

# Thermodynamics in finite time: A chemically driven engine

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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.<sup>1</sup> 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.<sup>2</sup> Two ways have been developed to evaluate these bounds, one by means of Legendre–Cartan transformations which yield absolute but not unique potentials,<sup>2</sup> and the other by direct determination of the extremal values of the process variables.<sup>3</sup> 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,<sup>3</sup> which is reviewed briefly in the next section.

One has several reasonable options when one chooses

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the variable whose extremum is to be determined. Curzon and Ahlborn<sup>4</sup> 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.<sup>5</sup> 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,<sup>2,3,6,7</sup> 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  $T_3$ .<sup>3</sup> The three dimensions of the space correspond to the three rates of heat flow into each of the respective reservoirs. They are designated

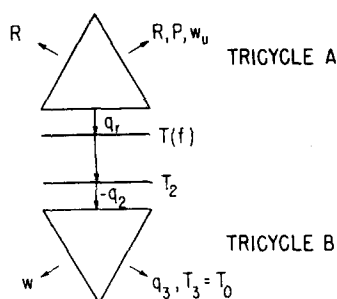


FIG. 1. A chemically driven engine as two coupled tricycles.

$q_1$ ,  $q_2$ , 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,  $w_u$  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  $R \rightarrow P$  occurs in a flow tube,

so that the time  $\tau$  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  $\tau$  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  $\rho_m$  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,<sup>8</sup> 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

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

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

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.

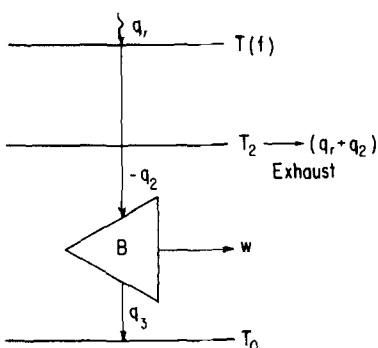


FIG. 2. A schematic diagram of a product mixture, initially at  $T(f)$ , transferring heat to the hot ( $T_2$ ) reservoir of a tricycle.

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  $R \rightarrow P$  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  $k' = A l_{0m} k_1$ . 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

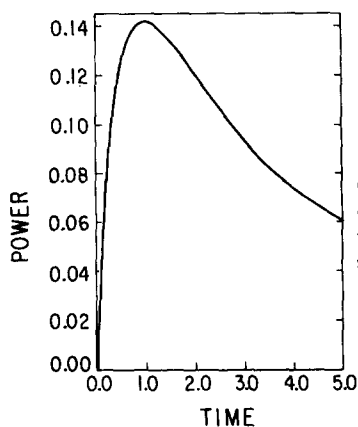


FIG. 3. The power produced (in units of  $CT_0f$ ) as a function of  $k'/f$ , which is proportional to the traversal time through the reactor, for Case I with first order kinetics, with  $u = 1$ .

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

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

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

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  $\eta$  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  $k_b$ :



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  $R \rightarrow P$  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,  $\epsilon$  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

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

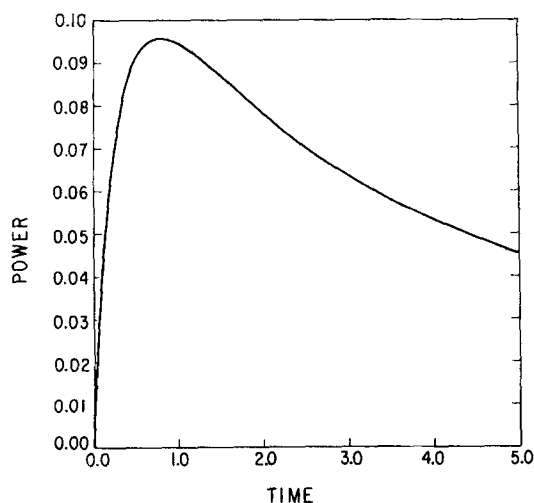


FIG. 4. The power produced (in units of  $CT_0f$ ) as a function of  $k_2R_0c'/f$  (proportional to the traversal time through the reactor) for Case I with second order kinetics, for  $u = 1$ .

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

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

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

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

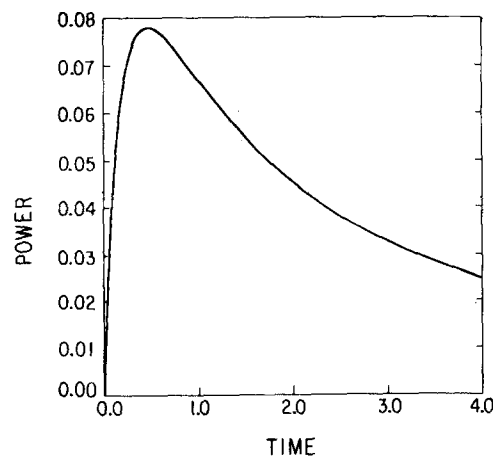


FIG. 5. The power produced (in units of  $Q'_m c' k X_0 y^{-1}$ ) as a function of reaction time (in units of  $y$ ) for a Case I system driven by a process which is first order in each of two reactants (X and Y) and second order overall, with  $u' = 1$  and  $X_0/Y_0 = 1/2$ .

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  $\int_{T_0}^{T_2} C_r(T) dT$  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 recently<sup>5</sup> 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.<sup>9</sup>

If the reaction  $R \rightarrow P$  were carried out isothermally at temperature  $T_0$  with molar entropy of reaction  $\Delta S_r$ , 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

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

When the second equation is rewritten as  $s = k' \Delta G/T_0$ , where  $\Delta G$  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:

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

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  $\eta$  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

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

and for second order kinetics

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

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.<sup>3-7,10</sup>

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.<sup>11</sup>

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.

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