

dence. We also need to examine whether any directional principles resembling the second law of thermodynamics apply when different states of the same total free energy are obtained in open and closed systems. Such problems are reserved for future consideration.

Acknowledgment. We thank Drs. Patrick De Kepper

and Dan Luss for helpful discussions. This work was supported in part by National Science Foundation Grants CHE8005500 to the University of Oregon and CHE8204085 to Brandeis University. R.N. also thanks the Max-Planck-Institut für Biophysikalische Chemie in Göttingen for hospitality during revisions of an initial version of the manuscript.

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 :

$$\Delta A = A(t_f) - A(t_i) \quad (3)$$

(1) J. W. Gibbs, "Collected Works", Vol. 1, Yale University Press, New Haven, CT, 1948, pp 49 ff.

(2) R. A. Gaggioli, Ed., "Thermodynamics: Second Law Analysis", American Chemical Society, Washington, DC, 1980.

(3) R. C. Tolman and P. C. Fine, *Rev. Mod. Phys.*, **20**, 51 (1948).

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

(4) J. H. Keenan, "Thermodynamics", MIT Press, Cambridge, MA, 1970.

(5) B. Andresen, P. Salamon, and R. S. Berry, *J. Chem. Phys.*, **66**, 1571 (1977).

(6) Y. B. Band, O. Kafri, P. Salamon, *J. Appl. Phys.*, **53**, 8 (1982).

(7) M. Mozurkewich and R. S. Berry, *J. Appl. Phys.*, **53**, 34 (1982).

(8) F. L. Curzon and B. Ahlborn, *Am. J. Phys.*, **43**, 22 (1975).

(9) A. Ben-Shaul and R. D. Levine, *J. Non-Equilib. Thermodyn.*, **4**, 363 (1979).

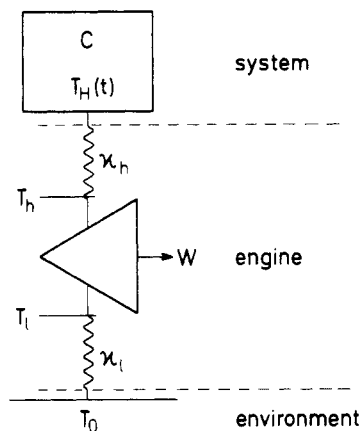


Figure 1. Schematic subdivision of a total system, in this case a finite heat reservoir of temperature $T_H(t)$ drained by an endoreversible engine into the environment at temperature T_0 . The internal reversible engine operates between $T_H(t)$ and $T_l(t)$.

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

For the endoreversible engine depicted in Figure 1 the maximum extractable power is⁸

$$\dot{W}_{\max} = \frac{\kappa_l \kappa_h}{\kappa_l + \kappa_h} (T_H^{1/2} - T_0^{1/2})^2 \quad (7)$$

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

$$dS/dt = \kappa(T - T_0)/T \quad dV/dt = aV \quad (13)$$

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

(10) P. Salamon and A. Nitzan, *J. Chem. Phys.*, **74**, 3546 (1981).

(11) P. Salamon, B. Andresen, and R. S. Berry, *Phys. Rev. A*, **15**, 2094 (1977).

(12) M. J. Ondrechen, B. Andresen, M. Mozurkewich, and R. S. Berry, *Am. J. Phys.*, **49**, 681 (1981).

(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).

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 $\{Y_{j0}, j=1,2,\dots\}$, 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

$$\dot{S}_{M\alpha} = \sigma_{\text{ah}} + \sigma_{\text{al}} + \dot{S}_{\text{m}\alpha} \quad (16)$$

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

$$\int_{t_i}^{t_i+\tau_\alpha} \dot{S}_{\text{m}\alpha}(t) dt = 0 \quad (17a)$$

where τ_α is the duration of one cycle of the machine labeled

by α , or, if the machine is a continuous-flow machine, the constraint becomes

$$\dot{S}_{\text{m}\alpha} = 0 \quad (17b)$$

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 $\dot{S}_{\text{m}\alpha}$, σ_{ah} , and σ_{al} . We shall take

$$\sigma_{\text{ah}} = -J_\alpha(Y_\alpha - Y_{\text{ah}}) \quad (18a)$$

$$\sigma_{\text{al}} = -J_{\alpha 0}(Y_{\alpha 0} - Y_{\alpha l}) \quad (18b)$$

$$\dot{S}_{\text{m}\alpha} = -J_\alpha Y_{\text{ah}} - J_{\alpha 0} Y_{\alpha l} \quad (19)$$

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_{ah} 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. $\dot{S}_{\text{m}\alpha}$ 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_{ah} '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_{ah} , the latter contains Y_{ah} , 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

$$\int_{t_i}^{t_i+\tau_\alpha} [J_\alpha Y_{\text{ah}} + J_{\alpha 0} Y_{\alpha l}] dt = 0 \quad (20a)$$

or

$$J_\alpha Y_{\text{ah}} + J_{\alpha 0} Y_{\alpha l} = 0 \quad (20b)$$

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 $\{Y_{\text{ah}}\}$ and $\{Y_{\alpha l}\}$. It is convenient to distinguish the equations for the subset $\{Y_\alpha\}$, which are coupled to the working devices (cf. eq 15), and the remainder, $\{Y_\lambda\}$:

(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.

$$\dot{Y}_\alpha = K_\alpha(Y_1, Y_2, \dots) + J_\alpha(Y_\alpha, u_\alpha) \quad (22a)$$

$$\dot{Y}_\lambda = K_\lambda(Y_1, Y_2, \dots) \quad (\lambda \neq \alpha) \quad (22b)$$

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 absence 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 we are 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 $\{Y_\beta\}$ 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.

IV. 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 function

$$L = V_f + \int_{t_i}^{t_f} (H - \sum_\beta \psi_\beta \dot{Y}_\beta) dt \quad (23)$$

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 change 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

$$\dot{\psi}_\beta = -\frac{\partial H}{\partial Y_\beta} = \left(\frac{\partial \sigma_{\alpha h}}{\partial Y_\beta} + (1 - \lambda_\alpha) \frac{\partial \dot{S}_{m\alpha}}{\partial Y_\beta} \right) \delta_{\alpha\beta} + \frac{\partial \sigma}{\partial Y_\beta} - \sum_\gamma \psi_\gamma \frac{\partial F_\gamma}{\partial Y_\beta} \quad (25)$$

$$\psi_\beta(t_f) = \partial V_f / \partial Y_\beta(t_f) \quad (26)$$

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 this 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 $Y_{\alpha l}$ yield

$$0 = \frac{\partial H}{\partial Y_{\alpha h}} = -\frac{\partial \sigma_{\alpha h}}{\partial Y_{\alpha h}} + (\lambda_\alpha - 1) \frac{\partial \dot{S}_{m\alpha}}{\partial Y_{\alpha h}} + \psi_\alpha \frac{\partial J_\alpha}{\partial Y_{\alpha h}} \quad (27)$$

$$0 = \frac{\partial H}{\partial Y_{\alpha l}} = -\frac{\partial \sigma_{\alpha l}}{\partial Y_{\alpha l}} + (\lambda_\alpha - 1) \frac{\partial \dot{S}_{m\alpha}}{\partial Y_{\alpha l}} \quad (28)$$

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 $Y_{\alpha l}(t_f)$ 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 , $Y_{\alpha h}$, $Y_{\alpha l}$, 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

(16) (a) 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.

way related to the usual linearization of the flux-force relation in nonequilibrium thermodynamics. In particular, \mathbf{M} 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

$$H = -\frac{1}{2} \sum_{\alpha} K_{\alpha} C_{\alpha}^2 - \frac{1}{2} \sum_{\alpha\beta} (Y_{\alpha} - Y_{\beta})^2 M_{\alpha\beta} + \sum_{\alpha} \psi_{\alpha} K_{\alpha} C_{\alpha} + \sum_{\alpha\beta} \psi_{\alpha} M_{\alpha\beta} (Y_{\beta} - Y_{\alpha}) \quad (30)$$

The variational principle leads to the results

$$\psi_{\alpha} = C_{\alpha}$$

$$\dot{C}_{\alpha} = \sum_{\beta} (M_{\alpha\beta} + M_{\beta\alpha}) (Y_{\alpha} - Y_{\beta}) - (\sum_{\beta} C_{\beta} M_{\beta\alpha} - C_{\alpha} \sum_{\beta} M_{\alpha\beta}) \sum_{\beta} (C_{\beta} - C_{\alpha}) M_{\alpha\beta} \quad (31)$$

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 a constant of motion along the optimal trajectory. This can be seen from the equations for \dot{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 the different subsystems do not interact. We find for each subsystem, when the final states $Y_{\alpha}(t_f)$ are not specified, that

$$\Delta A / T_0 = -2\Delta S_{\text{tot}} \quad (32)$$

so

$$|A / \Delta A| = \frac{1}{2} \quad (33)$$

and that $A(\tau)$ is proportional to the duration τ of the process. If the final state is prescribed

$$\Delta A / T_0 = (Y_{af} - Y_{ai}) N_{\alpha} Y_{\alpha 0}$$

$$C_{\alpha} = -N_{\alpha} Y_{\alpha 0}$$

$$Y_{af} - Y_{ai} = K_{\alpha} C_{\alpha} \tau$$

$$\Delta S_{\text{tot}} = \frac{1}{2} (Y_{af} - Y_{ai})^2 / (K_{\alpha}^2 \tau)$$

$$A / T_0 = (Y_{af} - Y_{ai}) N_{\alpha} Y_{\alpha 0} - \frac{1}{2} (Y_{af} - Y_{ai})^2 / (K_{\alpha}^2 \tau) \quad (34)$$

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 constant of motion connecting the control variables, and the trajectories of the optimal paths can be found from the optimal H . These trajectories have a characteristic form in the space with coordinates of the state variables $\{Y_{\alpha}\}$ and some 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.

VI. 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

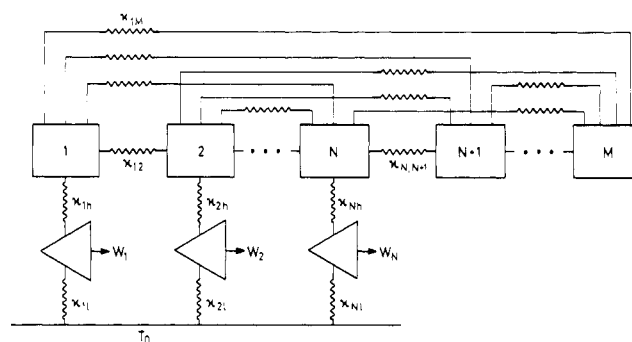


Figure 2. Thermal interaction of M reservoirs. The first N are also connected to the environment through endoreversible engines producing work W_1, \dots, W_N .

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 $\kappa_{\alpha l}$, and by the temperature of its working fluid at the two ends of the engine, $T_{\alpha h}$ and $T_{\alpha l}$. 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

$$\sigma_{\alpha h} = \dot{Q}_{\alpha h} \left(\frac{1}{T_{\alpha}} - \frac{1}{T_{\alpha h}} \right) \quad (37a)$$

$$\sigma_{\alpha l} = \dot{Q}_{\alpha l} \left(\frac{1}{T_0} - \frac{1}{T_{\alpha l}} \right) \quad (37b)$$

$$\dot{S}_{m\alpha} = 0 \quad (17b)$$

$$\sigma = -\sum_{j=1}^M T_j^{-1} \left(\sum_{r=1}^M \dot{Q}_{jr} \right) \quad (37c)$$

The constraint eq 20b becomes

$$\frac{\dot{Q}_{\alpha h}}{T_{\alpha h}} + \frac{\dot{Q}_{\alpha l}}{T_{\alpha l}} = 0 \quad (38)$$

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 $\dot{Q}_{\alpha l}$ given by linear laws, we have

$$\dot{Q}_{\alpha h} = \kappa_{\alpha h} (T_{\alpha h} - T_{\alpha}) \quad (40a)$$

$$\dot{Q}_{\alpha l} = \kappa_{\alpha l} (T_{\alpha l} - T_0) \quad (40b)$$

We now introduce the control variables

$$u_{ah} = T_{ah}/T_\alpha \quad u_{al} = T_{al}/T_0 \quad (41)$$

With these definitions the total entropy production of the heat engines becomes

$$\dot{S}_{tot} = \sum_{\alpha=1}^N [\kappa_{ah}(u_{ah} + u_{ah}^{-1} - 2) + \kappa_{al}(u_{al} + u_{al}^{-1} - 2)] + \sigma \quad (42)$$

and the Hamiltonian

$$H = -\sum_{\alpha=1}^N \left[\kappa_{ah} \left(u_{ah} + \frac{1 + \lambda_\alpha}{u_{ah}} - 2 - \lambda_\alpha \right) + \kappa_{al} \left(u_{al} + \frac{1 + \lambda_\alpha}{u_{al}} - 2 - \lambda_\alpha \right) \right] + \sum_{j=1}^M \left[\frac{1}{T_j} - \frac{\psi_j}{C_j} \right] \sum_{r=1}^M \dot{Q}_{jr} + \sum_{j=1}^M \frac{\psi_j}{C_j} \sum_{\alpha=1}^N \delta_{\alpha j} \dot{Q}_{\alpha h} \quad (43)$$

where

$$\dot{Q}_{\alpha h} = \kappa_{\alpha h} T_\alpha (u_{\alpha h} - 1) \quad (44)$$

and the λ_α are the Lagrange functions defined following eq 24.

Using eq 25–28 and eq 36 one can now show that

$$u_{al}(t) = \{1 + \lambda_\alpha(t)\}^{1/2} \quad \text{for } \kappa_{al} \neq 0 \quad (45)$$

$$1 - \frac{1 + \lambda_\alpha}{u_{ah}^2} - \frac{T_\alpha \psi_\alpha}{C_\alpha} = 0 \quad \text{for } \kappa_{ah} \neq 0 \quad (46)$$

$$\psi_j(t_f) = -C_j(1/T_0 - 1/T_{jf}) \quad (47)$$

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

$$(u_{al}/u_{ah})_f^2 = T_\alpha/T_0 \quad (48)$$

or

$$(T_{al}/T_{ah})_f = (T_0/T_{\alpha f})^{1/2} \quad \text{for } \kappa_{ah} \neq 0 \quad (49)$$

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 ψ_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}_{jr}^{NL} , the nonlinear part of \dot{Q}_{jr} , when \dot{Q}_{jr} is an odd function of $T_j - T_r$, vanishes, and

$$\sum_{j=1}^N T_j \psi_j$$

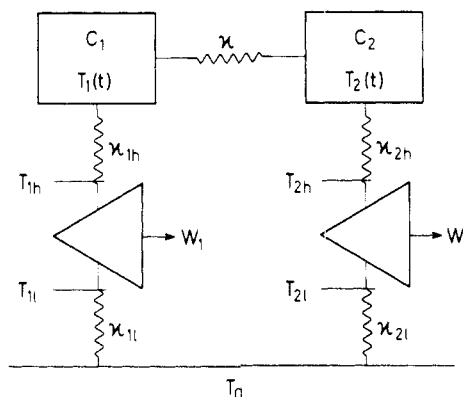


Figure 3. Model system consisting of two reservoirs at temperatures $T_1(t)$ and $T_2(t)$ and the environment at temperature T_0 . The reservoirs produce work through their respective engines in competition with internal relaxation through the conductance κ .

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_{jf} 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

$$\begin{aligned} \cos \theta &= [C_1(1 + \lambda_1)]^{1/2} / Ku_{1h} \\ \sin \theta &= [C_2(1 + \lambda_2)]^{1/2} / Ku_{2h} \end{aligned} \quad (56)$$

Loosely speaking, θ describes the relative rate of drainage

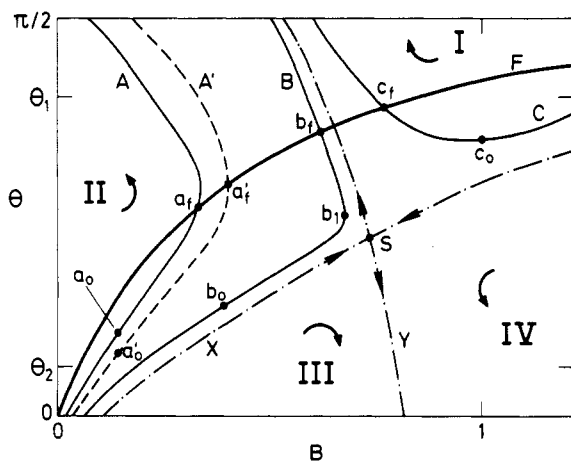


Figure 4. Idealized optimal time evolution paths for the model system. All final states lie on the heavy curve marked F, and the infinite-time paths are labeled X and Y. B and θ are defined in eq 55 and 56, respectively. Time direction in the four regions I–IV is shown by the arrows.

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 $B = T_2/T_{1i}$ 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_1 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 separatrices 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 separatrices 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 separatrices 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-

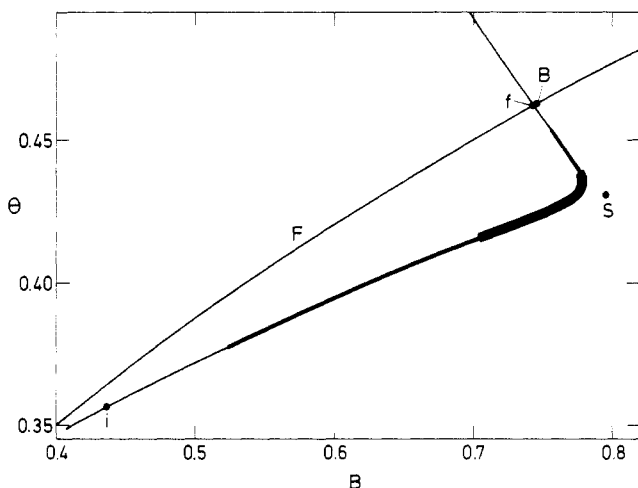


Figure 5. Calculated optimal time evolution path for the model system defined by $C_1/C_2 = 3$, $T_0 = 1$, $\kappa = 1$, and $\kappa_{\text{oh}} = \kappa_{\text{ol}} = 10$. The initial state is $T_{1i} = 8.8$, $T_{2i} = 4.0$, and the duration $\tau = 2$; 90% of this time is spent along the heavy segment 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.

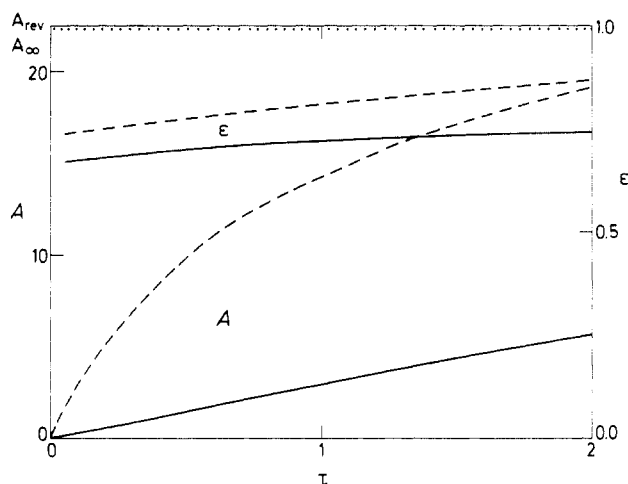


Figure 6. Finite-time availability, A (left scale), and effectiveness, ϵ , in producing this work (right scale) for the model system as a function of process duration, τ . The initial state is $T_{1i} = 10$, $T_{2i} = 5$, and the system is defined by $C_1/C_2 = 3$, $T_0 = 1$, $\kappa = 1$, and $\kappa_{\text{oh}} = \kappa_{\text{ol}} = 1$ (—) 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 ($\kappa = \kappa_{1h} = \kappa_{1l} = \kappa_{2h} = \kappa_{2l} = 1$) (—), a moderately strongly damped system, and for the engine conductances 10 times as large as the relaxation conductor ($\kappa = 1$, $\kappa_{1h} = \kappa_{1l} = \kappa_{2h} = \kappa_{2l} = 10$) (---), 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_{ol} remained constant within each cycle.

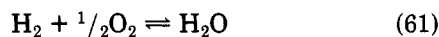
C. Other Interpretations. Apart from the general definition of finite-time availability, eq 5, the entire treatment so far has been in terms of heat flows and heat engines. However, the concepts and the model are not limited to mechanical systems. Rather, they can be given a number of other interpretations 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 $1/\kappa_{jh}$ and $1/\kappa_{jl}$ 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 thermally like 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

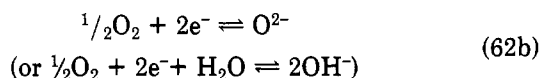
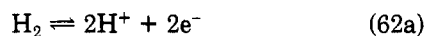
(19) H. T. Odum and R. C. Pinkerton, *Am. Sci.*, 43, 331 (1955).

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 \mathbf{T}_f whose optimal trajectory was less than a prescribed distance from the desired initial-state \mathbf{T}_i a time τ earlier, a simple linear two-dimensional extrapolation procedure was set up.

First a nonoptimal trajectory was integrated from \mathbf{T}_i for time τ to obtain an estimate of \mathbf{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 \mathbf{T}_i from these initial states with replacement of the trajectory which was furthest away from \mathbf{T}_i was repeated until the error was less than a prescribed value.

Vibrational Predissociation of H_2^- , D_2^- , and HD-Ar van der Waals Molecules

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(Received: December 22, 1982; In Final Form: March 15, 1983)

Accurate close-coupling calculations are performed for vibrationally predissociating states of $\text{H}_2\text{-Ar}$, $\text{D}_2\text{-Ar}$, and HD-Ar , using the best potential energy surface available. All the states examined have very small widths ($\Gamma \ll 10^{-6} \text{ cm}^{-1}$, corresponding to lifetimes $> 20 \mu\text{s}$). There is a pronounced tendency for predissociation to yield rotationally hot diatomic molecules, even for the $\text{H}_2\text{-Ar}$ and $\text{D}_2\text{-Ar}$ complexes where the present potential has no anisotropic terms of higher order than $P_2(\cos \theta)$. This near-resonant effect is particularly strong for HD-Ar , where all Legendre terms are present in the potential; in this case, about 50% of the HD products are formed in the highest two accessible rotational levels. There is some evidence for a rotational rainbow effect in the product rotational state distributions. Perturbation theory calculations which attempt to reproduce the accurate calculations are also reported. They successfully model the qualitative features of the close-coupling results, but are not quantitatively accurate even for these weakly coupled systems. It appears that this inadequacy is due to the need for a very accurate representation of the bound state wave function and to the neglect of important couplings between the different open channels. This conclusion is supported by the observation that very large basis sets are required to obtain convergence of the close-coupling calculations.

1. Introduction

van der Waals molecules whose monomers are internally

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excited often have enough energy to predissociate, and may do so by several mechanisms. Of particular interest here is vibrational predissociation (VP), where internal vibrational energy of one of the monomers is converted into rotational and/or translational energy of the fragments.