{X}, \quad \vec{X} = \underline{L}^{-1} \vec{j}, \quad (64)$$

where \underline{L} is the usual matrix of phenomenological coefficients. Then

$$\Delta S = \sum_i \vec{J}_i \underline{L}^{-1} \vec{J}_i / \tau_i = \sum_i \alpha_i / \tau_i, \quad (65)$$

where the $\{\alpha_i\}$ do not depend on time. Optimization of Eq. (65) subject to Eq. (27), $\tau = \sum_i \tau_i$ yields

$$\tau_i = \left(\tau / \sum_i \sqrt{\alpha_i} \right) \sqrt{\alpha_i}, \quad (66)$$

so that

$$\Delta S = \left(\sum_i \sqrt{\alpha_i} \right)^2 / \tau \quad (67)$$

and

$$dS_i/dt = \left(\sum_i \sqrt{\alpha_i} \right)^2 / \tau^2, \quad (68)$$

which is the same constant for all branches (Corollary 1'). The linearity of Eq. (64) and the constancy of \underline{L} correspond to the slow process limit in Sec. VII A.

X. DISCUSSION

In the sections above, we have repeatedly minimized the total entropy production in a heat-engine process subject to only thermal resistance losses.

We found that optimal operation implies constant entropy production rate on each branch. For slow operation, the requirement of minimum total entropy production implies that the entropy production rate is constant for the entire cycle.

The results further show that for optimal operation we should subject the working fluid to a constant thermal force on each branch. The required constant thermal force depends however on our choice of heat transfer law. If Newton's law of heat conduction holds, we need to hold T^{ex}/T constant. If we accept the heat-conduction law of irreversible thermodynamics, we need $(1/T) - (1/T^{ex}) = \text{constant}$. Newton's law is probably more reliable here.

Our solution for the one branch behavior of the optimal cycle is very general since we do not require any equations of state for the working fluid. The same is true for the long-time solution for the cycle as a whole. The general solution however, does depend on the detailed properties of the working fluid as was demonstrated in Sec. VIII. Note that in any case the results are not necessarily restricted to a gas in a cylinder and should apply for any engine.

The limitations imposed on the efficiency of operation for finite thermal conductance are significant. For realistic values of the parameters,¹⁹ $\sigma = 10 \text{ J/K}$ and $\kappa = 200 \text{ J/K sec}$ in a Carnot-type engine working between 700 and 300 K with a cycle time of $\tau = 1 \text{ sec}$, we find (see Appendix B) that the efficiency is reduced to 47% from the reversible value of 57%. The efficiencies of the best actual heat engine processes with similar σ and κ are 40%⁴ and thus compare favorably with the optimal engine with finite heat conductance.

The results described in the present paper differ in two important respects from previous work aimed at establishing limits on the quality of operation of finite time heat engines. The first difference is that our results apply to arbitrary heat engines, whereas most of the previous work^{1,3-7} dealt only with Carnot-type cycles, i.e., cycles working between two constant temperature reservoirs. The second difference is our choice of objective function. Previous works have maximized efficiency and power in finite time heat engines. We minimized the entropy production and showed that this is equivalent to minimizing the loss of availability. Both the relationship to properties of many steady-state systems²⁰ and the connection to practical minimization of loss of availability^{9c-9e} motivate this choice or criterion. It is, however, not equivalent to maximizing efficiency or power. For example, unlike the efficiency, the total entropy production criterion does not count heat at all temperatures equally. Efficiency and power by their nature define short-term goals. Total en-

ropy production or availability corresponds to a longer range goal of preserving natural resources. Each of these criteria of merit has legitimacy and defines operational goals for the engine. A quantitative comparison between these and other criteria of merit will be provided in another publication, where we also discuss the problem of choosing among these criteria under a given price schedule.^{9f}

The assumptions used in our formalism are standard. With few exceptions, mentioned below, the assumptions under which most optimal finite time operation problems have been attacked are, no friction, no internal dissipation, and neglect of inertial effects. An approach to optimal engine operation which takes friction into account has been described by three of us using the tricycle space formalism.³ A model which includes internal irreversibility in a simplified manner has been treated by Richter and Ross.²¹ The first of these works does not yield an explicit solution for the time operation of the engine, while the second is based on a highly simplified model. Inertial effects have been taken into account in Refs. 6 and 7.

In our model the working fluid is characterized by the single parameter σ , its entropy capacity. This is the simplest possible viewpoint short of using no parameters, as was done by Curzon and Ahlborn⁴ and in the tricycle formalism.³

Our result states that the "best process" is associated with a constant rate of entropy production. This is reminiscent of Prigogine's theorem of irreversible thermodynamics which states²² that the entropy production rate is minimum at near-equilibrium steady states. Both results are associated with variational principles. However the approach of Prigogine ("irreversible thermodynamics") involves instantaneous quantities while our formalism ("finite-time thermodynamics") investigates the extrema of integrals over time. It is interesting to note that both theorems are obtained under fairly similar assumptions. (In fact our results are in some sense more general; as we saw, the single branch results hold even when the phenomenological equations between flows and forces are nonlinear, so long as there is no internal dissipation.)

In the present work we limited ourselves to simple nonequilibrium situations. In particular, we disregarded irreversible processes associated with spatial inhomogeneities of the system. It will be interesting to investigate the generalization of the principle of constant entropy production rate to such cases which are encountered in processes involving internal dissipation.

Finally, we note that reversible bounds on work production have provided us with such fertile concepts as entropy and thermodynamic temperature.

The possibility of using finite time bounds as sources of new physical concepts should not be dismissed. We believe that the present article makes a start in this direction.

ACKNOWLEDGMENTS

B. A. is grateful for the hospitality shown him during his visit to Tel Aviv University and also wishes to acknowledge support from the Danish Science Foundation and NATO, for a travel grant, in connection with the preparation of this paper. A. N. and P. S. acknowledge the support of the Israel-U. S. Binational Science Foundation, Jerusalem. We thank Dr. I. Procaccia and Dr. A. Ben Shaul for helpful discussions. The manuscript was completed at the Aspen Center for Physics.

APPENDIX A: THE PROPORTIONALITY BETWEEN LOSS OF AVAILABILITY AND ENTROPY PRODUCTION

Here we prove that the loss of availability associated with an irreversible thermal interaction is proportional to the entropy production. Thus minimizing the loss of availability is equivalent to minimizing the entropy production.

First consider N systems, each with constant heat capacity C and at different temperatures T_i . When they interact to come to equilibrium at the common temperature T_f , their respective change of entropy is

$$\Delta S_i = \int_{T_i}^{T_f} C/T dT = C \ln(T_f/T_i). \quad (A1)$$

For a reversible interaction the total change in entropy vanishes:

$$\sum_i \Delta S_i = \sum_i C \ln(T_f/T_i) = C \left(N \ln T_f - \sum_i \ln T_i \right) = 0, \quad (A2)$$

which defines the final temperature

$$T_f = \left(\prod_i T_i \right)^{1/N}. \quad (A3)$$

The availability A of the collection of systems is the maximum work which can be obtained from their interaction. Conservation of energy yields

$$A = W_{\max} = - \sum_i Q_i = \sum_i C(T_i - T_f) = CN \left[\sum_i T_i/N - \left(\prod_i T_i \right)^{1/N} \right]. \quad (A4)$$

As an irreversible interaction between the sys-

tems, let two of them come to equilibrium without work production. Their common final temperature will be

$$T'_1 = T'_2 = \frac{1}{2}(T_1 + T_2) \quad (A5)$$

and the availability of the total system is

$$A' = CN \left[\sum_i T_i/N - \left(\frac{1}{4}(T_1 + T_2)^2 \prod_{i=3}^N T_i \right)^{1/N} \right]. \quad (A6)$$

The loss of availability is thus

$$\Delta A = A - A' = CN \left(\prod_{i=1}^N T_i \right)^{1/N} \left[\left(\frac{(T_1 + T_2)^2}{4T_1 T_2} \right)^{1/N} - 1 \right]. \quad (A7)$$

The entropy produced in the irreversible interaction is

$$\Delta S = \int_{T_1}^{T'_1} C/T dT + \int_{T_2}^{T'_2} C/T dT = C \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}, \quad (A8)$$

so that

$$\frac{\Delta A}{\Delta S} = N \left(\prod_i T_i \right)^{1/N} \left[\left(\frac{(T_1 + T_2)^2}{4T_1 T_2} \right)^{1/N} - 1 \right] / \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}. \quad (A9)$$

This depends not only on all the system temperatures but also on the nature of the irreversible process. However, in the limit of many systems we may use

$$\lim_{N \rightarrow \infty} \left(\frac{N(X^{1/N} - 1)}{\ln X} \right) = 1 \quad (A10)$$

to obtain

$$\frac{\Delta A}{\Delta S} = \left(\prod_i T_i \right)^{1/N}. \quad (A11)$$

Thus the geometric mean of the temperatures of systems provides the proportionality constant between the entropy production and the loss of availability. If all but a small number of systems have the same temperature T_0 , they constitute a reference reservoir, and then

$$\Delta A/\Delta S = T_0. \quad (A12)$$

We can prove Eq. (A12) also for the more general case of temperature-dependent heat capacities $C_i = C_i(T)$. As before, the common temperature T_f after a reversible interaction is obtained from

$$\sum_i \Delta S_i = \sum_i \int_{T_i}^{T_f} C_i(T)/T dT = 0, \quad (A13)$$

although we cannot give an explicit expression for T_f . As in Eq. (A4) the availability is

$$A = W_{\max} = - \sum_i Q_i = \sum_i \int_{T_i}^{T_f} C_i(T) dT. \quad (A14)$$

We now let systems 1 and 2 interact irreversibly to arrive at temperatures T'_1 and T'_2 . A subsequent reversible interaction between all system will lead to a different final temperature T_f' such that

$$\sum_i \Delta S_i' = \sum_i \int_{T_i'}^{T_f'} C_i(T)/T dT = 0. \quad (A15)$$

Taking the difference between Eqs. (A13) and (A15), we see that

$$\left(\int_{T_1}^{T'_1} + \int_{T_2}^{T'_2} + \sum_i \int_{T_i}^{T_f'} \right) C_i(T)/T dT = 0. \quad (A16)$$

Similarly, the loss of availability is

$$\Delta A = A - A' = - \left(\int_{T_1}^{T'_1} + \int_{T_2}^{T'_2} + \sum_i \int_{T_i}^{T_f'} \right) C_i(T) dT = - \sum_i \int_{T_i}^{T_f'} C_i(T) dT. \quad (A17)$$

The entropy produced is

$$\Delta S = \left(\int_{T_1}^{T'_1} + \int_{T_2}^{T'_2} \right) C_i(T)/T dT = - \sum_i \int_{T_i}^{T_f'} C_i(T)/T dT, \quad (A18)$$

so that

$$\frac{\Delta A}{\Delta S} = \left(\sum_i \int_{T_i}^{T_f'} C_i(T) dT \right) / \left(\sum_i \int_{T_i}^{T_f'} C_i(T)/T dT \right). \quad (A19)$$

Consider the case where all systems $i \geq 3$ are combined into a single reservoir of temperature T_0 and heat capacity C_0 . In the limit $C_1, C_2 \ll C_0$, we have $T_f \approx T_f' \approx T_0$, and

$$\Delta A/\Delta S = [C_0(T_0)(T_f - T_f')] / [(T_f - T_f')C_0(T_0)/T_0] = T_0, \quad (A20)$$

which again proves that the entropy production and the loss of availability are proportional to each other.

APPENDIX B: NUMERICAL RESULTS FOR THE FINITE-TIME CARNOT CYCLE

An important advantage of the formalism presented in this paper is that it allows one to calculate all quantities related to the finite-time operation of a model heat engine. Furthermore, the required calculations are well within the capacity of today's programmable calculators. Below we illustrate this feature of our formalism with the numerical results for an ideal-gas working fluid undergoing a Carnot cycle working between given temperatures T_1^{ex} and T_3^{ex} , with a given compres-

TABLE II. Numerical results for the finite-time Carnot cycle with minimum entropy production.

Given engine data	τ (sec)	η	T_1/T_f	T_1 (K)	T_3 (K)	Exact results			Constant σ results		
						W (J)	$4T_f \sigma^2/k\tau$ (J)	T_1/τ	T_1 (K)	T_3 (K)	σ (J/K)
$T_1^{ex} = 700$ K, $T_3^{ex} = 300$ K	0.5	0.1794	0.3926	496.9	407.7	16.78	1497	0.3356	469.6	398.8	17.22
$V^{\max}/V^{\min} = 10$, $\kappa = 209$ J/sec K	1	0.4671	0.4556	625.4	333.3	11.37	3321	0.4456	623.9	332.6	11.37
$\sigma_{rev} = 8.633$ J/K, $\eta_{rev} = 0.5714$	2	0.5293	0.4791	667.3	314.1	9.811	3465	0.4766	667.2	314.1	9.811
$T_{\min} = 0.47$ sec	4	0.5522	0.4896	684.7	306.6	9.184	3472	0.4890	684.6	306.6	9.184
$T_1^{ex} = 400$ K, $T_3^{ex} = 300$ K	1.35	0.0166	0.4426	347.1	341.3	19.06	109.7	0.4325	346.0	340.5	19.07
$V^{\max}/V^{\min} = 10$, $\kappa = 209$ J/sec K	2	0.1106	0.4616	366.3	325.7	17.80	721.2	0.4575	366.0	325.5	17.80
$\sigma_{rev} = 15.66$ J/K, $\eta_{rev} = 0.25$	4	0.1878	0.4812	384.1	312.0	16.66	1202	0.4801	384.1	311.9	16.66
$T_{\min} = 1.3$ sec	8	0.2205	0.4906	392.3	305.8	16.14	1396	0.4904	392.3	305.8	16.14
$T_1^{ex} = 400$ K, $T_3^{ex} = 300$ K	0.4	0.0246	0.4591	350.0	341.4	5.487	47.28	0.4340	347.2	339.6	5.522
$V^{\max}/V^{\min} = 2$, $\kappa = 209$ J/sec K	1	0.2075	0.4886	389.0	308.3	2.881	232.6	0.4862	389.0	308.3	2.881
$\sigma_{rev} = 2.189$ J/K, $\eta_{rev} = 0.25$	2	0.2319	0.4941	395.2	303.6	2.488	228.1	0.4941	395.2	303.6	2.488
$T_{\min} = 0.39$ sec	4	0.2416	0.4974	397.8	301.7	2.329	223.8	0.4972	397.8	301.7	2.329

sion ratio V^{\max}/V^{\min} , heat conductance $\kappa \equiv \kappa_1 = \kappa_2$, and cycle time τ . The results for a few representative values of the parameters are shown in Table II. Note that the results of the exact calculations and the constant σ calculations are very close even for very short times, e.g., the minimum cycle time τ_{\min} for the engine. (As the cycle time τ is decreased, the engine produces less work. τ_{\min} is defined as the cycle time for which zero work is produced.) Note further that the equation

$$W = W_{\text{rev}} - 4T_0 \sigma^2 / \kappa \tau \quad (\text{B1})$$

is valid to three significant figures for all our data. This means that the bound

$$W \leq W_{\text{rev}} - 4T_0 \sigma^2 / \kappa \tau \quad (\text{B2})$$

given for large times by Corollary 2 [Eq. (7)], may be assumed valid quite generally.

We now describe how the data in these tables were calculated. As shown in the example of Sec. VIII, the entropy capacity $\sigma = \sigma_1 = -\sigma_3$ of such an engine is related to the times τ_1 and τ_3 spent on the heat exchange branches of the cycle by Eqs. (44) and (45),

$$\sigma = \sigma_{\text{rev}} + C_v \ln \left(\frac{1 + \sigma/\kappa \tau_1}{1 - \sigma/\kappa \tau_3} \right), \quad (\text{B3})$$

where

$$\sigma_{\text{rev}} = R \ln(V^{\max}/V^{\min}) + C_v \ln(T_3^{\text{ex}}/T_1^{\text{ex}}). \quad (\text{B4})$$

Since we are given the total cycle time $\tau = \tau_1 + \tau_3$, our optimization problem is to find τ_1 such that the total entropy production [Eq. (26)]

$$\Delta S = \sum_i \frac{\sigma_i^2 / \kappa_i \tau_i}{1 + \sigma_i / \kappa_i \tau_i} = \frac{\sigma^2}{\kappa \tau_1 + \sigma} + \frac{\sigma^2}{\kappa \tau_3 - \sigma} \quad (\text{B5})$$

is minimized.

The numerical optimization proceeds as follows. Choosing a specific value of τ_1 , Eq. (B3) can be solved iteratively for σ by substituting a guess value σ_{guess} on the right-hand side of (B3), and using the resulting σ equal to the left-hand side of (B3) as the next guess. This iterative scheme converges quickly, and we can use the obtained value of σ to

evaluate ΔS by Eq. (B5). This procedure is repeated for different choices of τ_1 , until τ_1^{opt} is determined to the desired accuracy. Once τ_1^{opt} is known, we can evaluate σ and ΔS from Eqs. (B3)–(B5), and the other engine parameters from

$$T_1 = T_1^{\text{ex}} / (1 + \sigma / \kappa \tau_1), \quad (\text{B6})$$

$$T_3 = T_3^{\text{ex}} / (1 - \sigma / \kappa \tau_3), \quad (\text{B7})$$

$$\eta_{\text{rev}} = 1 - T_3^{\text{ex}} / T_1^{\text{ex}}, \quad (\text{B8})$$

$$\eta = 1 - T_3 / T_1, \quad (\text{B9})$$

$$W = \sigma(T_1 - T_3), \quad (\text{B10})$$

$$W_{\text{rev}} = \sigma T_1 \eta_{\text{rev}}, \quad (\text{B11})$$

where η denotes efficiency and W denotes work. The results of such calculations appear in Table II under the heading “exact results.” Alternatively, we can use the computational scheme by assuming that σ is a constant (Sec. VII C). Subject to this approximation, we can eliminate the search for τ_1^{opt} and use Eqs. (33) and (34) to find

$$\tau_1^{\text{opt}} = C \frac{|\sigma_i|}{\sqrt{\kappa_i}} - \frac{\sigma_i}{\kappa_i}, \quad (\text{B12})$$

with

$$C = \left(\tau + \sum_i \frac{\sigma_i}{\kappa_i} \right) / \left(\sum_i \frac{|\sigma_i|}{\sqrt{\kappa_i}} \right). \quad (\text{B13})$$

For our example, (B12) and (B13) reduce to

$$\tau_1^{\text{opt}} = \frac{1}{2} \tau - \sigma / \kappa, \quad (\text{B14})$$

$$\tau_2^{\text{opt}} = \frac{1}{2} \tau + \sigma / \kappa. \quad (\text{B15})$$

The iterative scheme for the constant σ calculations is based on Eqs. (B3), (B14), and (B15). A guess value of σ is used in Eqs. (B14) and (B15) to get τ_1 and τ_3 which give a better σ from Eq. (B3). This scheme is much faster as it eliminates the need to search for τ_1^{opt} . The results are presented in this table under the heading “constant- σ results.”

Since the results of both types of calculations depend only on the product $\kappa \tau$ rather than on the values of κ or τ separately, one can easily obtain results for κ' from the data in the table by altering the corresponding τ to $\tau' = \kappa \tau / \kappa'$.

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¹²L. Tisza, *Generalized Thermodynamics* (MIT Press, Cambridge, Mass., 1966).

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¹⁴Fixed mechanical coupling is defined by a constraint that some mechanical parameter of the working fluid remains constant. For a gaseous working fluid, the interesting special cases are isobaric ($P = \text{const}$), isometric ($V = \text{const}$), or polytropic ($PV^n = \text{const}$), but any $g(P, V) = \text{const}$ also satisfies our definition of fixed mechanical coupling. For different working fluids, such as may be used in cooling by adiabatic demagnetization for example, relevant cases of fixed mechanical coupl-

ing might involve constant magnetic field or constant magnetization.

¹⁵In Eq. (6) and in the remainder of the paper, S refers to the entropy of the universe, i.e., of system plus surroundings.

¹⁶For example consider a heat engine working between a heat source at constant temperature T_H and a heat sink at constant temperature T_C . If in one cycle the amount of heat Q^H is taken from the hot source and the amount Q^C is added to the cold source, then W_{rev} is the sum of the works associated with the reversible engines in which the hot and cold sources exchange the same heats Q^H and Q^C , and with the environment (of temperature T_0) playing the role of the other reservoir. Thus

$$W_{\text{rev}} = Q^H(1 - T_0/T_H) - Q^C(1 - T_0/T_C).$$

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8.6. The significance of Weinhold's length

J. Chem. Phys. **73**, 1001, 5407E (1980)

The significance of Weinhold's length

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Weinhold¹ proposed that a metric for the space of thermodynamic states is $\eta_{ij} = \partial^2 U / \partial X_i \partial X_j$, where X_i and X_j are extensive variables. Here we present an interpretation of the physical significance of this quantity as a metric, and clarify the two different ways in which η_{ij} has been used. The usual interpretation² of η_{ij} is as a second fundamental form, giving the "distance" between the surface of energy U , a function of the extensive variables $X_1 = S, X_2, \dots, X_n$,

$$U = U(X_1, \dots, X_n), \quad (1)$$

and the plane U_0 tangent to this surface at U_0 , where η_{ij} is evaluated. Thus, for a displacement of the system from the state specified by X_1^0, \dots, X_n^0 to the state at X_1, \dots, X_n , the difference between U and the plane tangent to U at U_0 , is, to second order,

$$U - U_0 = \frac{1}{2} \sum_{i,j} \frac{\partial^2 U}{\partial X_i \partial X_j} (X_i - X_i^0)(X_j - X_j^0). \quad (2)$$

Because the value of this form is the "distance" between the point (X_1, \dots, X_n, U) and the tangent plane, it can be identified as the availability of the system that can come from its displaced state into equilibrium with an environment at (X_1^0, \dots, X_n^0) .³ In this regard, η_{ij} is a second fundamental form.

Weinhold showed¹ that the laws of thermodynamics assure that η_{ij} also has the positivity required of a metric or first fundamental form on the surface of thermodynamic states.⁴ This property enabled him to re-

derive thermodynamic relations using simple geometric arguments.

Equation (2) shows that the length computed with η_{ij} treated as a second fundamental form is the availability. More precisely, when the displacements $(X_i - X_i^0)$ are small enough for Eq. (2) to hold, *as they are for fluctuations*, $\frac{1}{2} \sum \eta_{ij} (X_i - X_i^0)(X_j - X_j^0)$ gives the availability. This is the well-established physical interpretation of η_{ij} taken locally, i.e., in the vicinity of a single point on the surface.

Next we examine the physical significance of the lengths of paths based on η_{ij} as a metric taken globally. This interpretation follows from the general relation between length and metric, and from using η_{ij} as Weinhold does, as a first fundamental form. We shall see that the result is a change of velocity characteristic of the type of path.

Consider for simplicity a system of one component so $X_1 = S$ and $X_2 = V$ are the only independent extensive variables. Suppose further that the trajectory of the system is given parametrically as $S = S(\xi)$, $V = V(\xi)$. Then the length of the path from the state p_0 , V_0 to p_1 , V_1 is

$$L = \int_0^1 \left[\eta_{11} \left(\frac{dS}{d\xi} \right)^2 + 2\eta_{12} \frac{dS}{d\xi} \frac{dV}{d\xi} + \eta_{22} \left(\frac{dV}{d\xi} \right)^2 \right]^{1/2} d\xi. \quad (3)$$

Dimensionally, L is the square root of energy, or, if U is given as specific energy (energy per unit mass), then L has the dimensions of velocity.

To illustrate what L is, consider an ideal gas, for which

$$\eta = \begin{bmatrix} T/C_v & -p/C_v \\ -p/C_v & \gamma p/V \end{bmatrix},$$

the heat capacities are constant, $C_p - C_v = R$ and $C_p/C_v = \gamma$. For convenience, we define $\theta = mC_v/R$, half the number of quadratic degrees of freedom apart from the particle mass scaling factor m . A reversible or endoreversible⁵ process at constant volume gives

$$L^{(\nu)} = \int_0^1 \left[\frac{T}{C_v} \right]^{1/2} dS \\ = 2\sqrt{C_v} [\sqrt{T_1} - \sqrt{T_0}] = 2\sqrt{\frac{\theta}{3}} [v_1^{2/2} - v_0^{2/2}].$$

Note that v_1 and v_0 are gas-kinetic velocities at T_1 and T_0 , respectively. A reversible process at constant pressure gives

$$L^{(p)} = \int_0^1 \left[\frac{T}{C_v} \left(\frac{C_p}{V} \right)^2 \left(\frac{\partial V}{\partial \xi} \right)^2 - \frac{2p}{C_v} \frac{C_p}{V} \left(\frac{\partial V}{\partial \xi} \right) + \frac{\gamma p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 \right]^{1/2} d\xi \\ = \int_0^1 \left(\frac{\gamma}{\gamma-1} \right)^{1/2} \sqrt{\frac{p}{V}} dV \\ = 2\sqrt{C_p} [\sqrt{T_1} - \sqrt{T_0}] = 2\sqrt{\frac{\theta+1}{3}} [v_1^{2/2} - v_0^{2/2}],$$

where we assume $C_p = (\theta+1)R/m$.

A reversible process at constant temperature gives $L=0$, as expected because U is a function only of T .

A reversible adiabatic process gives

$$L^{(s)} = \int_0^1 \left[\frac{\gamma p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 \right]^{1/2} d\xi = \frac{2}{\gamma-1} \sqrt{\gamma p_0 V_0} \left[1 - \left(\frac{p_1}{p_0} \right)^{(\gamma-1)/2} \right],$$

which is the change in flow velocity of a gas undergoing

an isentropic expansion, e.g., in a rarefaction wave.⁶ In general, L is a change in a mean velocity, but characteristic of the constraints defining the path of the integral along which the length is measured. Incidentally for a solid whose equation of state is $V = V_0[1 + \alpha(T - T_0) - kp]$, $\eta_{11} = T/C_v$ as for the ideal gas, $\eta_{12} = \alpha T/kC_v$, and $\eta_{22} = (\alpha^2 T/kC_v) + 1/V_0 k$. The length L for an isochoric process is the same as for the gas; the length L for an isentropic process is of the form $L = \int [At + B]^{1/2} dV$.

We wish to thank Michael Mozurkewich for reading the manuscript.

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²P. Salamon, Doctoral Dissertation, The University of Chicago (1978) discusses this point specifically; standard texts on differential geometry, such as M. M. Lipschutz, *Differential Geometry* (McGraw-Hill, New York, 1969) or W. C. Graustein, *Differential Geometry* (Dover, New York, 1966), give general discussions of first and second fundamental forms. L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, Mass., 1966) discusses the subject and designates η_{ij} as the "stiffness" form.

³J. W. Gibbs, *Collected Works*, Vol. 1 (Yale Univ., New Haven, 1948); J. H. Keenan, *Thermodynamics* (MIT, Cambridge, Mass., 1970).

⁴The positivity of η fails at phase transitions; where these occur, there are lines along which η vanishes, which correspond to transformation of material from one phase to another without disrupting the equilibrium between system and environment. For further discussion see Ref. 1(b).

⁵"Endoreversible" is a term introduced by M. Rubin, *Phys. Rev. A* **19**, 1272 (1979) to characterize a thermodynamic system whose working substance undergoes reversible transformations, independent of whether the system is in equilibrium with its surroundings.

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Erratum: The significance of Weinhold's length

J. Chem Phys. **73**, 1001 (1980)

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The phrase following Eq. (1) should read "and the plane U_0 tangent to this surface. . . ." The left side of Eq. (2) should be " $U - U_0$ " rather than " $U - U_0^0$ ". The sentence comprising the next-to-last paragraph should read "A reversible process at a constant temperature T gives $L = (T/R)^{1/2} \Delta S$." The statement as made, " $L=0$," is incorrect.

8.7. Thermodynamics in finite time: Processes with temperature-dependent chemical reactions

J. Chem. Phys. 73, 5838 (1980)

Thermodynamics in finite time: Processes with temperature-dependent chemical reactions

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The thermodynamics of two chemical systems obeying Arrhenius law kinetics are studied from the viewpoint of finite time thermodynamics. The first is the determination of the maximum thermodynamic or chemical efficiency of a synthetic process whose heat input appears as preheating to overcome an activation barrier. The second is the determination of maximum power that can be obtained from an exothermic reaction carried out in a continuous flowsystem. The maximum power, achieved with a finite, nonzero flow rate, is a sensitive function of the activation energy of the reaction.

I. INTRODUCTION

Traditional thermodynamics provides bounds on the amounts of work and heat that can be exchanged between a system and its surroundings. In some situations, such as the generation of electric power from steam, the performances of real processes come close enough to their thermodynamic limits that we can use these limits as bases of useful criteria of merit. Many other processes operate at efficiencies or effectivenesses so far from the limits set by idealized reversible thermodynamic processes that traditional thermodynamic criteria are too weak to be of any significance for them. The disparity between actual performance and the corresponding reversible limit of a process is, in many instances, due to the nonzero rate of that process. Fortunately, for a large class of processes operating in finite time, one can construct functions that act like traditional thermodynamic potentials: The changes in these functions give the natural bounds on the work or heat that a system may exchange with its surroundings, for processes operating within certain constraints.¹ The difference between these extended potentials and traditional potentials is simply that the constraints used to obtain the new functions include constraints on time or rate, in addition to any of the traditional constraints that may apply on such variables as temperature, volume, or entropy. The "finite-time potentials" may be used to provide criteria of merit that are much more realistic than those derived for reversible processes, and even to exhibit how the optimal performance of a system depends on its rate. We refer to the construction of potentials for processes operating at finite rates, and to the determination of the process paths that would yield extremal values of heat or work, as the study of "finite time thermodynamics."

The first applications of finite time thermodynamics were to mechanical systems and heat engines.¹⁻⁸ More recently, the approach has been applied to systems undergoing changes of chemical potential, either through separation by distillation⁹ or by chemical reaction.¹⁰

The last example is the precursor of the work presented here: There we optimized the power of an engine driven by an exothermic chemical reaction with finite rate for the simplistic case in which the rate coefficients are temperature independent. That exercise was useful as the first example of finite time thermodynamic analysis in which the time constraints are rate coefficients of the working fluid, rather than parameters of the coupling between the system and its surroundings. However, it was clear when that work was being done that any reasonably realistic model would have to include the temperature dependence of the rate coefficients.

In the present work, we examine the optimization of two systems undergoing chemical reactions whose rate coefficients obey an Arrhenius law $k = A \exp(-E_a/T)$. (We absorb the gas constant into the activation energy.) The two examples are (1) the determination of the maximum fuel efficiency (thermodynamic efficiency in the usual meaning of work out per unit heat in from fuel) or chemical efficiency (amount of chemical product per unit heat in) from a chemical synthesis, and (2) the determination of maximum power obtainable from a heat engine driven by an exothermic chemical reaction. The first is treated in Sec. II, and the second in Sec. III.

Let us go through a qualitative argument as a preliminary illustration of how the finite rate of operation governs the performance of a process. We take the second example above, a heat engine driven by an exothermic reaction in a flow tube. If the rate coefficient is effectively independent of temperature, we know that maximum power is achieved with some positive flow rate.¹⁰ If the flow of reacting mixture is very slow, the reaction goes to completion in the flow tube, and the maximum heat per mole of starting material is produced, so that heat is transferred to the engine at a high temperature. However, if the flow is slow, the heat transferred per unit time is also small. On the other hand, if the flow is very fast, the reaction has insufficient time to go to completion, and heat transferred to the engine goes at a temperature below its maximum. Hence, the efficiency and power fall off at high flow rates. Between these two extremes is an intermediate flow rate for which the power produced is a maximum. This happens even if the rate coefficient of the heat-generating reaction is independent of temperature. For the more realistic case in which the rate of the reaction

obeys an Arrhenius law, one would expect the power production to be even more sensitive to the flow rate. Obviously, in an exothermic, Arrhenius-law reaction, a kind of cooperative effect is created; the heat of reaction increases the rate of reaction, which in turn produces heat at a faster rate.

II. OPTIMIZING THE EFFICIENCY OF A PREHEATED ISOTHERMAL CHEMICAL REACTION

Consider the reaction



of arbitrary order in any of the species $\{R_1, R_2, \dots, R_n\}$, i. e., R or any reaction intermediate:

$$\frac{dP}{dt} = k[R_1]^{a_1}[R_2]^{a_2} \dots [R_n]^{a_n}, \quad (2)$$

in which the rate coefficient k is given by an Arrhenius law

$$k = A \exp(-E_a/T). \quad (3)$$

For convenience, we express the activation energy in units of the gas constant, i. e., we write E_a to mean the activation energy divided by R , so E_a is expressed in K. Suppose further that the reaction mixture is preheated in order to start the reaction at a suitable rate, and that the reactants rapidly absorb and equilibrate all of the heat put in relative to the time scale of the chemical reaction.

Suppose the reaction mixture requires heat to raise its temperature from T_0 to T and to maintain its temperature at T thereafter. The first contribution to the total heat flow into the reaction mixture is

$$q = fQ = f \int_{T_0}^T C(T) dT, \quad (4)$$

where f is the flow rate of the reaction mixture (mol/time), and Q is the heat added to the reactants from outside sources to bring their temperature to T , in the same molar units used to define f ; $C(T)$ is the heat capacity of the mixture. Additional heat to maintain the temperature of the system must be supplied at a rate equal to the molar heat of reaction $\Delta H_r(T)$ times the rate of reaction:

$$\bar{q} \equiv q_{\text{thermodynamic}} = \Delta H_r(T) \frac{dP}{dt}. \quad (5)$$

The term \bar{q} is irrelevant to the remainder of the analysis and will be neglected hereafter.

The amount of product made per unit of heat provided from outside sources, which we call the *chemical efficiency*, is

$$\mathcal{E} = \frac{(dP/dt)}{Qf}. \quad (6)$$

The chemical efficiency is directly proportional to the thermodynamic efficiency η , the amount of useful chemical work performed per unit of heat supplied to drive the process. If $\Delta\mu$ is the change in chemical potential when 1 mol of P is made from reactants, then the two efficiencies are directly proportional, with $\Delta\mu$ the proportionality factor:

$$\mathcal{E} \cdot \Delta\mu = \eta. \quad (7)$$

In order to find the temperature at which \mathcal{E} is maximized, Q of Eq. (4) must first be calculated. For a reaction mixture with completely general heat capacity $C(T)$, the optimal temperature is a solution of $d\mathcal{E}/dT = 0$, which amounts to the integral equation

$$Q \equiv \int_{T_0}^T C(T) dT = \frac{C(T) T^2}{E_a}. \quad (8)$$

Equation (8) becomes a high-order polynomial equation if $C(T)$ is a polynomial in T , and one cannot expect to find a tractable analytic solution.

The problem would look simpler if one were to assume that the heat capacity of the mixture is constant over the entire temperature range from T_0 to T . However, the model implicitly presumes that $T \gg T_0$, so such an approximation would be foolhardy. Rather, it is better to assume that the reactants can be heated without reacting from T_0 to a higher temperature T' by the addition of a knowable quantity of heat Q' :

$$Q' = \int_{T_0}^{T'} C(T) dT. \quad (9)$$

Then we imagine that the mixture is heated (or cooled) over a short range of temperature, T' to T , short enough that the heat capacity of the mixture is constant. The total amount of heat added is thus

$$Q = Q' + \int_{T'}^T C dT = Q' + C(T - T'). \quad (10)$$

We define an effective temperature

$$\theta = T' - Q'/C \quad (11)$$

so

$$Q = C(T - \theta). \quad (12)$$

Presumably, one can find a suitable value for T' if one knows the approximate rate at which one wants to operate the process. Of course, once the optimal T is found, it is obligatory to check that it is indeed near enough to T' so that Eq. (10) is approximately valid. If it is not, one must choose a better T' and repeat the calculation.

We now wish to find the temperature T at which \mathcal{E} is maximized. In other words, we shall determine the amount of preheating that maximizes the chemical or thermodynamic efficiency of the synthesis. We construct $d\mathcal{E}/dT$ and set it equal to zero:

$$\begin{aligned} \frac{d\mathcal{E}}{dT} &= [Cf(T - \theta)A \mathcal{R}(E_a/T^2) \exp(-E_a/T) \\ &\quad - A \mathcal{R}Cf \exp(-E_a/T)] / [Cf(T - \theta)]^2 \\ &= 0, \end{aligned} \quad (13)$$

where

$$\mathcal{R} = \prod_{i=1}^n [R_i]^{a_i}. \quad (14)$$

The roots of Eq. (13) are the two temperatures T_+ and T_- for which extremal values of the efficiency \mathcal{E} are achieved:

$$T_{\pm} = \frac{1}{2} E_a \pm \frac{1}{2} \sqrt{E_a^2 - 4\theta E_a}. \quad (15)$$

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Note that, in general, E_a will be large relative to 4θ and that this is also a necessary condition for E_a to be independent of temperature. In the limit

$$E_a \gg 4\theta \quad (16)$$

the extremal value of \mathcal{E} occur at

$$T_+ \approx E_a - \theta, \quad (17)$$

$$T_- \approx \theta. \quad (18)$$

Note that $T_- = \theta \equiv T' - Q'/C$ corresponds to the uninteresting limit of no preheating [see Eq. (12)]. We now must find out if T_+ corresponds to a minimum or maximum \mathcal{E} . The second derivative of \mathcal{E} evaluated at $d\mathcal{E}/dT = 0$ is given by

$$\left. \frac{d^2\mathcal{E}}{dT^2} \right|_{T=T_+} = \frac{A\theta}{Cf} \exp(-E_a/T) (T - \theta)^{-3} \left(\frac{2\theta}{T} - 1 \right), \quad (19)$$

so that

$$\mathcal{E}'' > 0, \quad \text{for } T < 2\theta, \quad (20)$$

$$\mathcal{E}'' < 0, \quad \text{for } T > 2\theta. \quad (21)$$

Hence, preheating is advantageous when

$$T_+ \approx E_a - \theta > 2\theta, \quad (22)$$

or, in other words, when $E_a > 3\theta$. Thus, throughout the range of applicability of inequality (16), preheating to T_+ results in a local maximum in \mathcal{E} , corresponding to maximally efficient use of the input heat. Obviously, \mathcal{E} has a singularity at $T = \theta$ corresponding to no preheating, but the rate of reaction is presumably too low to permit operation at such a low temperature, at least for cases relevant to this analysis. Upon preheating to T_+ , the concomitant enhancement in rate is

$$\begin{aligned} \frac{(dP/dt)_{T=T_+}}{(dP/dt)_{T=T_0}} &= \exp \frac{E_a}{T_0} \exp \left(\frac{-1}{1 - \theta/E_a} \right) \\ &\approx \exp(E_a/T_0 - 1). \end{aligned} \quad (23)$$

Hence, preheating becomes increasingly advantageous for reactions with higher energy barriers.

At sufficiently high temperatures one must of course also consider the reverse reaction in Eq. (1) with its own Arrhenius rate equation. As shown in Ref. 10, this can be done by redefining some of the constants, so that our conclusions remain the same. However, the temperatures at which this is necessary are considerably above T_+ , since the activation energy for the reverse reaction is larger than E_a by $-\Delta H_r$, the molar heat of reaction.

III. AN ENGINE DRIVEN BY AN EXOTHERMIC ARRHENIUS-LAW REACTION

In the model termed case I of Ref. 10, the heat of reaction carried by the products of that chemical reaction is converted into work by a reversible engine. Because, in that model, the reaction product mixture has a finite heat capacity¹¹ independent of T , the efficiency of the reversible engine is

$$\eta = 1 - \frac{T_0}{T(f) - T_0} \ln [T(f)/T_0]. \quad (24)$$

Here, T_0 is the temperature of the cold reservoir of the engine and $T(f)$, a function of the flow rate f , is the temperature at which the hot product mixture enters the engine. We now analyze the power production of such an engine as a function of the flow rate f as we did in Ref. 10, except that we now include the temperature dependence of the rate coefficient of the reaction.

If no heat is lost from the reactor, all the heat released by the exothermic reaction, Q_m per mole of product, is used to heat the mixture whose heat capacity is C :

$$R_0 C \frac{dT}{dt} = Q_m \left(-\frac{dR}{dt} \right). \quad (25)$$

We consider a first order Arrhenius-law reaction $R \rightarrow P$ and let R and P indicate concentrations of these species as well as the species themselves with R_0 being the original (total) concentration of reactant. The rate of reaction is given by

$$\begin{aligned} -dR/dt &= RA \exp(-E_a/T) \\ &= kR. \end{aligned} \quad (26)$$

We define the extent of reaction

$$\epsilon = (R_0 - R)/R_0, \quad (27)$$

from which we transform Eq. (26) in the conventional way into

$$\begin{aligned} d\epsilon/dt &= (1 - \epsilon) A \exp(-E_a/T) \\ &= (1 - \epsilon) k, \end{aligned} \quad (28)$$

or

$$\epsilon = 1 - \exp \left(- \int k(t) dt \right). \quad (29)$$

This will be useful to us now to compare with the form with which we calculate the temperature of the products [Eq. (37)].

To calculate the temperature of the emerging product mixture the reactor is divided into a large number of cells of equal length. Temperature is assumed to be constant within each cell, and is given by

$$T_i = \frac{Q_m \epsilon_{i-1}}{C_i} + T_0 \quad (30)$$

for the i th cell, where ϵ_{i-1} is the extent of the reaction at the end of the $(i-1)$ th cell. The extent of reaction in the i th cell is

$$\epsilon_i = 1 - (1 - \epsilon_{i-1}) \exp(-k_i \Delta t). \quad (31)$$

The molar heat capacity in the i th cell C_i is the average of the heat capacities of the reactants and products C_r and C_p :

$$C_i = \epsilon_i C_p + (1 - \epsilon_i) C_r. \quad (32)$$

The dwell time in a single cell Δt is just the total traversal (or dwell) time in the reactor divided by the number of cells N :

$$\Delta t = t/N. \quad (33)$$

The traversal time t is inversely related to the flow rate f :

$$t = (S \cdot l) \rho_m / f, \quad (34)$$

where $(S \cdot l)$ is the reactor volume, and ρ_m is the density of the feed mixture. We assume the rate coefficient is constant within each cell:

$$k_i = A \exp(-E_a/T_i). \quad (35)$$

Note that Eq. (30) implies that there are no heat leaks—all heat produced in cells 1 through $(i-1)$ is used to heat the mixture to T_i —and that T_i is the temperature that fixes the rate coefficient throughout cell i .

The rate at which heat is released from the reaction at the end of the flow tube is therefore

$$q_{tot} = Q_m f \epsilon_N, \quad (36)$$

where the extent of reaction at the end of the N th cell is

$$\epsilon_N = 1 - \exp \left[- \left(\sum_{i=1}^N k_i \Delta t \right) \right], \quad (37)$$

which follows from the recursion relation (31). Equation (37) is the discrete form of Eq. (29), the ordinary integrated form of the first-order rate expression.

The power corresponding to Eq. (36) is

$$w(f) = q_{tot}(f) \eta(f). \quad (38)$$

The efficiency η is a function of the final temperature $T(f)$, which, in turn, is given by

$$T(f) = \frac{Q_m \epsilon_N}{C_N} + T_0. \quad (39)$$

Since flow rate and traversal time are related by Eq. (34), the power (38) also may be expressed as a function of t :

$$\begin{aligned} w(t) &= q_{tot}(t) \eta(t) \\ &= Q_m \left\{ 1 - \exp \left[- \sum_{i=1}^N k_i(t) \Delta t \right] \right\} (S l \rho_m / t) \\ &\quad \times \left\{ 1 - \frac{T_0}{T(t) - T_0} \ln \left[\frac{T(t)}{T_0} \right] \right\}. \end{aligned} \quad (40)$$

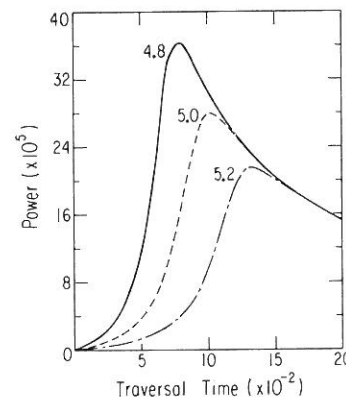


FIG. 1. Engine power (in units of Q_m per unit time) as a function of traversal time (equal to f^{-1} , i.e., $ASl\rho_m=1$) for a reversible engine driven by a first-order Arrhenius-law exothermic reaction with $Q_m/C_r T_0=1$, $C_p=C_r$, $T_0=300$ K, and for $E_a=4.8$ kcal/mol (—); 5.0 kcal/mol (---); and 5.2 kcal/mol (· · ·). The reactor was divided into 500 cells.

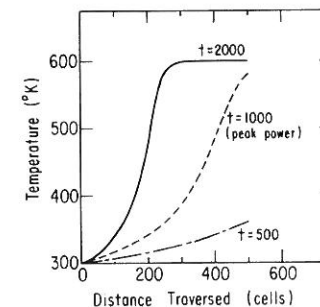


FIG. 2. Temperature (in K) as a function of distance traversed in the reactor (in cells) for a first-order Arrhenius-law reaction with $Q_m/C_r T_0=1$, $C_p=C_r$, $T_0=300$ K, and $E_a=5.0$ kcal/mol for traversal times (equal to f^{-1}) of 2000 (—); 1000 (---); and 500 (· · ·). $t=1000$ corresponds to maximum engine power.

This is a form for the power from which one can readily carry out computations.

Figure 1 shows the power, as a function of traversal time, in units of Q_m per unit time. The time unit is taken as that of the traversal time f^{-1} , i.e., with $ASl\rho_m=1$. For this figure, we have taken $Q_m/C_r T_0=1$, $C_{reactants}=C_{products}=C$, and $T_0=300$ K. The calculations were performed with 500 cells. Power functions w are shown for three values of the activation energy E_a (4.8, 5.0, and 5.2 kcal/mol). (For convenience, we use conventional chemical units for E_a to designate the curves.) The power changes so rapidly as a function of this absolute parameter that these three rather closely spaced values seemed sufficient to illustrate the results and still allow us to display the curves on linear scales.

In some respects the curve of power versus traversal time of an engine driven by an Arrhenius-law reaction resembles that of the constant rate coefficient case.¹⁰ Maximum power is achieved for a finite, positive dwell time. The power function again depends upon $Q_m/C_r T_0$. As in Ref. 10, a larger value for $Q_m/C_r T_0$ results in a higher maximum power achieved at an earlier time (i.e., at a higher flow rate). However, we now find a strong dependence of the power function upon the activation energy. From Fig. 1 one observes that small changes in the activation energy significantly shift both the value of the maximum power and the flow rate required to achieve that maximum.

In the present case the temperature profile within the reactor tube is also quite sensitive to the flow rate or traversal time. Figure 2 shows the temperature, in K, of the reaction mixture as a function of the distance traversed in the reactor, measured in cells, for the case where $E_a=5.0$ kcal/mol and for $t=500$, 1000, and 2000 (in units of f^{-1}). All other parameters are the same as in Fig. 1. The time $t=1000$ is very close to the one which produces maximum power for $E_a=5.0$ kcal/mol. The highest temperature obtainable, in this case 600 K, is limited by the value chosen for $Q_m/C_r T_0$. At the flow rate giving peak power, in this case corresponding to a dwell time of 1000, the temperature at the

end of the flow tube is only slightly less than the maximum temperature. At slower flow rates, the maximum temperature is attained before the mixture reaches the end of the tube, whereas at faster flow rates, the final temperature is not even close to the maximum. Curves of the general sort of Fig. 2 are well known in chemical kinetics, e. g., in the temperature profile of a premixed flame.¹²

As in Sec. II the reverse reaction P → R has been disregarded, partly because it can be included with limited effort¹⁰ if necessary, and partly because combustion processes have large heats of reaction and thus require very large temperatures to proceed in reverse at appreciable rates.

IV. DISCUSSION

The two examples examined above illustrate the trade-off between rapid rate of operation and thermodynamic efficiency in energy conversion processes. In the first example, an Arrhenius-law chemical synthesis, we showed that for typical values for the activation energy, there is a temperature to which the reactants may be preheated so as to maximize $(dP/dt)/q$. Equation (17) gives this temperature. There is second formal solution; $(dP/dt)/q$ has a singularity at $q=0$ (no preheating), but this will often correspond to an undesirably slow rate of synthesis.

From the second example it was found that the power produced by an engine driven by an exothermic Arrhenius-law reaction behaves in some ways like the case of a temperature independent rate, which corresponds to $E_a=0$. The maximum power is obtained at some finite, positive dwell time (or finite, positive flow rate). The more exothermic the reaction, i. e., the higher the value for Q_m/CT_0 , the higher the maximum power and the less time required to achieve the maximum power. The present system also shows a strong dependence of the power versus dwell time curve upon E_a . The higher the energy barrier, the longer it takes to attain the maximum power; the peak power also drops dramatically as E_a increases. The initial slope of the power versus time function is also decreased as the energy barrier increases. However, in the limit of long dwell time the power does not depend upon activation energy (cf. Figure 1); the three curves join at t large. This is the limit in which the reaction reaches completion before the mixture emerges from the reactor.

Along the reactor tube there is a sudden "burst" of heat, with a corresponding rapid rise in temperature, if the flow rate is sufficiently slow (see Fig. 2). This is caused by a cooperative effect characteristic of exothermic activated reactions. Maximum power is achieved at that flow rate which allows the burst in temperature to occur just before the end of the flow tube.

We can find the point of maximum extent where $d\epsilon/dt=0$; this is always $t=\infty$ where the reaction has come to equilibrium, and

$$T(\infty) \equiv T_\infty = T_0 + Q_m/C. \quad (41)$$

The second derivative $d^2\epsilon/dt^2=0$ provides the point of steepest rise of the temperature, the "reaction front." The general solution contains two exponential integrals but for large activation energy E_a (as in combustion) this time t_f behaves as

$$t_f \sim E_a^{-1} e^{E_a/T_0}. \quad (42)$$

The width of the reaction front, taken as the inverse of the slope of the extent at this point,

$$\Delta t_f \equiv \left(\frac{d\epsilon}{dt} \Big|_{t_f} \right)^{-1} \quad (43)$$

behaves for large E_a as

$$\Delta t_f \sim E_a e^{E_a/T_\infty}. \quad (44)$$

Thus, both t_f and Δt_f become infinite in the limit of large activation barriers, but the relative width becomes sharper with increasing E_a in this limit:

$$\frac{\Delta t_f}{t_f} \sim E_a^2 \exp \left[E_a \left(\frac{1}{T_\infty} - \frac{1}{T_0} \right) \right], \quad (45)$$

since the inverse temperature difference is negative. This means that, for a fixed length flow tube, the reaction front becomes increasingly localized, and one should be careful not to operate the combustor too close to the maximum power condition (i. e., with the wave front at the end of the flow tube), since small fluctuations easily could displace the sharp reaction front outside the tube.

The temperature dependence of the rate coefficient is well recognized by engineers to be a most important consideration in determining how to carry out an exothermic reaction in a flow system.^{12,13} Indeed, the power of an engine driven by such a reaction is limited by the activation energy of the reaction except in the limit of slow flow rates.

ACKNOWLEDGMENTS

We thank C. H. Barkelew for his suggestions. This research was supported by a grant from the Shell Companies Foundation and a travel grant from NATO. We also wish to thank the Aspen Center for Physics for its hospitality during part of the course of this work, and R. S. B. wishes to express his appreciation to the Laboratoire de Photophysique Moléculaire, where he was working when this manuscript was completed.

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Maximum work from a finite reservoir by sequential Carnot cycles

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The production of work from a heat source with finite heat capacity is discussed. We examine the conversion of heat from such a source first by a single Carnot engine and then by a sequence of Carnot engines. The optimum values of the operating temperatures of these engines are calculated. The work production and efficiency of a sequence with an arbitrary number of engines is derived, and it is shown that the maximum available work can be extracted only when the number of cycles in the sequence becomes infinite. The results illustrate the importance of recovery or bottoming processes in the optimization of work-producing systems. In addition, the present model illuminates one practical limitation of the Carnot cycle: The Carnot efficiency is only obtainable from a heat source with infinite heat capacity. However, another cycle, somewhat reminiscent of the Otto and Brayton cycles, is derived which will provide the maximum efficiency for a heat source with a finite heat capacity.

INTRODUCTION

It is well known that Carnot engines have little practical use because of the large volumes they sweep out on the adiabatic branches. This limitation takes expression in a low value of the work ratio, the net work per cycle divided by the work done in the expansion stroke. For the Carnot engine, the expansion stroke is the hot isotherm plus the adiabatic expansion. Recall that the work done on the ideal Carnot engine in adiabatic compression equals the work done by the engine in adiabatic expansion. Moreover this work ratio is sensitive to irreversibilities, especially to mechanical friction.^{1,2} Investigations of the optimum performance and irreversibilities of engines operating in finite time have only very recently been reported.³⁻⁶ While the Carnot cycle (i.e., a cycle consisting of two adiabats and two isotherms) delivers the maximum work in an infinitely slow cycle when irreversibilities are present, it is not the optimum cycle for processes operating in finite time.^{5,6}

However, even if a Carnot engine is operated reversibly, the Carnot efficiency

$$\eta_{\text{Carnot}} = (T^{\text{high}} - T^{\text{low}}) / T^{\text{high}} \quad (1)$$

cannot be realized if the heat which drives the engine is supplied by a source with finite heat capacity. As heat is withdrawn from the source, its temperature drops and the available work decreases.

Consider a Carnot engine operating between two reservoirs with temperatures T^H and T^L . Suppose that the source with constant heat capacity C is initially at temperature T^S , with $T^S > T^H > T^L$. Suppose next that the source transfers its heat to the reservoir at T^H , while its temperature drops from T^S to T^H , and the source and reservoir are then disconnected. The heat transferred to the engine is $C(T^S - T^H)$. This heat may then be converted into work with efficiency $(T^H - T^L)/T^H$. If T^H is set high (i.e., close to T^S) the heat transferred to the engine is small, but it will be converted into work with high efficiency. Conversely, if T^H is set low (i.e., close to T^L), a larger amount of heat is transferred to the engine, but it is converted into work with low efficiency.

In this paper we investigate a system with heat supplied by a source with finite, constant heat capacity and in which this heat is converted into work in two different ways: in the first case, by a single Carnot engine; and in the second case, by a sequence of Carnot cycles. The optimum value for T^H , the upper temperature of each engine, is derived both for the single engine case and for a sequence of N Carnot cycles. The work produced by an arbitrary number of optimized engines is calculated, and it is shown that the maximum work is extracted (i.e., the effectiveness of the system becomes unity) only by an infinite number of Carnot cycles ($N \rightarrow \infty$). From our expression for the work in the limit $N \rightarrow \infty$, it is apparent that for a finite heat source originally at T^S and a cold reservoir at T^L , the Carnot efficiency $(T^S - T^L)/T^S$ is unobtainable, even by an infinite number of sequential Carnot engines. Finally, the reversible cycle which achieves the maximum efficiency from a finite hot reservoir is constructed, and some practical consequences of our results are discussed.

ONE-ENGINE OPTIMIZATION

For the case where work is produced by a single Carnot engine, the work is given by

$$W = C(T^S - T^H)(T^H - T^L)/T^H, \quad (2)$$

$$W = C[T^S + T^L - T^H - (T^S T^L / T^H)]. \quad (3)$$

The temperatures T^S and T^L , which might be, for example, the flame temperature of a combustion process and ambient temperature, respectively, are regarded as fixed and T^H is the variable parameter. The upper temperature T^H for which the work is maximized is the solution to

$$\frac{dW}{dT^H} = C[T^S T^L / (T^H)^2 - 1] = 0. \quad (4)$$

The optimum value for T^H is then

$$T^H(1) = (T^S T^L)^{1/2}; \quad (5)$$

the script letters denote the optimum value, and 1 in parentheses denotes one Carnot cycle.

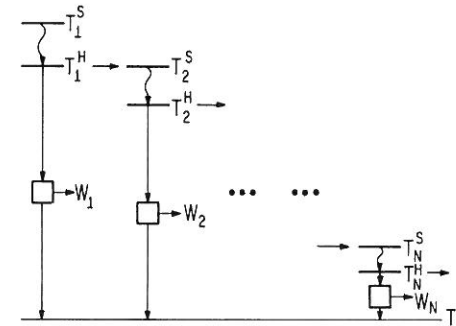


Fig. 1. Sequence of N Carnot cycles. Heat is supplied to each engine at T_i^H from a source initially at T^S . The source is disconnected from the i th engine at T_i^H and then becomes the source for the $(i + 1)$ th engine.

N-ENGINE OPTIMIZATION

In the one-engine case, the heat source is disconnected from the hot reservoir of the system at T^H . This means that a significant amount of the original availability is not recovered, because $C(T^H - T^L)$ units of heat are discarded unless extraneous processes can utilize this lower-grade heat. Naturally, the effectiveness can be improved if engines are added to the system (see Fig. 1). The high temperature T_i^H of the first cycle becomes the source temperature of the second cycle T_2^S and so on so that

$$T_i^H = T_{i+1}^S \quad (6)$$

for $1 \leq i \leq (N - 1)$, where the subscripts denote the element of the sequence and where N is the total number of cycles in the sequence.⁷

The work produced by the i th cycle in the sequence is [cf. Eq. (3)]

$$W_i = C[T_i^S + T^L - T_i^H - (T_i^S T^L / T_i^H)]. \quad (7)$$

The total work for the N -cycle sequence is

$$W(N) = \sum_{i=1}^N W_i, \quad (8)$$

which, using Eqs. (6) and (7), becomes

$$W(N) = C \sum_{i=1}^N (-T_i^S T^L / T_i^H) + CT^L N + CT_1^S - CT_N^H. \quad (9)$$

We wish to find the values for the elements of the set $\{T_1^H, T_2^H, \dots, T_N^H\}$ for which $W(N)$ is maximized. This is, in effect, a problem in discrete optimal control, albeit exceedingly simple, since the only variable in the N -cycle problem is T_1^H . This is because T_2^H may be fixed as the optimum T^H for the one-cycle problem, \dots , and T_N^H may be fixed by optimization of the $(N - 1)$ -cycle problem. In other words, any T_i^H may be optimized independently of any engines with index less than i .

Hence, for the two-cycle case,

$$W(2) = -C(T_1^S T^L / T_1^H) - C(T_2^H T^L / T_2^H) + 2CT^L + CT_1^S - CT_2^H, \quad (10)$$

but the optimum value for T_2^H is given by

$$T_2^H(2) = \sqrt{T_1^S T^L} = \sqrt{T_1^H T^L}. \quad (11)$$

If T_2^H , the high temperature of the second cycle of the two-cycle sequence, is fixed at this optimum value, then $T_1^H(2)$ is the solution to

$$\frac{dW(2)}{dT_1^H} = C[T_1^S T^L / (T_1^H)^2 - (T_1^H)^{-1/2} (T^L)^{1/2}] = 0, \quad (12)$$

given by

$$T_1^H(2) = [(T_1^S)^2 T^L]^{1/3} = T_1^S [T^L / T_1^S]^{1/3}. \quad (13)$$

It is straightforward to prove that, for an N -cycle sequence with the high temperature of each cycle optimized, the optimum value for $T_1^H(N)$, the upper temperature of the first engine in the sequence, is

$$T_1^H(N) = [(T_1^S)^N T^L]^{1/(N+1)} = T_1^S [T^L / T_1^S]^{1/(N+1)}. \quad (14)$$

Equation (14) has already been shown to be true for $N = 1$ and 2; we prove it by induction for an arbitrary N . It is easiest to prove the case for N engines from the case for $N - 1$ if we count backwards. First, we suppose that Eq. (14) gives the optimum upper temperature of engine 1 for any sequence if the total number of cycles in the sequence is any integer between 1 and $N - 1$ inclusive, and if all engines in the sequence with index ≥ 2 have already been optimized. We then must show that Eq. (14) holds for a sequence of N cycles (provided, of course, that the upper temperatures of engines 2 through N in this sequence have been set at their optimum values). Since each engine may be optimized independently of engines of lower index, we start with engine N in the N -cycle sequence (see Fig. 1) and then proceed to engines $N - 1, N - 2, \dots, 2$ (i.e., we work from right to left in Fig. 1). We have assumed that Eq. (14) is true for any sequence with 1 through $N - 1$ cycles; this gives the optimum upper temperature for $2 \leq i \leq N$ in the N -engine problem:

$$T_i^H(N) = T_i^S (T^L / T_i^S)^{1/(N-i+2)}. \quad (15)$$

We now wish to recast Eq. (15) in terms of T_1^H , the upper temperature of the first engine. To do this we use Eq. (15) with $i = 2$ and substitute Eq. (6) to find the optimized upper temperature of the second engine:

$$T_2^H(N) = T_1^H (T^L / T_1^H)^{1/N}. \quad (16)$$

We also need to express $T_i^H(N)$ for $3 \leq i \leq N$ in terms of T_1^H ; hence, we must prove Eq. (18) below. Equation (18) has already been shown to be true for $i = 2$ [see Eq. (16)]; we prove it for $3 \leq i \leq N$ by induction on i . It is assumed that, for the $(i - 1)$ th engine,

$$T_{i-1}^H(N) = T_1^H (T^L / T_1^H)^{(i-2)/N} = T_1^S. \quad (17)$$

We substitute Eq. (17) into Eq. (15) to express the optimized upper temperature of the i th engine in the sequence as a function of T_1^H :

$$T_i^H(N) = T_1^H (T^L / T_1^H)^{(i-1)/N}. \quad (18)$$

Finally, substitution of Eq. (18) into the expression for the work produced by the N -cycle sequence, Eq. (9) yields

$$W(N) = C[-T_1^S T^L / T_1^H - N(T_1^H)^{1/N} (T^L)^{(N-1)/N} + T^L N + T_1^S]. \quad (19)$$

Again, setting the first derivative of W with respect to T_1^H equal to zero, one obtains

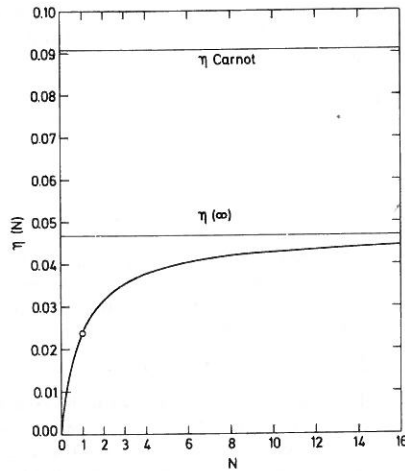


Fig. 2. Thermal efficiency of optimized N sequence of Carnot engines for a range of N . Also shown are the reversible efficiencies of conversion from a finite capacity heat source, $\eta(\infty)$, and from an infinite capacity heat source, η_{Carnot} . The initial ratio of reservoir temperatures is $T_1^S/T^L = 1.1$.

$$C\{T_1^S T^L / [T^H(N)]^2 - [T^L/T^H(N)]^{(N-1)/N}\} = 0, \quad (20)$$

from which Eq. (14) follows.

Hence, if each cycle in the N -member sequence has been optimized [i.e., the upper temperature has been fixed according to Eq. (15)], the maximum work obtainable by this sequence from a source with constant heat capacity initially at T_1^S is

$$W(N) = C[-(N+1)T^L(T_1^S/T^L)^{1/(N+1)} + NT^L + T_1^S], \quad (21)$$

The upper limit of this function is achieved for $N \rightarrow \infty$. We rewrite Eq. (21) as

$$W(N) = C\{T_1^S - T^L - T^L(N+1) \times [(T_1^S/T^L)^{1/(N+1)} - 1]\} \quad (22)$$

and use that

$$\lim_{N \rightarrow \infty} N(x^{1/N} - 1) = \ln x \quad (23)$$

to obtain

$$W(\infty) = C[T_1^S - T^L - T^L \ln(T_1^S/T^L)], \quad (24)$$

which is the maximum (reversible) work extractable from the finite capacity heat reservoir, since it is equal to the availability of the original material at T_1^S (Ref. 8):

$$W = C \int_{T^L}^{T_1^S} \left(1 - \frac{T^L}{T}\right) dT. \quad (25)$$

This quantity is considerably larger than the maximum work extractable with a single Carnot cycle [combine Eqs. (3) and (5) or use Eq. (21) directly]:

$$W(1) = C(\sqrt{T_1^S} - \sqrt{T^L})^2. \quad (26)$$

The corresponding efficiency of the sequence, $W(N)/Q$ (from source), is

$$\eta(N) = W(N)/[C(T_1^S - T^L)], \quad (27)$$

which is plotted versus N in Fig. 2 for $T_1^S/T^L = 1.1$. Clearly $\eta(N)$ and $W(N)$ have the same functional dependence upon N , they are both increasing functions. In the limit $N \rightarrow \infty$ we have

$$\eta(\infty) = 1 - \frac{T^L}{T_1^S - T^L} \ln(T_1^S/T^L) \quad (28)$$

$$= 1 + \frac{1 - \eta_c}{\eta_c} \ln(1 - \eta_c), \quad (29)$$

where

$$\eta_c \equiv \eta_{\text{Carnot}} = (T_1^S - T^L)/T_1^S. \quad (30)$$

The values of $\eta(\infty)$ and η_c are also indicated on Fig. 2 to emphasize the inferiority of $\eta(1)$ (circled). To see more clearly how $\eta(\infty)$ deviates from the Carnot efficiency, we may rewrite Eq. (29) as

$$\eta(\infty) = \eta_c - (1 - \eta_c) \sum_{j=1}^{\infty} \frac{\eta_c^j}{j+1}. \quad (31)$$

This relationship is depicted in Fig. 3. Since every term in the summation on the right-hand side of Eq. (31) is positive, we have

$$\eta(\infty) < \eta_c. \quad (32)$$

In other words, the efficiency of the infinite sequence of engines producing work from a finite hot reservoir originally at T_1^S and a cold reservoir at constant temperature T^L will always be smaller than the efficiency of a single Carnot engine operating between two infinite reservoirs at T_1^S and T^L . Hence the classical Carnot efficiency (derived for systems operating between infinite reservoirs) is not really useful for the establishment of criteria of merit for heat engines operating with finite heat capacity heat sources. For such engines, the Carnot efficiency is unobtainable.

REVERSIBLE CYCLE

The reversible limit $N \rightarrow \infty$ was in Eq. (24) derived as an infinite sequence of Carnot cycles. Viewed as a single

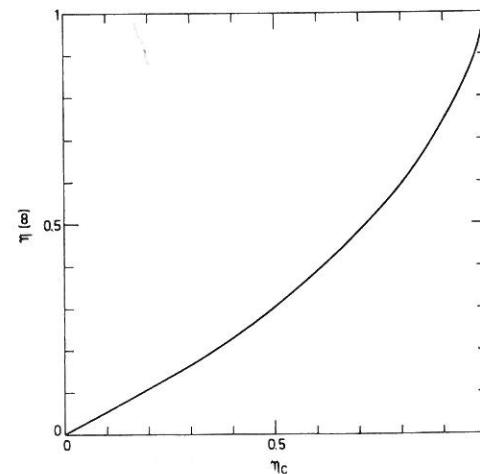


Fig. 3. Thermal efficiency for reversible conversion of energy from a finite capacity heat source versus the efficiency for an infinite capacity heat source (Carnot efficiency) at the same initial temperatures.

overall cycle, none of the common "named" heat cycles behave this way. We will here construct a cycle (specify its branches) which achieves this reversible energy conversion from a finite capacity heat reservoir.

The low-temperature heat exchange is with an infinite capacity reservoir (at T^L) for which an isothermal branch is appropriate. The high-temperature reservoir has heat capacity C , i.e., from the point of view of the engine $-dQ/dT = C$, which, combined with the energy conservation equation for an ideal gas,

$$dQ = C_r dT + (RT/V)dV, \quad (33)$$

yields

$$\frac{-dV}{V} = \frac{C + C_r}{R} \frac{dT}{T}, \quad (34)$$

or in integrated form

$$V = V_0 \left(\frac{T_0}{T}\right)^{(C+C_r)/R}, \quad (35)$$

where V_0 and T_0 are size constants. This defines a polytrope with $PV^{1+R/(C+C_r)} = \text{const}$. The special cases $C = 0, \infty, -C_r$, and $-C_r$ reproduce the usual adiabat, isotherm, isometric, and isobar, respectively. These two heat exchange branches can now be joined by a reversible adiabat to form the complete reversible finite-heat-capacity reservoir cycle whose PV and TS diagrams are shown in Fig. 4. A finite capacity low-temperature reservoir will of course only change the isotherm into another polytrope with $PV^{1+R/(C+C_r)} = \text{const}$. The constructed cycle is a hybrid between a Carnot cycle (isothermal part) and something reminiscent of a Brayton or Otto cycle (polytropic part). The exact behavior depends on the relationship between the gas and reservoir heat capacities, C_r and C , and on the constraints on the reservoir that define what kind of heat capacity C represents, e.g., constant volume, constant pressure, constant surface tension, etc.

Let us close with a remark regarding the comparison of a single large engine with a set of engines of the type described here. The polycycle is, in effect, a series of cycles, each using the waste heat from the one before. Cycles using waste heat are generally called bottoming cycles. The advantage of the polycycle comes from its ability to convert heat to work without requiring the extremely large volumes and compression ratios that a single engine would call for. The work produced by the polycycle relative to the total energy flow (its work ratio) and the compression ratio are necessarily less than the corresponding quantities for the Carnot cycle, because some heat is accepted at less than the maximum temperature. In particular the work efficiency in terms of the swept volume depends strongly upon the initial temperature gap available and the reservoir heat capacity. The largest "volume efficiency," the work divided by $(V_{\text{max}} - V_{\text{min}})$, is achieved for

$$\frac{R}{C + C_r} = 1 + \ln \left(\frac{T_1^S}{T^L} \right) / \left(1 - \frac{T_1^S}{T^L} \right), \quad (36)$$

which makes the polycycle particularly appropriate for bottoming cycles and other conversion of large quantities of low-grade heat into work. For large temperature ratios (T_1^S/T^L) the rapidly increasing compression ratio can make the cycle extremely sensitive to friction losses from the piston.

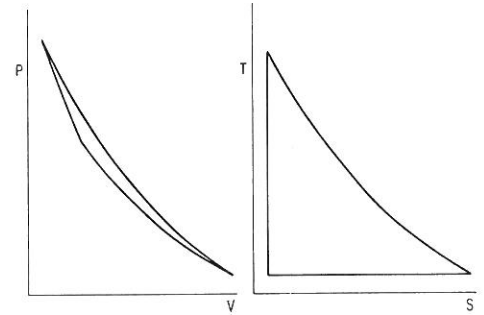


Fig. 4. PV and TS diagrams for the ideal gas reversible polycycle which extracts the maximum possible work from a finite-heat-capacity reservoir. The left branch is the adiabat, the bottom one the isotherm, and the upper-right branch the polytrope. Coordinate scales are arbitrary.

DISCUSSION

We have seen that the maximum work extractable from a heat source with finite heat capacity, Eq. (24) is considerably larger than that extractable from the same source by a single Carnot cycle, Eq. (26). Nevertheless, the efficiency corresponding to Eq. (24) is less than that of a Carnot engine operating between two infinite heat capacity reservoirs at T_1^S and T^L . These results have proved to be important in, for example, the determination of the maximum power which can be produced from a combustion process with finite rate.⁹ Indeed, the heat which drives most real engines is supplied by a source with finite heat capacity.

Some common cycles, such as the Otto or the Rankine, exchange heat along paths with changing temperatures. Such cycles have lower Carnot efficiencies than cycles such as the Carnot or Stirling, where heat exchange occurs isothermally. The lower efficiencies of the former are sometimes cited as evidence for their inferiority relative to the latter type.¹⁰ The above results show that this claim is only justified when infinite heat reservoirs are involved. For finite heat capacity sources it is best to accept the heat in a non-isothermal manner, following the temperature drop of the reservoir, rather than to accept it at some fixed temperature and discard the remaining temperature drop. Thus for this case a new cycle with a high-temperature polytrope matched to the reservoir heat capacity, and not a Carnot cycle, is actually the best.

The optimum value for the upper temperature of a given cycle depends, as one might expect, upon the number of succeeding (higher index) cycles in the sequence. The addition of recovery or bottoming processes permits one to operate optimally by extracting less heat in each cycle; thus each cycle is operated at as high a temperature as possible.

Efforts in the newly established field of finite-time thermodynamics have demonstrated that the efficiencies of real energy conversion processes are limited by finite-time and finite-rate constraints when irreversibilities are present (see, e.g., Refs. 3-6 and 9). The results of the present work show that even in the realm of reversible thermodynamics, the efficiencies of real engines will be limited by the finite heat capacity of the heat source.

ACKNOWLEDGMENTS

We would like to thank the Shell Companies Foundation and Exxon, USA for support of this research, and acknowledge a NATO travel grant. We are grateful for the hospitality of the Aspen Center for Physics, where part of this work was performed.

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¹Joseph H. Keenan, *Thermodynamics* (MIT, Cambridge, MA, 1970), Chap. XII.

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⁷Note that other cycles that do not use isothermal branches, e.g., the Rankine cycle, are essentially of this sort, with N large.

⁸See, e.g., H. B. Callen, *Thermodynamics* (Wiley, New York, 1960), p. 73.

⁹M. J. Ondrechen, R. S. Berry, and B. Andresen, *J. Chem. Phys.* **72**, 5118 (1980).

¹⁰For example, Ref. 1, p. 180.

8.9. Optimal staging of endoreversible heat engines

J. Appl. Phys. **53**, 1 (1982)

Optimal staging of endoreversible heat engines

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(Received 25 February 1981; accepted for publication 19 August 1981)

One way to classify performance indices of irreversible heat engines is according to how the indices change when one engine is replaced by two (or more) of the same kind in series. We investigate the performance of two endoreversible engines (i.e., heat engines with the only irreversibility being heat resistance to the surroundings) which are put in series to form a single engine, whose power output is maximized. In this unconstrained optimization the interface between the two stages, which for the present model is the intermediate temperature and the relative timing of the two engines, is arbitrary and can be used to satisfy other, nonthermodynamic constraints. Adding any constraint on the volume of the working gas does not lift this indeterminacy. The optimum composite system is equivalent to a single endoreversible engine, thus displaying a sequencing property similar to Carnot engines.

PACS numbers: 05.70.Ln, 05.70.Ce

I. INTRODUCTION

The bounds on performance criteria in classical thermodynamics are provided by reversible processes. These bounds are of great interest because they are generally independent of the particular machinery employed to perform the processes which attain the bounds. The general study of irreversible engines has in part been stimulated by the fact that classical reversible thermodynamics provides bounds that are usually too optimistic to be useful benchmarks for real processes. The problem, of course, is that the inevitable losses associated with operating machinery at nonvanishing rates are neglected. Several previous studies¹⁻⁸ have attempted to repair this situation by incorporating the most important losses into the reference process.

In addition to the bounds there are other features of reversible processes which require reexamination when irreversibilities are considered. For example, the maximum efficiency for extracting work from a system composed of two heat reservoirs is the same whether one uses a single Carnot engine or several Carnot engines in series, parallel, or any combination thereof. In this paper we examine how performance criteria are affected for a class of irreversible engines when one such engine is replaced by two of these engines in series, by which we mean that the low-temperature reservoir of one engine is the high-temperature reservoir of the next (Fig. 1).

Unlike reversible engines, irreversible engines generally must be operated differently when different performance indices are optimized. Our purpose in studying the sequencing of irreversible engines was originally to see if it was possible to classify performance indices by their sequencing properties. We had expected different behavior depending on whether, for example, we maximized efficiency or average power output. As will be shown in this paper, this did not happen. Despite the more complex behavior of irreversible engines, they display a sequencing property similar to Carnot engines.

The class of engines we shall study are endoreversible⁹ heat engines where the only irreversibility is due to heat resistances between the heat reservoirs and the reversible (e.g., Carnot) engine. We call such engines CA engines because the efficiency at maximum-average-power output was first calculated by Curzon and Ahlborn.¹ Complete, unconstrained optimizations of engines with only heat resistance losses, but without assuming a specific work cycle, were carried out in Refs. 5 and 6 for systems without and with volume constraints. In the present paper we investigate the optimal staging of two CA engines. There is some practical inspiration for this model from machines like two-stage refrigerators, which are usually employed to make liquid air,¹⁰ multistage compressors for high pressure, and power plant turbines, which are often sequenced for high, medium, and low pressure.

We should emphasize that this is not an unrestricted optimization (as in Refs. 5 and 6) since each of the engines are required to be of CA type. We use the CA-engine because it is the simplest irreversible engine. Furthermore, the CA-engine is not as unrealistic as it may appear at first sight. For example, the requirement that the isentropic branches occur in negligible time means that they must occur on a time scale that is fast compared to the slow rates for heat leaks to the environment but slow compared to the rapid internal relaxation of pressure gradients in the working fluid. An analysis of reversible, adiabatic branches may be found in Ref. 11.

The plan of this paper is as follows. In Sec. II we review the results for a single CA engine and consider a simple example of the sequencing of two CA engines. This example is made simple because the reservoir connecting the two engines is taken to have a constant temperature. In Sec. III, we present the detailed specification of the model we study. In Secs. IV and V the optimal cycle for maximum average power is computed. For those not interested in the mathematical details the results are presented and discussed starting with Eq. (62). In Sec. VI we consider the performance criteria of

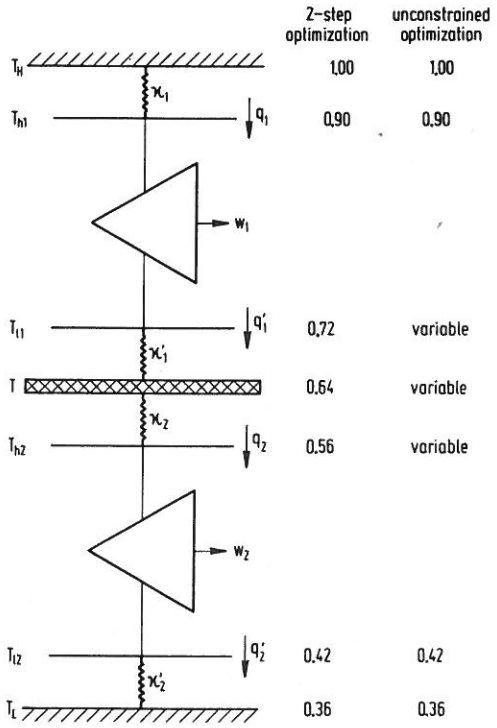


FIG. 1. Two staged CA engines. In the numerical examples T_H and T_L are the same as in Fig. 2. The first column results from the staging of two individually optimized CA engines with the intermediate temperature T a constant. The second column results from an unconstrained optimization of the whole system.

maximum efficiency, maximum effectiveness, and minimum entropy production. Finally Sec. VII contains our conclusions.

II. A SIMPLE EXAMPLE OF SEQUENCING

For comparison let us recapitulate the results for a single CA engine operating at maximum power¹ between reservoirs at temperatures T_H and T_L (see Fig. 2). The actual operating temperatures for the reversible cycle are

$$T_h = \frac{1}{2}T_H(1 + x), \tag{1}$$

$$T_l = \frac{1}{2}T_L(1 + x^{-1}), \tag{2}$$

where

$$x = (T_L/T_H)^{1/2}, \tag{3}$$

when the heat conductances κ and κ' are the same. The corresponding thermal efficiency is calculated to be

$$\eta_0 = 1 - x = 1 - (T_L/T_H)^{1/2} \tag{4}$$

at the maximum-average-power output

$$w_{max} = \frac{1}{4}\kappa T_H(1 - x)^2 = \frac{1}{4}\kappa(\sqrt{T_H} - \sqrt{T_L})^2, \tag{5}$$

where the engine is in contact with each reservoir for half the cycling period, and the adiabatic branches have a negligible

duration. Note the resemblance between Eq. (3) and the Carnot efficiency $\eta_{max} = 1 - T_L/T_H$. A numerical example with $T_H = 1.00$ and $T_L = 0.36$ is indicated on Fig. 2.

Next let us put two CA engines on top of each other, separated by a reservoir at temperature T (see Fig. 1), but requiring that, on the average, this reservoir does not act as a heat source or sink. For simplicity we again take all the heat conductances equal and assume each engine operates at maximum average power output. Then, if the average rate of heat withdrawn from T_H is q_1 , and we define

$$y = (T/T_H)^{1/2}, \tag{6}$$

the average power output of the top engine is

$$w_1 = (1 - y)q_1. \tag{7}$$

Since the average heat flow out of the top engine and into the bottom engine is yq_1 , the average power output of the second engine is

$$w_2 = (1 - x/y)(yq_1) = (y - x)q_1, \tag{8}$$

since $x/y = (T_L/T)^{1/2}$. Thus the total average power production is

$$w = w_1 + w_2 = (1 - x)q_1. \tag{9}$$

Note that Eq. (8) leads to the same efficiency as a single CA engine operated between the reservoirs T_H and T_L . This is just the same results one finds for Carnot engines; there is no change in efficiency if a single engine operating between two given reservoirs is replaced by staged engines. In the Appendix we show that this result follows simply from the fact that the output of one engine is the input of the second engine and the fact that at maximum power output $1 - \eta$ is a ratio of the form $F(T_L)/F(T_H)$.

The intermediate temperatures can be calculated from analogs of Eq. (1) and the requirement that

$$q_1 = \frac{\kappa}{4}T(y^{-1} - 1) \tag{10}$$

equals

$$q_2 = \frac{\kappa}{4}T(1 - x/y). \tag{11}$$

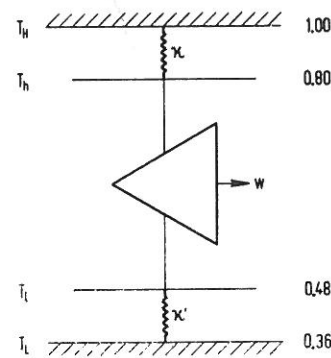


FIG. 2. A single CA engine operated between reservoirs T_H and T_L . In the example at right we have taken $T_H = 1.00$ and $T_L = 0.36$.

The results are

$$\begin{aligned} T_{h1} &= \frac{1}{4}T_H(3 + x), & T_{h2} &= \frac{1}{8}T_H(1 + x)(1 + 3x), \\ T_{i1} &= \frac{1}{8}T_H(1 + x)(3 + x), & T_{i2} &= T_H x(1 + 3x), \\ T &= \frac{1}{4}T_H(1 + x)^2. \end{aligned} \tag{12}$$

If we now calculate q_1 for the staged engines we find

$$q_1 = \frac{\kappa}{8}T_H(1 - x), \tag{13}$$

which is half the result for a single engine with the same cycling time. Thus the staged engines generate half the average power or, what is the same thing, do half the work in one period that the single engine does when they have the same heat conductances κ . This factor is easy to understand. If we call the thermal resistance of a CA engine $1/\kappa_h + 1/\kappa_l$, where κ_h (κ_l) is the heat conductance at the high-(low)temperature end of the engine, then if $\kappa_h = \kappa_l = \kappa$ for all engines, the staged engine has twice the thermal resistance that the single engine does.

The numerical values, with the same choice of reservoir temperatures as in Fig. 2, are indicated in the first column on Fig. 1. The reason for this little exercise, besides the interesting result of unchanged efficiency [Eq. (8)], is to provide a comparison for the less restricted results of the following sections, where all the intermediate temperatures are optimized simultaneously and permitted to vary in time.

Finally, note that with the exception of one temperature, T_H say, only temperature ratios enter into the calculation. As a consequence, an arbitrary number of engines may be squeezed in between T_H and T_L . The overall efficiency will remain unchanged, see Appendix, but the average power generated will decrease.

III. MODEL

The system we want to study is depicted in Fig. 1. It consists of two CA engines operating between the fixed-temperature reservoirs at T_H and T_L and coupled through the intermediate reservoir at $T(t)$. The important difference from the system described in Sec. II is that this reservoir has a finite heat capacity C , and its temperature may therefore vary in time as the CA engines go through their cycles. The heat conductances linking the reservoirs to the reversible engines are all constant. Each of the CA engines are assumed to contain a reversible (e.g., Carnot) engine with is in contact with the hot reservoir (through κ_i , $i = 1$ or 2) for the period t_i and in contact with the cold reservoir (through κ'_i) for the period $\tau - t_i$, so that the total cycle time for both is τ . However, cycle 2 is shifted t_0 in time relative to cycle 1. The adiabatic branches, not slowed down by heat transfer, are assumed to transpire in zero time. Thus one period is divided into four segments:

- $t \in [0, t_0]$: engine 1 connected to T_H , engine 2 to T_L ,
- $t \in [t_0, t_1]$: engine 1 connected to T_H , engine 2 to T ,
- $t \in [t_1, t_2 + t_0]$: engine 1 connected to T , engine 2 to T ,
- $t \in [t_2 + t_0, \tau]$: engine 1 connected to T , engine 2 to T_L .

(This is for $0 < t_1 < t_2$, as will be assumed in the rest of the paper. In case $t_1 < t_0 < \tau$ the segments come in the order 3, 1, 4, 2 without affecting any of our conclusions.) Figure 3

shows a possible time variation of the temperature of the intermediate reservoir, $T(t)$ and of the "isotherms" of the two reversible engines.

In the search for the time sequence which produces the maximum average power, $W/\tau = (W_1 + W_2)/\tau$, we keep the reservoir temperatures T_H and T_L and the cycle time τ fixed while letting all the other quantities vary: T_{h1} , T_{i1} , T , T_{h2} , T_{i2} , t_1 , t_2 , t_0 . The variables are connected through the requirements of heat balance in the intermediate reservoir,

$$C\dot{T} = \kappa'_1(T_{i1} - T) - \kappa_2(T - T_{h2}), \tag{14}$$

and reversibility of the internal engines,

$$\begin{aligned} \Delta S_1 &= \int_0^{t_1} \kappa_1(T_H - T_{h1})/T_{h1} dt \\ &\quad - \int_{t_1}^{\tau} \kappa'_1(T_{i1} - T)/T_{i1} dt = 0, \end{aligned} \tag{15}$$

$$\begin{aligned} \Delta S_2 &= \int_{t_0}^{t_0+t_2} \kappa_2(T - T_{h2})/T_{h2} dt \\ &\quad - \int_{t_1+t_0}^{\tau} \kappa'_2(T_{i2} - T_L)/T_{i2} dt = 0. \end{aligned}$$

The average power produced is $\bar{w} = (W_1 + W_2)/\tau$, where

$$\begin{aligned} W_1 &= \int_0^{t_1} \kappa_1(T_H - T_{h1}) dt \\ &\quad - \int_{t_1}^{\tau} \kappa'_1(T_{i1} - T) dt, \\ W_2 &= \int_{t_0}^{t_0+t_2} \kappa_2(T - T_{h2}) dt \\ &\quad - \int_{t_1+t_0}^{\tau} \kappa'_2(T_{i2} - T_L) dt. \end{aligned} \tag{16}$$

The optimization will be carried out by the method of optimal control¹² with $W = W_1 + W_2$ as the objective function

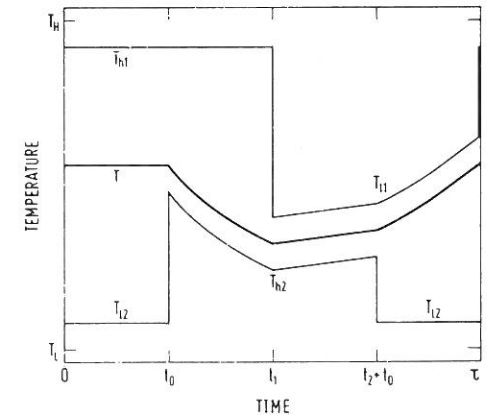


FIG. 3. Temperature sequence during one period for the system shown in Fig. 1 resulting from unconstrained optimization, i.e., corresponding to the last column of Fig. 1.

and Eqs. (13) and (14) as constraints, so that the Hamiltonian¹² of the problem H is defined by

$$\int_0^\tau H dt = W_1 + W_2 + \int_{t_0}^\tau \psi \kappa_1' (T_{11} - T) dt - \int_{t_0}^{t_2+t_0} \psi \kappa_2' (T - T_{h2}) dt - \lambda_1 \Delta S_1 - \lambda_2 \Delta S_2. \quad (16)$$

H is constant throughout the cycle. λ_1 and λ_2 are ordinary Lagrange multipliers corresponding to the integral constraints [Eq. (14)], whereas $\psi(t)$ is the adjoint variable associated with $T(t)$ via the differential constraint, Eq. (13). The connection between the two is the Hamiltonian equations

$$\dot{\psi} = -\frac{\partial H}{\partial T}, \quad (17)$$

$$\dot{T} = \frac{\partial H}{\partial \psi}.$$

The remaining optimality equations are

$$\frac{\partial H}{\partial T_{h1}} = \frac{\partial H}{\partial T_{11}} = \frac{\partial H}{\partial T_{h2}} = \frac{\partial H}{\partial T_{12}} = 0, \quad (18)$$

which must be solved for each of the four time segments. When joining those into a complete cycle we can further take advantage of the continuity of $T(t)$ and $\psi(t)$ across the switching points.

We will for simplicity set $\kappa_1 = \kappa_1' = \kappa_2 = \kappa_2' = 1$ and $C = 1$ in the following derivation and only quote the general results at the end.

IV. SINGLE-BRANCH OPTIMIZATIONS

A. Branch 1, $t \in [0, t_0]$

Neither engine is connected to T during this time segment, so the Hamiltonian is simply

$$H = (T_H - T_{h1})(1 - \lambda_1/T_{h1}) - (T_{12} - T_L)(1 - \lambda_2/T_{12}) \quad (19)$$

and

$$\dot{\psi} = -\frac{\partial H}{\partial T} = 0, \quad (20)$$

$$\frac{\partial H}{\partial T_{h1}} = -1 + \lambda_1(T_h/T_{h1}^2) = 0, \quad (21)$$

$$\frac{\partial H}{\partial T_{12}} = -1 + \lambda_2(T_L/T_{12}^2) = 0,$$

which makes

$$\psi(t) = \text{const} \equiv \psi_0, \quad (22)$$

$$\lambda_1 = T_{h1}^2/T_H, \quad (23a)$$

$$\lambda_2 = T_{12}^2/T_L. \quad (23b)$$

Thus T_{h1} and T_{12} are constant in this interval, and H becomes

$$H = (T_H - T_{h1})^2/T_H + (T_{12} - T_L)^2/T_L = T_H(1 - R_1)^2 + T_L\left(\frac{1}{r_2} - 1\right)^2, \quad (24)$$

where we have introduced the dimensionless ratios

$$R_1 = T_{h1}/T_H, \quad (25a)$$

$$r_2 = T_L/T_{12}.$$

Later we will need the corresponding ratios

$$R_2 = T_{h2}/T, \quad (25b)$$

$$r_1 = T/T_{11}.$$

These ratios may be time dependent, but they are all less than one. Since the intermediate reservoir is isolated during this segment its temperature is constant, $T(t) = T_0$.

B. Branch 2, $t \in [t_0, t_1]$

Only engine 2 is connected to T , so

$$H = (T_H - T_{h1})(1 - \lambda_1/T_{h1}) + (T - T_{h2})(1 - \lambda_2/T_{h2}) - \psi(T - T_{h2}), \quad (26)$$

$$\psi = -1 + \lambda_2/T_{h2} + \psi, \quad (27)$$

$$\frac{\partial H}{\partial T_{h1}} = 1 + \lambda_1 T_H/T_{h1}^2 = 0, \quad (28a)$$

$$\frac{\partial H}{\partial T_{h2}} = -1 + \lambda_2 T/T_{h2}^2 + \psi = 0. \quad (28b)$$

Eq. (28a) gives the same result for this branch as Eq. (23a),

$$\lambda_1 = T_{h1}^2/T_H = T_H R_1^2, \quad (29)$$

whereas Eq. (28b) can be solved for ψ ,

$$\psi = 1 - \lambda_2 T/T_{h2}, \quad (30)$$

which simplifies the Hamiltonian to

$$H = T_H(1 - R_1)^2 + T_L \frac{1}{r_2} \left(\frac{1}{R_2} - 1\right)^2. \quad (31)$$

Since this must have the same (constant) value as in the previous branch, Eq. (24), the ratio R_2 must also be constant and equal to

$$R_2 = (2 - r_2)^{-1}. \quad (32)$$

Now Eq. (13) can be solved for $T(t)$,

$$\dot{T} = -T + T_{h2} = -\nu T, \quad (33)$$

where

$$\nu = 1 - R_2, \quad (34)$$

to give

$$T(t) = T_0 e^{-\nu(t-t_0)} \quad (35)$$

and, through Eq. (30),

$$\psi(t) = 1 - (T_L/T_0)(1/r_2 R_2^2) e^{\nu(t-t_0)}. \quad (36)$$

C. Branch 3, $t \in [t_1, t_1 + t_0]$

Here both engines are connected to T , and arguments analogous to the ones we have just used yield

$$r_1 = \text{const}, \quad (37)$$

$$R_2 = \text{const}, \quad (38)$$

$$T_{h2}^2/T_{11}^2 = r_1^2 R_2^2 = \lambda_2/\lambda_1, \quad (39)$$

$$T(t) = T(t_1) e^{-\nu(t-t_1)},$$

$$\psi(t) = 1 - [T_H/T(t)] r_1^2 R_1^2 e^{\nu(t-t_1)} = [T_L/T(t)] r_2^{-2} R_2^{-2} e^{\nu(t-t_1)}, \quad (40)$$

where

$$\gamma = 2 - (1/r_1) - R_2. \quad (41)$$

Using our earlier definition of x in Eq. (2), Eq. (38) assumes the very symmetric form

$$x = r_1 R_1 r_2 R_2. \quad (42)$$

D. Branch 4, $t \in [t_2 + t_0, \tau]$

This branch is very similar to branch 2 with the roles of the engines interchanged. The solutions are

$$\lambda_2 = T_{12}^2/T_L = T_L/r_2^2, \quad (43)$$

$$r_1 = \text{const} = 2 - (1/R_1), \quad (44)$$

$$T(t) = T(t_2 + t_0) e^{-\mu(t-t_2-t_0)}, \quad (45)$$

$$\psi(t) = 1 - \frac{T_H}{T(t_2 + t_0)} r_1^2 R_1^2 e^{\mu(t-t_2-t_0)}, \quad (46)$$

with

$$\mu = 1 - (1/r_1). \quad (47)$$

V. CLOSING OF CYCLE

The solutions on the four time segments may now be joined into a complete cycle by invoking the continuity of $T(t)$ and $\psi(t)$ across the switching points. From this requirement we deduce that

(i) the integration constant T_0 of Eq. (35) is the same as the constant temperature T_0 in segment 1.

(ii) ψ_0 , Eq. (22) can be found from Eq. (36),

$$\psi_0 = \psi(t_0) = 1 - (T_L/T_0) r_2^{-2} R_2^{-2}. \quad (48)$$

(iii) $T_{h2}(t)$ is continuous at t_1 . This is not a trivial statement, since only the state functions $T(t)$ and $\psi(t)$ are required to be continuous, whereas the other functions in principle could contain jumps, caused by jumps in the control functions.

(iv) $T_{11}(t)$ is continuous at $t_2 + t_0$.

The constancy of H , λ_1 and λ_2 have already been used several times. It should be emphasized that the constancy of H ensures the continuity of T_{h1} at t_0 and of T_{12} at τ and thus makes all the ratios r_1 , R_1 , r_2 , R_2 constant in their respective intervals of applicability. Finally, the periodicity and continuity of $T(t)$ implies that

$$T(0+) = T(\tau-),$$

or

$$T_0 = T_0 e^{-\nu(t_1-t_0) - \gamma(t_2-t_0) + \mu(\tau-t_2-t_0) - \mu(\tau-t_2-t_0)} \quad (49)$$

and gives a relation between t_1 and t_2

$$\begin{aligned} \nu(t_1 - t_0) + \gamma(t_2 + t_0 - t_1) + \mu(\tau - t_2 - t_0) \\ = (1 - R_2)(t_1 - t_0) + [2 - (1/r_1) - R_2](t_2 + t_0 - t_1) \\ + [1 - (1/r_1)](\tau - t_2 - t_0) \\ = (1 - R_2)t_2 + [1 - (1/r_1)](\tau - t_1) = 0. \end{aligned} \quad (50)$$

Note that both T_0 and t_0 have dropped out of this equation.

Our four temperature ratios are connected through

Eqs. (32), (42), and (44), so all the expressions can be given in terms of one of them, say R_1 . Then

$$r_1 = 2 - 1/R_1, \quad (44)$$

$$r_2 = 2x/(x - 1 + 2R_1), \quad (51)$$

$$R_2 = \frac{1}{2}[1 + x/(2R_1 - 1)], \quad (52)$$

and

$$\nu = \frac{1}{2}[1 - x/(2R_1 - 1)], \quad (53)$$

$$\gamma = \frac{1}{2}[3 - (2R_1 + x)/(2R_1 - 1)], \quad (54)$$

$$\mu = 1 - R_1/(2R_1 - 1), \quad (55)$$

while the adjoint variable is related to the temperature T in all time segments as follows,

$$\psi(t) = 1 - (2R_1 - 1)^2 T_H/T(t). \quad (56)$$

A possible time variation for all temperatures involved is shown in Fig. 3, and a numerical example with T_H and T_L as specified in the Introduction is listed in the second column of Fig. 1.

At this point there are two equations left, Eqs. (14), which we use to determine t_1 and t_2 .

$$\Delta S_1 = t_1 \left(\frac{1}{R_1} - 1\right) - (\tau - t_1)(1 - r_1) = 0 \quad (57)$$

$$\Rightarrow t_1 = \frac{1}{2}\tau \quad (58)$$

and

$$\Delta S_2 = t_2 \left(\frac{1}{R_2} - 1\right) - (\tau - t_2)(1 - r_2) = 0 \quad (59)$$

$$\Rightarrow t_2 = \frac{1}{2}\tau. \quad (60)$$

Combining this with Eq. (50) we finally obtain the last piece in our puzzle,

$$R_1 = \frac{1}{4}(3 + x), \quad (61)$$

from which all the other quantities may be calculated.

The average power produced by this optimal composite engine is $w = W/\tau$, where

$$\begin{aligned} W = \frac{\tau}{2} T_H(1 - R_1) - \left(\frac{1}{r_1} - 1\right) \int_{\tau/2}^{\tau} T(t) dt + (1 - R_2) \\ \times \int_0^{\tau/2+t_0} T(t) dt - \frac{\tau}{2} T_L \left(\frac{1}{r_2} - 1\right) = \frac{\tau}{8} T_H(1 - x)^2, \end{aligned} \quad (62)$$

at efficiency

$$\eta = \frac{w}{q_1} = \frac{[T_H(1 - x)^2]}{[T_H(1 - x)]} = 1 - x, \quad (63)$$

which is exactly the CA efficiency (cf. the Introduction). This is a most remarkable result, especially when one notes that the final results are independent of T_0 and t_0 . This means that the relative phase of the two engines (t_0) as well as the intermediate temperature, T (as long as it is between T_{h1} and T_{12} , which are fixed) are immaterial. Even if one of the engines deviates from maximum power output, the other will exactly compensate for this (through a changed temperature range) to make the composite engine appear as a single CA engine. The staging of two CA engines, as described in Sec. II, is but one choice of the intermediate temperature T . It is worth repeating that the results presented above are for equal heat conductances, κ_1 , κ_1' , κ_2 , κ_2' , which greatly simpli-

fies the expressions and, e.g., makes $\gamma = 0$, i.e., all temperatures are constant in time segment 3 where both engines are connected to the intermediate reservoir.

The practical implications of this result are that

(1) There is no thermodynamic basis for choosing between a single-stage and a multi-stage machine with the same overall heat resistances, i.e., referring to Figs. 1 and 2,

$$\kappa^{-1} + \kappa'^{-1} = \kappa_1^{-1} + \kappa_1'^{-1} + \kappa_2^{-1} + \kappa_2'^{-1}, \quad (64)$$

for a fixed cycle time τ . Of course if one uses the maximum conductivity in all cases so all κ 's are equal, then the right-hand side of Eq. (64) is twice as large as the left-hand side and, consequently, w is half as large for the sequenced engines as for the single engine.

(2) There is no thermodynamic basis for choosing the phasing or the intermediate temperature in a two-stage system (within the limits mentioned above).

Both questions must be settled by engineering preferences or limits such as size of the machinery, materials strength, and complexity.

One possible additional constraint which could be added to this problem to make it more realistic concerns the volume swept by the two engines, e.g., the total volume or the sum of the compression ratios. So far the "internal" engines (triangles in Figs. 1 and 2) have only been assumed to be reversible and exchange heat isothermally, but if we want to consider the volume behavior, we must specify the precise type of cycle used and the equation of state of the working fluid. Only the Carnot, Stirling, and Ericsson cycles qualify as exchanging heat isothermally (cf. the pressure-volume (PV) and temperature-entropy (TS) diagrams in Ref. 7). Let us for simplicity choose an ideal gas in a Carnot engine. Then

$$\begin{aligned} Q_1 &= \kappa_1 t_1 (T_H - T_{h1}) \\ &= n_1 R T_{h1} [\ln(V_{11}/V_{h1}) - (\gamma - 1)^{-1} \ln(T_{h1}/T_{l1})], \end{aligned} \quad (65)$$

where n_1 is the number of moles of gas in the engine, V_{11}/V_{h1} is the compression ratio, and $\gamma = C_p/C_v$ the ratio of heat capacities. A similar equation holds for engine 2, and it makes no difference that the branch in contact with T is not truly isothermal, because the other isotherm is, and two branches are sufficient to completely define the endpoints of the cycle. Eq. (65) can easily be solved for n_1 to correspond to any desired temperatures and compression ratio, so any volume constraint carries with it the freedom of adjusting the amount of working fluid, and T_0 and t_0 are still indeterminate. The choice must again be made on engineering grounds.

VI. OTHER OBJECTIVE FUNCTIONS

The above analysis was carried out in order to maximize the power output of the engine (as was done in Ref. 1). Other objective functions, like efficiency, effectiveness, and entropy production, can be treated in a completely analogous way by adding extra constraints to the Hamiltonian, Eq. (16). For example, maximizing the efficiency $\eta = W/Q_1$ can be done by maximizing W subject to fixed $Q_1 = t_1 \kappa_1 (T_H - T_{h1}) = \text{const}$. Doing that, the efficiency becomes

$$\eta = 1 - x^2 / \left(1 - \frac{8Q_1}{T_H \tau} \right). \quad (66)$$

Its natural limits are

$$\eta \rightarrow 1 - x^2 = \eta_{\text{rev}} \quad \text{for } Q_1 \rightarrow 0 \quad \text{or } \tau \rightarrow \infty, \quad (67)$$

and

$$\eta \rightarrow -\infty \quad \text{for } Q_1 \rightarrow T_H \tau / 8, \quad (68)$$

so that the efficiency approaches the Carnot efficiency for very slow operation and decreases for increased heat input. For a single engine a similar optimization yields

$$\eta = 1 - x^2 / \left(1 - \frac{4Q_1}{T_H \tau} \right). \quad (69)$$

Thus the efficiency of the staged system is less than that for a single-stage engine operating between the same high- and low-temperature reservoirs with the same period and heat influx Q_1 . The difference is the factor of 8, rather than 4 for the single stage, multiplying Q_1 in Eq. (66). For our example with $T_L/T_H = 0.36$ and taking $4Q_1/T_H \tau = 0.1$, the maximum efficiency of the single engine is $\eta_{\text{max}} = 0.60$ while for the two-stage engine it is $\eta_{\text{max}} = 0.55$. If in this example one takes $T/T_H = 0.64$, the efficiency of the two stages is $\eta_1 = 0.29$ and $\eta_2 = 0.37$, and $1 - \eta_{\text{max}} = (1 - \eta_1)(1 - \eta_2)$ as required by Eq. (A4). Thus staging the engines while keeping the heat influx the same decreases the efficiency as would be expected from the increase in thermal resistance.

The effectiveness, $\epsilon = W/W_{\text{rev}}$, differs, in this case, from the efficiency only by a constant, since

$$W_{\text{rev}} = Q_1(1 - x^2), \quad (70)$$

and its optimal behavior is identical to the one just quoted for η .

It is easy to show that minimizing the entropy production per cycle for fixed Q_1 is the same as maximizing the effectiveness for fixed Q_1 . To see this we observe that the total entropy production per cycle is

$$\Delta S = \frac{Q_2}{T_L} - \frac{Q_1}{T_H}. \quad (71)$$

Since the actual work done per cycle is $W = Q_1 - Q_2$,

$$\Delta S = -\frac{W}{T_L} + \frac{Q_1}{T_L} \left(1 - \frac{T_L}{T_H} \right). \quad (72)$$

Using Eq. (70) and the definition of effectiveness, we then find

$$\begin{aligned} \Delta S &= (W_{\text{rev}} - W)/T_L \\ &= (1 - \epsilon)W_{\text{rev}}/T_L, \end{aligned} \quad (73)$$

where W_{rev} and T_L are constant, so that minimum ΔS corresponds to maximum ϵ .

VII. CONCLUSIONS

Using a model for a two-stage thermal engine, we have determined the configuration which produces the most power. We have found that the interface between the two stages (temperature and timing) is, within limits, arbitrary and can be used to satisfy other, nonthermodynamic constraints. The building block in finite-time thermodynamics is the CA en-

gine, which in many respects behaves similarly to the Carnot engine of reversible thermodynamics. Thus CA engines can be staged to form an overall CA engine, and the unconstrained staging optimization also yields CA behavior. This is the first attempt to look at composite systems in finite-time thermodynamics and should facilitate its application to more complex systems based on the models solved so far.

ACKNOWLEDGMENTS

We would like to thank the Aspen Center for Physics for providing the excellent surroundings which brought us together and stimulated us during this work. B.A. also wants to thank NATO for a travel grant.

APPENDIX

In this appendix, we provide a derivation of the result of Sec. II in a simple way that illustrates the importance of the heat output and input of successive engines being equal and of the form of $1 - \eta$.

Consider a sequence of N engines. The efficiency of the j^{th} engine is

$$\eta_j = 1 - Q'_j/Q_j, \quad (A1)$$

where Q_j is the heat input per cycle, and Q'_j is the heat output per cycle. Now suppose

$$Q'_j = Q_{j+1} \quad \text{for } j = 1, 2, \dots, N-1. \quad (A2)$$

Then

$$(1 - \eta_1) \dots (1 - \eta_N) = Q'_N/Q_1. \quad (A3)$$

But the efficiency of the entire engine is just given by

$$\eta = 1 - Q'_N/Q_1, \quad \text{so} \quad (A4)$$

$$1 - \eta = (1 - \eta_1) \dots (1 - \eta_N).$$

Next suppose that, if we optimize the operation of a single engine for some choice of objective function such as maximum average power output, that

$$1 - \eta = f(T_L)/f(T_H), \quad (A5)$$

where T_H is the temperature of the high-temperature reservoir and T_L is the temperature of the low-temperature reservoir. Suppose we select a series of reservoir temperatures

$$T_H = T_1 > T_2 > \dots > T_{N+1} = T_L, \quad (A6)$$

and operate each sequenced engine in its optimal mode so that

$$1 - \eta_j = f(T_{j+1})/f(T_j), \quad (A7)$$

then Eq. (A4) implies that

$$1 - \eta = f(T_{N+1})/f(T_1) = f(T_L)/f(T_H), \quad (A8)$$

That is, the efficiency of the sequenced engines equals that of a single engine. This is the case for Carnot engines where $f(T) = AT$ and CA engines, where $f(T) = B\sqrt{T}$. It does not follow that the work done per cycle is the same for the sequenced engines as for the single engine.

If η is not itself an extremum, then the individual engines in the sequenced case need not be operated optimally in order for the overall efficiency to be equal to $1 - f(T_L)/f(T_H)$. This occurs if the average power is maximized.⁵ Thus there is some freedom in selecting the operation of the individual engines. If the objective function is the efficiency itself, then it is clear from Eq. (A4) that each engine must be operated at maximum efficiency; however, even in this case the intermediate reservoir temperatures may be selected arbitrarily provided they remain ordered according to Eq. (A6).

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8.10. Thermodynamic constraints in economic analysis

Chapter 20 of *Self-organization and dissipative structures: Applications in the physical and social sciences*, edited by W. C. Schieve and P. M. Allen (University of Texas Press, Austin, Texas, 1982), p.323

20. Thermodynamic Constraints in Economic Analysis

R. Stephen Berry and Bjarne Andresen

INTRODUCTION

The incorporation of thermodynamics into economic analysis has been a tantalizing but elusive objective to scientists and economists. On one hand scientists have seen thermodynamics as a source not only of boundary constraints for processes, but also of criteria of merit, a notion that has sometimes captivated its proponents so deeply that it has led them to advance energy theories of value. On the other hand, economists have seen in the mathematical structure of thermodynamics the basis for a powerful analogic representation of equilibrium, and Nicholas Georgescu-Roegen, a participant in this conference, has been working for several years toward incorporating the physical content of the second law of thermodynamics into economic thinking.

This paper reviews work (largely but not entirely of the group at Chicago) by scientists and economists establishing some of the connections between the physical content of thermodynamics (and its extensions) and the analysis of economic behavior. First, we examine the role of thermodynamic bounds in some simple economic analyses, particularly of production and consumption. This examination will give us some insights into energy theories of value and the difference between their implications for choice and those of conventional economics. Next we examine the constraints themselves. The traditional bounds set by Carnot cycles are not always meaningful because the constraints associated with operating processes at finite rates often impose bounds to work or heat that are far lower than those of reversible processes. Moreover, the physical function one wants to optimize is not necessarily a conventional thermodynamic quantity, such as efficiency or effectiveness; it may be the power produced, for example. Hence we shall examine how finite time constraints can be introduced into thermodynamics. Finally,

we shall see how the introduction of thermodynamic considerations affects economic decisions, in a few particular cases.

THERMODYNAMIC CONSTRAINTS IN THE ECONOMIC ANALYSIS OF PRODUCTION

For the scientists, this section begins with a brief introduction to some simple, standard economists' ideas; for the nonscientists, a bit of explanation of thermodynamic ideas is then given. To both groups, we beg patience for belaboring the obvious.

For clarity, this argument is presented largely in terms of an idealized producer who uses two input factors, call them E and L , to make a product Q . The extension of the argument to systems of more than two input factors or to more than one product is straightforward. For simplicity, we assume capital is fixed; its discounted present value could be included as a third input factor if investment in new capital were of concern. Suppose that E and L are substitutable for each other, at least over a limited range. Suppose also that the amount of output Q is given by a function called the production function

$$Q = Q(E, L) . \quad (1)$$

We can therefore represent Q in a space with axes defined by E and L , as in fig. 20.1. As is common in most economic analyses, we assume that Q is convex toward the axes of E and L wherever it represents a real process. (This assumption can be modified to allow for wiggles in Q but such elaboration adds little to the argument.) The general form of Q is that of the curves Q_1 and Q_2 of fig. 20.1. Each of these is a curve of constant quantity of output and is called an *isoquant*. Note that Q_1 is less than Q_2 and that every point in the quadrant shown lies on one isoquant.

We assume that the prices of E and L are independent of the amount purchased of each. Then for any total expenditure, the purchasable amounts of E and L lie on a straight line of the form

$$L = -pE + L_{\max} , \quad (2)$$

where p , the negative of the slope of the line, is the price of E , relative to the price of L :

$$p = -(dL/dE) = (dm/dE)/(dm/dL) , \quad (3)$$

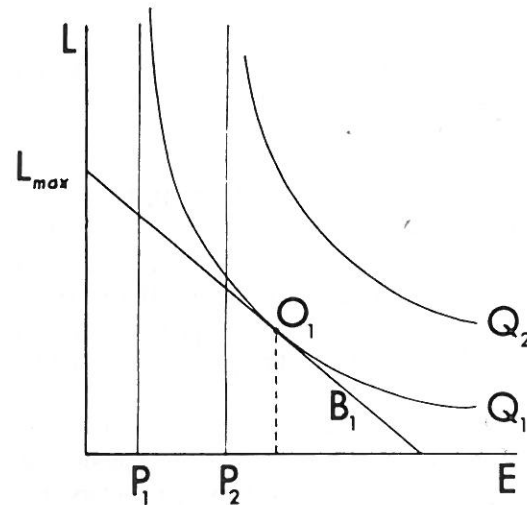


Fig. 20.1. Production isoquants Q_1 and Q_2 ($Q_1 < Q_2$) with two substitutable input factors L and E . The asymptotes of E for Q_1 and Q_2 are P_1 and P_2 . Given the budget line B_1 , the optimum operating point is O_1 .

where dm/dE and dm/dL are the unit prices of E and L in terms of a common (presumably monetary) numeraire. The lines of constant total expenditure are called *budget lines*; in fig. 20.1, B_1 is such a line.

It is a well-known elementary theorem of the economics of production that, if our assumed conditions hold, the maximum production is achieved for a given budget, or a given level of production is achieved at a minimum budget, if the producer operates at that point where his budget line is tangent to his product isoquant. If B_1 is the budget line, then the optimum operating point is O_1 on isoquant Q_1 .

All other points on B_1 are on isoquants corresponding to lower amounts of product than Q_1 . Similarly, if Q_1 is the desired isoquant (and the price of E relative to that of L fixes the slopes of all the budget lines to be equal to that shown for B_1) then O_1 is again the optimal operating point because B_1 is the budget line of lowest total expenditure that can be reached on Q_1 . This completes the required course in elementary economics.

To bring thermodynamics into the argument, we suppose that the input factor E is a fuel or other good that has associated with its use a set of thermodynamic quantities, such as a heat of combustion, a change of internal and free energy, a loss of availability, and so forth. (*Availability* is the maximum work that can be obtained from a system when it comes from a state tem-

porarily constrained out of equilibrium with its surroundings to a state in equilibrium with its surroundings.) We also suppose that L is a good, such as labor, used for control purposes, whose thermodynamic changes are zero or negligibly small in the process that makes Q . We could attribute changes of thermodynamic quantities to L as well as to E , but this would complicate the discussion unnecessarily.

Since the energy requirement is proportional to the amount of product, each isoquant has its own asymptote parallel to the L -axis, but, for fuel-consuming or endothermic processes, displaced to the right of that axis. The most thermodynamically effective systems imaginable, with no consideration of cost, equipment, or controls, are those that operate at their asymptotes. If these asymptotes are determined in the conventional manner for the thermodynamic systems, they correspond to the unattainable limits of infinitely slow reversible processes. Hence it is useful to think in terms of operating points near, rather than at the asymptotic limits. The distance along the E -axis from the operating point to the asymptote is the thermodynamic "surcharge." More strictly, the ratio of the distances along the E -axis, P_1/E_1 , of fig. 20.1 is the thermodynamic effectiveness of the process, the minimum work required to produce Q_1 divided by the actual work used to manufacture the same amount of product.

A theorem and a corollary relate the economic optimality of our production system to its thermodynamic effectiveness (or efficiency, if one rescales the E axis appropriately).¹ First, suppose one asks for the necessary and sufficient conditions that an economically efficient production system operates "close" to its asymptote. More precisely, what are the conditions that its effectiveness be $(1 + \epsilon)^{-1}$, or that the consumption of E be $(1 + \epsilon)P$? The necessary and sufficient condition is that the budget line has a slope dL/dE that falls at least as steeply as the slope of the isoquant at the point $E = (1 + \epsilon)P$. In other words, the thermodynamic factor E must be expensive enough to justify operating at or to the left of the point $[(1 + \epsilon)P, L_0]$, as shown in fig. 20.2. This constitutes the theorem.

The corollary is an extension of the theorem and requires that we know the production function $Q(E, L)$. The theorem requires only that we know the slope of Q near $(1 + \epsilon)P$ and that Q be convex toward the axis. The corollary states that knowing the function $Q(E, L)$ and the budget line we can predict the economically optimal thermodynamic effectiveness of the system; it is precisely P/E_0 , where P is the asymptote of E and E_0 is the consumption of E at the economically optimal operating point. This is illustrated in figure 20.2, for the special case where $E_0 = (1 + \epsilon)P$.

This analysis exposes very clearly how the consequences of energy theories of value differ from those of traditional economic optimization. One sometimes encounters these descendants of the labor theory of value among

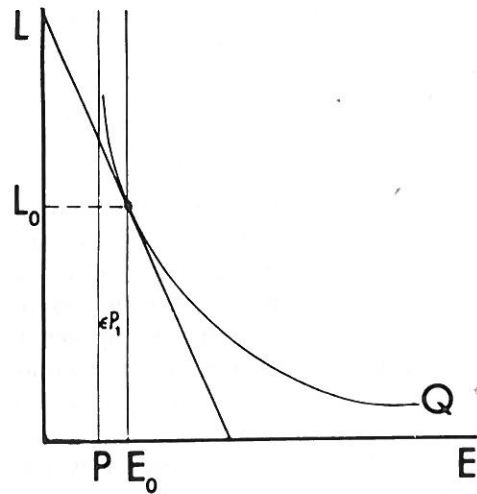


Fig. 20.2. A production system like that in fig. 20.1, with the optimal operating point at $E = E_o = (1 + \epsilon)P$, i.e., "within ϵ " of its asymptote on the E -axis.

the more zealous expressions of concerned analysis of energy use.^{2,3,4} One form of an energy theory of value would have us set a value to ϵ and ask, given a budget line and a family of isoquants, for example, B , Q_1 , and Q_2 of fig. 20.3, what is the highest isoquant that can be reached on B having a thermodynamic effectiveness greater than or equal to $(1 + \epsilon)^{-1}$? The answer is Q_1 , as shown in fig. 20.3, with the operating point α marked as a square. The economic optimum lies at β , on the isoquant Q_2 . The difference $Q_2 - Q_1$ is the penalty in output paid to satisfy the condition on the thermodynamic effectiveness.

Simple as these theorems are, they offer some possible applications. In general one knows one's budget line and can determine the thermodynamic effectiveness from engineering data at hand. From these, one can predict the slope of the production function at the economically optimal operating point. Hence if one believes one knows the production function, one can evaluate its slope at the operating point, which is just the substitutability, $(\partial L / \partial E)_Q$, and determine immediately whether the assumption of economic optimality is being met. If the production function has a steeper negative slope than the budget line, then one is operating at such a point as α of fig. 20.3 and is operating at too high a thermodynamic effectiveness; if the budget line is declining faster, as at the intersection of Q_1 and B , then one can raise the output by increasing thermodynamic efficiency.

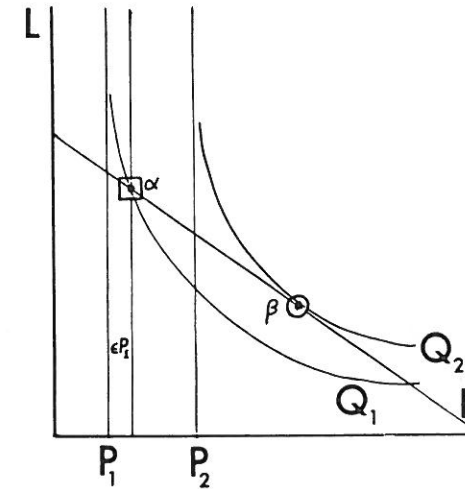


Fig. 20.3. Production isoquants and a budget line to illustrate how one form of energy theory of value differs from conventional economic optimization. The economist chooses point β for his operation; the advocate of the energy theory of value chooses point α , producing Q_1 , less than the economist's Q_2 , at the same expenditure.

The test just proposed is predicated on a knowledge of the production function, which may be asking for more than one has. Let us push the argument back a step to examine how we infer the form of the production function.⁵ Typically, one knows a few operating points yielding the same output, such as the three shown in fig. 20.4. One obtains the form of the isoquants by fitting those points to an assumed analytic form having the desired convexity property. If one neglects the constraint that $E \geq P$, then conventionally adopted functions such as the CES (constant elasticity of substitution) would yield an isoquant Q' ; with the thermodynamic constraint, one fits the points to the curve Q . It is quite apparent that Q falls more steeply than Q' in the region shown. (What happens at larger E depends on the form chosen for Q and Q' .) This fact implies that estimates of the optimum operating point at E prices higher than those yielding points α , β and γ will be further to the left if one uses the family of curves of the form Q' than if one uses curves of the form Q . In other words, if the production system is operating in a region near enough to the thermodynamic limit to make the function Q' flatter than the function Q , the producer will underestimate the economically efficient amount of E (read energy or fuel for E , of course) if he neglects the effects of the natural thermodynamic limit. The reason underlying this apparent para-

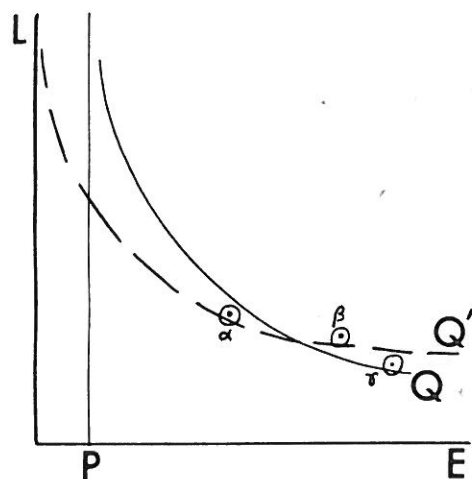


Fig. 20.4. Illustration of the fitting of "observed" points α , β , γ to formal representations of production functions without consideration of thermodynamic limits (Q') and with these limits (Q).

dox is that the substitutability of L by E , $-(\partial L/\partial E)_Q$, is greater with Q than is implied by Q' and that, if the productivity of L is constant, the real productivity, $(\partial Q/\partial E)_L$, of E is less than is implied by the family of curves with the shape of Q' .

THE NATURE OF THERMODYNAMIC CONSTRAINTS

We have seen how the existence of a thermodynamic limit affects the behavior of a production system and the producer who uses an economic analysis to optimize his operating point. How does one locate the asymptote?

The natural starting point is to choose the traditional thermodynamic limit. This is certainly a lower bound, but it is not necessarily the most useful lower bound. If one underestimates the value of the asymptote P , then one is liable to make the same errors, admittedly to a lesser degree, that one makes by forgetting that P is not zero. Because we carry out production processes at finite rates, we can be quite sure that $P(r)$, the lower bound on E to produce Q at a rate $r = \dot{Q}$, is greater than $P(0)$, the bound on E for a reversible process. The relevant questions at this point are "How do we find $P(r)$? What is the difference between $P(0)$ and $P(r)$ and when is that difference significant?"

How does $P(r)$ depend on r ?" Then we can go on to ask what path the process must take to yield or approach $P(r)$.

These questions bring us directly to a substantive problem of thermodynamics. A meaningful bound $P(r)$ must be the equivalent of a thermodynamic potential, in the sense that if the constraints are specified defining the range of allowable processes, then $P(r)$ is the extremal value of the work (maximum if it is work extracted to a work reservoir, minimum if it is work done on the system) in the allowable space, and within that space, $P(r)$ must depend only on the initial and final points and of course on the rate r . The one complication beyond the conventional definition of a thermodynamic potential is the inclusion of a constraint on the rate or time for the process. It was shown⁶ that such functions $P(r)$ exist and that they can be constructed by a fairly simple transformation, a natural generalization of a Legendre transformation⁷; strictly, one generates integrals of motion in the sense of Cartan.⁸ Naturally if one introduces time constraints in addition to the traditional constraints on temperature, pressure, entropy, and so on, the parameters of the thermodynamic system—its heat capacities and the other relevant equilibrium parameters—must be augmented by parameters giving its relevant time responses (heat conductance, frictional coefficient, chemical rate constraints, and so forth). To get more physics out, we must put more physics in. It has been possible, in the cases studied until now, to choose a time scale so that only one or, at most, two or three relaxation processes are relevant. For example heat conduction between the system and its reservoirs may be the one significant rate process, whenever internal relaxation processes of the working fluid are rapid enough to establish internal thermal equilibrium in the fluid. If technological and time constraints do not fully determine the potential $P(r)$, one may include others, for example the constraint of fixed budget. The difference between two points of a potential function chosen this way will be the energy required to carry out the process at the specified (average) rate, r , at the lowest possible cost.

To illustrate the significance of letting the process proceed at nonvanishing rates, let us look at the performance of an idealized auto engine operating between a high combustion temperature and the ambient temperature. This example becomes a rich nonlinear system when it is transformed into an extremal problem for operating an engine at a finite rate. Suppose we attribute three loss processes to the engine: friction, a finite heat conductance between reservoirs and system, and a heat leak into the low-temperature reservoir. Suppose the friction is taken to be linear in velocity or quadratic in the power (corresponding to a thick lubricant layer), and heat transfer between system and reservoirs follows Newton's law: the rate of heat flow is directly proportional to the temperature difference. Then the power, w , continuous or average, delivered by such an engine, is expressible in terms of the reservoir tem-

peratures T_H and T_L , the rate of heat flow $-q$ from the hot reservoir, the heat resistance $\rho/2$, the friction coefficient α , and the rate of heat leak q_0 :

$$w = -\alpha \left(\frac{T_H - T_L - q\rho}{T_H - q\rho} \right)^2 - \left(\frac{T_H - T_L}{T_H} \right) q + \frac{T_L}{T_H} \left(\frac{\rho^2}{T_H - q\rho} \right) - q_0. \quad (4)$$

Let us choose to make power an extremum. We obtain a quartic equation whose four solutions are most naturally expressed in terms of the temperature difference

$$\Delta T \equiv q\rho \quad (5)$$

and a ratio of heat resistance to friction

$$\nu = \rho/2\alpha, \quad (6)$$

as

$$\Delta T = T_H \pm \sqrt{T_H T_L} \quad (7)$$

and

$$\frac{1}{2} \left[-\nu + T_H - T_L \mp \sqrt{(\nu + T_H + T_L)^2 - 4T_H T_L} \right]. \quad (8)$$

The general form of the solution can be shown conveniently in a contour diagram of ρw , essentially the power on a plane with axes ΔT that we can interpret as a scaled axis for q , and ν , that we can interpret as the inverse of friction. Such a contour diagram is shown in fig. 20.5. The figure is drawn for $T_H/T_L = 9$. The light lines are contours of equal power for fixed ρ . The heavy solid lines give the maximal power solutions; the heavy dotted lines give minima. "Solutions" for $\Delta T > 9$ correspond to physically inadmissible regions, because they would violate the Second Law. Solutions with $\Delta T < 0$ correspond to the engine acting as a heat pump. Note that in the admissible heat engine region, there are two regimes. Over most of this region shown, to the left of $\nu \sim -4$, there is only a single maximum to ρw ; this is the region in which the power is limited by the rate of heat transfer. To the right, there are two (equal) maxima and one minimum of ρw , corresponding to each value of

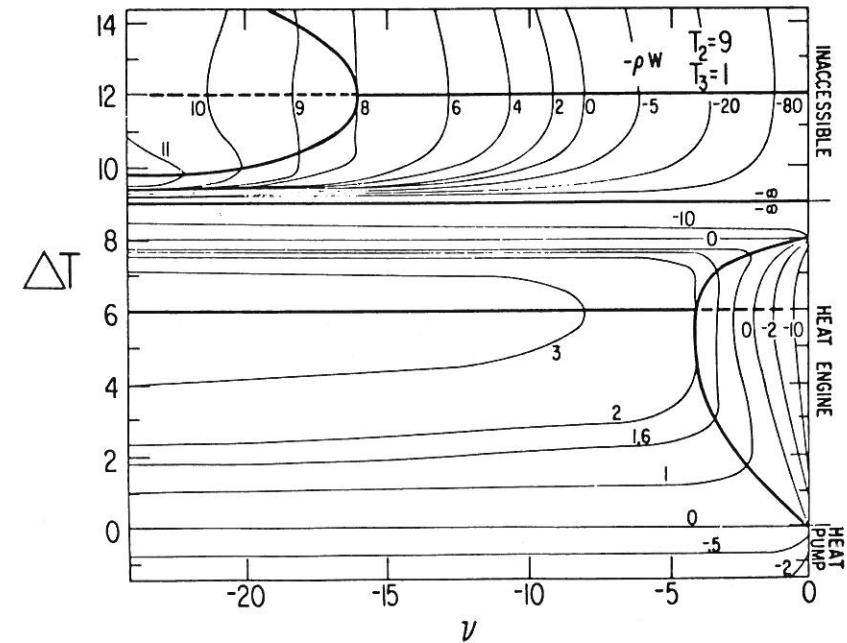


Fig. 20.5. Contours of power production for a two-reservoir heat engine with finite heat conductance to its reservoirs and friction. Heavy solid lines are maxima of power; heavy dotted lines are minima. The ordinate ΔT is ρq , and the abscissa ν is $\rho/2\alpha$, essentially the inverse of the friction, as explained in the text.

ν , but to different values of ΔT or q . The system exhibits a bifurcation point at $(\Delta T = 6, \nu \sim -4)$; as friction increases, the system enters sharply into the friction-dominated region. In this region the maxima of ρw correspond to two quite different rates of heat input and, therefore, to two quite different efficiencies.

We can translate this model into real-world numbers using values appropriate for an automobile engine.⁹ Suppose that the combustion temperature $T_H = 2700$ K and the ambient $T_L = 300$ K; we take realistic values for $\rho = -1$ K/kW and $\alpha = 4.167 \times 10^{-4}$ kW⁻¹, which correspond to $q = 1800$ kW and $w = 600$ kW at the bifurcation point that separates the regions dominated by friction and by heat resistance. The efficiency of this system at the bifurcation point is only 33 percent, compared with a Carnot efficiency (i.e., reversible operation) for these two reservoirs of 89 percent. If the engine is improved so that the friction coefficient is halved, then w goes up to 1,200 kW with the same heat consumption as before, to give an efficiency of 67 percent;

if on the other hand α is doubled, then a power output of only 300 kW is obtained with $q = 706$ kW or 2,294 kW, corresponding to efficiencies of 42 percent and 13 percent. In short, the penalty in the thermodynamic efficiency for operating the engine at a finite rate so as to maximize power is, for the most favorable case described here, 89 percent minus 67 percent or 22 percent. If one maximizes efficiency rather than power, one achieves a different set of optimal operating conditions. These conditions follow approximately the same qualitative behavior as those that maximize the power.

Another illustration of rate dependence is the operation of a heat engine between two thermal reservoirs with finite heat conductance to each of them. The maximum power is extracted from this system at an intermediate rate of operation where the increase in power with rate is balanced against the increased temperature drops across the thermal resistances. The efficiency at this point is $1 - \sqrt{T_{\text{high}}/T_{\text{low}}}$ as opposed to the traditional Carnot efficiency $1 - T_{\text{high}}/T_{\text{low}}$. Note that this result is independent of the thermal resistance, which is not true for the power produced.

So far we have concentrated on the optimization of power produced for the heat cycles, but that is but one of an infinite number of possible objective functions. Other desires might be to maximize the efficiency or minimize the entropy production. Even more likely, the goal might be nontechnical, in particular the minimizing of unit cost or total cost of operation or a weighted combination of all these possibilities. The choice is completely open and will generally lead to different optimal behavior for different objective functions.¹⁰ An example is given in fig. 20.6 where we again consider a heat engine with thermal resistances to its reservoirs. The figure shows the optimal allocation of time between the hot (τ_1) and cold (τ_2) isothermal branches of the cycle when (a) the total entropy production is minimized, (b) the efficiency is a maximum, and (c) the power produced is maximized. The constraint of fixed cycle time $\tau_1 + \tau_2$ forces the operating point to lie on the diagonal indicated. Positive work is only produced for times above the hyperbola. Clearly, the different objective functions require different operating conditions (allocation of time), and, under conditions of very short time, it may even be possible to optimize one function but not another.

The preceding thermodynamic analysis has produced limits on various quantities of choice for the process considered, either directly or as the difference between values of a potential function in the initial and final states. However, no indication is given of how this optimal performance is achieved. Finding the time path of that process is an entirely different, and much more difficult, project usually solved by optimal control theory. Although that information is essential for the actual operation of the process, we only need the limiting values of energy consumption and similar values for the economic analysis and will bypass further discussion of the optimal path.

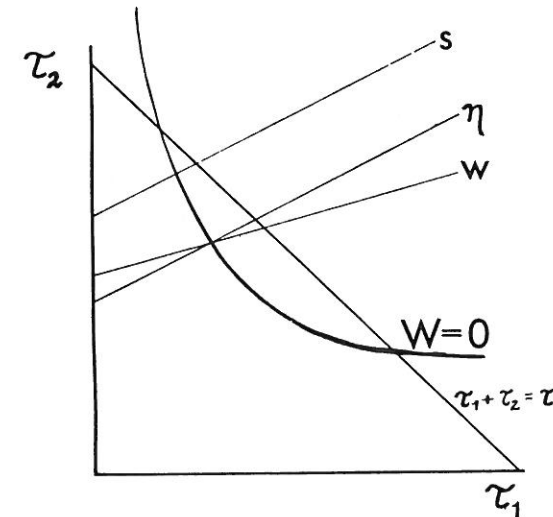


Fig. 20.6. General form of the extremals for a Carnot-like heat engine with finite heat conductance that may spend time τ_1 in contact with T_H and τ_2 in contact with T_L . The parallel lines marked s and η correspond to minimal entropy production and maximum efficiency; the line marked w corresponds to maximum power. The hyperbola divides the region of positive work (above) from a region in which the work would be negative. Any engine with a fixed period lies on a line $\tau_1 + \tau_2 = \tau$, a constant.

In this section we have looked at the thermodynamic behavior of processes proceeding at nonvanishing rate and found the energy requirements to depend strongly on the time period allocated for the process. In the terms of the previous section, the proper asymptote to use in the economic analysis of a technology is often a sensitive function of the rate at which we want the product delivered.

APPLICATION OF CONSTRAINTS

The thermodynamic constraints for finite time operation described in the previous section can be used in the economic analysis in two different ways:

1. One can calculate the total cost C of producing the quantity Q of product in a given time, consisting of the capital cost for a plant of a certain size plus the operating cost for optimal operation at a rate r necessary to produce Q . Obviously, there is a tradeoff between a larger plant operating at a lower rate (and therefore usually at a higher efficiency) and the capital cost of that

plant, so one can find the economic optimum by either minimizing C for fixed Q or maximizing Q for fixed C .

2. One can add information about the operating and capital costs as functions of rate to the definition of the extremal equations and solve them with constrained product quality Q .

Both procedures will arrive at the same optimum, so it is a matter of taste whether one prefers the black-box approach of 2 or is interested in the intermediate physical information of 1.

This problem can be made more precise and realistic by taking into account discounting, changing productivity of capital and the dependence of productivities on the rate of production. Here, we merely give a formal statement of the problem, not a solution. Let the objective function π be the net profit, the difference between revenue R and cost C . The discount rate is r ; $P_Q(t)$ is the unit price of product Q at time t ; \dot{Q} and \dot{C} are the time rates of change of physical output Q and cost C . Thus

$$\begin{aligned} \Pi &= R - C \\ &= \int_0^T \dot{Q}(t) p_Q(t) e^{-rt} dt - \int_0^T \dot{C}(t) e^{-rt} dt \end{aligned}$$

where the total cost per unit time is the sum of the input costs

$$\dot{C} = \sum_j I_j(t) p_j(t).$$

For example we may take a three-input production system with capital K , materials M , and energy E . Let us suppose that the cost of capital bought at time t is fully paid at that time; the forward costs are included in the cost. Then

$$C(\tau) = \int_0^{\tau} \left[\dot{K}(t) p_K(t) + \dot{M}(t) p_M(t) + \dot{E}(t) p_E(t) \right] e^{-rt} dt,$$

although one might choose to use different exogenous discount rates for the different input factors in special cases.

The output rate $\dot{Q}(t)$ is a function of the amount of capital $K(t)$ and of its distribution of vintage and productivity. We denote $\phi(t'-t'')$ the output rate at t' per unit of capital purchased at t'' . Thus

$$\dot{Q}(t') = \int_0^{t'} \dot{K}(t'') \phi(t'-t'') dt''.$$

Our finite-time thermodynamics enters in the physical basis of the function $\phi(t'-t'')$. To be as precise as possible, we designate ϕ as a *rate-of-production function*, a relation between rate of production and rate of use of

input factors (and possibly of amounts of inputs as well in some cases) to distinguish it from a relation between amounts of output and amounts of input factors. Note that ϕ is presumed here to relate physical variables. Then for our three-factor system, we require that $\phi(t'-t'')$ be a function of $\dot{E}(t')$, of $\dot{M}(t')$ and of a set of parameters $\lambda_i(t'-t'')$ that characterize the rate-of-production function. Strictly, then ϕ is a functional, rather than a simple function.

The problem is then one of finding the maximum of π , the objective function, by suitable adjustment of the control functions \dot{K} , \dot{M} and \dot{E} . We may suppose $\dot{Q}(t)$ is given exogenously; the functional $\phi[\dot{M}, \dot{E}; \lambda_i(t'-t'')]$ connects \dot{M} and \dot{E} and, thus, can be treated as a constraint. The usual constraints on positivity of \dot{M} and \dot{E} apply. At this point, one can begin making approximations and introduce empirical or theoretical ϕ s and reduce the problem to a simple enough form to be soluble.

As an example, one might use for one's ϕ a function like that of a Carnot-like heat engine operating between two reservoirs at temperatures T_H and T_L , at a finite rate τ^{-1} per cycle but with finite, nonzero heat conductance κ connecting the engine to its reservoirs and with minimum loss of availability.¹⁰ The heat conductance can be interpreted as K . Such an engine has an extremum of useful power—a maximum of power if it produces work or a minimum of power required if it acts as a consumer of work—equal to

$$\dot{W} = W_{\text{reversible}} - T_L \left(\sum_{\text{branches } i} |\sigma_i| \right)^2 / \kappa \tau.$$

Here $|\sigma_i|$ is the absolute value of the entropy carried in branch i of the process and is characteristic of the particular machine. The amount of materials and fuel or energy consumed of course enter in the σ s. In the simplest case, we neglect M altogether and \dot{E} is simply the fuel consumed per cycle, expressed in units of heat per cycle, which is, in turn, $T_H \sigma_1$, where σ_1 is the entropy transported in the hot isothermal branch of the cycle. The reversible work in this system is the Carnot work $[1 - (T_L/T_H)] T_H \sigma_1$. Entropy is only transported in two branches of the Carnot-like cycle and the amounts in the two branches are the same, so

$$\begin{aligned} \dot{W} &= \left[1 - (T_L/T_H) \right] T_H \sigma_1 - T_L (2\sigma_1)^2 / \kappa \tau \\ &= \left[1 - (T_L/T_H) \right] \dot{E} - [4T_L/T_H^2 \kappa \tau] \dot{E}^2. \end{aligned}$$

If the output Q is taken to be power, then this expression is precisely a physical rate-of-production function connecting the physical inputs of rate of fuel consumption \dot{E} and capital K , in the form of heat conductance, with the salable output \dot{W} .

Formal application of an economic constraint to the problem of finding a thermodynamic extremum leads to a simple corollary to a general and elementary theorem of economics.¹¹ Suppose we want to find the extremum of the change of a generalized potential ΔP , with P a function of the parameters X_1, \dots, X_n , which may include rate or time per unit as well as the usual parameters of a thermodynamic system. Additionally, suppose one constraint is a fixed budget, $C(X_1, \dots, X_n) = \text{constant}$. Then the fundamental variational equation is

$$d(\Delta P) - \lambda dC = 0, \quad (9)$$

or, for each parameter X_i ,

$$\frac{\partial \Delta P}{\partial X_i} = \lambda \frac{\partial C}{\partial X_i}. \quad (10)$$

This equality in turn implies that the constant λ satisfies

$$\lambda = dC/d\Delta P = \frac{\partial C/\partial X_i}{\partial \Delta P/\partial X_i} \text{ for all } i, \quad (11)$$

that is that the ratio of marginal cost of each factor to its marginal thermodynamic (work) productivity is a constant, the same for all factors, and equal to the marginal cost of optimally produced work.

Finally, we can look toward using thermodynamic optima, especially those based on finite time constraints, as guides for the allocation of research and development effort. Even without carrying out optimal control analyses of the paths that would yield the extremal values of work, we can determine the minimum fuel requirements of processes, per unit of product, or the maximum work delivered per unit of fuel for engines for operations at nonzero rates and compare them with the fuel per unit output of actual operations. The analyses tell us immediately whether the operating rates are optimal and, as in the example of the engine given in the previous section, which physical parameters should be changed to bring the system to a more nearly optimal condition. At a more fundamental level, we can see from the comparison of real and ideal requirements of fuel per unit output which processes have the potential for large improvements and which are already operating so near their ther-

modynamic limits that new technology based on the same ideal model can only yield a very small increment of fuel saving, for example. The generation of electricity from steam is in the latter category; modern generating systems operate so near to their Carnot efficiencies that we cannot possibly achieve large reductions in fuel use (so long as we use available materials) by technological improvement. Such processes as the manufacture of ammonia operate at thermodynamic levels only about one-third as efficient as their ideal reversible limits. We may be able to make technological changes to reduce the apparent inefficiencies of these systems. Their minimum energy requirements, however, are not yet known when they are constrained to produce products at their present rates. We do not really know yet how much we could hypothetically improve the technology of manufacturing ammonia, if we constrain the process to produce at the rate it now does. Finding the answers to such questions will be a next step toward using thermodynamics to guide practical policy choices.

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8.11. Availability for finite-time processes: General theory and a model

J. Phys. Chem. **87**, 2704 (1983)

Availability for Finite-Time Processes. General Theory and a Model

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(Received: December 20, 1982; In Final Form: March 2, 1983)

The concept of availability as an upper bound to the work that can be extracted from a given system in connection with specified surroundings is extended to processes constrained to operate at nonzero rates or in finite times. Such analyses are facilitated by the introduction of generic models which describe a whole range of systems in such a way that the optimal performance of the generic model is an upper bound to the performance of the real systems. The effects of the time constraint are explored in general and in more detail for a generic model in which extraction of work competes with internal relaxation. Extensions to nonmechanical systems are indicated. We hereby wish to establish the finite-time availability as a standard of performance more useful than the traditional availability based on reversible processes.

I. Introduction

One of the classic problems of thermodynamics has been the determination of the maximum work that might be extracted when a prepared system is allowed to undergo a transformation from its initial state to a designated final state. When that final state is defined by the condition of equilibrium between the system and some environment, the maximum extractable work is generally known now as the availability A (other names are exergy and essergy). This is a convenient shortening of "available work", the original name for this quantity when it was first introduced by Gibbs.¹ Availability, unlike the usual thermodynamic potentials, provides a general expression for the maximum extractable work, an expression that does not depend on the nature of the constraints on the process, so long as the limit of the process is reversible. This general expression, first given by Gibbs, remains the basis of "second-law analyses" of performance, whose criterion is the ratio of the actual work performed to the change of availability of the system when it undergoes its transformation from

initial to final state.² This ratio is called the "effectiveness" or the "second-law efficiency".

The formal solution to the more general problem of finding the work for an arbitrary transformation of a system was given as an equality; in the form derived by Tolman and Fine³

$$W = -\Delta A - T_0 \int_{t_i}^{t_f} \dot{S}_{\text{tot}} dt \quad (1)$$

Here the availability

$$A = U - T_0 S + P_0 V - \sum_j \mu_{0j} N_j \quad (2)$$

for a process in which the system approaches equilibrium with an environment whose temperature is T_0 , pressure is P_0 , and chemical potential of species j is μ_{0j} .

The change of availability ΔA is taken between the initial time t_i and the final time t_f :

$$\Delta A = A(t_f) - A(t_i) \quad (3)$$

The time rate of change of entropy, \dot{S}_{tot} , is that of system and environment together. It is never negative; however, if the process is reversible, $\dot{S}_{\text{tot}} = 0$, and

$$W_{\text{rev}} = -\Delta A \quad (4)$$

Note also that eq 1 is satisfied in general, and the condition $W = -\Delta A$ is satisfied for reversible processes, whether or not the system has reached equilibrium with the environment at t_f .

Our purpose here is to extend the concept of availability to provide a bound to the work that can be obtained when a system is allowed to approach equilibrium with an environment for a finite interval of time. The traditional expression 4 may sometimes be inadequate, or even misleading, if the process under consideration is only of interest when it operates at rates for which its entropic losses are considerable. On the other hand, the general equation 1 is likely to be either hollow, as in the event that we do not know all the contributions to the entropy production, or completely determined. We shall work essentially with eq 1 but from a viewpoint quite different from that associated with its derivation^{1,4} or from that of the familiar uses of availability.²

Traditionally, we suppose we know the sources of entropy production and can treat eq 1 as a fully determined expression when computing the work that a system can do. Alternatively, when using availability as a tool for engineering analysis, we evaluate A from eq 2 at suitable points of a process and compare it with W in order to determine at which process stages large amounts of potential work are lost. These stages then may be redesigned to improve their performance, either by reducing their losses of availability or by using their availability changes to supply useful work or heat.

The viewpoint that we introduce here begins with the supposition that we can find generic models for processes with time or rate constraints. Each of these generic models is characterized by its own mechanism of entropy production; each is intended as an idealization one level more realistic than a reversible model. The Carnot engine, the archetype of all generic models for thermodynamic processes, reproduces only certain of the properties of real engines. Other standard reversible cycles such as the air-standard Stirling, Brayton, Otto, etc., cycles have been useful for describing the limiting behavior of real heat engines. Recently, models have been introduced which, by incorporating specific mechanisms of entropy production, become models of real processes that are more realistic than the reversible standard cycles.⁵⁻⁷

We suppose, in accord with the findings of Andresen et al.,⁵ that the entropy production for a system of interest will be dominated by that represented by some generic model. The choice of the entropy production mechanisms which are included in the model is dictated by the requirement that they are essential for the operation of the device that extracts work from the system or that they are inescapable because of the structure of the system. The generalization of availability from eq 1 is then expressed in terms of a variational form. Suppose the system is to go through a process Σ with a set of constraints g_j expressed in terms of the system's extensive variables X_1, \dots and conjugate intensive variables Y_1, \dots and that the environment toward which the system moves has intensive

variables Y_{10}, \dots . Then

an upper bound to the work that can be obtained from a process Σ in the time τ , subject to a set of constraints $g_j(X_1, \dots, X_n, Y_1, \dots, Y_n, \tau) = 0$, is given by the finite-time availability

$$A(\Sigma_0; \tau) = \max W(\Sigma_0; \tau) \quad (5)$$

where Σ_0 is an idealized generic process suitable for modeling the realistic process Σ

$$W(\Sigma_0; \tau) = -\Delta A(\Sigma_0) - T_0 \int_0^\tau \dot{S}_{\text{tot}}(\Sigma_0; t) dt \quad (6)$$

and the work $W(\Sigma_0; \tau)$ of the generic process is computed as in eq 1 from the known initial state and the entropy production implied or specified by the definition of the generic process.

An example illustrating this definition will be given in section III.

One such generic process Σ_0 is the endoreversible two-reservoir heat engine with finite heat conductances between the reservoirs and the system. When this process is further specified to have four branches, two isotherms and two adiabats, it is the familiar Curzon-Ahlborn engine.⁸ A second generic process is the two-reservoir heat engine with friction and a heat leak. It might seem that the heat leak should be treated separately, but it turns out that these two "nonidealities" can be treated simultaneously and still yield a transparent solution that describes the examples of pure friction and pure heat leak as natural limiting cases.⁵

This approach will justify itself if the concept of generic, finite-time models is successful in the sense that many real processes can be described as "imperfect" variations of one or more such processes, and the generic models are well-defined limiting cases for the real processes. At least two kinds of evidence support this view. One is the utility of the standard reversible cycles. Another is the result of ref 5, that optimized two-reservoir heat engines with finite heat conductances, heat leaks, and friction fall into two classes sharply separated by a classical bifurcation: one class is dominated by friction and the other by heat conductance, and their characteristics are quite different.

In discussing expressions 5 and 6, we used the clause " Σ_0 is a generic process suitable for modeling Σ ". The meaning of "suitable" must be made more precise. Here, we intend it to mean that, within the constraints of the real process Σ and its generic model Σ_0 , it is not possible to change Σ to produce more work than Σ_0 produces. The problem of constructing model processes that are suitable in this sense is the subject of a future communication. One must, of course, show that a generic model is suitable before one relies on it. The need for such proofs has been made clear with the example given by Ben-Shaul and Levine⁹ of a process in which speeding up a relaxation process yields more work rather than less work. We have been able to show, however, that for large classes of processes, both microscopic and macroscopic in nature, suitable generic models may be constructed.

Some processes are defined with no freedom in the selection of the final state. (We assume, in the spirit of the definition of availability, that the initial state of the system is always well-defined.) Other processes are defined so that the final state may be chosen from within some set of states in order to optimize the chosen objective function such as A . It is a truism, but nonetheless an important point, that in the former case determining the finite-time

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(9) A. Ben-Shaul and R. D. Levine, *J. Non-Equilib. Thermodyn.*, **4**, 363 (1979).

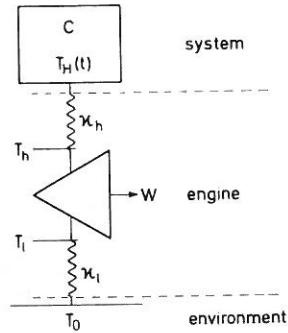


Figure 1. Schematic subdivision of a total system, in this case a finite heat reservoir of temperature $T_H(t)$ drained by an endoreversible engine into the environment at temperature T_0 . The internal reversible engine operates between $T_H(t)$ and $T_I(t)$.

availability is merely a matter of minimizing the total entropy production in order to maximize $W(\tau)$. In the latter case, variational techniques also determine the final state and, thereby, the ordinary availability A_f of that final state. We shall provide examples of both sorts of problems in section VI.

The choice of what one optimizes, the objective function or functional, is a matter of some importance. Among the thermodynamic quantities—as opposed to economic quantities—that one may choose are $A(\tau)$, the objective function to which this paper is devoted, the effectiveness ϵ , the efficiency η , the average power generation, and the entropy production ΔS . For many purposes, notably for engineering design, cost or net revenue is the desired objective function. It is important to recognize that different choices of objective functions usually give different results.^{5,10} For example, in the two-reservoir system, if the heat absorbed from the hot reservoir is fixed, then the max ϵ occurs at the max η , but, under other constraints, these maxima differ.

As we have pointed out in the past, one can approach the maximization of work either by finding its extremal value in a manner that sidesteps finding how to obtain that maximum^{5,11} or by finding the path that yields the maximum work.¹²⁻¹⁴ The former is illustrated in the next section, in which we find $A(\tau)$ for three generic models. The latter is described in sections III-VI, where we construct and analyze a system of coupled finite heat reservoirs and engines whose initial state is not in equilibrium. This particular system has a characteristic that makes it especially useful as a generic model; namely, it has a constant of the motion in its time evolution. The concluding section also outlines how to extend the generic model to chemical as well as other systems.

II. Performance Bound without Path

The simplest way of obtaining the time-dependent availability $A(\tau)$ without performing a full time-path optimization is to make use of energy calculations based on conservation equations^{5,8} or thermodynamic potentials.¹¹

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(11) P. Salamon, B. Andresen, and R. S. Berry, *Phys. Rev. A*, **15**, 2094 (1977).

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(13) M. H. Rubin and B. Andresen, *J. Appl. Phys.*, **53**, 1 (1982).

(14) M. J. Ondrechen, M. H. Rubin, and Y. B. Band, *J. Chem. Phys.*, **78**, 4721 (1983).

For the endoreversible engine depicted in Figure 1 the maximum extractable power is⁸

$$\dot{W}_{\max} = \frac{\kappa_i \kappa_h}{\kappa_i + \kappa_h} (T_H^{1/2} - T_0^{1/2})^2 \quad (7)$$

If the hot reservoir at T_H is infinite, this power can be sustained indefinitely, and the time-dependent availability of the system operating for the interval τ becomes

$$A(\tau) = W_{\max}(\tau) = \kappa (T_H^{1/2} - T_0^{1/2})^2 \tau \quad (8)$$

linear in the total operating time τ . By contrast, since both the driving reservoir and the environment are infinite, so is the traditional availability. This proportionality of the finite-time availability to time, $A(\tau) \propto \tau$, is general for all systems with infinite reservoirs since they are not degraded. This holds as well for systems with the more complicated loss mechanisms of ref 5.

Next, consider extracting the maximum work from a finite reservoir (heat capacity C), originally at temperature T_H by connecting Carnot engines between it and the environment at T_0 ; each engine accepts heat at a fixed upper temperature.¹² We assume that we can switch engines once per time unit. Then the extractable work as a function of the number of engines in the sequence¹² becomes the time-dependent availability for the system:

$$A(\tau) = CT_0 [T_H/T_0 - 1 - (\tau + 1) \{ (T_H/T_0)^{1/(\tau+1)} - 1 \}] \quad (9)$$

Finally, if one has a finite-time potential,¹¹ P , then

$$A(\tau) = P(A) - P(B) \quad (10)$$

where B is the most distant point in thermodynamic space which can be reached from A in time τ . Note that this does not require any knowledge about how to get from A to B . One example of this is "Example 4: Quasistatic expansion" of ref 11, where we found

$$P = c_1 T + c_2 V^2 + c_3 \ln V \quad (11)$$

c_1, c_2, c_3 are constants. In this case

$$A(\tau) = c_1 (T_A - T_B) + c_2 (V_A^2 - V_B^2) + c_3 \ln (V_A/V_B) \quad (12)$$

where T_B and V_B are determined by integrating the constraint equations¹¹

$$dS/dt = \kappa (T - T_0)/T \quad dV/dt = \alpha V \quad (13)$$

for the duration τ .

This no-path procedure for finding $A(\tau)$ is very convenient when some of the above conditions are fulfilled. However, if the system is nonsteady and no potentials are available, it is necessary to perform a full optimization from which the desired time path also emerges. This is done in the following sections.

III. Thermodynamic Problem

We now construct a system intended to be a generic model for real complex systems in local thermal equilibrium providing work in competition with internal relaxation.

To determine the time-dependent availability $A(\tau)$ we must calculate the maximum work that can be extracted from a system in a stable environment. We begin with the equation for the work done by the system, eq 1-3, and recall that the process is of fixed duration $\tau = t_f - t_i$.

The analysis of thermodynamic processes in terms of availability usually begins with an arbitrary division of the (isolated) total system into two interacting parts: the environment, characterized by unchanging intensive variables, and the system of interest.⁴ To do our analysis of

irreversible processes, we find it more convenient to divide the total system into three parts: the environment, the system = internal reservoirs and interfaces, and the engines that perform useful work, as indicated with the example of Figure 1. This division helps to isolate irreversibilities and to clarify the basis of the somewhat arbitrary choices of generic processes for the representation of irreversible systems. This arbitrariness does not occur when reversible processes are used since all reversible heat engines using the same set of heat reservoirs will perform the same amount of work per unit heat absorbed.

With this division of the isolated system, the rate of total entropy production consists of two parts: the rate of entropy production in the system, σ , and the rate of entropy production in the devices that are used to perform useful work \dot{S}_M

$$\dot{S}_{\text{tot}} = \sigma + \dot{S}_M \quad (14)$$

σ is taken to be a function of a set of intensive thermodynamic variables $\{Y_\beta, \beta=1,2,\dots\}$. Contributions from leaks directly between system and environment are assumed to be included in \dot{S}_M . Our system may be composed of several parts so that, for example, several Y_β 's may correspond to temperatures. In contrast, the environment is characterized by a set of intensive parameters $\{Y_j, j=1,2,\dots\}$, where each j labels a physically distinct, intensive variable. Recall that the subscript zero is used to refer to the environment.

Next the rate of entropy increase of the working devices, \dot{S}_M , must be specified. Some subset of the Y_β will be coupled to working devices which in turn are coupled to the environment. We shall write

$$\dot{S}_M = \sum_\alpha \dot{S}_{M\alpha} \quad (15)$$

where the sum is understood to be over this subset. Up to this point our entire discussion has been quite general but purely formal, subject only to the requirement that our system is describable in terms of thermodynamic variables. As explained in section I, we must make a choice of generic processes that will serve as standard processes. Each generic system is associated with a particular form of its $\dot{S}_{M\alpha}$. In our case we choose to write

$$\dot{S}_{M\alpha} = \sigma_{\alpha h} + \sigma_{\alpha l} + \dot{S}_{m\alpha} \quad (16)$$

where we describe the engine in terms of a "higher" part¹⁵ which is in contact with the system, a "lower" part which is in contact with the environment, and a part associated with the internal, work-producing machine (see Figure 1). In general, this division is arbitrary; however, in our case we shall see that the arbitrariness is eliminated.

We require that each machine operate endoreversibly. This means that the work is produced by the internal machine which operates reversibly between the upper and lower parts of the working device. In such a machine all the entropy production occurs on its boundary and arises from the conditions necessary to produce nonzero fluxes J_α into and out of the device. An immediate consequence of this requirement is that we obtain a constraint equation for each flux path

$$\int_{t_i}^{t_i+\tau} \dot{S}_{m\alpha}(t) dt = 0 \quad (17a)$$

where τ_α is the duration of one cycle of the machine labeled

(15) The expression "higher" part does not mean that the reservoirs are necessarily of a higher temperature than the environment, but should rather be taken pictorially, cf. Figure 1. A refrigeration system with some $T_\alpha < T_0$ is equally well treated by this formalism.

by α , or, if the machine is a continuous-flow machine, the constraint becomes

$$\dot{S}_{m\alpha} = 0 \quad (17b)$$

The transport of heat across the boundary is essential to the finite-time operation of the machine and is associated with an inevitable irreversibility. In other processes required to operate in finite time, one finds other essential irreversibilities, often a single kind that dominates the loss processes. One illustration is the diffusion to and from electrodes in nonturbulent batteries.

To complete the definition of $\dot{S}_{M\alpha}$ it is necessary to specify $\sigma_{\alpha h}$, $\sigma_{\alpha l}$, and $\sigma_{\alpha i}$. We shall take

$$\sigma_{\alpha h} = -J_\alpha (Y_\alpha - Y_{\alpha h}) \quad (18a)$$

$$\sigma_{\alpha l} = -J_{\alpha 0} (Y_{\alpha 0} - Y_{\alpha l}) \quad (18b)$$

$$\dot{S}_{m\alpha} = -J_\alpha Y_{\alpha h} - J_{\alpha 0} Y_{\alpha l} \quad (19)$$

where J_α is the α -th flux into the system, Y_α is the conjugate force, $J_{\alpha 0}$ is the α -th flux into the environment, and $Y_{\alpha h}$ and $Y_{\alpha l}$ characterize the state of the internal engine at different parts of the cycle. For convenience the environmental thermodynamic variable corresponding to Y_α has been labeled with α . We recognize $J_\alpha Y_\alpha$ and $J_{\alpha 0} Y_{\alpha 0}$ as the entropy flowing out of the engine into the system and the environment, respectively. $\dot{S}_{m\alpha}$ is composed of the entropy flow out of the upper and lower parts of the internal engine.

The operation of the engine is determined by the regulation of the $Y_{\alpha h}$'s and $Y_{\alpha l}$'s. They are a subset of the control variables; we denote the entire set of these variables for all the working devices by u . The controls are usually restricted to some bounded set U in a k -dimensional Euclidean space. In order to determine the optimum process we must determine u . The set u may also contain rate coefficients or transport coefficients which appear in the fluxes, J_α . For example heat flow into and out of a machine is governed by the thermal conductances of the walls of the engine; transport of matter may be governed by diffusion coefficients, and electric current by conductances. If these parameters are treated as bounded control variables, they usually lead to boundary extrema; that is, the system usually yields the extrema of the desired property when the parameters take on their maximum values, or when the device is turned off—which is equivalent to setting some conductances to zero. Thus, the flux J_α will depend on Y_α and $u_{\alpha h}$, the latter contains $Y_{\alpha h}$, and the flux $J_{\alpha 0}$ will depend on $Y_{\alpha 0}$ and $u_{\alpha l}$.

Note that eq 19 when substituted into eq 17a or 17b becomes

$$\int_{t_i}^{t_i+\tau} [J_\alpha Y_{\alpha h} + J_{\alpha 0} Y_{\alpha l}] dt = 0 \quad (20a)$$

or

$$J_\alpha Y_{\alpha h} + J_{\alpha 0} Y_{\alpha l} = 0 \quad (20b)$$

With eq 14-20 we have now formally specified all the sources of the entropy production. The final step necessary to complete the formulation of our problem is to specify the dynamics, given by the equations of motion of the set $\{Y_\beta\}$ which determines the state of the system:

$$\dot{Y}_\beta = F_\beta(Y_1, Y_2, \dots, u) \quad (21)$$

where we recall that u is the complete set of control variables including the $\{Y_{\alpha h}\}$ and $\{Y_{\alpha l}\}$. It is convenient to distinguish the equations for the subset $\{Y_{\alpha l}\}$, which are coupled to the working devices (cf. eq 15), and the remainder, $\{Y_\lambda\}$:

$$\dot{Y}_\alpha = K_\alpha(Y_1, Y_2, \dots) + J_\alpha(Y_\alpha, u_\alpha) \quad (22a)$$

$$\dot{Y}_\lambda = K_\lambda(Y_1, Y_2, \dots) \quad (\lambda \neq \alpha) \quad (22b)$$

where J_α is the flux introduced in eq 18a. The K 's reflect the internal coupling of the system and assure that, in the presence of the working devices, the interacting parts of the system relax toward equilibrium.

This completes our general formulation of the problem. We must now determine how to regulate the controls in order to extract the maximum work from the system when it is given the system in a specified initial state $\{Y_\beta(0)\}$ and any other constraints that are to be imposed. For example, we may require that some subset of the variables β take predetermined values at t_f . This is now a well-defined problem in optimal control theory. In the next section we outline its formulation and solution.

7. Optimal Control Problem

In this section we outline the mathematical formulation and solution to the problem discussed in the previous section. In the standard fashion^{16,17} we write a variational action

$$L = V_f + \int_{t_i}^{t_f} (H - \sum_\beta \psi_\beta \dot{Y}_\beta) dt \quad (23)$$

where the Hamiltonian is given by

$$H = -\dot{S}_{\text{tot}} + \sum_\alpha \lambda_\alpha \dot{S}_{m\alpha} + \sum_\beta \psi_\beta F_\beta \quad (24)$$

with \dot{S}_{tot} defined by eq 14–16, 18, and 19, and $\dot{S}_{m\alpha}$ given by eq 19. The sets $\{\psi_\beta\}$ and $\{\lambda_\alpha\}$ are Lagrange functions which are introduced to enforce the constraints 22 and 20.

If a constraint of the form of eq 20a is used, then the corresponding λ_α is constant over each cycle but may range from cycle to cycle. The quantity V_f is a function of the thermodynamic variables of the system at the end of the process. In the case that interests us here, eq 1 shows that V_f is $-\Delta A/T_0$, where the temperature of the environment has been divided out for convenience.

The equations of motion which determine the optimal path are found by obtaining the extrema of L . The variation with respect to Y_β gives

$$\begin{aligned} 0 &= -\frac{\partial H}{\partial Y_\beta} = \\ &= \left(\frac{\partial \sigma_{\alpha\beta}}{\partial Y_\beta} + (1 - \lambda_\alpha) \frac{\partial \dot{S}_{m\alpha}}{\partial Y_\beta} \right) \delta_{\alpha\beta} + \frac{\partial \sigma}{\partial Y_\beta} - \sum_\gamma \psi_\gamma \frac{\partial F_\gamma}{\partial Y_\beta} \quad (25) \\ \psi_\beta(t_f) &= \partial V_f / \partial Y_\beta(t_f) \quad (26) \end{aligned}$$

where $\delta_{\alpha\beta}$ is zero if Y_β is not in the set $\{Y_\alpha\}$ defined before eq 15 and is 1 otherwise. Equation 26 comes from the variation of the final value of the system variable Y_β . If its value is not free, then eq 26 is replaced by the requirement $Y_\beta(t_f) = Y_{\beta f}$, where $Y_{\beta f}$ is specified.

The variation with respect to the controls is complicated by the fact that conductances often appear linearly in the fluxes and, therefore, in H . The variation with respect to such linear control variables requires special handling.^{16–18} We simply quote the result that the conductances that appear linearly in H take either their maximum value or their minimum value of zero. In the latter case the machine whose conductance vanishes decouples from either the system, the environment, or both. Finally, the varia-

tions with respect to $Y_{\alpha h}$ and $Y_{\alpha i}$ yield

$$0 = \frac{\partial H}{\partial Y_{\alpha h}} = -\frac{\partial \sigma_{\alpha h}}{\partial Y_{\alpha h}} + (\lambda_\alpha - 1) \frac{\partial \dot{S}_{m\alpha}}{\partial Y_{\alpha h}} + \psi_\alpha \frac{\partial J_\alpha}{\partial Y_{\alpha h}} \quad (27)$$

$$0 = \frac{\partial H}{\partial Y_{\alpha i}} = -\frac{\partial \sigma_{\alpha i}}{\partial Y_{\alpha i}} + (\lambda_\alpha - 1) \frac{\partial \dot{S}_{m\alpha}}{\partial Y_{\alpha i}} \quad (28)$$

where the form of F_β given in eq 22 has been used to obtain the last term in eq 27.

Equations 17, 22, and 25–28 determine the optimal solution once the J_α 's and the K 's in eq 22, the initial conditions $Y_\beta(t_i)$, and any final condition $Y_\beta(t_f)$ are specified. In general, these equations are nonlinear and must be solved numerically.

Equations 27 and 28 prove an interesting result when $Y_\alpha(t_f)$ is not specified but is determined from the optimization process. At $t = t_f$ eq 26 may be combined with these equations to eliminate $\psi_\alpha(t_f)$ and $\lambda_\alpha(t_f)$. We then get a relation connecting $Y_\alpha(t_f)$, $Y_{\alpha h}(t_f)$, and $Y_{\alpha i}(t_f)$ independent of the remaining variables (except the conductances for the α -flux path). The general equation is not very informative, but a specific example is provided by eq 49. Such a relation is easy to understand physically. As t approaches t_f , there is a time at which the internal relaxation time of the variable Y_α becomes long compared to the remaining extraction time, in which case it becomes irrelevant that the α -th subsystem is coupled to the rest of the system. From that point on, the engine should be run in the mode optimal for the decoupled boundary subsystem. Thus, the condition just depends on the α -th engine and α -th subsystem. Furthermore, as t approaches t_f , and the engines no longer interact with one another, more work is produced by having all the work-producing engines operate than by having some idle. Earlier on in the process, the effects of flows between subsystems sometimes may make it optimal to have some engines not running or even running backward, as heat pumps.

V. A Linear Model

The equations of section IV become nonlinear because of the nonlinearity of the entropy production $\dot{S}_{m\alpha}$. Equations 27, 28, and 17 lead to a nonlinear relation connecting Y_α , $Y_{\alpha h}$, $Y_{\alpha i}$, and ψ_α . For this reason it is useful to study a very simple model using eq 1 before we examine the results of the detailed calculations in the next section.

We introduce a generalized linear model through the following set of equations:

$$\dot{S}_{\text{tot}} = \frac{1}{2} \sum_\alpha (Y_{\alpha c} - Y_\alpha) J_\alpha + \frac{1}{2} \sum_{\alpha\beta} (Y_\beta - Y_\alpha) K_{\alpha\beta}$$

$$\Delta A/T_0 = \sum_\alpha (Y_{\alpha f} - Y_{\alpha i}) N_\alpha Y_{\alpha 0}$$

$$\dot{Y}_\alpha = J_\alpha + \sum_\beta K_{\alpha\beta}$$

$$J_\alpha = K_\alpha (Y_{\alpha c} - Y_\alpha) \quad K_{\alpha\beta} = M_{\alpha\beta} (Y_\beta - Y_\alpha) \quad (29)$$

where quantities K_α , $M_{\alpha\beta}$, and N_α are all constants, and $Y_{\alpha i}$ and $Y_{\alpha f}$ are the initial and final values of Y_α . The $Y_{\alpha c}$ are control variables. The condition that \dot{S}_{tot} be nonnegative requires that $K_\alpha \geq 0$ and that the symmetric part of the matrix \mathbf{M} be nonnegative. It is clear that the diagonal elements of \mathbf{M} do not enter the problem and so are simply set to zero.

This model makes no explicit mention of the working device which is hidden in J_α . The machine has been devised so that it operates at a rate proportional to the deviation from equilibrium of the subsystem to which it is connected. $K_{\alpha\beta}$ is the flux between the α and β subsystem. We wish to emphasize that our linear model is not in any

way related to the usual linearization of the flux-force relation in nonequilibrium thermodynamics. In particular, it is not required to be a symmetric matrix. Inspection of eq 29 shows that $Y_{\alpha c}$ always appears in the combination $Y_{\alpha c} - Y_\alpha = C_\alpha$ which we take as our control variable. Then the Hamiltonian for this model is

$$\begin{aligned} &= -\frac{1}{2} \sum_\alpha K_\alpha C_\alpha^2 - \frac{1}{2} \sum_{\alpha\beta} (Y_\alpha - Y_\beta)^2 M_{\alpha\beta} + \sum_\alpha \psi_\alpha K_\alpha C_\alpha + \\ &\quad \sum_{\alpha\beta} \psi_\alpha M_{\alpha\beta} (Y_\beta - Y_\alpha) \quad (30) \end{aligned}$$

The variational principle leads to the results

$$\begin{aligned} \psi_\alpha &= C_\alpha \\ &= \sum_\beta (M_{\alpha\beta} + M_{\beta\alpha}) (Y_\alpha - Y_\beta) - \\ &\quad (\sum_\beta C_\beta M_{\beta\alpha} - C_\alpha \sum_\beta M_{\alpha\beta}) \sum_\beta (C_\beta - C_\alpha) M_{\alpha\beta} \quad (31) \end{aligned}$$

Thus, the equations for Y_α and C_α are sets of coupled, linear, first-order differential equations. Note that $\sum_\alpha C_\alpha$ is constant of motion along the optimal trajectory. This can be seen from the equations for C_α directly and is a manifestation of the invariance of the Hamiltonian with respect to the transformation $Y_\alpha \rightarrow Y_\alpha + D$ for all α , where D is a constant. The general solution of these equations is a linear combination of a steady-state term plus terms with exponential time dependence.

A particularly simple case is obtained if \mathbf{M} is zero. Then different subsystems do not interact. We find for each subsystem, when the final states $Y_\alpha(t_f)$ are not specified, that

$$\Delta A/T_0 = -2\Delta S_{\text{tot}} \quad (32)$$

$$|A/\Delta A| = \frac{1}{2} \quad (33)$$

and that $A(\tau)$ is proportional to the duration τ of the process. If the final state is prescribed

$$\Delta A/T_0 = (Y_{\alpha f} - Y_{\alpha i}) N_\alpha Y_{\alpha 0}$$

$$C_\alpha = -N_\alpha Y_{\alpha 0}$$

$$Y_{\alpha f} - Y_{\alpha i} = K_\alpha C_\alpha \tau$$

$$\Delta S_{\text{tot}} = \frac{1}{2} (Y_{\alpha f} - Y_{\alpha i})^2 / (K_\alpha^2 \tau)$$

$$T_0 = (Y_{\alpha f} - Y_{\alpha i}) N_\alpha Y_{\alpha 0} - \frac{1}{2} (Y_{\alpha f} - Y_{\alpha i})^2 / (K_\alpha^2 \tau) \quad (34)$$

In this case, if $\tau \rightarrow \infty$, we get a reversible process. There is no contradiction between results 33 and 34 in the limit $\tau \rightarrow \infty$, because ΔA is fixed in the latter but increases with τ in the former.

The simple linear model presented in this section has many features in common with the more physical case discussed in the next section. In particular, there is a local instant of motion connecting the control variables, and the trajectories of the optimal paths can be found from the extremal H . These trajectories have a characteristic form in the space with coordinates of the state variables $\{Y_\alpha\}$ and the set of independent variables describing the controls $\{C_\alpha\}$ (in the next section there is one such variable, the angle θ). These trajectories are of the type that are associated with unstable systems where stationary states are saddle points. We do not pursue the linear problem any further here.

I. A More Complex Generic Model. An Internally Relaxing System

A. General Description. In this section we apply the general formalism of sections III and IV to the case of an

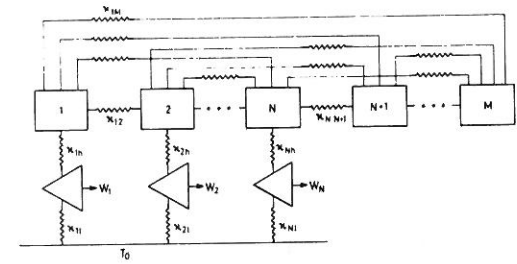


Figure 2. Thermal interaction of M reservoirs. The first N are also connected to the environment through endoreversible engines producing work W_1, \dots, W_N .

internally relaxing system. The system is composed of M finite heat reservoirs that are characterized by their heat capacities C_j and their temperatures T_j . These reservoirs are connected, as shown in Figure 2, by heat conductors with the heat flow from j to r given by a linear law

$$\dot{Q}_{jr} = \kappa_{jr} (T_j - T_r) \quad (35)$$

Some of the reservoirs are also drained by heat engines to the environment, as described below. Thus, the system is completely characterized by a set of fixed parameters $\{C_j, \kappa_{jr}\}$, and its state is given by the state vector $\mathbf{T} = (T_1, \dots, T_M)$. The environment is an infinite heat reservoir whose temperature is T_0 . The engines are continuous-flow endoreversible engines of the type shown in Figure 1. The α -th engine is characterized by its heat conductances, $\kappa_{\alpha h}$ and $\kappa_{\alpha i}$, and by the temperature of its working fluid at the two ends of the engine, $T_{\alpha h}$ and $T_{\alpha i}$. We assume $\alpha = 1, 2, \dots, N$, where $N \leq M$; i.e., we number the reservoirs such that the first N are connected to the engines.

For this example, V_f of eq 23 is $(A_i - A_f)/T_0$, where the availability

$$A = \sum_{n=1}^M C_n [T_n - T_0 - T_0 \ln (T_n/T_0)] \quad (36)$$

and \dot{S}_{tot} , according to eq 14–18, consists of the terms

$$\sigma_{\alpha h} = \dot{Q}_{\alpha h} \left(\frac{1}{T_\alpha} - \frac{1}{T_{\alpha h}} \right) \quad (37a)$$

$$\sigma_{\alpha i} = \dot{Q}_{\alpha i} \left(\frac{1}{T_0} - \frac{1}{T_{\alpha i}} \right) \quad (37b)$$

$$\dot{S}_{m\alpha} = 0 \quad (17b)$$

$$\sigma = -\sum_{j=1}^M T_j^{-1} \left(\sum_{r=1}^M \dot{Q}_{jr} \right) \quad (37c)$$

The constraint eq 20b becomes

$$\frac{\dot{Q}_{\alpha h}}{T_{\alpha h}} + \frac{\dot{Q}_{\alpha i}}{T_{\alpha i}} = 0 \quad (38)$$

Finally, the equations of motion (eq 22) become

$$\dot{T}_j = -\frac{1}{C_j} \sum_{r=1}^M \dot{Q}_{jr} + \sum_{\alpha} \delta_{\alpha j} \frac{1}{C_j} \dot{Q}_{\alpha h} \quad (39)$$

where $\delta_{\alpha j}$ is the Kronecker delta function.

With the $\dot{Q}_{\alpha h}$ and $\dot{Q}_{\alpha i}$ given by linear laws, we have

$$\dot{Q}_{\alpha h} = \kappa_{\alpha h} (T_{\alpha h} - T_\alpha) \quad (40a)$$

$$\dot{Q}_{\alpha i} = \kappa_{\alpha i} (T_{\alpha i} - T_0) \quad (40b)$$

We now introduce the control variables

(16) M. H. Rubin, *Phys. Rev. A*, **19**, 1272 (1979); (b) *ibid.*, **19**, 1277 (1979).

(17) M. H. Rubin, *Phys. Rev. A*, **22**, 1741 (1980).

(18) A. E. Bryson, Jr., and Y. Ho, "Applied Optimal Control", Hemisphere, Washington, DC, 1975.

$$u_{ah} = T_{ah}/T_\alpha \quad u_{ai} = T_{ai}/T_0 \quad (41)$$

With these definitions the total entropy production of the heat engines becomes

$$\dot{S}_{tot} = \sum_{\alpha=1}^N [\kappa_{ah}(u_{ah} + u_{ah}^{-1} - 2) + \kappa_{ai}(u_{ai} + u_{ai}^{-1} - 2)] + \sigma \quad (42)$$

and the Hamiltonian

$$H = -\sum_{\alpha=1}^N \left[\kappa_{ah} \left(u_{ah} + \frac{1 + \lambda_\alpha}{u_{ah}} - 2 - \lambda_\alpha \right) + \kappa_{ai} \left(u_{ai} + \frac{1 + \lambda_\alpha}{u_{ai}} - 2 - \lambda_\alpha \right) \right] + \sum_{j=1}^M \left[\frac{1}{T_j} - \frac{\psi_j}{C_j} \right] \sum_{r=1}^M \dot{Q}_{jr} + \sum_{j=1}^M \frac{\psi_j}{C_j} \sum_{\alpha=1}^N \delta_{\alpha j} \dot{Q}_{ah} \quad (43)$$

where

$$\dot{Q}_{ah} = \kappa_{ah} T_\alpha (u_{ah} - 1) \quad (44)$$

and the λ_α are the Lagrange functions defined following eq 24.

Using eq 25–28 and eq 36 one can now show that

$$u_{ai}(t) = [1 + \lambda_\alpha(t)]^{1/2} \quad \text{for } \kappa_{ai} \neq 0 \quad (45)$$

$$1 - \frac{1 + \lambda_\alpha}{u_{ah}^2} - \frac{T_\alpha \psi_\alpha}{C_\alpha} = 0 \quad \text{for } \kappa_{ah} \neq 0 \quad (46)$$

$$\psi_j(t_f) = -C_j(1/T_0 - 1/T_{jf}) \quad (47)$$

if $T_{jf} = T_j(t_f)$ is not specified by the process and therefore is free to be varied.

If we combine eq 45–47, we have

$$(u_{ai}/u_{ah})_f^2 = T_\alpha/T_0 \quad (48)$$

or

$$(T_{ai}/T_{ah})_f = (T_0/T_{ai})^{1/2} \quad \text{for } \kappa_{ah} \neq 0 \quad (49)$$

This is precisely the operating condition for a single engine connected to a system composed of a single reservoir, as we expect on physical grounds from the discussion at the end of section IV.

From eq 39 and the equations for $\dot{\psi}_j$ one can show that

$$\frac{d}{dt} \sum_{j=1}^N \psi_j T_j = \sum_{j=1}^N \frac{1}{C_j T_j} (-C_j + T_j \psi_j) \dot{Q}_j^{NL} \quad (50)$$

where the nonlinear contribution

$$\dot{Q}_j^{NL} = \sum_{r=1}^N \left[\dot{Q}_{jr} - T_j \frac{\partial \dot{Q}_{jr}}{\partial T_j} - T_r \frac{\partial \dot{Q}_{jr}}{\partial T_r} \right] \quad (51)$$

If \dot{Q}_{jr} depends only on the temperature difference $T_j - T_r$, and $\dot{Q}_{jr} = f_{jr}(T_j - T_r) = -f_{rj}(T_r - T_j)$, then

$$\dot{Q}_j^{NL} = \sum_{r=1}^N [\dot{Q}_{jr} - (T_j - T_r) \dot{Q}'_{jr}] \quad (52)$$

where the prime denotes the derivative with respect to the temperature argument of \dot{Q}_{jr} . Note that in our model, where \dot{Q}_{jr} is linear in $T_j - T_r$, \dot{Q}_j^{NL} , the nonlinear part of \dot{Q}_{jr} , when \dot{Q}_{jr} is an odd function of $T_j - T_r$, vanishes, and

$$\sum_{j=1}^N T_j \psi_j$$

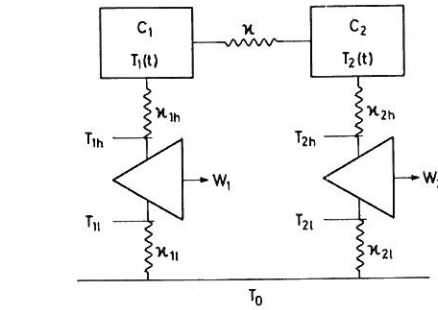


Figure 3. Model system consisting of two reservoirs at temperatures $T_1(t)$ and $T_2(t)$ and the environment at temperature T_0 . The reservoirs produce work through their respective engines in competition with internal relaxation through the conductance κ .

is a constant of motion. It is clear from the derivation that the existence of this constant depends critically on the linearity of \dot{Q}_{jr} .

In order to interpret this constant, we evaluate it at $t = t_f$. If we assume that all the final temperatures T_{jf} are free, then eq 47 may be used in evaluating the constant, and we find

$$\sum_{j=1}^N \psi_j T_j = \frac{-1}{T_0} \sum_{j=1}^N C_j (T_{jf} - T_0) \quad (53)$$

Each individual term $C_j(T_{jf} - T_0)$ is the thermal energy remaining in the j -th reservoir compared to its energy when it is in equilibrium with the environment. Thus, the constant is the negative of the remaining total energy divided by the temperature of the environment. If this remaining energy were all to go as heat into the environment, then the increase in entropy of the environment would be exactly the negative of this constant.

If all the final temperatures are not free, then the constant does not have so simple an interpretation because ψ_{jr} must be computed by using the final-state condition $T_j(t_f) = T_{jf}$, the given value of T_j at $t = t_f$.

We have completed the solution of this problem for the case of $M = N = 2$ and now summarize the result of this calculation.

B. Two-Reservoir System. For $M = N = 2$ the system is shown in Figure 3. We want to extract the maximum work in time τ starting with reservoirs 1 and 2 at temperatures T_{1i} and T_{2i} , thus leaving the final temperatures T_{1f} and T_{2f} free for the optimization. Then eq 53 is a constant of motion which we use to define K

$$K^2 = T_0^{-1} \sum_{j=1}^2 C_j T_j \quad (54)$$

Another constant of motion is of course H , eq 43. In order to simplify the variational equations 25–28, constraint equations 38, and equations of motion 39 as far as possible, we define the reduced variables

$$B = T_2/T_1 \quad (55)$$

and the angle θ through

$$\begin{aligned} \cos \theta &= [C_1(1 + \lambda_1)]^{1/2} / K u_{1h} \\ \sin \theta &= [C_2(1 + \lambda_2)]^{1/2} / K u_{2h} \end{aligned} \quad (56)$$

Loosely speaking, θ describes the relative rate of drainage

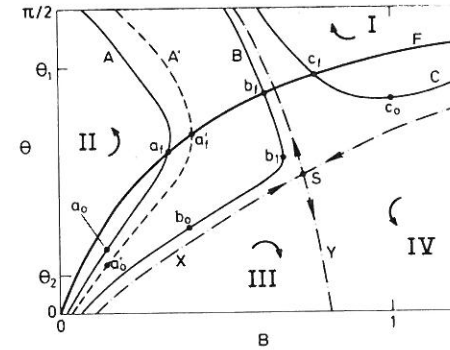


Figure 4. Idealized optimal time evolution paths for the model system. All final states lie on the heavy curve marked F, and the infinite-time paths are labeled X and Y. B and θ are defined in eq 55 and 56, respectively. Time direction in the four regions I–IV is shown by the arrows.

of the two reservoirs. Then an optimal trajectory in the (B, θ) plane is obtained by using the constancy of

$$H = \kappa_1 \left(1 - \frac{K \cos \theta}{C_1^{1/2}} \right)^2 + \kappa_2 \left(1 - \frac{K \sin \theta}{C_2^{1/2}} \right)^2 + \kappa(1-B)K^2 \left(\frac{\cos^2 \theta}{C_1} - \frac{\sin^2 \theta}{BC_2} \right) \quad (57)$$

where

$$\kappa_i = \kappa_{ih} \kappa_{il} / (\kappa_{ih} + \kappa_{il}) \quad (58)$$

The time evolution is obtained from either

$$\dot{\theta} = \frac{d\theta}{dt} = \kappa \left(\frac{\tan^2 \theta}{C_2} - \frac{B^2}{C_1} \right) / 2B \tan \theta \quad (59a)$$

or

$$\dot{B} = \frac{dB}{dt} = \left[\frac{\kappa_1}{C_1} \left(1 - \frac{C_1^{1/2}}{K \cos \theta} \right) - \frac{\kappa_2}{C_2} \left(1 - \frac{C_2^{1/2}}{K \sin \theta} \right) \right] B + \kappa \left(\frac{B}{C_1} + \frac{1}{C_2} \right) (1-B) \quad (59b)$$

A few idealized optimal trajectories are shown in Figure 4. Equation 53 applied to eq 27 in the final situation yields

$$B_f = (C_1/C_2) \tan^2 \theta_f \quad (60)$$

so that all final states must be on the heavy curve in Figure 4. This provides the last bit of information necessary to fully determine a trajectory. A similar “initial-state curve” unfortunately does not exist, which means that the optimal solution—as is usually the case—must be calculated by starting from the final state. The final state may be chosen arbitrarily, but only one such choice yields precisely the trajectory that hits the desired initial state at a time τ earlier. Consequently, the problem has to be solved by iteration, e.g., as an extrapolation problem (see Appendix for the procedure used).

Let us now look at some features of the optimal trajectories. Trajectory A in Figure 4 starts with a given $B = T_{2i}/T_{1i}$ at point a_0 and evolves to a_f in time τ . If, starting from the same initial B , the process were allowed a time $\tau' > \tau$, it would begin with a different θ and follow another

trajectory, A' from a_0' to a_f' , completely different from A, and thereby produce more work than the sum of the contributions from A and an optimal extension from τ to τ' . Thus, it is imperative to know from the outset how much time is available. Trajectory B is an example showing that an optimal trajectory does not necessarily approach equilibrium between the reservoirs ($B = 1$), but may increase the temperature difference, as happens between points b_i and b_f . It is even possible to start with equal temperatures and evolve along the optimal trajectory to unequal reservoir temperatures as on trajectory C. This, of course, requires some asymmetry in the system, such as different heat capacities or conductances for the two reservoirs.

For very long process times the optimal trajectories approach the curves X and Y which intersect at the “stationary” point S, where $\dot{\theta} = \dot{B} = 0$. (Note that $\dot{\theta} = \dot{B} = 0$ do not imply $T_1 = T_2 = 0$, so S is not in general a point of static equilibrium; it is only a kind of steady state.) A point on a typical slow trajectory thus moves along next to X and slows down as it approaches S (from left or right depending on the initial condition), spends most of the available time in the neighborhood of S, and just before time is up, moves up to the final-state curve close to Y. The curves X and Y are called separatrixes because they divide the B - θ plane into the four regions I–IV with different types of trajectories. Thus, the final-state points b_f and c_f describe very similar conditions, whereas the initial states b_0 and c_0 are quite different. Obviously, no optimal trajectory crosses a separatrix because that would require infinite time. There is a symmetry between the regions I and III, and similarly between II and IV, such that any optimal trajectory in I by interchange of all parameters connected with the two engines and reservoirs is transformed into an optimal trajectory in III and vice versa. (The separatrixes depend on the final state, so the stationary point S may be situated above or below the final-state curve.) Thus, it is only necessary to investigate trajectories in two of these regions; we chose I and II. The time direction of the optimal trajectories is as indicated by the arrows in Figure 4.

When θ is less than some value θ_2 , engine 2 reverses and acts as a heat pump. This is observed in extreme cases when $T_1 \gg T_2$ so that it is advantageous to expend some work in the initial phase to keep down the temperature difference $T_1 - T_2$, and thereby minimize the losses in κ , while reaping more work later from combined higher temperature reservoirs. An analogous reversal in engine 1 occurs when $\theta > \theta_1$.

The somewhat idealized curves of Figure 4 have been used to clarify the variations among optimal trajectories. Numerically calculated optimal trajectories with realistic system parameters (an example is shown in Figure 5) have all these interesting effects squeezed into a very small region around the stationary point. In addition, the separatrixes depend on the final state, so it is somewhat incorrect to show all the trajectories A, A', B, C in the same figure. However, for our qualitative discussion it has sufficed. In order to show its time evolution, a heavy line indicates that part of the optimal trajectory in Figure 5 where 90% of the total duration is spent, and 50% is spent in the extra-heavy-line segment.

Probably the most interesting aspect of the finite-time availability $A(\tau)$ is how it depends on the process time τ for a fixed initial state. The results of two such calculations are shown in Figure 6; the left scale is for A, and the right scale for the effectiveness $\epsilon = W/\Delta A$, i.e., the maximal captured work divided by the corresponding drop in or-

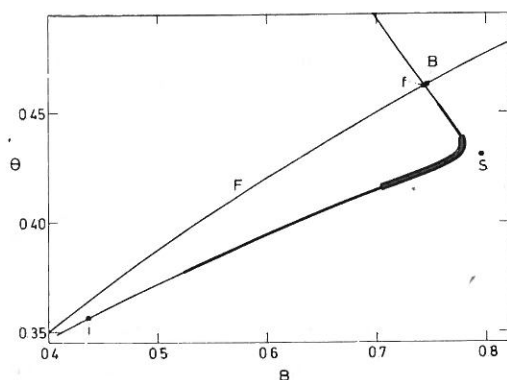


Figure 5. Calculated optimal time evolution path for the model system defined by $C_1/C_2 = 3$, $T_0 = 1$, $\kappa = 1$, and $\kappa_{\text{th}} = \kappa_{\text{el}} = 10$. The initial state is $T_{1i} = 8.8$, $T_{2i} = 4.0$, and the duration $\tau = 2$; 90% of this time is spent along the heavy segment and 50% along the extra-heavy segment. F is the curve of final states, f the present final state, i the initial state, S the "stationary" point, and B the intersection of the separatrix Y and F; i.e., region II is to the left and region I to the right.

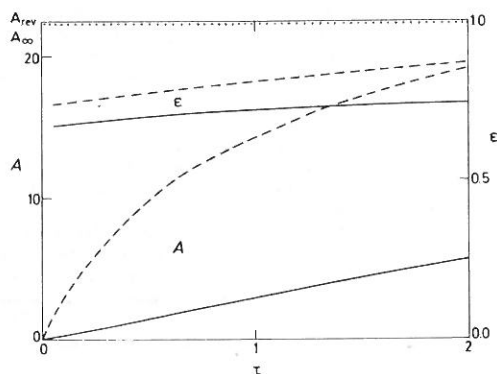


Figure 6. Finite-time availability, A (left scale), and effectiveness, ϵ , in producing this work (right scale) for the model system as a function of process duration, τ . The initial state is $T_{1i} = 10$, $T_{2i} = 5$, and the system is defined by $C_1/C_2 = 3$, $T_0 = 1$, $\kappa = 1$, and $\kappa_{\text{th}} = \kappa_{\text{el}} = 1$ (—) or 10 (---). The units of A and τ are arbitrary.

dinary availability. The upper line labeled A_{rev} is the total availability of the initial state and hence the maximum work that could be extracted reversibly with the environment at T_0 . This is not the upper limit to A , $A(\infty)$, because the finite conductance κ always permits the two reservoirs to come to thermal equilibrium, whether or not the engines run infinitely slowly. The true limit, A_∞ , is only the same as A_{rev} when the initial state $T_{1i} = T_{2i}$, that is, when the initial constrained state of the system is in internal equilibrium. If that internal equilibrium condition is not met, the infinite-time limit of finite-time thermodynamics does not correspond to the limit of reversible thermodynamics, by which we mean that no entropy is produced in any part of the system. The two pairs of curves are for all conductances equal ($\lambda = \lambda_{1h} = \lambda_{1l} = \lambda_{2h} = \lambda_{2l} = 1$) (—), a moderately strongly damped system, and for the engine conductances 10 times as large as the relaxation conductor ($\lambda = 1$, $\lambda_{1h} = \lambda_{1l} = \lambda_{2h} = \lambda_{2l} = 10$) (---), a weakly damped system. As is evident from Figure 6, $A \propto \tau$ for short times and only slowly approaches the upper limit A_∞ . Similarly the approach of ϵ to 1 is also slow, even more so than A , but it starts out with a nonzero value, generally in the

neighborhood of $1/2$. The rationale of this is that, with work as our objective function, the optimization first attempts to increase W and later ϵ .

These results are distinctly different from those obtained by reversible thermodynamics: (1) $A(\tau) \ll A_{\text{rev}}$, except for very long times τ ; (2) even $A(\infty) < A_{\text{rev}}$, unless $T_{1i} = T_{2i}$; (3) in most situations, when all five conductances are of the same order of magnitude, roughly only half of the drop in availability of the two reservoirs is captured as work, compared to $\epsilon = 1$ for reversible operation (cf. the linear model of section V, eq 33). This effectiveness of one-half has actually been proposed as a general conjecture for all power-producing systems.¹⁹ In the general case of many interacting systems (see Figure 2) the finite-time effects would be even greater.

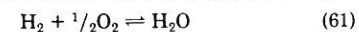
The calculations reported here are for continuous-flow engines, using the instantaneous constraint equation 17b. A few exploratory calculations were also carried out with the cycle-averaged constraint 17a. Differences were very small, the most significant being that the lower internal temperatures T_{el} remained constant within each cycle.

C. Other Interpretations. Apart from the general definition of finite-time availability, eq 5, the entire treatment so far has been in terms of heat flows and heat engines. However, the concepts and the model are not limited to mechanical systems. Rather, they can be given a number of other interpretations simply by renaming the variables or by modifying the equations of motion or constraint equations slightly. The general conclusions remain unchanged. For example, to treat a hydraulic system, the resistors $1/\kappa_{1h}$ and $1/\kappa_{1l}$ can be directly translated into viscosity of the fluid in the pipes, κ_{ij} are leaks between reservoirs, and the reservoirs are compressed fluid reservoirs. Turbine configurations come in this category too. In a realistic description there must, of course, be a generator system to charge the reservoirs in addition to the engine system. This can be viewed simply as the model operated in reverse with the initial temperatures/pressures below the final ones. For lightly damped systems this "mirror image" will behave similarly to its engine counterpart. However, strongly damped systems show no resemblance between forward and backward optimal operation. An analogous behavior was observed for an engine with thermal resistance, friction, and heat leak⁵ where a bifurcation separated the engine performance into a single-optimum thermally dominated region and a double-optimum frictionally dominated region, whereas heat pump operation was thermallike at all rates.

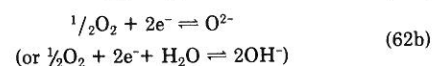
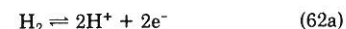
Furthermore, the model of Figure 3 may be translated into molecular physics to describe the interaction of two degrees of freedom of a molecule. We may take reservoir 1 to be vibrational excitation and reservoir 2 rotational excitation, for example. In the two-reservoir model each degree of freedom must either be thermally distributed, i.e., be described by an internal temperature, T_{vib} or T_{rot} , or consist of only two energy levels, whereas the general model of Figure 2 can handle any distribution. Then energy flow through κ becomes internal relaxation, the two engines may be lasers with light carrying away the work, the surrounding resistors represent the molecular rate constants, and finally T_0 is the temperature of the surrounding translational heat bath. This model is akin to the lasing system of ref 9 but, as a two-reservoir model, does not contain sufficient detail to reproduce the surprising conclusion obtained there that increasing a particular rate of relaxation increases work output. Actually adding such connections— κ_{ij} in the notation of Figure

2—must be taken as a change in the generic model as defined in eq 5 and can therefore indeed increase work output.

As a last example consider the two reservoirs to contain chemical substances which can react, e.g., according to



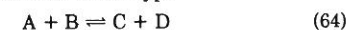
The substances need not be spatially separated. Then the temperatures of Figure 3 translate into chemical potentials or, for simplicity, into concentrations c_α . Each engine is a chemical half-reaction



which operates reversibly. If the process is heterogeneous as in a typical fuel cell, the resistors represent diffusion to and from the catalytic surfaces according to Fick's law

$$j_\alpha = D_\alpha(c'_\alpha - c_\alpha) \quad (63)$$

for each substance α , where D_α is the diffusion constant and c'_α and c_α are the concentrations on the catalytic surface and in the reaction mixture, respectively. In the example above c_{H^+} and c_{OH^-} are considered to be their equilibrium values represented by the environment. Note that eq 63 is completely analogous to the thermal equation 40. The relaxation resistor κ represents uncatalyzed (uncaptured) reaction between the reactants. Looked at this way our model describes how to obtain the most energy from, e.g., a fuel cell in time τ . If energy is no objective, but one wants a reaction of the type



consider it implemented as two pairs of half-reactions back

to back such that the work output of one drives the other. The description using half-reactions is purely to emphasize the analogy with the thermal treatment in the previous sections. Finite-time availability is just as important in homogeneous reactions, and we believe that the notion of nonvanishing rate will be very useful for designing and describing chemical reactions in general.

Acknowledgment. Part of this work was performed while M.H.R. was on sabbatical visits to the University of Chicago and the University of Copenhagen. He wishes to express his gratitude to his hosts at both institutions and to the National Science Foundation and the Danish Science Foundation for their financial support. B.A. wants to thank NATO for a travel grant. Part of this work was carried out at the Aspen Center for Physics, whose hospitality we appreciate. We thank Peter Salamon for his helpful comments.

Appendix

Extrapolation Procedure to Initial State. As mentioned in section VIB, the optimal control problem has to be solved backward from a guessed final state even though it is the initial state which is specified. In order to find that final-state T_f whose optimal trajectory was less than a prescribed distance from the desired initial-state T_i , a time τ earlier, a simple linear two-dimensional extrapolation procedure was set up.

First a nonoptimal trajectory was integrated from T_i for time τ to obtain an estimate of T_f which, along with two other points in the vicinity of this estimate, formed starting points from which optimal trajectories were calculated backward. Two-dimensional extrapolation in T_f from these initial states with replacement of the trajectory which was furthest away from T_i was repeated until the error was less than a prescribed value.

(19) H. T. Odum and R. C. Pinkerton, *Am. Sci.*, **43**, 331 (1955).

*The reader my expectant mind projected
was, gentle reader, not a bit like you.
So if this book was less than you expected,
believe me, I've been disillusioned too.*

(Piet Hein: Grooks VI)

FINITE-TIME THERMODYNAMICS

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1983

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