

Finite-Time Optimization of Chemical Reactions: $nA \rightleftharpoons mB$

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We investigate the optimization of chemical reactions of the type $nA \rightleftharpoons mB$ in a closed container. The goal is to produce a maximal amount of A or B within a given finite time. The controls are taken to be volume and temperature, restricted to allowed regions in (V, β) -space with $\beta = 1/kT$. We show that the optimal path is achieved by choosing V and β such that, for the current amounts of reaction products N_A and N_B , the reaction rate $f(N_B, N_A, V, \beta) = dN_B/dt$ is at all times maximal or minimal. For different combinations of endo/exothermicity and activation energies switches between extremal values of V and/or β may be included in the optimal path. The resulting paths are described qualitatively for general values of n and m , while the reactions $2NH_3 \rightleftharpoons N_2 + 3H_2$, $N_2O_4 \rightleftharpoons 2NO_2$, and $2NO_2 \rightleftharpoons N_2 + 2O_2$ are used as concrete examples. It is observed that the optimal and equilibrium paths differ by a constant $\Delta\beta$; a possible connection with a constant thermodynamic speed path is discussed.

I. Introduction

In the past 15 years continued interest has been shown in the effects of restricting physical processes involving thermodynamic quantities to a finite duration τ . This theory of finite-time thermodynamics was originally applied to the study of Carnot engines,^{1–8} but was subsequently extended to simple chemical reactions,^{9,10} diffusion,¹¹ phase change,¹² message encoding,¹³ economics,¹⁴ etc. In all of these cases there has been a felicitous marriage between thermodynamics and optimization theory due to the fruitful questions that are posed by the introduction of finite time. For example, “Given that only a finite time is available to achieve a certain goal, how should this be accomplished such as to produce as little entropy as possible during the process” or “Given again a finite time, how can a maximal amount of work be produced during the process?”

It is natural to extend this line of thought to include processes involving chemical potentials such as chemical reactions, distillation, and other separation processes. In this paper we address the case of chemical reactions with controllable rates. The natural question that arises is how to produce a maximal amount of the desired product (or how to lose as little as possible) when the total duration of the process is fixed. A second point of interest is how to produce a given amount of material within a given time such that the work consumption or entropy production is minimal.

Here we concentrate on the question of maximization of the desired component. The reaction $nA \rightleftharpoons mB$ is chosen as a paradigm since it exhibits all the features of interest as far as the finite-time optimization with volume and temperature as controls is concerned. The more general reaction $\sum \alpha_i A_i \rightleftharpoons \sum \alpha_j A_j$ will reduce to the simpler case if the components A_i are chosen in the appropriate stoichiometric amounts. In general the difference between the two reactions will be one of complexity and not one of principle. More fundamental differences occur if, for example, consecutive reactions of the type $nA \rightleftharpoons mB \rightleftharpoons lC$ are being considered. We refer to a future publication¹⁵ for these kinds of reactions.

Of course, the question of the maximization of a desired reaction product has been addressed before.^{16–18} Here we study the general solution in sufficient analytical detail to allow us to

connect the results to the basic concepts of finite-time thermodynamics. For all the reactions considered the distance between the optimal and the equilibrium curves in (N, β) -space, $\Delta\beta = \beta^*(N) - \beta^0(N)$, is found to be constant, a result reminiscent of the constant thermodynamic speed of optimal paths in finite-time thermodynamic analyses where entropy production or availability loss are minimized. However, this distance does not approach zero as the duration τ becomes infinite, unlike usual finite-time thermodynamic expansions.

II. Determination of the Optimal Paths

The determination of the optimal procedure to produce the maximal amount of A or B for the reaction $nA \rightleftharpoons mB$ falls into two natural parts: (1) mathematical description of the reaction and formulation of the optimization problem; (2) solution of the optimization problem.

A. Mathematical Description of the Reaction. For the purpose of this study we specify the following conditions for the chemical reaction.

(1) The reaction chamber is closed; that is, neither of the two substances A and B is added or removed during the process, whereas energy and volume may flow as determined. Thus, mass conservation holds, and we can always calculate the amount of, for example, A present from our knowledge of the amount of B and the initial load.

(2) The reactor is well-stirred, and thus no concentration or temperature gradients exist within the reactor.

(3) The reaction rate is assumed to follow an Arrhenius-type expression,

$$\frac{dN_B}{dt} \equiv f(N_B, V, \beta) = V \left[a e^{-\beta E_A} \left(\frac{N_A}{V} \right)^n - b e^{-\beta E_B} \left(\frac{N_B}{V} \right)^m \right] \quad (1)$$

with forward and backward activation energies E_A and E_B , respectively. The exothermicity of the forward reaction is then $\Delta = E_B - E_A$. Further, N_B is the amount of B; $N_A = N_0 - (n/m)N_B$ is the amount of A, where N_0 is the total amount of material if all the material were present as A; and $\beta = 1/kT$ is the inverse temperature. The constants a and b are related to the collision frequencies. Without restriction of generality we can always assume that $m \geq n$. This rate expression results if the reaction is assumed to proceed by random collisions of n units of A to produce m units of B and vice versa. (If n or m

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equals 1, it is assumed that the corresponding dissociation can nevertheless occur, e.g. due to the presence of an inert gas of constant density or due to the presence of a catalyst.)

(4) The parameters that can be controlled in order to achieve the desired optimization are the volume V and the (inverse) temperature β .

(5) We will consider two types of constraints on these controls: (i) $V \in [V_0, V_1]$ and $T \in [T_0, T_1]$ (or $\beta \in [\beta_1, \beta_0]$); (ii) pressure p is constant and $\beta \in [\beta_1, \beta_0]$. In this second case we also assume that the ideal gas law holds, $p = (N_A + N_B)/V\beta$.

In both cases we allow for an instantaneous adjustment of the controls if the optimal path demands this. Clearly this is an approximation, but it is reasonable within the context of this paper, and in most realistic cases a jump in the control values can be replaced by a fast change without major effect on the optimal path.

We are now ready to formulate the optimization problem, and to make the description as concise as possible, we will consider the maximization of B; A as desired substance as well as the opposite situation of minimization emerge by simple symmetry.

Maximize the amount of product B at the end of the reaction duration τ by adjusting the volume and temperature along the path:

$$\max_{V(t), \beta(t)} N_B(\tau) \equiv N_B(0) + \int_0^\tau f(N_B, V, \beta) dt \quad (2)$$

with $f(N_B, V, \beta)$ given by eq 1 and V and β appropriately restricted.

B. Solution of the Optimization Problem. We will use the indirect optimization method developed by Rozonoer and Tsirlin,¹⁹ which is applicable to optimization problems of the form

$$\max_{u(t)} I[u(t), \tau] = \int_0^\tau f_0(x, u) dt \quad (3)$$

with

$$\dot{x} = f_1(x, u), \quad x(0) = x_0, \quad x(\tau) = x_\tau \quad (4)$$

and where $u(t)$ is the control, and $x(t)$ is the state. If $x(t)$ is monotonic in the interval $[0, \tau]$, we can change the integration over time t into an integration over amount x :

$$I[u(t), \tau] = \int_{x_0}^{x_\tau} \frac{f_0(x, u)}{f_1(x, u)} dx \quad (5)$$

with

$$\int_{x_0}^{x_\tau} \frac{1}{f_1(x, u)} dx = \tau = \frac{\tau}{x_\tau - x_0} \int_{x_0}^{x_\tau} dx \quad (6)$$

Application of the Euler–Lagrange equations to this dual optimization problem leads to the following necessary condition:

$$\frac{\partial f_0}{\partial u} f_1 - f_0 \frac{\partial f_1}{\partial u} = \lambda \frac{\partial f_1}{\partial u} \quad (7)$$

where λ is the Lagrange multiplier corresponding to the constraint. Rozonoer and Tsirlin¹⁹ have shown that the monotonicity of $x(t)$ also makes this condition sufficient.

Equation 7 is an algebraic equation for u with possibly several solutions $u_i(x, \lambda)$. Maximization of $I[u(t)]$ will now be achieved by choosing for each value of x the solution $u_i(x, \lambda)$ which

generates the largest integrand f_0/f_1 . This results in a piecewise continuous solution $u^*(x, \lambda)$. It remains to determine λ , which can be found by solving the time constraint

$$\tau = \int_{x_0}^{x_\tau} \frac{1}{f_1(x, u^*(x, \lambda))} dx \quad (8)$$

The application of this method to the problem we consider in eq 2 is straightforward. The controls V and β correspond to u , while x represents N_B . The two functions f_0 and f_1 are the same, and thus the solution of eq 7 is given by either $\lambda = 0$ or $\partial f_1 / \partial u = 0$. Since $\lambda = 0$ corresponds to the trivial statement that $N_B(t) = N_B(0) + \int dt N_B$, i.e. without any rate constraint, the optimal path will be given by

$$\frac{\partial f_1}{\partial u} = 0 \quad (9)$$

Thus, the optimal path will consist of maximizing the reaction rate $f(N_B, V, \beta)$ for each value of N_B .

Integrating eq 1 using the optimal values $V^*(N_B)$ and $\beta^*(N_B)$ results in a monotonically increasing or decreasing function $N_B^*(t)$, which makes eq 9 both a necessary and a sufficient condition for the determination of the optimal path.¹⁹ We conclude that the problem of finding the optimal path in (V, β) -space for the maximal production of substance B can always be reduced to finding the maximum of a function of two variables $f(V, \beta)$ where the location of the optimum is parameterized by N_B . This general prescription is in agreement with earlier optimization results on a more qualitative basis.^{16–18}

III. The Optimal Paths for the Reaction $nA \rightleftharpoons mB$

In the previous section we have shown that the determination of the optimal path is equivalent to determining the values of V and β for which the reaction rate $f(N_B, V, \beta)$ is maximal at every point of the path. This result is actually quite general and applies to all reactions of the type $\sum \alpha_i A_i \rightleftharpoons \sum \alpha_j A_j$, the only difference being that N_B is replaced by the standard reaction coordinate ξ . However, to demonstrate the main features that occur in many such optimal paths, we have restricted ourselves to the case $nA \rightleftharpoons mB$ where the reaction rate is assumed to be given by eq 1 and the constraints on V and β are as outlined in subsection II.A.

In principle, eight different optimization situations occur whether (1) the desired product to be maximized is A or B (since $m \geq n$ was arbitrarily chosen in section II.A.3); (2) the initial content $N_A(0)$ is small (≈ 0) or large ($\approx N_0$); or (3) the forward reaction $nA \rightarrow mB$ is exothermic ($\Delta > 0$) or endothermic ($\Delta < 0$). In addition, a number of special cases may arise if $m = n$ and/or $n = 1$ and for certain relative values of the activation energies.

Whereas the exact description of the optimal paths in sections IV and V covers all situations, our written discussion will limit itself to the case where B is the desired product in order to avoid confusion. The other case results by symmetry.

For sufficiently small initial amounts of B the optimal reaction rate is positive over the whole allowed range of V and β . Clearly we want it to remain positive for “as long as possible” (measured in N_B), and for large τ the final optimal values of V and β will thus correspond to the equilibrium situation ($f = 0$) that gives the largest amount of B for the allowed range of V and β . At this value of N_B the reaction rate f for the remaining part of the allowed region is negative.

On the other hand, for sufficiently large initial amounts of B the reaction rate is negative over the whole allowed range of V and β . Now we want f to reach the equilibrium value ($f = 0$)

TABLE 1: Optimal Paths (Read Vertically) for All Possible Reaction Conditions When V and β Are Constrained to the Intervals $V \in [V_0, V_1]$ and $\beta \in [\beta_1, \beta_0]$ (or $T \in [T_0, T_1]$)^a

	product B		product A	
	small $N(0)$	large $N(0)$	small $N(0)$	large $N(0)$
$\Delta < 0$				
$m > n > 1$	(V_0, β_1) $\rightarrow (V^V(\beta_1), \beta_1)$ $\rightarrow (V_1, \beta_1)$	(V_1, β_0) $\rightarrow (V_1, \beta_1)$	(V_0, β_1) $\rightarrow (V_0, \beta^{\beta}(V_0))$ $\rightarrow (V_0, \beta_0)$	(V_1, β_0) $\rightarrow (V_0, \beta_0)$
$m > n = 1$	(V_1, β_1)	(V_1, β_0) $\rightarrow (V_1, \beta_1)$	(V_0, β_1) $\rightarrow (V_0, \beta^{\beta}(V_0))$ $\rightarrow (V_0, \beta_0)$	(V_0, β_0)
$m = n > 1$	(V_0, β_1)	(V_1, β_0) $\rightarrow (V_1, \beta_1)$	(V_0, β_1) $\rightarrow (V_0, \beta^{\beta}(V_0))$ $\rightarrow (V_0, \beta_0)$	(V_1, β_0)
$m = n = 1$	(V, β_1)	(V, β_0) $\rightarrow (V, \beta_1)$	(V, β_1) $\rightarrow (V, \beta^{\beta}(V))$ $\rightarrow (V, \beta_0)$	(V, β_0)
$\Delta > 0$				
$m > n > 1$	(V_0, β_1) $\rightarrow (V^V(\beta_1), \beta_1)$ $\rightarrow (V_1, \beta_1)$ $\rightarrow (V_1, \beta^{\beta}(V_1))$ \rightarrow any point on $(V^{\beta}, \beta^{\beta})$ $\rightarrow (V_0, \beta^{\beta}(V_0))$ $\rightarrow (V_0, \beta_0)$ $\rightarrow (V^V(\beta_0), \beta_0)$ $\rightarrow (V_1, \beta_0)$	(V_1, β_0)	(V_0, β_1)	(V_1, β_0) [$\rightarrow (V_0, \beta_0)$]
$m > n = 1$	(V_1, β_1) $\rightarrow (V_1, \beta^{\beta}(V_1))$ $\rightarrow (V_1, \beta_0)$	(V_1, β_0)	(V_0, β_1)	(V_1, β_0) $\rightarrow (V_0, \beta_1)$
$m = n > 1$	(V_0, β_1) $\rightarrow (V_0, \beta^{\beta}(V_0))$ $\rightarrow (V_0, \beta_0)$	(V_1, β_0)	(V_0, β_1)	(V_1, β_0) $\rightarrow (V_1, \beta_1)$
$m = n = 1$	(V, β_1) $\rightarrow (V, \beta^{\beta}(V))$ $\rightarrow (V, \beta_0)$	(V, β_0)	(V, β_1)	(V, β_0) $\rightarrow (V, \beta_1)$

^a Branches in brackets may not be included in the optimal path. For the exothermic ($\Delta > 0$) case $m > n > 1$, $<$ indicates intermediate branches when $E_B/E_A < (m-1)/(n-1)$ and similarly with the relational operator replaced by $=$ and $>$. The initial and final branches are the same for all values of E_B/E_A .

“as quickly as possible” (measured in N_B), i.e. with as little loss of B as possible, and thus for large τ the final optimal values of V and β are those where $f = 0$ appears for the first time (measured in N_B). These are, of course, identical with the optimal final values one would reach when beginning with a small amount of B. For shorter durations τ equilibrium is never reached, and the optimal path is chosen to minimize the absolute value of f at all times.

Note, however, that these final values of V and β are only guaranteed to be optimal when the reaction reaches equilibrium for $\tau \rightarrow \infty$. This makes it imperative for the case of finite available time τ not just to simply choose the final optimal values of V and β associated with the largest amount of B at equilibrium but instead to choose always those values of V and β that maximize the reaction rate at any given instant.

The general procedure for constructing the optimal path is then as follows.

(1) Determine the location of the interior maxima and the zeroes of the reaction rate as functions of N_B as well as the behavior of the reaction rate for β , $V \rightarrow 0$ and ∞ .

(2) Compare the values of f at the boundary of the allowed regions (boundary extrema) with the values at the interior extrema in order to determine the absolute maximum. Of special interest are the values of N_B at which two such local extrema become identical, since this indicates that a switch in the controls should take place. Although the exact values of these N_B can only be determined numerically because they

generally require the solution of transcendental equations, it is nearly always possible to use analytical estimates to predict whether such a jump will occur somewhere along the optimal path for a given set of parameters, m , n , E_A , E_B , a , b , β_0 , β_1 , V_0 , and V_1 .

(3) Determine the range of parameters which will give the same optimal path as a means to classify the solutions.

In sections IV and V we will, after a short description of the behavior of the reaction rate as a function of N_B , list the different cases in tabular form. The optimal path is parametrized by N_B and will consist of a sequence of branches, each one being either an internal extremum or a control boundary. Switches from one branch to the next may occur when they intersect. Thus, the optimal path “ $\beta_0 \rightarrow \beta^{\beta_2}(N_B) \rightarrow \beta_1$ ” is to be interpreted as follows: “Start at $\beta = \beta_0$; when a value of N_B is reached such that $f(\beta_0) = f(\beta^{\beta_2}(N_B))$, switch to $\beta = \beta^{\beta_2}(N_B)$; when a value of N_B is reached such that $f(\beta^{\beta_2}(N_B)) = f(\beta_1)$, switch to β_1 and remain there until the end of the prescribed duration” (the quantities are derived in the appendices).

For the sake of compactness we have in Table 1 combined many cases whose optimal paths consist of only segments of a more general path, valid for a somewhat larger region in parameter space; usually it is quite obvious from the specific choice of parameters which path applies. For the description of this multitude we employ brackets and braces. Braces enclose two branches separated by a comma and indicate that one of those branches will occur at this step of the path.

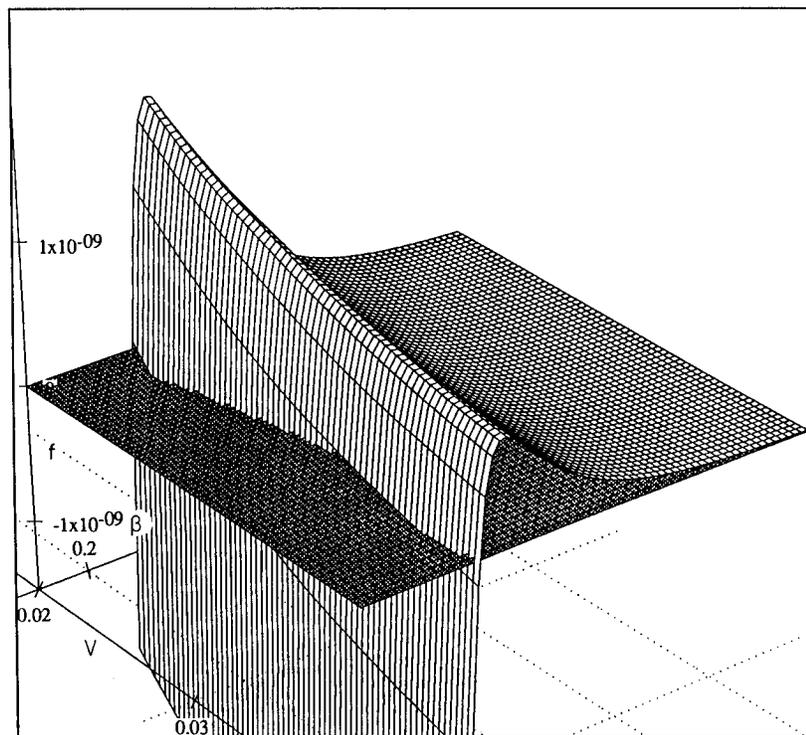


Figure 1. Plot of the reaction rate $f(N_B, V, \beta)$ at fixed N_B for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ with constrained ranges of V and β . Maximal rate is on the left V boundary, the ridge is the (V^β, β^β) curve, and equilibrium (V^0, β^0) is at the intersection with the base plane.

Brackets enclose branches of the optimal path that vanish for certain choices of the parameter values. Thus, the path “ $\{\beta_0, \beta_1\} \rightarrow \{\beta_1, \beta_0\}$ ” has the following interpretation: “Start at β_0 or β_1 depending on whether $f(\beta_0)$ or $f(\beta_1)$ is larger; if at some point $f(\beta_0) = f(\beta_1)$, switch to β_1 or β_0 , respectively; if $f(\beta_0) = f(\beta_1)$ never occurs, then stay on the original branch”.

IV. Constraint 1: $V \in [V_0, V_1]$, $\beta \in [\beta_1, \beta_0]$

In Figure 1 we have sketched a typical reaction rate $f(N_B, V, \beta)$ as a function of V and β for a fixed value of N_B . To visualize the optimal paths associated with constraint 1, we sketch for some value of N_B the curves in the (V, β) -plane where the reaction rate $f(N_B, V, \beta)$ or its partial derivative with respect to V and β vanishes (Figures 2 and 3). Depending on the values of the particle numbers m and n and whether the process is exothermic or endothermic ($\Delta > 0$ or $\Delta < 0$), the graphs will

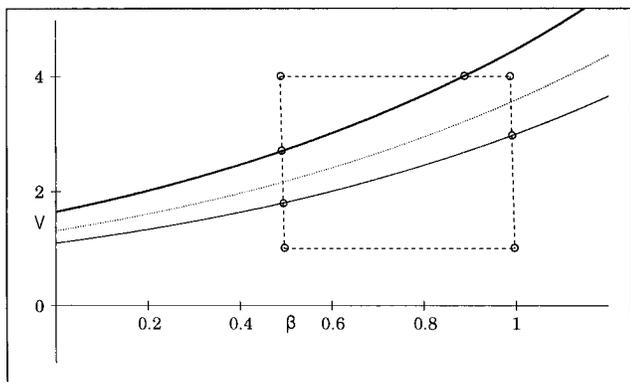


Figure 2. Plot of the points of zero reaction rate (V^0, β^0) , eq A7, (\cdots) and the lines of critical points for constant β (V^V, β^V) , eq A8, ($-$) and for constant V (V^β, β^β) , eq A9, ($-$) for an endothermic ($\Delta < 0$) reaction at a particular value of N_B . If $n = 1$, the thick curve (V^V, β^V) is not present. A possible allowed range of volume and temperature values is indicated by the dashed rectangle. The eight possible switching points are marked with circles.

be different. For each of these cases the optimal path may further depend on the allowed ranges of V and β . The formulas necessary for the discussion are listed in Appendix 1, the optimal paths and their switches are presented in Table 1, and the resulting limiting behaviors of f are found in Table 4.

A. $\Delta < 0$ (Endothermic Reaction). 1. $m > n > 1$ (Figure 2). The three curves (V^0, β^0) , (V^V, β^V) , and (V^β, β^β) , which represent the points where the reaction rate f and its partial derivatives with respect to V and β vanish, respectively, are specially marked in Figure 2. From eqs A7, A8, and A9 in Appendix 1 we see that they differ only by their prefactors and therefore never cross. As a consequence, no interior extremum of f exists, and the optimal path will always lie on the boundary of the allowed region in (V, β) -space. This location can be either

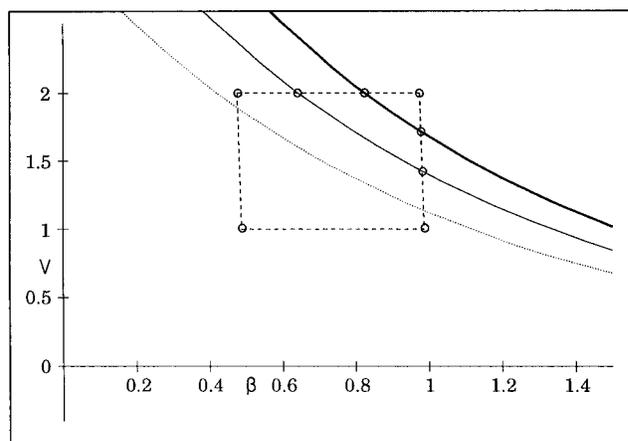


Figure 3. Plot of the points of zero reaction rate (V^0, β^0) , eq A7, (\cdots) and the lines of critical points for constant β (V^V, β^V) , eq A8, ($-$) and for constant V (V^β, β^β) , eq A9, ($-$) for an exothermic ($\Delta > 0$) reaction at a particular value of N_B . If $n = 1$, the thick curve (V^V, β^V) is not present. A possible allowed range of volume and temperature values is indicated by the dashed rectangle. The eight possible switching points are marked with circles. Note that if $E_B(n-1)/E_A(m-1) = 1$, (V^V, β^V) is identical to (V^β, β^β) and represents a line of interior maxima.

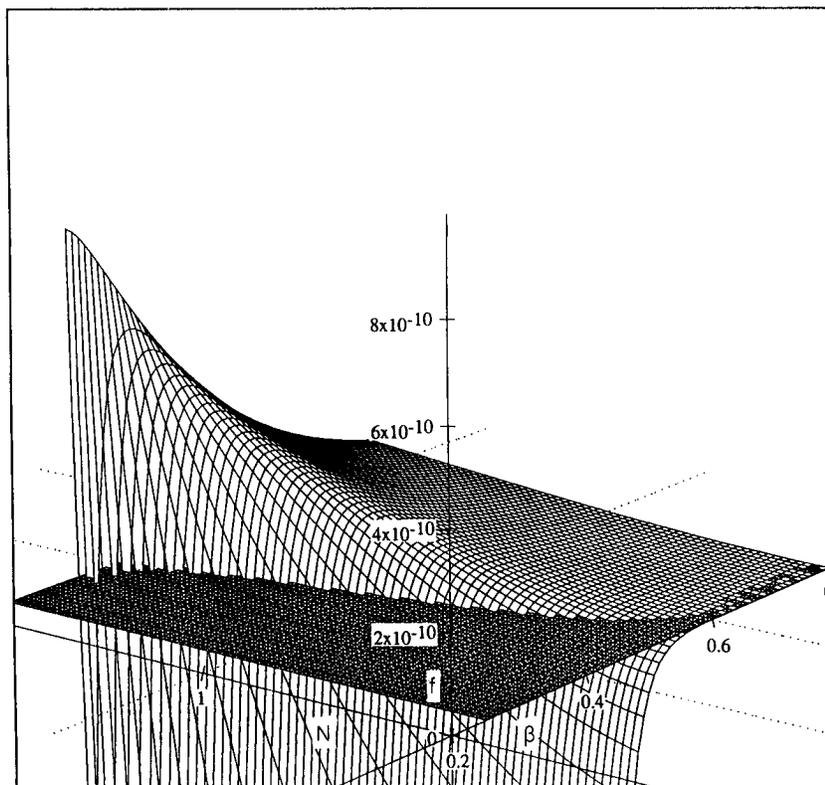


Figure 4. Plot of the reaction rate $f(N_B, \beta)$ for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ with constant pressure p and constrained range of β . Maximal rate is on the ridge, equilibrium at the intersection with the base plane.

one of its corners or the intersection of (V^V, β^V) or (V^β, β^β) with the boundary. Those eight points are marked with circles in Figure 2. As N_B changes, the three curves will gradually move, leading to changes in the optimal values of V and β as functions of N_B and to switches from one optimal segment to another, i.e. from one of the eight possible extremum points to another.

2. $m > n = 1$ (Figure 2). The only difference from case 1 is the lack of curve (V^V, β^V) , since f is monotonically increasing with V for all values of β (eq A3').

3. $m = n > 1$. In this case (V^V, β^V) has become identical to (V^0, β^0) (eqs A7', A8'). The limiting behavior of $f(V)$ depends on β . The curve (V^β, β^β) is a line of relative minima in the β -direction.

4. $m = n = 1$. The reaction rate is volume independent. The optimal path is the same as in case 3 above with all reference to volume removed.

B. $\Delta > 0$ (Exothermic Reaction). 1. $m > n > 1$ (Figure 3). From eqs A7, A8, and A9 in Appendix 1 we see that the three curves of (V^0, β^0) , (V^V, β^V) , and (V^β, β^β) again differ only by their prefactors. Except for the special case $E_B/E_A = (m-1)/(n-1)$, when (V^V, β^V) and (V^β, β^β) are identical, these curves will never cross. As a consequence, no interior extremum of f exists, and the optimal path will again always lie on the boundary of the allowed region in (V, β) -space, either at one of its corners or at the intersection of (V^V, β^V) or (V^β, β^β) with the boundary. In the special case $E_B/E_A = (m-1)/(n-1)$ we find that f has a line of relative maxima along the curve $(V^\beta, \beta^\beta) = (V^V, \beta^V)$.

2. $m > n = 1$ (Figure 3). We note that again curve (V^V, β^V) is missing.

3. $m = n > 1$. As in case A.3 above, (V^V, β^V) has become identical to (V^0, β^0) . The difference from the endothermic case is that (V^β, β^β) now is a line of relative maxima in the β -direction. Again the limiting behavior of $f(V)$ depends on β . The optimal

paths are identical to those for $\Delta < 0$ (with the roles of N_A and N_B exchanged).

4. $m = n = 1$. The reaction rate is volume independent. The optimal path is the same as in case 3 above with all reference to volume removed.

V. Constraint 2: $p = (N_A + N_B)/V\beta = \text{Constant}$, $\beta \in [\beta_0]$

The major difference from the previous constraint is the fact that the number of independent variables is reduced to one. As a consequence, however, the functional form of $f(N_B, \beta)$ is more complex, as can be seen in Figure 4, which depicts the reaction rate as a function of N_B and β . Depending on the values of β_1 and β_0 , we find up to three interior extrema (solutions of eq A15) and up to two zeroes (solutions of eq A14) of the reaction rate f as a function of β for a given value of N_B , making the analysis rather involved and tedious. Thus, we will not discuss all the possible variations the optimal path can take for each special case. We hope that the discussion below will allow the interested reader to deal with special cases of interest personally. The formulas necessary for the discussion are listed in Appendix 2.

A. $\Delta < 0$ (Endothermic Reaction). 1. $m > n > 1$ (Figure 5). From eq A14 in Appendix 2 we see that, in addition to $\beta^0 = 0$ and $\beta^0 = \infty$, exactly one solution $\beta^0(N_B)$ exists for all values of N_B . The location of $\beta^0(N_B)$ varies continuously with N_B ; its limiting locations when $N_B \rightarrow 0$, and when $N_A \rightarrow 0$, as for all the other cases, are given in Table 4. Similarly eq A15 gives exactly two solutions, in addition to $\beta^\beta = 0$ (if $n > 2$) and $\beta^\beta = \infty$: β^{β_1} (relative maximum, $f(\beta^{\beta_1}) > 0$) and β^{β_2} (relative minimum, $f(\beta^{\beta_2}) < 0$) for all values of N_B . We find furthermore that $\beta^{\beta_1} < \beta^0 < \beta^{\beta_2}$ and that they vary continuously as functions of N_B . See again Table 4 for the limiting values. Combined

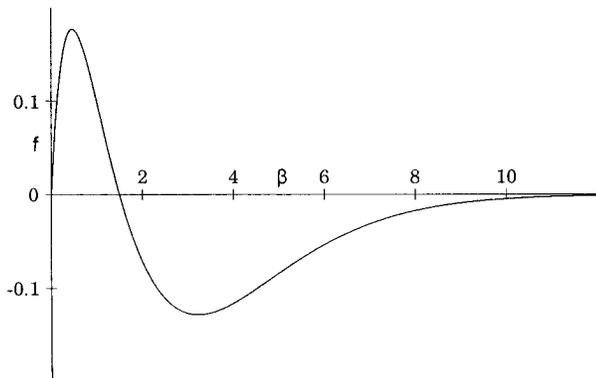


Figure 5. Plot of the reaction rate $f(\beta)$ for an endothermic ($\Delta < 0$) reaction with $m > n > 1$ at constant pressure p . Varying N_B deforms the curve but leaves the number of roots and extrema invariant.

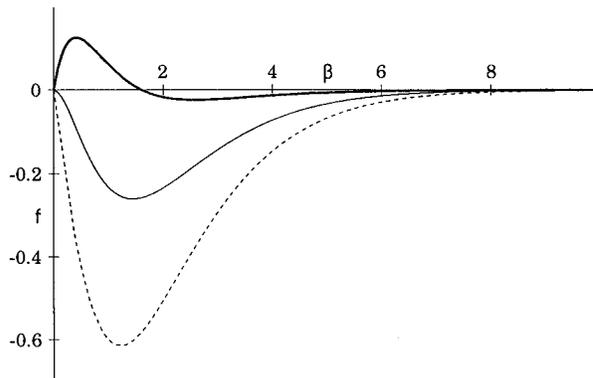


Figure 6. Plot of the reaction rate $f(\beta)$ for an endothermic ($\Delta < 0$) reaction with $m = n > 1$ at constant pressure p for three different values N_B . Note how one of the roots and extrema disappears as N_B increases.

with the behavior of the reaction rate for large and small values of β , this determines the optimal paths as summarized in Table 2.

2. $m > n = 1$. In addition to $\beta^0 = \infty$, one solution $\beta^0(N_B)$ of eq A14 exists for all values of N_B , and its location varies continuously with N_B . However, under these conditions eq A15 gives just one solution β^{β_2} (relative minimum, $f(\beta^{\beta_2}) < 0$), besides $\beta^\beta = \infty$, for all values of N_B . As opposed to case A.1 above, $f(\beta=0)$ is positive here. We find also that $\beta^0 < \beta^{\beta_2}$ and that it varies continuously as function of N_B .

3. $m = n > 1$ (Figure 6). Here eq A14 can be solved exactly to yield one solution, $\beta^0 = (1/\Delta) \ln(h(N_B))$. Equation A15 has two solutions, β^{β_1} (relative maximum, $f(\beta^{\beta_1}) > 0$) and β^{β_2} (relative minimum, $f(\beta^{\beta_2}) < 0$). We find again that $\beta^{\beta_1} < \beta^0 < \beta^{\beta_2}$ and that they vary continuously as functions of N_B . Clearly the solution β^{β_1} is only of relevance if $h(N_B) < 1$ (N_B small), since $\beta^{\beta_1} < 0$ if $(h(N_B))$ is defined in eq A13).

4. $m = n = 1$. Since the problem is volume independent, the requirement of constant pressure is irrelevant, and the solution is identical to the one presented in section IV.A.4.

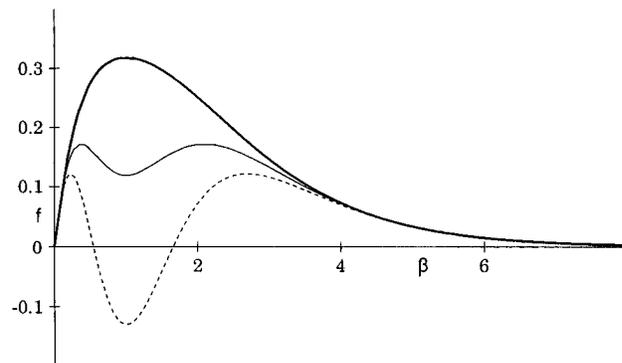


Figure 7. Plot of the reaction rate $f(\beta)$ for an exothermic ($\Delta > 0$) reaction with $m > n > 1$ and $E_B(n-1)/E_A(m-1) = 1$ at constant pressure p for three different values N_B . Note how the single maximum splits up as N_B increases, and h (eq A13) goes through the sequence $h(N_B) < h^{\text{ex}}$ (—), $h^{\text{ex}} < h(N_B) < h^{\text{c}}$ (—), $h(N_B) > h^{\text{c}}$ (---).

B. $\Delta > 0$ (Exothermic Reaction). 1. $m > n > 1$ (Figure 7). Besides $\beta^0 = 0$ and $\beta^0 = \infty$, eq A14 now has zero, one, or two solutions $\beta^0(N_B)$ depending on the value of $h(N_B)$ (defined

TABLE 2: Optimal Branches (Read Vertically) for All Possible Reaction Conditions When Pressure p Is Constant and β Is Constrained to the Interval $B \in [\beta_1, \beta_0]$ (or $T \in [T_0, T_1]$)^a

	product B						product A					
	small $N(0)$			large $N(0)$			small $N(0)$			large $N(0)$		
	low	mid	high	low	mid	high	low	mid	high	low	mid	high
$\Delta < 0$												
$m > n > 1$	β_0 $\rightarrow \beta^{\beta_1}$ $\rightarrow \beta_1$	β^{β_1} $\rightarrow \beta_1$	β_1	β_1	\dagger	β_0 $\rightarrow \beta_1$	β_0	β^{β_2} $\rightarrow \beta_0$	β_1 $\rightarrow \beta^{\beta_2}$ $\rightarrow \beta_0$	β_1 $\rightarrow \beta_0$	\ddagger	β_0
$m > n = 1$	β_1	β_1	β_1	β_1	\dagger	β_0 $\rightarrow \beta_1$	β_0	β^{β_2} $\rightarrow \beta_0$	β_1 $\rightarrow \beta^{\beta_2}$ $\rightarrow \beta_0$	β_0	β_0	β_0
$m = n > 1$	β_0 $\rightarrow \beta^{\beta_1}$ $\rightarrow \beta_1$	β^{β_1} $\rightarrow \beta_1$	β_1	β_1	\dagger	β_0 $\rightarrow \beta_1$	β_0	β^{β_2} $\rightarrow \beta_0$	β_1 $\rightarrow \beta^{\beta_2}$ $\rightarrow \beta_0$	β_1 $\rightarrow \beta_0$	\ddagger	β_0
$m = n = 1$	β_1	β_1	β_1	β_0	β_0	β_0	β_1	β_1	β_1	β_0	β_0	β_0
$\Delta > 0$												
$m > n > 1$	see Table 3											
$m > n = 1$	see Table 3											
$m = n > 1$	β_0	β^{β_2} $\rightarrow \beta_0$	β_1 $\rightarrow \beta^{\beta_2}$ $\rightarrow \beta_0$	β_1 $\rightarrow \beta_0$	\dagger	β_0	β_0 $\rightarrow \beta^{\beta_1}$ $\rightarrow \beta_1$	β^{β_1} $\rightarrow \beta_1$	β_1	β_1	\ddagger	β_0 $\rightarrow \beta_1$
$m = n = 1$	β_1	β_1	β_1	β_0	β_0	β_0	β_1	β_1	β_1	β_0	β_0	β_0

^a Column headings low/mid/high refer to the barrier heights in the appropriate direction of reaction, i.e. $E_A < (n-1)/\beta_0$; $(n-1)/\beta_0 < E_A < (n-1)/\beta_1$; $E_A > (n-1)/\beta_1$, respectively, or $E_B < (m-1)/\beta_0$; $(m-1)/\beta_0 < E_B < (m-1)/\beta_1$; $E_B > (m-1)/\beta_1$. Branches marked \dagger are identical to those for low barrier height if $f(\beta_0) < f(\beta_1)$ and to those for high barrier height if $f(\beta_0) > f(\beta_1)$. \ddagger signals the opposite relationship.

TABLE 3: Optimal Branches for Exothermic ($\Delta > 0$) Reactions with Stoichiometry $m > n > 1$ and $m > n = 1$ When Pressure p Is Constant and β Is Constrained to the Interval $\beta \in [\beta_1, \beta_0]$ (or $T \in [T_0, T_1]$)^a

	product B		product A	
	small $N(0)$	large $N(0)$	small $N(0)$	large $N(0)$
$m > n > 1$				
$E_B/E_A < (m-1)/(n-1)$				
$\beta_0 < \beta^c$	$[[\beta_0 \rightarrow] \beta_1 \rightarrow] \beta_1$	$[\beta_0 \rightarrow] \beta_1$	$[[\beta_1 \rightarrow] \beta_2 \rightarrow] \beta_0$	$[\beta_1 \rightarrow] \beta_0$
$\beta_1 < \beta^A, \beta^c < \beta_0$	$\beta_1 \rightarrow [\beta_1 \rightarrow]$ $[\beta_3 \rightarrow] \beta_0$	$\{\beta_0, \beta_1\}$ $[\rightarrow \{\beta_1, \beta_0\}]$	$[\beta_1 \rightarrow] \beta_2$	$[[\beta_0 \rightarrow] \beta_1 \rightarrow]$ $\beta_0 \rightarrow \beta_2$
$\beta^A < \beta_1 < \beta^c < \beta_0$	$\beta_1 [\rightarrow \{\beta_0, \beta_3\}]$	$\{\beta_0, \beta_1\}$ $[\rightarrow \{\beta_1, \beta_0\}]$	$[\beta_1 \rightarrow] \beta_2$	$\beta_0 \rightarrow \beta_2$
$\beta^c < \beta_1$	$\beta_1 \rightarrow [\beta_3 \rightarrow] \beta_0$	β_0	β_1	$\beta_0 \rightarrow [\beta_2 \rightarrow] \beta_1$
$E_B/E_A = (m-1)/(n-1)$				
$\beta_0 < \beta^c$	$\beta_0 \rightarrow \beta_1 \rightarrow \beta_1$	β_1	β_0	$\beta_1 \rightarrow \beta_0$
$\beta_1 < \beta^c < \beta_0$	$\beta_c \rightarrow \{\beta_1, \beta_3\} \rightarrow$ $\{\beta_0, \beta_1\}$	$\{\beta_0, \beta_1\}$ $[\rightarrow \{\beta_1, \beta_0\}]$	$\beta^c [= \beta_2]$	$\{\beta_0, \beta_1\}$ $[\rightarrow \{\beta_1, \beta_0\}]$
$\beta^c < \beta_1$	$\beta_1 \rightarrow \beta_3 \rightarrow \beta_0$	β_0	β_1	$\beta_0 \rightarrow \beta_1$
$E_B/E_A > (m-1)/(n-1)$				
$\beta_1 < \beta^c$	$[[\beta_1 \rightarrow] \beta_3 \rightarrow] \beta_0$	$[\beta_1 \rightarrow] \beta_0$	$[[\beta_0 \rightarrow] \beta_2 \rightarrow] \beta_1$	$[\beta_0 \rightarrow] \beta_1$
$\beta_0 < \beta^B, \beta^c < \beta_1$	$\beta_3 \rightarrow [\beta_0 \rightarrow]$ $[\beta_1 \rightarrow] \beta_1$	$\{\beta_0, \beta_1\}$ $[\rightarrow \{\beta_1, \beta_0\}]$	$[\beta_0 \rightarrow] \beta_2$	$[[\beta_1 \rightarrow] \beta_0 \rightarrow]$ $\beta_1 \rightarrow \beta_2$
$\beta^B < \beta_0 < \beta^c < \beta_1$	$\beta_0 \rightarrow \{\beta_1, \beta_3\}$	$\{\beta_0, \beta_1\}$ $[\rightarrow \{\beta_1, \beta_0\}]$	$[\beta_0 \rightarrow] \beta_2$	$\beta_1 \rightarrow \beta_2$
$\beta^c < \beta_0$	$\beta_0 \rightarrow [\beta_1 \rightarrow] \beta_1$	β_1	β_0	$\beta_1 \rightarrow [\beta_2 \rightarrow] \beta_0$
$m > n = 1$				
$\beta_0 < \beta^c$	β_1	$[\beta_0 \rightarrow] \beta_1$	$[[\beta_1 \rightarrow] \beta_2 \rightarrow] \beta_0$	β_0
$\beta_1 < \beta^c < \beta_0$	$[[\beta_1 \rightarrow] [\beta_3 \rightarrow]]$ $\beta_0 \rightarrow \beta_1$	$\{\beta_0, \beta_1\}$ $[\rightarrow \{\beta_1, \beta_0\}]$	$[\beta_1 \rightarrow] \beta_2$	$\beta_0 \rightarrow \beta_2$
$\beta^c < \beta_1$	$\beta_1 \rightarrow [\beta_3 \rightarrow] \beta_0$	β_0	β_1	$\beta_0 \rightarrow [\beta_2 \rightarrow] \beta_1$

^a Branches in brackets may not be included in the optimal path. Branches in braces are alternatives.

in eq A13) relative to the critical value

$$h^c = \left(\frac{e\Delta}{m-n} \right)^{m-n} \quad (10)$$

Correspondingly, we define $\beta^c = (m-n)/\Delta \equiv \beta_1^0 \equiv \beta_2^0$ at the critical point. The locations of these solutions vary continuously with N_B . Similarly, in addition to $\beta^B = 0$ (if $n > 2$) and $\beta^B = \infty$, eq A15 gives one, two, or three solutions β^{β_i} depending on the value of $h(N_B)$ relative to a critical value h^{ex} . It is found that $h^{\text{ex}} < h^c$ and that the β^{β_i} vary continuously as functions of N_B . However, their limiting locations depend on the value of E_B/E_A relative to $(m-1)/(n-1)$. (See Table 4.) We observe that β^{β_1} and β^{β_3} are always relative maxima with $f(\beta^{\beta_1})$ and $f(\beta^{\beta_3})$ positive. In general, the exact location of $(\beta^{\text{ex}}, h^{\text{ex}})$ has to be found numerically from eq A15 and its β -derivative. If $E_B/E_A = (m-1)/(n-1)$, we can calculate h^{ex} and β^{ex} explicitly:

$$h^{\text{ex}} = \left(\frac{e\Delta}{m-n} \right)^{m-n} \frac{n-1}{m-1} = \frac{n-1}{m-1} h^c \quad (11)$$

$$\beta^{\text{ex}} = \beta^c \quad (12)$$

Then β^{β_2} is a relative maximum or minimum depending on whether $h < h^{\text{ex}}$ or $h > h^{\text{ex}}$; for all other values of E_B/E_A , β^{β_2} is a relative minimum throughout. Furthermore, $f(\beta^{\beta_2}) > 0$ when $h < h^c$ ($f(\beta^{\beta_2}) < 0$ when $h > h^c$).

Together with the limiting behavior of the reaction rate for large and small values of β the critical points and zeroes of f determine the optimal paths. However, the situation is now rather involved (cf. Table 3) since there are many possibilities for β and β_0 to be placed with relation to the location of the zeroes and critical points of the reaction rate. We note that the optimal paths of case $E_B/E_A > (m-1)/(n-1)$ follow from

the analysis of the case $E_B/E_A < (m-1)/(n-1)$ since the order of the four special temperatures $\beta^A = (n-1)/E_A$, $\beta^B = (m-1)/E_B$, $\beta^c = (m-n)/\Delta$, and β^{ex} is just reversed: $\beta^A < \beta^B < \beta^c < \beta^{\text{ex}}$ for $E_B/E_A < (m-1)/(n-1)$, while $\beta^A > \beta^B > \beta^c > \beta^{\text{ex}}$ for $E_B/E_A > (m-1)/(n-1)$. Thus, in the optimal paths, β_0 and β_1 change roles, as do β^{β_1} and β^{β_3} .

2. $m > n = 1$. The zero, one, or two solutions $\beta^0(N_B)$ of eq A14 behave in the same way as in case 1 ($m > n > 1$) with n put equal to 1 in all the formulas. However, we note that $f(\beta=0) > 0$ and $f_\beta(\beta=0) < 0$, leading to the removal of the relative maximum β^{β_1} . This agrees with the fact that only zero, one, or two solutions of $f_\beta(\beta^{(1)}) = 0$ (eq A15) exist depending on whether h is smaller than, equal to, or larger than h^{ex} . We find as before that $h^{\text{ex}} < h^c$ and that the β^{β_i} vary continuously as functions of N_B . As far as the dependence of E_B/E_A is concerned, the only case which is relevant is $E_B/E_A < (m-1)/(n-1)$ since $(m-1)/(n-1) \rightarrow \infty$ for $n \rightarrow 1$.

As before, the exact location of $(\beta^{\text{ex}}, h^{\text{ex}})$ has to be found numerically from solving eqs A15 and its β -derivative. We observe that β^{β_3} is always a relative maximum with $f(\beta^{\beta_3})$ positive, and β^{β_2} is always a relative minimum with $f(\beta^{\beta_2}) > 0$ when $h < h^c$ ($f(\beta^{\beta_2}) < 0$ when $h > h^c$). Again the optimal paths are rather involved since there are many possibilities for β_1 and β_0 to be placed with relation to the location of the zeroes and critical points of the reaction rate.

3. $m = n > 1$. The optimal paths for this case are identical to the ones discussed for $\Delta < 0$ with the roles of N_A and N_B exchanged.

4. $m = n = 1$. Since the problem is volume independent, the requirement of constant pressure is irrelevant and the solution is identical to the one presented in section IV.B.4.

TABLE 4: Limiting Behavior of the Reaction Rate f when $V \rightarrow 0$ and ∞ and When $\beta \rightarrow \infty$ ($T \rightarrow 0$) (left); Limiting Behavior of the Roots and Extrema of the Reaction Rate (right)^a

	$f(N_B, V, \beta)$			β^0_i			β^{β_i}		
	$V \rightarrow 0$	$V \rightarrow \infty$	$\beta \rightarrow \infty$	$N_B \rightarrow 0$	$h \rightarrow h^{\text{ex}}$	$N_A \rightarrow 0$	$N_B \rightarrow 0$	$h \rightarrow h^{\text{ex}}$	$N_A \rightarrow 0$
$\Delta < 0$									
$m > n > 1$	$-\infty$	0^+	0^-	∞		0	$(n-1)/E_A$ ∞		0 $(m-1)/E_B$
$m > n = 1$	$-\infty$	q	0^-	∞		0	\bullet ∞	\bullet	\bullet $(m-1)/E_B$
$m = n > 1$	∞^\ddagger $-\infty^\ddagger$	$0^{+\ddagger}$ $0^{-\ddagger}$	0^-	∞	0^*	$-\infty$	$(m-1)/E_A$ ∞	0^*	$-\infty$ $(m-1)/E_B$
$m = n = 1$			0^-						
$\Delta > 0$									
$m > n > 1$	$-\infty$	0^+	0^+		β^{c-**} β^{c+**}	0 ∞	$(n-1)/E_A$	∞	0
$<$								$\beta^{\text{ex-}}$	$(m-1)/E_B$
$<$								$\beta^{\text{ex+}}$	∞
$=$								β^c	0
$=$							β^c	β^c	β^c
$=$								β^{c+}	∞
$>$								$\beta^{\text{ex-}}$	0
$>$								$\beta^{\text{ex+}}$	$(m-1)/E_B$
$>$							$(n-1)/E_A$		∞
$m > n = 1$	$-\infty$	q	0^+		β^{c-**} β^{c+**}	0 ∞	\bullet	\bullet $\beta^{\text{ex-}}$ $\beta^{\text{ex+}}$	\bullet $(m-1)/E_B$ ∞
$m = n > 1$	∞^\ddagger $-\infty^\ddagger$	$0^{+\ddagger}$ $0^{-\ddagger}$	0^+	∞	0^*	$-\infty$	∞ $(m-1)/E_A$	0^*	$(m-1)/E_B$ $-\infty$
$m = n = 1$			0^+						

^a \ddagger is for $\beta > \beta^V$, \ddagger is for $\beta < \beta^V$. For brevity we define $q = (aN_A e^{-\beta E_A})^-$. When $\beta \rightarrow 0$ ($T \rightarrow \infty$), f approaches a finite value, positive or negative, which depends not only on the parameters but also on the instantaneous product concentration. Roots and extrema marked with \bullet do not exist. The entries marked with $*$ are for the limit $h \rightarrow 1$, while $**$ indicates $h \rightarrow h^c$. For the exothermic ($\Delta > 0$) case $m > n > 1$, $<$ indicates intermediate branches when $E_B/E_A < (m-1)/(n-1)$ and similarly with the relational operator replaced by $=$ and $>$.

VI. Realistic Examples

To illustrate the qualitative description of the optimal paths given in the previous two subsections we now apply the analysis to three chemical reactions, $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, and $2\text{NO}_2 \rightleftharpoons \text{N}_2 + 2\text{O}_2$. In all cases we will model the reactions using the simple reaction equation eq 1 together with the simplifying assumptions mentioned (ideal gas law, constant activation energies, etc.).

A. $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$. The desired quantity is ammonia, and it is assumed that we begin with initially 2 mol combined of nitrogen and hydrogen in the appropriate stoichiometric ratio (1:3), i.e. 0.5 mol N_2 plus 1.5 mol H_2 , corresponding to 1 mol NH_3 . From the literature²⁰ we take the following constants (at pressures of about 250 atm and temperatures of about 820 K): $E_A = 167$ kJ/mol, $E_B = 58.6$ kJ/mol, $b/a = 5.43 \times 10^{-5}$ m⁶/mol². (We note that 1 kJ/mol corresponds to a temperature of about 120 K.) Thus, we have the following quantities of interest: $m = 4$, $n = 2$, $E_A = 167$ kJ/mol, $E_B = 58.6$ kJ/mol, $\Delta = -108$ kJ/mol, $(n-1)/E_A = 0.006$ mol/kJ, $(m-1)/E_B = 0.0512$ mol/kJ, $b/a = 5.43 \times 10^{-15}$ m⁶/mol², $N_0 = 1$ mol.

We consider two constraints.

(i) $V_0 = 0.005$ m³, $V_1 = 0.02$ m³, $\beta_0 = 0.3$ mol/kJ ($T_0 = 400$ K), $\beta_1 = 0.1$ mol/kJ ($T_1 = 1200$ K). This corresponds to the case of desired product A in small initial amounts in section IV.A.1 and Table 1 such that the optimal reaction path is the following: The volume should be $V = V_0 = 0.005$ m³ throughout. The temperature should initially be $\beta = \beta_1 = 0.1$ mol/kJ. When N_B has decreased to 1.985 mol, corresponding to a product of $N_A = 0.0075$ mol, a continuous switch to $\beta(N_B) = (-1/\Delta) \ln[(V_0^{m-n}/g(N_B)) (E_A/E_B)] = 0.2029 - 0.0185 \ln[N_B^2/(2 - N_B)]$ mol/kJ is possible. Finally, when N_B has

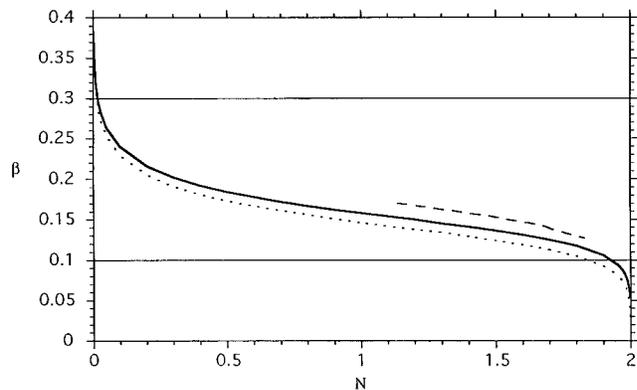


Figure 8. Plot of the optimal temperature path $\beta^*(N_B)$ for ammonia at $p = 256$ atm, $0.1 \leq \beta \leq 0.3$ mol/kJ (—). As a comparison, $\beta^*(N_B)$ for realistic data taken from ref 21 is also shown (---) as well as the equilibrium path $\beta^0(N_B)$ (···).

reached 0.1 mol, the temperature switches smoothly to $\beta = \beta_0 = 0.3$ mol/kJ and stays at that value.

(ii) $p = 256$ atm = 2.59×10^7 Pa, $\beta_0 = 0.3$ mol/kJ ($T_0 = 400$ K), $\beta_1 = 0.1$ mol/kJ ($T_1 = 1200$ K). This corresponds to the case of desired product A in small initial amounts with a high barrier height in section V.A.1 and Table 2 since $\beta_1 > (m-1)/E_B$. The optimal path then starts with an initial temperature $\beta = \beta_1 = 0.1$ mol/kJ. When N_B has decreased to 1.93 mol, corresponding to a product of $N_A = 0.035$ mol, the temperature switches smoothly to $\beta = \beta^{\beta_2}(N_B)$, which may be found by solving eq A15. At $N_B = 0.017$ mol it switches off the internal extremum to $\beta = \beta_0 = 0.3$ mol/kJ and stays at that value.

In Figure 8 we plot the optimal path $\beta(N_B)$ for $p = 256$ atm and $\beta \in [0.1, 0.3]$ mol/kJ. On the same graph we show the

optimal path that was found numerically in ref 21 using the best available data for the activation coefficients and equation of state. The similarity between the two curves is impressive considering the highly simplified reaction equation and equation of state used in our calculation. The agreement could be improved further if the numerical values for the effective activation energies of the modern catalysts were available, since a lowering of the activation energies E_A and E_B would result in an upward shift of the optimal curve $\beta^*(N_B)$ in Figure 8. The main effect of the more accurate kinetic information will be the time allocation along the optimal path rather than the path in (V, β) -space itself.

B. $N_2O_4 \rightleftharpoons 2NO_2$. The desired quantity is the dimer N_2O_4 , and it is assumed that we begin with initially 2 mol of nitrogen dioxide. From the literature²⁰ we take the following constants (at pressures of about 1 atm and temperatures of about 300 K): $E_A = 46.25$ kJ/mol, $E_B = 7.16$ kJ/mol, $b/a = 1.35 \times 10^{-10}$ m³/mol. Thus, we have the following quantities of interest: $m = 2$, $n = 1$, $E_A = 46.25$ kJ/mol, $E_B = 7.16$ kJ/mol, $\Delta = -39.1$ kJ/mol, $(m - 1)/E_B = 0.14$ mol/kJ, $b/a = 1.35 \times 10^{-10}$ m³/mol, $N_0 = 1$ mol.

We consider two constraints.

(i) $V_0 = 0.02$ m³, $V_1 = 0.04$ m³, $\beta_0 = 0.4$ mol/kJ ($T_0 = 300$ K), $\beta_1 = 0.35$ mol/kJ ($T_1 = 340$ K). This corresponds to the case of desired product A in small initial amounts in section IV.A.2 and Table 1 such that the optimal reaction path is the following: The volume should be $V = V_0 = 0.02$ m³ throughout. The temperature should initially be $\beta = \beta_1 = 0.35$ mol/kJ. When N_B has decreased to 1.99 mol, it switches smoothly to $\beta(N_B) = (-1/\Delta) \ln[(V_0^{m-n}/g(N_B)) (E_A/E_B)] = 0.5112 - 0.0256 \ln[N_B^2/(2 - N_B)]$ mol/kJ. When N_B has fallen to 1.95 mol, the temperature switches further to $\beta = \beta_0 = 0.4$ mol/kJ and stays at that value.

(ii) $p = 1$ atm = 1.013×10^5 Pa, $\beta_0 = 0.4$ mol/kJ ($T_0 = 300$ K), $\beta_1 = 0.35$ mol/kJ ($T_1 = 340$ K). This corresponds to the case of desired product A in small initial amounts with a high barrier height in section V.A.2 and Table 2 since $\beta_1 > (m - 1)/E_B$. The optimal path then starts at temperature $\beta = \beta_1 = 0.35$ mol/kJ. When N_B has dropped to 1.90 mol, it switches to $\beta = \beta_2(N_B)$, again found by solving eq A15. When $N_B = 1.483$ mol, the temperature switches to $\beta = \beta_0 = 0.4$ mol/kJ and stays at that value.

C. $2NO_2 \rightleftharpoons N_2 + 2O_2$. The desired quantity is the molecules N_2 and O_2 , and it is assumed that we begin with initially 1 mol of nitrogen dioxide. From the literature²⁰ we take the following constants (at pressures of about 1 atm and temperatures of about 300 K): $\Delta = 67.7$ kJ/mol, $E_B = 945$ kJ/mol, $b/a = 477$ m³/mol. The value for E_B corresponds to the heat of formation of N_2 from two single nitrogen atoms. Thus, we have the following quantities of interest: $m = 3$, $n = 2$, $E_A = 877.3$ kJ/mol, $E_B = 945$ kJ/mol, $\Delta = 67.7$ kJ/mol, $(m - 1)/E_B = 0.0021$ mol/kJ, $(n - 1)/E_A = 0.0011$ mol/kJ, $\beta^c = (m - n)/\Delta = 0.0147$ mol/kJ, $h^c = 184.03$ kJ/mol, $\beta^{ex} = 0.0159$ mol/kJ, $h^{ex} = 183.46$ kJ/mol, $b/a = 477$ m³/mol, $N_0 = 1$ mol.

We consider two constraints.

(i) $V_0 = 0.004$ m³, $V_1 = 0.04$ m³, $\beta_0 = 0.4$ mol/kJ ($T_0 = 300$ K), $\beta_1 = 0.1$ mol/kJ ($T_1 = 1200$ K). This corresponds to the case of desired product B in small initial amounts and with $E_B/E_A < (m - 1)/(n - 1)$ in section IV.B.1 and Table 1 such that the optimal reaction path is the following: For the combined content of N_2 plus O_2 , N_B increasing to 0.144 mol, found by solving eq A8, the optimal conditions are $\beta^* = \beta_1 = 0.1$ mol/kJ and V^* and $V_0 = 0.004$ m³. As the reaction proceeds to the range $0.144 < N_B < 0.288$ mol, again calculated from eq A8, β^* remains at $\beta_1 = 0.1$ mol/kJ, while V^* evolves along $V^V(N_B)$

$= 1.095N_B^3/(1 - (2/3)N_B)^2$ m³. In the following $0.288 < N_B < 0.343$ mol, both β^* and V^* remain fixed at $\beta^* = \beta_1 = 0.1$ mol/kJ and $V^* = V_1 = 0.04$ m³. At the end of that range a smooth switch to $\beta^\beta(V_1)$ occurs with β^* found from eq A9, $\beta^* = 0.1397 + 0.0148 \ln[N_B^3/(1 - (2/3)N_B)^2]$ mol/kJ and $V^* = V_1 = 0.04$ m³. Finally, at $N_B > 1.4996$ mol the optimal path switches to the constant $\beta^* = \beta_0 = 0.4$ mol/kJ and $V^* = V_1 = 0.04$ m³.

(ii) $p = 1.013 \times 10^5$ Pa, $\beta_0 = 0.25$ mol/kJ ($T_0 = 480$ K), $\beta_1 = 0.1$ mol/kJ ($T_1 = 1200$ K). This corresponds to the case of desired product B in small initial amounts in section V.B.1 and Table 2 since $\beta_1 > \beta^{ex}$ and $(E_B/E_A) < (m - 1)/(n - 1)$. The optimal path then starts at temperature $\beta^* = \beta_1 = 0.1$ mol/kJ. When N_B has increased to 0.4569 mol, the third solution of eq A15, $\beta^\beta_3(N_B)$ has become equal to β_1 and a switch to that branch occurs. When $N_B = 1.4487$ mol, the optimal path switches off that branch again to $\beta^* = \beta_0 = 0.25$ mol/kJ and stays at that value.

VII. Discussion

A. Generality of the Results. In section III we have presented a qualitative description of the optimal reaction paths for all reactions of type $nA \rightleftharpoons mB$, illustrated in section VI with three numerical examples where the transition points along the optimal path were calculated from the parameters of the reaction. As we pointed out earlier, the result of the optimization procedure in section II is more general and applies to all reactions of the type $\sum \alpha_i A_i \rightleftharpoons \sum \alpha_j A_j$. We observe further that our derivation never referred to the special structure of eq 1, and thus, in principle, any empirical reaction rate can be used as long as it is only a function of N_B , V , and T . This would permit the inclusion of realistic equations of state plus the temperature and pressure dependence of the activation coefficients in our analysis.

However, the method we used in section II does not generalize in a straightforward manner to several variables (reaction coordinates). Therefore, reactions of the type $nA \rightleftharpoons mB \rightleftharpoons lC$ with B as the desired product will have to be treated differently. The optimal choice of controls is then not necessarily the one that maximizes the reaction rate at any given moment.¹⁵

B. Thermodynamic Distance. The classical way to approach chemical reactions is from the point of view of equilibrium. As we have seen in this paper, for the case of finite duration of the reactions the crucial quantity has turned out to be the reaction rate instead, where the case of equilibrium ($f = 0$) is never attained in finite time, although we have spoken of reaching equilibrium as fast or slowly as possible measured in N_B coordinates. Such a use of thermodynamic quantities as a measure of distance from some (infinite-time) state of the system and/or as a proper time along the path of the process is well-known in finite-time thermodynamics.²² Here one speaks of the thermodynamic distance which measures the distance in the space of thermodynamic coordinates between the system in its current state and some ghost equilibrium state which it strives toward (usually this relaxation requires an infinite time). In a quantitative description a thermodynamic metric \mathbf{M} is introduced,^{22,23} consisting of the second derivatives of one of the extensive variables with respect to all the others, e.g. the entropy metric

$$\mathbf{M}_S = - \left\{ \frac{\partial^2 S}{\partial X_i \partial X_j} \right\} \quad (13)$$

where the X may be energy U , volume V , particle number N , etc.

In our example a reasonable choice of such a ghost equilibrium state corresponds to the values of V and T (or just T , if constraint 2 applies) for which the current N_B is the equilibrium value. We have plotted the curve of equilibrium values $\beta^0(N_B)$ for the ammonia reaction (reaction A in section VI) under the constraint of constant pressure $p = 256$ atm in Figure 8 and find that over almost the entire range of values of N_B the numerical distance in the β -direction between the optimal and the equilibrium path is nearly constant and equals 0.012 ± 0.001 mol/kJ. Such a constant value of the distance to the equilibrium state has also been observed in ref 21, although those data cover only a much shorter range of N_B values (also plotted in Figure 8). We have also performed the same analysis for reactions B and C in section VI (both forward and backward), and we find again that the distance between $\beta^*(N_B)$ and $\beta^0(N_B)$ is approximately constant (wherever $\beta^0(N_B)$ exists) and equals 0.053 ± 0.002 mol/kJ and 0.00111 ± 0.00002 mol/kJ (forward)/ 0.0021 ± 0.0001 mol/kJ (backward), respectively.

An immediate interpretation of this constant $\Delta\beta$ would be to identify it with a lag distance in the (N_B, β) -space in analogy to that defined in ref 22 and found to be constant for an optimal process based on thermodynamic length. However, this interpretation encounters serious difficulties. On a formal level, whereas the internal energy U and entropy S form “good metrics” (i.e. with the same sign everywhere) due to the traditional principles of an equilibrium system having minimum energy/maximum entropy, no such extremum principle exists for particle number N . The straightforward connection between $\Delta N = N^*(\beta) - N^0(\beta)$ and $\Delta\beta$ would be made via $\partial^2 N / \partial \beta^2$, but $\partial^2 N / \partial \beta^2$ changes sign at least once over the full range of β , $[0, \infty]$, so a metric based on this quantity is not useful. Consequently, the usual optimality criterion²² of constant thermodynamic speed cannot be applied, and the amazing constancy of $\Delta\beta$ must have a different interpretation.

On a more practical level one should notice two important aspects which distinguish our finite-time optimization from traditional problems in finite-time thermodynamics to which the concept of thermodynamic length has been applied.

(i) The system does not move between two predefined thermodynamic states, $N(0)$ and $N(\tau)$, while some other quantity, e.g. entropy or availability, is produced/lost in an optimal fashion due to the finite time available. Instead the task calls for the maximization of $N(\tau)$, where the only constraints are the finite duration τ and the reaction rate $f(N, \beta)$. In other words, our final state is also part of the optimization, not just the intervening path.

(ii) No matter how much time τ available, the optimal path will never approach the equilibrium curve. That is, $\Delta\beta$ is not a function of τ , and $\Delta\beta \not\rightarrow 0$ as $\tau \rightarrow \infty$ precisely because the final state $N(\tau)$ is not fixed but part of the optimization.

As a consequence, we suggest that the proper reference curve with respect to which a thermodynamic distance is to be defined and measured is the optimal path, i.e. the curve of maximum reaction rate. Similarly, the quantity that should be minimized due to deviations from the optimal path (e.g. if only a finite number of temperature adjustments are allowed) is the amount of “underproduced” material compared to the optimal path, or, correspondingly, the extra time necessary to produce the same amount of product as along the optimal path. The treatment then will be analogous to the study of quasistatic processes with a finite number of steps.²⁴ Note that along the optimal path $\partial^2 f / \partial \beta^2$ is always of only one sign (away from the boundary).

Similarly, we expect that the optimal path will proceed with constant thermodynamic speed, i.e. will keep a constant thermodynamic distance—measured in the entropy metric—away

from the equilibrium curve if we minimize, for example, the entropy production during a chemical reaction that results in a well-prescribed amount of reaction products. This is analogous to the standard posing of the problem in finite-time thermodynamics.

Nevertheless, the question remains whether the approximate constancy of $\Delta\beta$ is a general consequence of the optimization. Clearly, if and when it can be shown that optimality implies a constant $\Delta\beta$, this optimality criterion could then be used to determine the optimal path for those systems of chemical reactions that do not yield easily to optimization methods like the one used in section 2. This will be of special importance since for general chemical systems it is considerably easier to determine the curve of equilibrium values than the actual optimal path.

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Appendix 1: Extremal Points for Constraint 1

The general rate equation taken from eq 1 is

$$f(N_B, V, \beta) = a e^{-\beta E_A} \frac{N_A^n}{V^{n-1}} \left(1 - e^{-\beta \Delta} \frac{g}{V^{m-n}} \right) \quad (\text{A1})$$

with the additional definition

$$g(N_B) = \frac{b N_B^m}{a N_A^n} \quad (\text{A2})$$

Remember that mass conservation implies that $N_A = N_0 - (n/m)N_B$. We also require the partial derivatives

$$f_V = \frac{\partial f}{\partial V} = -a e^{-\beta E_A} \frac{N_A^n}{V^n} \left[(n-1) - (m-1) e^{-\beta \Delta} \frac{g}{V^{m-n}} \right] \quad (\text{A3})$$

$$f_{VV} = \frac{\partial^2 f}{\partial V^2} = a e^{-\beta E_A} \frac{N_A^n}{V^{n+1}} \left[n(n-1) - m(m-1) e^{-\beta \Delta} \frac{g}{V^{m-n}} \right] \quad (\text{A4})$$

$$f_\beta = \frac{\partial f}{\partial \beta} = -a e^{-\beta E_A} \frac{N_A^n}{V^{n-1}} \left[E_A - E_B e^{-\beta \Delta} \frac{g}{V^{m-n}} \right] \quad (\text{A5})$$

$$f_{\beta\beta} = \frac{\partial^2 f}{\partial \beta^2} = a e^{-\beta E_A} \frac{N_A^n}{V^{n-1}} \left[E_A^2 - E_B^2 e^{-\beta \Delta} \frac{g}{V^{m-n}} \right] \quad (\text{A6})$$

Using eqs A1, A3, and A5, one can determine the critical points of f and the points of zero reaction rate:

$$f(V^0, \beta^0) = 0 \Leftrightarrow V^0(\beta^0) = \exp\left(-\frac{\beta^0 \Delta}{m-n}\right) g(N_B)^{1/(m-n)} \quad (\text{A7})$$

$$f_V(V^V, \beta^V) = 0 \Leftrightarrow V^V(\beta^V) = \left(\frac{m-1}{n-1}\right)^{1/(m-n)} \exp\left(-\frac{\beta^V \Delta}{m-n}\right) g(N_B)^{1/(m-n)} \quad (\text{A8})$$

$$f_{\beta}(V^{\beta}, \beta^{\beta}) = 0 \Leftrightarrow$$

$$V^{\beta}(\beta^{\beta}) = \left(\frac{E_B}{E_A}\right)^{1/(m-n)} \exp\left(-\frac{\beta^{\beta}\Delta}{m-n}\right) g(N_B)^{1/(m-n)} \quad (\text{A9})$$

Note the special cases

$$m = n > 1: \quad \beta^0(V) = \frac{\ln(g(N_B))}{\Delta} \quad (\text{A7}')$$

$$\beta^V(V) = \frac{\ln(g(N_B))}{\Delta} \quad (\text{A8}')$$

$$\beta^{\beta}(V) = \frac{\ln(g(N_B))}{\Delta} + \frac{\ln(E_B/E_A)}{\Delta} \quad (\text{A9}')$$

$$m > n = 1: \quad f_V(V, \beta) > 0 \Leftrightarrow f \text{ increases monotonically} \\ \text{with } V \text{ for all } \beta \quad (\text{A3}')$$

$$m = n = 1: \quad f(V, \beta) = f(\beta), \text{ i.e. the problem is} \\ \text{volume independent} \quad (\text{A1}')$$

From $f_{\beta\beta}$ we can further conclude that $(V^{\beta}, \beta^{\beta})$ are local minima in the β -direction if $\Delta < 0$ and local maxima in the β -direction if $\Delta > 0$. From f_{VV} follows that (V^V, β^V) are always local maxima in the V -direction if $m > n > 1$. If $m = n > 1$, then $\beta^V(V)$ corresponds to a line of saddle points, and

$$f_V > 0 \text{ for } \beta < \beta^V \\ f_V < 0 \text{ for } \beta > \beta^V \quad (\text{A10})$$

Appendix 2: Extremal Points for Constraint 2

Entering the constant pressure $p = (N_A + N_B)/V\beta$ into the general rate equation, eq 1, and taking the β -derivative, we arrive at

$$f(N_B, \beta) = a \frac{N_A^n}{(N_A + N_B)^{n-1}} p^{n-1} \beta^{n-1} e^{-\beta E_A} (1 - h \beta^{m-n} e^{-\beta \Delta}) \quad (\text{A11})$$

and

$$f_{\beta} = \frac{\partial f}{\partial \beta} = a \frac{N_A^n}{(N_A + N_B)^{n-1}} p^{n-1} \beta^{n-2} e^{-\beta E_A} [n - 1 - \beta E_A - \\ h(m - 1 - \beta E_B) \beta^{m-n} e^{-\beta \Delta}] \quad (\text{A12})$$

with the definition

$$h(N_B) = \frac{b}{a} \frac{N_B^m}{N_A^n (N_A + N_B)^{m-n}} p^{m-n} \quad (\text{A13})$$

The zeroes and critical points of the reaction rate now follow:

$$f(\beta^0) = 0 \Leftrightarrow \beta^0 = 0 \text{ if } n > 1 \text{ or } \beta^0 = \infty \text{ or} \\ e^{\beta^0 \Delta} = h(\beta^0)^{m-n} \quad (\text{A14})$$

$$f_{\beta}(\beta^{\beta}) = 0 \Leftrightarrow \beta^{\beta} = 0 \text{ if } n \geq 2 \text{ or } \beta^{\beta} = \infty \text{ or} \\ (n - 1 - \beta^{\beta} E_A) e^{\beta^{\beta} \Delta} - \\ h(m - 1 - \beta^{\beta} E_B) (\beta^{\beta})^{m-n} = 0 \quad (\text{A15})$$

In general the number of solutions (in addition to $\beta = 0$ and ∞) to eqs A14 and A15 will depend on the value of $h(N_B)$.

The limiting values of f are

$$f(\beta \rightarrow \infty) = \begin{cases} 0^+ & \text{for } \Delta > 0 \\ 0^- & \text{for } \Delta < 0 \end{cases} \quad (\text{A16})$$

$$f(\beta=0) = \begin{cases} 0 & \text{for } n > 1 \\ aN_A & \text{for } m > n = 1 \\ aN_A - bN_B & \text{for } m = n = 1 \end{cases} \quad (\text{A17})$$

Similarly,

$$f_{\beta}(\beta \rightarrow \infty) = \begin{cases} 0^- & \text{for } \Delta > 0 \\ 0^+ & \text{for } \Delta < 0 \end{cases} \quad (\text{A18})$$

$$f_{\beta}(\beta=0) = \begin{cases} 0 & \text{for } n > 2 \\ \frac{N_A^2}{a(N_A + N_B)p} & \text{for } m > n = 2 \\ \frac{(aN_A^2 - bN_B^2)}{(N_A + N_B)p} & \text{for } m = n = 2 \\ -aN_A E_A & \text{for } m > 2, n = 1 \\ -b \frac{N_B^2}{N_A + N_B} p - aN_A E_A & \text{for } m = 2, n = 1 \\ bN_B E_B - aN_A E_A & \text{for } m = n = 1 \end{cases} \quad (\text{A19})$$

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