

Thermodynamics in finite time: Processes with temperature-dependent chemical reactions

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The thermodynamics of two chemical systems obeying Arrhenius law kinetics are studied from the viewpoint of finite time thermodynamics. The first is the determination of the maximum thermodynamic or chemical efficiency of a synthetic process whose heat input appears as preheating to overcome an activation barrier. The second is the determination of maximum power that can be obtained from an exothermic reaction carried out in a continuous flowsystem. The maximum power, achieved with a finite, nonzero flow rate, is a sensitive function of the activation energy of the reaction.

I. INTRODUCTION

Traditional thermodynamics provides bounds on the amounts of work and heat that can be exchanged between a system and its surroundings. In some situations, such as the generation of electric power from steam, the performances of real processes come close enough to their thermodynamic limits that we can use these limits as bases of useful criteria of merit. Many other processes operate at efficiencies or effectivenesses so far from the limits set by idealized reversible thermodynamic processes that traditional thermodynamic criteria are too weak to be of any significance for them. The disparity between actual performance and the corresponding reversible limit of a process is, in many instances, due to the nonzero rate of that process. Fortunately, for a large class of processes operating in finite time, one can construct functions that act like traditional thermodynamic potentials: The changes in these functions give the natural bounds on the work or heat that a system may exchange with its surroundings, for processes operating within certain constraints.¹ The difference between these extended potentials and traditional potentials is simply that the constraints used to obtain the new functions include constraints on time or rate, in addition to any of the traditional constraints that may apply on such variables as temperature, volume, or entropy. The "finite-time potentials" may be used to provide criteria of merit that are much more realistic than those derived for reversible processes, and even to exhibit how the optimal performance of a system depends on its rate. We refer to the construction of potentials for processes operating at finite rates, and to the determination of the process paths that would yield extremal values of heat or work, as the study of "finite time thermodynamics."

The first applications of finite time thermodynamics were to mechanical systems and heat engines.¹⁻⁸ More recently, the approach has been applied to systems undergoing changes of chemical potential, either through separation by distillation⁹ or by chemical reaction.¹⁰

The last example is the precursor of the work presented here: There we optimized the power of an engine driven by an exothermic chemical reaction with finite rate for the simplistic case in which the rate coefficients are temperature independent. That exercise was useful as the first example of finite time thermodynamic analysis in which the time constraints are rate coefficients of the working fluid, rather than parameters of the coupling between the system and its surroundings. However, it was clear when that work was being done that any reasonably realistic model would have to include the temperature dependence of the rate coefficients.

In the present work, we examine the optimization of two systems undergoing chemical reactions whose rate coefficients obey an Arrhenius law $k = A \exp(-E_a/T)$. (We absorb the gas constant into the activation energy.) The two examples are (1) the determination of the maximum fuel efficiency (thermodynamic efficiency in the usual meaning of work out per unit heat in from fuel) or chemical efficiency (amount of chemical product per unit heat in) from a chemical synthesis, and (2) the determination of maximum power obtainable from a heat engine driven by an exothermic chemical reaction. The first is treated in Sec. II, and the second in Sec. III.

Let us go through a qualitative argument as a preliminary illustration of how the finite rate of operation governs the performance of a process. We take the second example above, a heat engine driven by an exothermic reaction in a flow tube. If the rate coefficient is effectively independent of temperature, we know that maximum power is achieved with some positive flow rate.¹⁰ If the flow of reacting mixture is very slow, the reaction goes to completion in the flow tube, and the maximum heat per mole of starting material is produced, so that heat is transferred to the engine at a high temperature. However, if the flow is slow, the heat transferred per unit time is also small. On the other hand, if the flow is very fast, the reaction has insufficient time to go to completion, and heat transferred to the engine goes at a temperature below its maximum. Hence, the efficiency and power fall off at high flow rates. Between these two extremes is an intermediate flow rate for which the power produced is a maximum. This happens even if the rate coefficient of the heat-generating reaction is independent of temperature. For the more realistic case in which the rate of the reaction

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obeys an Arrhenius law, one would expect the power production to be even more sensitive to the flow rate. Obviously, in an exothermic, Arrhenius-law reaction, a kind of cooperative effect is created; the heat of reaction increases the rate of reaction, which in turn produces heat at a faster rate.

II. OPTIMIZING THE EFFICIENCY OF A PREHEATED ISOTHERMAL CHEMICAL REACTION

Consider the reaction



of arbitrary order in any of the species $\{R_1, R_2, \dots, R_n\}$, i. e., R or any reaction intermediate:

$$\frac{dP}{dt} = k[R_1]^{a_1}[R_2]^{a_2} \cdots [R_n]^{a_n}, \quad (2)$$

in which the rate coefficient k is given by an Arrhenius law

$$k = A \exp(-E_a/T). \quad (3)$$

For convenience, we express the activation energy in units of the gas constant, i. e., we write E_a to mean the activation energy divided by R , so E_a is expressed in K. Suppose further that the reaction mixture is preheated in order to start the reaction at a suitable rate, and that the reactants rapidly absorb and equilibrate all of the heat put in relative to the time scale of the chemical reaction.

Suppose the reaction mixture requires heat to raise its temperature from T_0 to T and to maintain its temperature at T thereafter. The first contribution to the total heat flow into the reaction mixture is

$$q = fQ = f \int_{T_0}^T C(T) dT, \quad (4)$$

where f is the flow rate of the reaction mixture (mol/time), and Q is the heat added to the reactants from outside sources to bring their temperature to T , in the same molar units used to define f ; $C(T)$ is the heat capacity of the mixture. Additional heat to maintain the temperature of the system must be supplied at a rate equal to the molar heat of reaction $\Delta H_r(T)$ times the rate of reaction:

$$\bar{q} \equiv q_{\text{thermodynamic}} = \Delta H_r(T) \frac{dP}{dt}. \quad (5)$$

The term \bar{q} is irrelevant to the remainder of the analysis and will be neglected hereafter.

The amount of product made per unit of heat provided from outside sources, which we call the *chemical efficiency*, is

$$\mathcal{E} = \frac{(dP/dt)}{Qf}. \quad (6)$$

The chemical efficiency is directly proportional to the thermodynamic efficiency η , the amount of useful chemical work performed per unit of heat supplied to drive the process. If $\Delta\mu$ is the change in chemical potential when 1 mol of P is made from reactants, then the two efficiencies are directly proportional, with $\Delta\mu$ the proportionality factor:

$$\mathcal{E} \cdot \Delta\mu = \eta. \quad (7)$$

In order to find the temperature at which \mathcal{E} is maximized, Q of Eq. (4) must first be calculated. For a reaction mixture with completely general heat capacity $C(T)$, the optimal temperature is a solution of $d\mathcal{E}/dT = 0$, which amounts to the integral equation

$$Q \equiv \int_{T_0}^T C(T) dT = \frac{C(T) T^2}{E_a}. \quad (8)$$

Equation (8) becomes a high-order polynomial equation if $C(T)$ is a polynomial in T , and one cannot expect to find a tractable analytic solution.

The problem would look simpler if one were to assume that the heat capacity of the mixture is constant over the entire temperature range from T_0 to T . However, the model implicitly presumes that $T \gg T_0$, so such an approximation would be foolhardy. Rather, it is better to assume that the reactants can be heated without reacting from T_0 to a higher temperature T' by the addition of a knowable quantity of heat Q' :

$$Q' = \int_{T_0}^{T'} C(T) dT. \quad (9)$$

Then we imagine that the mixture is heated (or cooled) over a short range of temperature, T' to T , short enough that the heat capacity of the mixture is constant. The total amount of heat added is thus

$$\begin{aligned} Q &= Q' + \int_{T'}^T C dT \\ &= Q' + C(T - T'). \end{aligned} \quad (10)$$

We define an effective temperature

$$\theta = T' - Q'/C \quad (11)$$

so

$$Q = C(T - \theta). \quad (12)$$

Presumably, one can find a suitable value for T' if one knows the approximate rate at which one wants to operate the process. Of course, once the optimal T is found, it is obligatory to check that it is indeed near enough to T' so that Eq. (10) is approximately valid. If it is not, one must choose a better T' and repeat the calculation.

We now wish to find the temperature T at which \mathcal{E} is maximized. In other words, we shall determine the amount of preheating that maximizes the chemical or thermodynamic efficiency of the synthesis. We construct $d\mathcal{E}/dT$ and set it equal to zero:

$$\begin{aligned} \frac{d\mathcal{E}}{dT} &= [Cf(T - \theta) A \mathcal{R}(E_a/T^2) \exp(-E_a/T) \\ &\quad - A \mathcal{R} Cf \exp(-E_a/T)] / [Cf(T - \theta)]^2 \\ &= 0, \end{aligned} \quad (13)$$

where

$$\mathcal{R} = \prod_{i=1}^n [R_i]^{a_i}. \quad (14)$$

The roots of Eq. (13) are the two temperatures T_+ and T_- for which extremal values of the efficiency \mathcal{E} are achieved:

$$T_{\pm} = \frac{1}{2} E_a \pm \frac{1}{2} \sqrt{E_a^2 - 4\theta E_a}. \quad (15)$$

Note that, in general, E_a will be large relative to 4θ and that this is also a necessary condition for E_a to be independent of temperature. In the limit

$$E_a \gg 4\theta \quad (16)$$

the extremal value of \mathcal{E} occur at

$$T_+ \cong E_a - \theta, \quad (17)$$

$$T_- \cong \theta. \quad (18)$$

Note that $T_- = \theta \equiv T' - Q'/C$ corresponds to the uninteresting limit of no preheating [see Eq. (12)]. We now must find out if T_+ corresponds to a minimum or maximum \mathcal{E} . The second derivative of \mathcal{E} evaluated at $d\mathcal{E}/dT = 0$ is given by

$$\left. \frac{d^2\mathcal{E}}{dT^2} \right|_{\mathcal{E}'=0} = \frac{A\mathcal{R}}{Cf} \exp(-E_a/T) (T - \theta)^{-3} \left(\frac{2\theta}{T} - 1 \right), \quad (19)$$

so that

$$\mathcal{E}'' > 0, \quad \text{for } T < 2\theta, \quad (20)$$

$$\mathcal{E}'' < 0, \quad \text{for } T > 2\theta. \quad (21)$$

Hence, preheating is advantageous when

$$T_+ \approx E_a - \theta > 2\theta, \quad (22)$$

or, in other words, when $E_a > 3\theta$. Thus, throughout the range of applicability of inequality (16), preheating to T_+ results in a local maximum in \mathcal{E} , corresponding to maximally efficient use of the input heat. Obviously, \mathcal{E} has a singularity at $T = \theta$ corresponding to no preheating, but the rate of reaction is presumably too low to permit operation at such a low temperature, at least for cases relevant to this analysis. Upon preheating to T_+ the concomitant enhancement in rate is

$$\begin{aligned} \frac{(dP/dt)_{T=T_+}}{(dP/dt)_{T=T_0}} &= \exp \frac{E_a}{T_0} \exp \left(\frac{-1}{1 - \theta/E_a} \right) \\ &\approx \exp(E_a/T_0 - 1). \end{aligned} \quad (23)$$

Hence, preheating becomes increasingly advantageous for reactions with higher energy barriers.

At sufficiently high temperatures one must of course also consider the reverse reaction in Eq. (1) with its own Arrhenius rate equation. As shown in Ref. 10, this can be done by redefining some of the constants, so that our conclusions remain the same. However, the temperatures at which this is necessary are considerably above T_+ , since the activation energy for the reverse reaction is larger than E_a by $-\Delta H_r$, the molar heat of reaction.

III. AN ENGINE DRIVEN BY AN EXOTHERMIC ARRHENIUS-LAW REACTION

In the model termed case I of Ref. 10, the heat of reaction carried by the products of that chemical reaction is converted into work by a reversible engine. Because, in that model, the reaction product mixture has a finite heat capacity¹¹ independent of T , the efficiency of the reversible engine is

$$\eta = 1 - \frac{T_0}{T(f) - T_0} \ln[T(f)/T_0]. \quad (24)$$

Here, T_0 is the temperature of the cold reservoir of the engine and $T(f)$, a function of the flow rate f , is the temperature at which the hot product mixture enters the engine. We now analyze the power production of such an engine as a function of the flow rate f as we did in Ref. 10, except that we now include the temperature dependence of the rate coefficient of the reaction.

If no heat is lost from the reactor, all the heat released by the exothermic reaction, Q_m per mole of product, is used to heat the mixture whose heat capacity is C :

$$R_0 C \frac{dT}{dt} = Q_m \left(-\frac{dR}{dt} \right). \quad (25)$$

We consider a first order Arrhenius-law reaction $R \rightarrow P$ and let R and P indicate concentrations of these species as well as the species themselves with R_0 being the original (total) concentration of reactant. The rate of reaction is given by

$$\begin{aligned} -dR/dt &= RA \exp(-E_a/T) \\ &= kR. \end{aligned} \quad (26)$$

We define the extent of reaction

$$\epsilon = (R_0 - R)/R_0, \quad (27)$$

from which we transform Eq. (26) in the conventional way into

$$\begin{aligned} d\epsilon/dt &= (1 - \epsilon) A \exp(-E_a/T) \\ &= (1 - \epsilon) k, \end{aligned} \quad (28)$$

or

$$\epsilon = 1 - \exp \left(-\int k(t) dt \right). \quad (29)$$

This will be useful to us now to compare with the form with which we calculate the temperature of the products [Eq. (37)].

To calculate the temperature of the emerging product mixture the reactor is divided into a large number of cells of equal length. Temperature is assumed to be constant within each cell, and is given by

$$T_i = \frac{Q_m \epsilon_{i-1}}{C_i} + T_0 \quad (30)$$

for the i th cell, where ϵ_{i-1} is the extent of the reaction at the end of the $(i-1)$ th cell. The extent of reaction in the i th cell is

$$\epsilon_i = 1 - (1 - \epsilon_{i-1}) \exp(-k_i \Delta t). \quad (31)$$

The molar heat capacity in the i th cell C_i is the average of the heat capacities of the reactants and products C_r and C_p :

$$C_i = \epsilon_i C_p + (1 - \epsilon_i) C_r. \quad (32)$$

The dwell time in a single cell Δt is just the total traversal (or dwell) time in the reactor divided by the number of cells N :

$$\Delta t = t/N. \quad (33)$$

The traversal time t is inversely related to the flow rate f :

$$t = (S \cdot l) \rho_m / f, \quad (34)$$

where $(S \cdot l)$ is the reactor volume, and ρ_m is the density of the feed mixture. We assume the rate coefficient is constant within each cell:

$$k_i = A \exp(-E_a/T_i). \quad (35)$$

Note that Eq. (30) implies that there are no heat leaks—all heat produced in cells 1 through $(i-1)$ is used to heat the mixture to T_i —and that T_i is the temperature that fixes the rate coefficient throughout cell i .

The rate at which heat is released from the reaction at the end of the flow tube is therefore

$$q_{tot} = Q_m f \epsilon_N, \quad (36)$$

where the extent of reaction at the end of the N th cell is

$$\epsilon_N = 1 - \exp\left[-\left(\sum_{i=1}^N k_i \Delta t\right)\right], \quad (37)$$

which follows from the recursion relation (31). Equation (37) is the discrete form of Eq. (29), the ordinary integrated form of the first-order rate expression.

The power corresponding to Eq. (36) is

$$w(f) = q_{tot}(f) \eta(f). \quad (38)$$

The efficiency η is a function of the final temperature $T(f)$, which, in turn, is given by

$$T(f) = \frac{Q_m \epsilon_N}{C_N} + T_0. \quad (39)$$

Since flow rate and traversal time are related by Eq. (34), the power (38) also may be expressed as a function of t :

$$\begin{aligned} w(t) &= q_{tot}(t) \eta(t) \\ &= Q_m \left\{ 1 - \exp\left[-\sum_1^N k_i(t) \Delta t\right] \right\} (Sl\rho_m/t) \\ &\quad \times \left\{ 1 - \frac{T_0}{T(t) - T_0} \ln\left[\frac{T(t)}{T_0}\right] \right\}. \end{aligned} \quad (40)$$

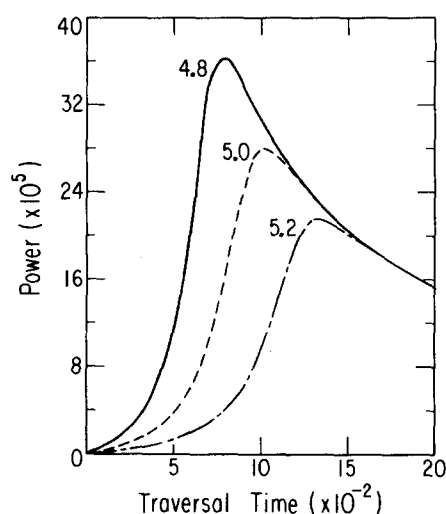


FIG. 1. Engine power (in units of Q_m per unit time) as a function of traversal time (equal to f^{-1} , i. e., $ASl\rho_m=1$) for a reversible engine driven by a first-order Arrhenius-law exothermic reaction with $Q_m/C_r T_0=1$, $C_p=C_r$, $T_0=300$ K, and for $E_a=4.8$ kcal/mol (—); 5.0 kcal/mol (---); and 5.2 kcal/mol (-.-.). The reactor was divided into 500 cells.

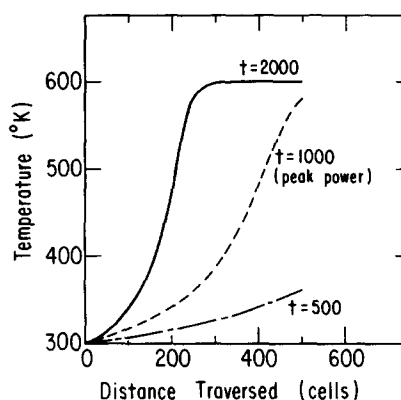


FIG. 2. Temperature (in K) as a function of distance traversed in the reactor (in cells) for a first-order Arrhenius-law reaction with $Q_m/C_r T_0=1$, $C_p=C_r$, $T_0=300$ K, and $E_a=5.0$ kcal/mol for traversal times (equal to f^{-1}) of 2000 (—); 1000 (---); and 500 (-.-.). $t=1000$ corresponds to maximum engine power.

This is a form for the power from which one can readily carry out computations.

Figure 1 shows the power, as a function of traversalal time, in units of Q_m per unit time. The time unit is taken as that of the traversalal time f^{-1} , i. e., with $ASl\rho_m=1$. For this figure, we have taken $Q_m/CT_0=1$, $C_{\text{reactants}}=C_{\text{products}}=C$, and $T_0=300$ K. The calculations were performed with 500 cells. Power functions w are shown for three values of the activation energy E_a (4.8, 5.0, and 5.2 kcal/mol). (For convenience, we use conventional chemical units for E_a to designate the curves.) The power changes so rapidly as a function of this absolute parameter that these three rather closely spaced values seemed sufficient to illustrate the results and still allow us to display the curves on linear scales.

In some respects the curve of power versus traversalal time of an engine driven by an Arrhenius-law reaction resembles that of the constant rate coefficient case.¹⁰ Maximum power is achieved for a finite, positive dwell time. The power function again depends upon Q_m/CT_0 . As in Ref. 10, a larger value for Q_m/CT_0 results in a higher maximum power achieved at an earlier time (i. e., at a higher flow rate). However, we now find a strong dependence of the power function upon the activation energy. From Fig. 1 one observes that small changes in the activation energy significantly shift both the value of the maximum power and the flow rate required to achieve that maximum.

In the present case the temperature profile within the reactor tube is also quite sensitive to the flow rate or traversalal time. Figure 2 shows the temperature, in K, of the reaction mixture as a function of the distance traversed in the reactor, measured in cells, for the case where $E_a=5.0$ kcal/mol and for $t=500$, 1000, and 2000 (in units of f^{-1}). All other parameters are the same as in Fig. 1. The time $t=1000$ is very close to the one which produces maximum power for $E_a=5.0$ kcal/mol. The highest temperature obtainable, in this case 600 K, is limited by the value chosen for Q_m/CT_0 . At the flow rate giving peak power, in this case corresponding to a dwell time of 1000, the temperature at the

end of the flow tube is only slightly less than the maximum temperature. At slower flow rates, the maximum temperature is attained before the mixture reaches the end of the tube, whereas at faster flow rates, the final temperature is not even close to the maximum. Curves of the general sort of Fig. 2 are well known in chemical kinetics, e. g., in the temperature profile of a premixed flame.¹²

As in Sec. II the reverse reaction $P \rightarrow R$ has been disregarded, partly because it can be included with limited effort¹⁰ if necessary, and partly because combustion processes have large heats of reaction and thus require very large temperatures to proceed in reverse at appreciable rates.

IV. DISCUSSION

The two examples examined above illustrate the trade-off between rapid rate of operation and thermodynamic efficiency in energy conversion processes. In the first example, an Arrhenius-law chemical synthesis, we showed that for typical values for the activation energy, there is a temperature to which the reactants may be preheated so as to maximize $(dP/dt)/q$. Equation (17) gives this temperature. There is second formal solution; $(dP/dt)/q$ has a singularity at $q=0$ (no preheating), but this will often correspond to an undesirably slow rate of synthesis.

From the second example it was found that the power produced by an engine driven by an exothermic Arrhenius-law reaction behaves in some ways like the case of a temperature independent rate, which corresponds to $E_a=0$. The maximum power is obtained at some finite, positive dwell time (or finite, positive flow rate). The more exothermic the reaction, i. e., the higher the value for Q_m/CT_0 , the higher the maximum power and the less time required to achieve the maximum power. The present system also shows a strong dependence of the power versus dwell time curve upon E_a . The higher the energy barrier, the longer it takes to attain the maximum power; the peak power also drops dramatically as E_a increases. The initial slope of the power versus time function is also decreased as the energy barrier increases. However, in the limit of long dwell time the power does not depend upon activation energy (cf. Figure 1); the three curves join at t large. This is the limit in which the reaction reaches completion before the mixture emerges from the reactor.

Along the reactor tube there is a sudden "burst" of heat, with a corresponding rapid rise in temperature, if the flow rate is sufficiently slow (see Fig. 2). This is caused by a cooperative effect characteristic of exothermic activated reactions. Maximum power is achieved at that flow rate which allows the burst in temperature to occur just before the end of the flow tube.

We can find the point of maximum extent where $d\epsilon/dt=0$; this is always $t=\infty$ where the reaction has come to equilibrium, and

$$T(\infty) \equiv T_\infty = T_0 + Q_m/C. \quad (41)$$

The second derivative $d^2\epsilon/dt^2=0$ provides the point of steepest rise of the temperature, the "reaction front." The general solution contains two exponential integrals but for large activation energy E_a (as in combustion) this time t_f behaves as

$$t_f \sim E_a^{-1} e^{E_a/T_0}. \quad (42)$$

The width of the reaction front, taken as the inverse of the slope of the extent at this point,

$$\Delta t_f \equiv \left(\frac{d\epsilon}{dt} \Big|_{t_f} \right)^{-1} \quad (43)$$

behaves for large E_a as

$$\Delta t_f \sim E_a e^{E_a/T_\infty}. \quad (44)$$

Thus, both t_f and Δt_f become infinite in the limit of large activation barriers, but the relative width becomes sharper with increasing E_a in this limit:

$$\frac{\Delta t_f}{t_f} \sim E_a^2 \exp \left[E_a \left(\frac{1}{T_\infty} - \frac{1}{T_0} \right) \right], \quad (45)$$

since the inverse temperature difference is negative. This means that, for a fixed length flow tube, the reaction front becomes increasingly localized, and one should be careful not to operate the combustor too close to the maximum power condition (i. e., with the wave front at the end of the flow tube), since small fluctuations easily could displace the sharp reaction front outside the tube.

The temperature dependence of the rate coefficient is well recognized by engineers to be a most important consideration in determining how to carry out an exothermic reaction in a flow system.^{12,13} Indeed, the power of an engine driven by such a reaction is limited by the activation energy of the reaction except in the limit of slow flow rates.

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