

Optimal Behavior of Consecutive Chemical Reactions $A \rightleftharpoons B \rightleftharpoons C^\dagger$ Thor A. Bak,[‡] Peter Salamon,[§] and Bjarne Andresen^{*,§,||}

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We analyze the maximum obtainable yield of B, starting from A in the consecutive chemical reactions $A \rightleftharpoons B \rightleftharpoons C$. We use the temperature as the control variable for a given process duration. We show that all optimal paths start with a branch at infinite temperature and derive a curve on which switching from this temperature to lower temperatures is possible. We also show that the production rate of B at the end of the reaction is equal to the incremental gain of B when the path is re-optimized for increased duration. Finally, we show that for a given set of parameters, there is a unique “maximum useful time” which may be infinite. If a duration longer than this “maximum useful time” is specified, then all reactions should be shut off for that excess amount of time, a situation that makes most optimization routines become unstable.

1. Introduction

Already a half-century ago, several authors^{1–11} considered the question of improving the yield of a chemical reaction taking place in a tubular reactor by adjusting the temperature in various parts of the reactor. The papers most pertinent to the present work are those of Bilous and Amundson³ and Aris.^{8–11} Since then, numerical and approximate techniques have become widespread.¹² Analytical approaches to understanding the structure of possible solutions, on the other hand, have met with grave difficulties and have been abandoned in favor of an engineering approach that can solve specific real-world problems of industrial interest. This circumstance, in which the search for general principles is abandoned in favor of the explicit solution of practical problems, is reminiscent of the state of energy conversion technology in the early 1970s, when R. Stephen Berry and others¹³ approached thermodynamics with the aim of extracting general principles for what is possible given the constraint of finite time. Not unlike now, practical engineering optimizations were technically up to the task of designing real applications, but there was a lack of general results concerning limits to what is possible in finite time. This paper is offered in a similar spirit. We strive to increase the analytic understanding of the possible control of chemical reactions for maximal yield with a focus on finite time. We hope our efforts are a fitting tribute in this volume dedicated to Berry's 70th birthday.

By considering a reaction in a tubular reactor, through which the reacting material is pumped and along which the temperature varies, we are in effect considering a reaction at a temperature that varies with time. If there is only one chemical reaction going on, the more or less obvious answer to the problem of getting maximum yield is to adjust the temperature so that the reaction rate is as large as possible at each point of the reactor. This, in most cases, just means keeping the temperature as high as

possible. In the following, we let the temperature be infinite, but by this we simply mean “as high as possible, other conditions taken into account”.

Aris⁸ solved the problem of two consecutive reactions using the method of dynamic programming rather than the functional differentiation used by Bilous and Amundson.³ In this paper, we use the method of optimal control theory, on the problem $A \rightleftharpoons B \rightleftharpoons C$ and derive some new conclusions regarding its optimal control.

2. System

We consider the system of first-order chemical reactions



with rate constants k_i , $i = 1..4$ depending on temperature T through Arrhenius expressions, $k_i = s_i e^{-E_i/kT}$ with activation energies E_i and collision factors s_i . These are taken to be constants, whereas the temperature T varies with time.

Starting from pure A, our objective is to produce as much B as possible within a given duration τ by varying the temperature appropriately over the time span $[0, \tau]$. We do not put any restrictions on the temperature, except that it must be positive, and we assume that it can be changed freely and instantaneously as needed.

3. Optimization Procedure

We use optimal control theory¹⁴ to derive the optimal temperature path. To avoid the omnipresent exponential functions in the rate constants, it is convenient to change the control variable from T to

$$u = e^{-1/kT} \quad (2)$$

with u restricted to the interval $[0, 1]$ corresponding to the temperature interval $[0, \infty]$ so that

$$k_i = s_i u^{E_i} \quad (3)$$

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Our objective function to be maximized is thus

$$B(\tau) = \int_0^\tau \frac{dB}{dt} dt \quad (4)$$

subject to the three constraints

$$\frac{dA}{dt} = -k_1A + k_2B \quad (5)$$

$$\frac{dB}{dt} = k_1A - k_2B - k_3B + k_4C \stackrel{\text{def}}{=} F \quad (6)$$

$$A + B + C = 1 \quad (7)$$

and with initial conditions

$$A(0) = 1, B(0) = C(0) = 0 \quad (8)$$

Substituting C from eq 7 into eq 6, the Hamiltonian for this system becomes

$$H = \lambda(-k_1A + k_2B) + \mu[(k_1 - k_4)A - (k_2 + k_3 + k_4)B + k_4] \quad (9)$$

where μ is the combined multiplier from the dynamic eq 6 and the objective function in eq 4. The Hamiltonian equations to be solved are then

$$\begin{aligned} \frac{\partial H}{\partial A} &= -\frac{d\lambda}{dt} \cdot \frac{\partial H}{\partial B} = -\frac{d\mu}{dt}, \\ \frac{\partial H}{\partial \lambda} &= \frac{dA}{dt} \cdot \frac{\partial H}{\partial \mu} = \frac{dB}{dt} \end{aligned} \quad (10)$$

subject to the boundary conditions eq 8 and

$$\lambda(\tau) = 0; \mu(\tau) = 1 \quad (11)$$

The control $u(t)$ is determined by

$$u = \operatorname{argmax}_u H \quad (12)$$

where $\operatorname{argmax} H$ means the value of u that results in the maximum possible value of H . The Hamiltonian H depends on the "temperature" u through the rate constants k_i .

4. Consequences of Optimality

Our first observation is valid much more generally than the example considered here. We first note that the Hamiltonian in any problem without explicit time dependence except for a constrained total time τ equals the incremental yield of the objective function by increasing the duration of the process

$$H = \frac{dB^*}{d\tau} \quad (13)$$

where B^* is the optimal value of the objective function B over possible controls of duration τ . It then follows that when we are maximizing the yield of one chemical, say B, without regard for the final values of other species, the marginal yield per unit of time spent is exactly equal to the rate of B production at that instant. That is

$$\frac{dB^*}{dt} = \left. \frac{dB}{dt} \right|_{t=\tau} \quad (14)$$

This follows by substituting the boundary conditions eq 11 into the Hamiltonian expression eq 9 and identifying the resulting expression as dB/dt . This observation is generally true, provided that the objective function coincides with the final value of one

of the state variables, and none of the other state variables have constrained final values, a common occurrence for chemical systems. One implication of this result is that, to first order, one can always simply continue on the optimal trajectory past the final duration without re-optimizing.

Although our ultimate aim is primarily to understand the effects of finite time limitations, consider for a moment the problem with unconstrained duration τ . For this case, the Hamiltonian must vanish and so will the final reaction rate. Suppose there is a finite optimal duration τ^* . Then any duration $\tau > \tau^*$ is also optimal because we can ensure the same yield by proceeding as before up to time τ^* and then setting the temperature to 0 ($u = 0$). Thus, the structure of such problems is highly unusual in the sense that they have a *maximal useful time* τ_{mut} . Any time allocated beyond τ_{mut} is spent at 0 temperature with the reactions shut off. Note that $u = 0$ implies that the Hamiltonian is zero and all of the dynamical equations give zero derivatives. As expected on physical grounds, the process is frozen. Such $u = 0$ branches can be added to any optimal process and still have the results satisfy all the conditions of optimality. In fact, for solutions corresponding to $H = 0$, such branches can be spliced in anywhere along the process, once the constrained time τ exceeds the maximum useful time. This fact serves to confound numerical algorithms for the solution.

It follows from eq 13 that for any for any $\tau < \tau_{\text{mut}}$, H is a positive constant. Plugging our initial conditions into H , we find that

$$H = (\mu_0 - \lambda_0)s_1u^{E_1} \quad (15)$$

The only consistent solution of eq 12 for $t = 0$ is then $u = 1$, i.e., for $\tau < \tau_{\text{mut}}$, the optimal control starts with infinite temperature.

How long should the system remain at $u = 1$? This is a difficult but chemically interesting question. The $u = 1$ trajectory is followed as long as this value of u maximizes the Hamiltonian. This situation can change either abruptly, by a better maximum showing up at another value of u resulting in a jump to that temperature, or gradually, by the minimum moving off from the boundary $u = 1$. Both of these cases are illustrated by numerical solutions in the next section. For the case where this change is gradual, we can derive an asymptotic switching curve. At the instant where the optimal control leaves $u = 1$, we must have

$$\left. \frac{\partial H}{\partial u} \right|_{u=1} = 0 \quad (16)$$

For a fixed value of H , this must be solved together with $H(u = 1) = H_0$ to find the switching curve which in general depends on the values of λ and μ . In the long time limit, when $H \rightarrow 0$, the dependence on λ and μ drop out and we find the conic section

$$\alpha A^2 + (\alpha + \beta + \gamma)AB + (\alpha + \delta)B^2 - \alpha A - \beta B = 0 \quad (17)$$

with

$$\begin{aligned} \alpha &= s_1s_4(E_1 - E_4) \\ \beta &= s_2s_4(E_4 - E_2) \\ \gamma &= s_1s_3(E_1 - E_3) \\ \delta &= s_2s_3(E_3 - E_2) \end{aligned} \quad (18)$$

Note that these curves always pass through $(A,B) = (0,0)$ and $(1,0)$.

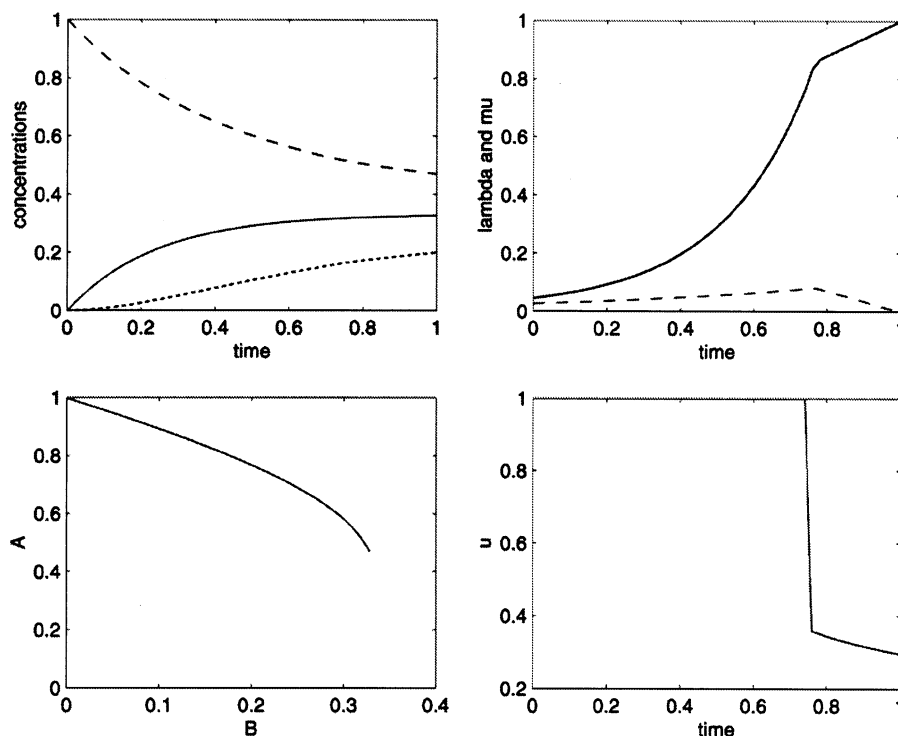


Figure 1. Optimal time sequences of the concentrations A , B , and C (frame a: dashed, solid, dotted) as well as the conjugate variables λ and μ (frame b: dashed and solid) for activation energies $E = (1, 2, 1, 3)$, collision factors $s = (0.7, 0.7, 0.7, 0.7)$ and duration $\tau = 1$. Frame c shows the phase relationship, A as function of B , for the optimal path. Frame d shows the time evolution of the control u (“temperature”) which produces the optimum yield.

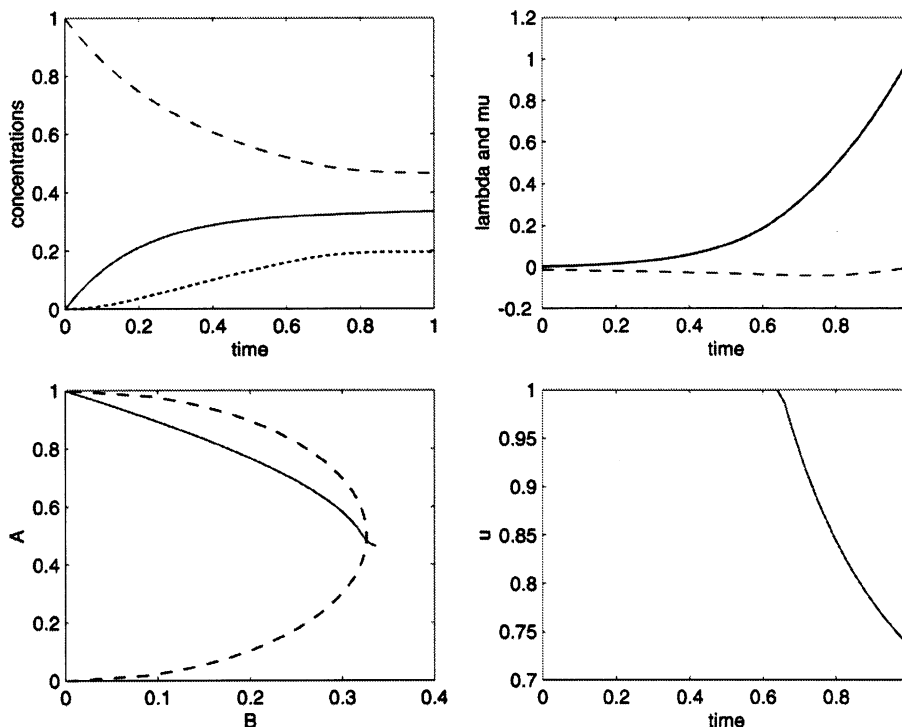


Figure 2. Optimal solution for activation energies $E=(2, 1, 3, 1)$, collision factors $s = (0.6, 0.6, 0.6, 0.6)$, and duration $\tau = 1$. The nomenclature is the same as in Figure 1 except that in frame c the switching condition from the boundary branch $u=1$ is shown dashed.

5. Numerical Optimization

We present two numerical examples of this boundary value problem solved using Krotov’s method,¹⁵ in which alternately the state differential equations (in A and B) are integrated in the forward time direction and the conjugate differential equations (in λ and μ) are integrated in the backward direction. In this way, each set of equations starts with its given boundary

conditions. After each iteration back and forth, the u that maximizes H is determined at each point along the trajectory. This method is much more efficient than the conventional “shooting method” and usually converges in just a few iterations as long as τ is not too long, i.e., as long as time is at a premium, such that it must be used carefully. For long reaction times, one or more periods of standstill may be required, as explained

above. This indeterminacy made it impossible to obtain numerical solutions for durations $\tau > \tau_{\text{mut}}$.

Figure 1, parts a and b, shows the optimal time sequences of the concentrations A , B , and C , as well as the conjugate variables λ and μ for the case in which the activation energies and collision factors used are $E = (1, 2, 1, 3)$, $s = (0.7, 0.7, 0.7, 0.7)$, and $\tau = 1$. Frame c of Figure 1 shows the phase plot of A vs B . Frame d of Figure 1 contains the control u ("temperature") which produces the optimum. This represents a system where B is more stable than A , and C is more stable still. Thus, without control, the final product would be C . The optimal path calls for a relatively long period at infinite temperature, after which the temperature jumps to a much lower value to prevent loss into C (see frame d).

Figure 2 with $E = (2, 1, 3, 1)$, $s = (0.6, 0.6, 0.6, 0.6)$, and $\tau = 1$ is the opposite case where A is the most stable substance. Again, the optimal path starts with a fairly long period at infinite temperature but then gradually breaks away to lower values as B should be favored over C (Figure 2, frame d). The cooling begins when the phase trajectory of A vs B crosses the switching curve shown in frame c of Figure 2.

6. Conclusions

The consecutive chemical reactions $A \rightleftharpoons B \rightleftharpoons C$ have been analyzed both numerically and analytically. Starting with pure A and maximizing the amount of B at the end of the given process duration, we find that all optimal paths start at infinite temperature ($u = 1$). Depending on the energy barriers and the collision factors, the optimal temperature may subsequently switch to either a finite temperature (internal optimum) or zero temperature ($u = 0$) if the "maximum useful time" is exceeded. For certain sets of parameter values, the production rate dB/dt will approach zero asymptotically for long process durations; for others, it will become zero for finite durations. If such an internal zero exists, then the optimization becomes indeterminate for longer durations because the required periods of shutting off the reaction can equally well appear anywhere during the process.

The final value of the production rate dB/dt was shown to equal the marginal productivity of additional time allocated

dB^*/dt . This shows that continuing along a path optimized for duration τ will, to first order, result in the same yield as re-optimizing for a longer duration. We remark that maximizing the yield of B for a given duration and minimizing the duration for a given yield are dual problems and thus equivalent,¹⁶ a fact that does not seem to be appreciated in recent engineering literature.¹²

The present line of development should be considered part of the continuing effort along R. Stephen Berry's original vision of finite-time thermodynamics¹³ as the exploration of general bounds on what can be achieved in finite time. Although the problem discussed in this article does not concern the energetics of the process directly, it is an attempt to find how much of A can be turned into B in a given time and thus belongs to the realm of finite-time thermodynamics. Although we have found several interesting conclusions regarding this simple system, much more remains unanswered.

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