

On the Error of the Quasi-Steady-State Approximation

T. Turányi,^{†,‡} A. S. Tomlin,[†] and M. J. Pilling^{*,†}

School of Chemistry, The University of Leeds, Leeds, LS2 9JT, UK, and Central Research Institute for Chemistry, P.O. Box 17, H-1525 Budapest, Hungary

Received: July 24, 1992; In Final Form: October 6, 1992

Application of the quasi-steady-state approximation (QSSA) in chemical kinetics allows the concentration of some species (QSSA species) to be calculated not only via the solution of kinetic differential equations but also from the concentration of other species using algebraic equations. The difference in the concentrations of QSSA species obtained from the two calculations, at a single time point, is called the instantaneous QSSA error. This error represents a continuous perturbation of the calculated trajectory and causes an overall error in the concentrations of non-QSSA species as well. Two equations are given for the calculation of the instantaneous error. Initial selection of QSSA species can be based on the first equation, which predicts the instantaneous error of a single species. The second more involved error equation takes into account the interaction of errors of selected species and gives the instantaneous error for a group of QSSA species. Successful application of the QSSA requires that the overall error of important species be small. In some cases a small instantaneous error in the QSSA species can be magnified and results in large overall error. Such "pathological" cases can be detected by the calculation of the initial concentration sensitivity matrix. Those species, which induce large overall error, have to be excluded from the group of the QSSA species. The relation of the QSSA to the lifetime of species and to the stiffness of ODEs is also discussed. The use of the error formulas is illustrated by the application of the QSSA for a propane pyrolysis mechanism and briefly for the combustion of H₂.

1. Introduction

1.1. Definition of the QSSA. The kinetics of a spatially homogeneous reaction system can be described by the following system of ordinary differential equations (more exactly by an initial value problem):

$$dc/dt = f(c, k), \quad c(0) = c_0 \quad (1)$$

where c is the n -dimensional vector of concentrations of species \mathcal{C} , and k is the m -dimensional vector of parameters.

The application of the quasi-steady-state approximation (QSSA) involves the replacement of some of the differential equations by algebraic equations, by assigning the right-hand side of the differential equations to zero. The solution of this differential-algebraic system of equations should be real, positive, and in good accordance with the solution of the original system of ordinary differential equations.

1.2. Summary of Previous Results Concerning the Application of the QSSA. The QSSA was first applied in 1913 to chemical kinetic schemes by Bodenstein¹ and by Chapman and Underhill.² Its application spread after the publication of a further article by Bodenstein,³ and the QSSA is often referred to as the Bodenstein method. In the Russian literature it is also known as the Bodenstein–Semenov method, since Semenov^{4–6} was the first to apply it to substantially nonstationary processes and to restrict its use to only some of the intermediates rather than to all of them.

The QSSA has been applied for several purposes during the history of chemical kinetics: in the precomputer age (1913 to ≈1960) it was used to obtain approximate analytical solutions for systems of kinetic differential equations. In the next era (≈1960 to 1971) the computer was available to chemists, but efficient programs did not exist for the solution of the stiff differential equations which frequently occur in chemical kinetics. The QSSA was therefore used for the conversion of stiff differential equations into nonstiff systems.^{7,8} Nowadays stiff ordinary differential equations can be solved numerically in most

practical cases, making this application less important. It has been suggested that the QSSA is therefore a redundant technique and that its use should be discontinued.^{9–13}

Even if such an argument were valid, an understanding of the basis and applicability of the QSSA would still be needed, as has been emphasised by Côme:¹⁴ "since the QSSA has been used to elucidate most reaction mechanisms and to determine [many] rate coefficients of elementary processes, a fundamental answer to the question of the validity of the approximation seems desirable".

Further, the QSSA remains a powerful tool for the simplification of reaction structures. Indeed, recent years have witnessed the renaissance of the application of the QSSA for kinetic simulations. The speed of computers enables the simulation of spatially inhomogeneous chemical kinetic systems, which are of great practical importance in atmospheric and in combustion chemistry. However, these models require a precise yet realistic description of chemical processes. In flame modeling for example, Peters^{15–20} derived reduced chemical schemes with the extensive use of the QSSA, and this method is now widely used^{21,22} for obtaining small chemical kinetic models for fluid dynamic calculations. The Peters method, however, does not include a general recipe for the selection of QSSA species.

General conditions for the application of the QSSA have been sought for a long time. In several articles, the same kinetic system has been simulated with and without the application of QSSA and the results have been compared (see refs 11, 12, and 23–28). Unfortunately these investigations have given information about the applicability of the QSSA only for specific reaction systems, at the circumstances investigated, and for the QSSA species selected. No general rules could be formulated, and in some cases the results from the two calculations did not agree but no reasons were given. Other researchers have investigated the applicability of the QSSA for small reaction systems.^{29–34} Their results are general for the system investigated but cannot be transferred to other systems. In particular, the application of the QSSA to the Michaelis–Menten scheme was the topic of several studies (see, e.g., refs 35–40). The most advanced example of

[†] The University of Leeds.

[‡] Central Research Institute for Chemistry.

this approach considers a scheme in which the steps represent general elementary reaction types.⁴¹

The most frequently applied method for the general investigation of the QSSA is based on singular perturbation theory.^{30,35,40-47} A review of such investigations is given by Klonowski.³⁸ The main result, given by the Tihonov theorem,⁴⁸ lists conditions, fulfilled in most chemical kinetic systems, which represent necessary conditions for the approximation of the solution of the kinetic differential equation by the QSSA solution. Time scales are related to variables (species concentrations), and the QSSA species are characterized by a short characteristic time. However, this mathematical technique seems to be ineffective for the calculation of the QSSA error for large systems.

Principal component analysis of either the concentration or rate sensitivity matrices has been employed to investigate the parameter combinations that reflect the influence of QSSA species through their reactions.^{49,50} A geometrical picture of the QSSA has been developed by Fraser et al.,^{37,51-53} the central idea being that the solution of the kinetic differential equations is attracted by smooth surfaces, the slow manifolds \mathcal{M} which can be approximated by the QSSA solution. A detailed analysis is given for several reversibly connected, rapidly equilibrating networks, coupled to an irreversible consuming reaction.

Discussion in the chemical literature has provided insight into the QSSA without rigorous mathematical proof. For example, Williams⁵⁴ concludes that the QSSA is applicable for a species if the sums of rates of its consuming and producing reactions are both much higher than its net production rate. A common idea in the literature however, is that the radicals and the QSSA species are the same. This empirical observation is applicable in most cases, but there are noticeable breakdowns. For example, (see, e.g., ref 7), the QSSA is not applicable at low conversions for radical Br in the H₂-Br₂ reaction system. The QSSA is not always applicable in atmospheric chemical systems for peroxy radicals,¹¹ which are not very reactive at ambient temperature. It is also not applicable in several combustion systems⁵⁵⁻⁵⁷ for H, despite its high reactivity. On the other hand, the belief that it can only be applied to radicals, has unnecessarily limited its usage. For example, under some circumstances, the QSSA is applicable for the molecule diallyl in a propane pyrolysis model.⁵⁸

1.3. Outline. In this paper we seek general methods for the selection of QSSA species via a discussion of the source of errors induced by the quasi steady-state approximation. In section 2 we introduce definitions of QSSA species and their errors. In section 3 error formulas are given for the rapid calculation of the deviation of the QSSA species concentrations from the full ODE solution at a specific time point. This "instantaneous error" can be calculated for a single species or for a group of selected QSSA species. In section 4 we examine a dynamic picture which serves to illustrate the physical interpretation of the QSSA. Section 5 discusses the propagation of QSSA errors and how "pathological" QSSA species, whose errors spread quickly to other species, can be identified. In section 6 we summarize an algorithm for identifying QSSA species, and in section 7 introduce the connections between the QSSA error and the species lifetime. In section 8 the effect of the removal of QSSA species on the stiffness of a system is discussed, and in section 9 we investigate some practical methods for the solution of the resulting set of algebraic equations and the application of the QSSA in mechanism reduction. In section 10 we illustrate the method with reference to a scheme describing low-conversion propane cracking and briefly to a scheme describing the oxidation of hydrogen in a flow reactor. Here we compare the actual errors, i.e. the deviation of the concentrations calculated from the differential-algebraic scheme and from the full differential scheme, with the estimated error calculated from the formulae derived in the previous sections. Finally, in section 11, we summarize and draw conclusions.

2. Errors in the Application of the QSSA

For simplicity, we restrict our investigations to spatially homogeneous systems. The conclusions can be extended to spatially inhomogeneous systems.

According to the QSSA, the group of species corresponding to the concentration vector \mathbf{c} in eq 1 can be classified into two groups: $\mathcal{C} = (\mathcal{C}^{(1)}, \mathcal{C}^{(2)})$, where $\mathcal{C}^{(1)}$ are the non-QSSA species and $\mathcal{C}^{(2)}$ are the QSSA species. The concentrations of the species calculated from eq 1 are $\mathbf{c}^{(1)}$ and $\mathbf{c}^{(2)}$, respectively. Hence $\mathbf{c} = (\mathbf{c}^{(1)}, \mathbf{c}^{(2)})^T$ and the corresponding rates of change of concentration are $\mathbf{f}^{(1)}$ and $\mathbf{f}^{(2)}$, respectively. Let the matrix $\mathbf{J}(t)$ with elements $\partial f_i / \partial c_j$ denote the Jacobian of eq 1. Submatrices of the Jacobian will also be used according to the following partitioning:

$$\mathbf{J} = \begin{pmatrix} \mathbf{J}^{(11)} & \mathbf{J}^{(12)} \\ \mathbf{J}^{(21)} & \mathbf{J}^{(22)} \end{pmatrix} = \begin{pmatrix} \frac{\partial \mathbf{f}^{(1)}}{\partial \mathbf{c}^{(1)}} & \frac{\partial \mathbf{f}^{(1)}}{\partial \mathbf{c}^{(2)}} \\ \frac{\partial \mathbf{f}^{(2)}}{\partial \mathbf{c}^{(1)}} & \frac{\partial \mathbf{f}^{(2)}}{\partial \mathbf{c}^{(2)}} \end{pmatrix} \quad (2)$$

The application of the QSSA converts eq 1 into the following system of differential-algebraic equations:

$$d\mathbf{C}^{(1)}/dt = \mathbf{f}^{(1)}(\mathbf{C}, \mathbf{k}) \quad (3)$$

$$0 = \mathbf{f}^{(2)}(\mathbf{C}, \mathbf{k}) \quad (4)$$

$$\mathbf{C}(0) = \mathbf{c}_0$$

The concentrations of the species calculated from eqs 3 and 4 are defined as the QSSA concentrations $\mathbf{C}^{(1)}$ and $\mathbf{C}^{(2)}$, respectively. It is assumed that eq 4 has at least one real positive root. The set of algebraic equations need not necessarily be linear; quadratic terms arise, for example, if the QSSA species are coupled through certain reactions. More than one solution may then be possible, and for systems with multiple roots, the nearest root to the exact concentration is selected. Equation 4 can be considered as an equation for the steady state of a reaction scheme, where the non-QSSA species have constant concentration (external species). A discussion of conditions for the existence and uniqueness of steady-states of chemical reaction systems can be found in section 4.4 of ref 59. A trivial requirement is that all the QSSA species have to be intermediates.

If the QSSA species are selected properly, the solution of the system of differential equations 3, connected to algebraic equations 4, does not differ significantly from the solution of system 1 during the time interval of application. The key question is the selection of the group of QSSA species. This selection depends on the tolerated error in concentration from the QSSA solution and therefore an assessment of the error of the application of the QSSA is required. The unavailability of a method to calculate such error estimates, other than via a simulation of the mechanism with and without the application of the QSSA, has been one of the major criticisms of the QSSA.⁶⁰

In the majority of chemical kinetic simulations, most of the species concentrations are zero at the beginning of the simulation. One practical observation is that the QSSA can be applied only after a time period called the induction period. The difference in the QSSA species concentrations at the starting time of the application of the QSSA, calculated from eq 1 and eqs 4 and 3, is the *instantaneous* error of the quasi-steady-state approximation. If the concentration-time curves of non-QSSA species, obtained by the solution of ODE 1 and eqs 3 and 4 were exactly the same, i.e., $\mathbf{C}^{(1)} = \mathbf{c}^{(1)}$, the instantaneous error could be obtained at any subsequent time in exactly the same way.

While the instantaneous error refers only to the QSSA species, in practice the concentrations of non-QSSA species are also affected by the application of the quasi-steady-state approximation. The *overall* QSSA error is the difference in the calculated

concentrations of all species, with and without the application of the QSSA. The error in the QSSA species concentrations implies a continuous perturbation of the calculated trajectories. This results in a change in the other species concentrations which propagates back through eq 4 to the QSSA species so that their overall error can be different from their instantaneous error. However, if the overall error of non-QSSA species is small, the overall error of QSSA species is close to their instantaneous error.

From a practical point of view, each species of a kinetic mechanism can be classified into one of the important, necessary and redundant categories.⁶¹ The modeller is interested only in the concentration of important species but the calculation of the concentration of necessary species is also required because of their coupling to important species. Redundant species are those species which can be removed from the scheme with no significant effect on the important species, and can be identified through a Jacobian analysis. The reduced mechanism contains only important and necessary species. The *overall error of important species* is the central measure of the applicability of quasi-steady-state approximation. Usually, the important species are non-QSSA species and hence the calculation of the instantaneous error is not enough. However, small instantaneous errors usually imply small overall errors.

3. Calculation of the Instantaneous Error

Frank-Kamenetskii⁶² was the first to investigate general criteria for the applicability of the QSSA which could be applied to any mechanism and to any number of intermediate species. The starting point of his ideas is reproduced below, using the notation and terminology introduced in the previous section.

Let $\mathbf{C} = (\mathbf{c}^{(1)}, \mathbf{C}^{(2)})$ be the concentration of species calculated from eqs 3 and 4, i.e., assume that the overall error of non-QSSA species is negligible. Let $\Delta \mathbf{c}^{(2)}$ denote the instantaneous error of QSSA species, i.e., $\Delta \mathbf{c}^{(2)} = \mathbf{c}^{(2)} - \mathbf{C}^{(2)}$, and i and k the indexes of the QSSA species.

A Taylor series approximation of dc_i/dt around C_i gives eq 5 (neglecting the second and higher order terms). [Note that in

$$dc_i/dt = [f_i(\mathbf{c}, \mathbf{k})]_{\mathbf{c}=\mathbf{C}} + \sum_k [\partial f_i(\mathbf{c}, \mathbf{k}) / \partial c_k]_{\mathbf{c}=\mathbf{C}} \Delta c_k \quad (5)$$

a real mechanism the order of an elementary reaction is never higher than three, in most cases being only one or two, and thus the second derivatives are either equal to zero or contain second-order rate coefficients. The third and fourth terms of the Taylor series therefore provide only a small contribution to dc_i/dt if Δc_i is small. Hence, the truncation of the Taylor series after the second term is, in most practical cases, a good approximation.]

The definition of the QSSA in eq 4 implies that $[f_i(\mathbf{c}, \mathbf{k})]_{\mathbf{c}=\mathbf{C}} = 0$ and eq 5 can be rearranged into the following form:

$$\Delta c_i^s = \frac{1}{J_{ii}} \frac{dc_i}{dt} - \frac{1}{J_{ii}} \sum_{k \neq i} J_{ik} \Delta c_k^s \quad (6)$$

where $J_{ik} = [\partial f_i(\mathbf{c}, \mathbf{k}) / \partial c_k]_{\mathbf{c}=\mathbf{C}}$. From now on Δc_i^s will denote an approximated error derived from eq 6, and Δc_i the real error derived from the difference in solutions of eq 1 and eqs 3 and 4.

Frank-Kamenetskii did not use eq 6 for the calculation of the instantaneous error directly, but, based on this equation and using several approximations, he concluded that species i is a QSSA species, in most practical cases, if $\max_j |d \ln c_j / dt|$ is smaller than $|\partial f_i / \partial c_i|_{\mathbf{c}=\mathbf{C}}$, where j denotes the index of any species.

In this paper the approximation of the instantaneous error based on eq 5 is exploited. Using a matrix formalism, eq 5 can also be rearranged into the form

$$d\mathbf{c}^{(2)} / dt = \mathbf{J}^{(22)} \Delta \mathbf{c}^{s(2)} \quad (7)$$

Equation 7 represents a set of linear algebraic equations for $\Delta \mathbf{c}^{s(2)}$

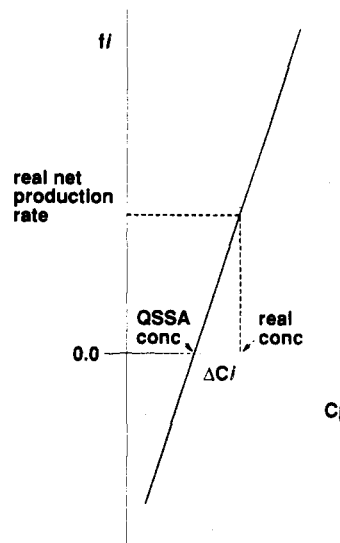


Figure 1. Schematic plot of the actual and QSSA values of f_i against c_i for a QSSA species, showing that small errors are possible even for large actual values of f_i provided the slope of f_i , given by $\partial f_i / \partial c_i$ is steep.

whose solution gives the instantaneous error of the quasi-steady-state approximation for each of the group of QSSA species.

The second term on the right-hand side of eq 6 corresponds to the interaction of the instantaneous errors of QSSA species. If this interaction is neglected, eq 6 can be simplified and a separate equation for the approximate instantaneous error Δc_i^s of each individual species is obtained:

$$dc_i/dt = J_{ii} \Delta c_i^s \quad (8)$$

This equation is equivalent to eq 6 if a single QSSA species rather than a group of QSSA species is considered.

Equation 8 shows that the quasi-steady-state approximation does not imply that the net production rate of a QSSA species is zero. Clearly f_i is zero when c_i is equal to the QSSA concentration C_i and $\Delta c_i^s = 0$. However, Δc_i^s can still be small, even if f_i is nonzero, provided $|\partial f_i / \partial c_i| = |J_{ii}|$ is large (see eq 8); indeed, substantial values of f_i can be tolerated provided $|J_{ii}|$ is itself sufficiently large. This point is illustrated schematically in Figure 1, which shows a plot of f_i vs c_i and demonstrates that Δc_i^s is small for large f_i , if the slope $|\partial f_i / \partial c_i|$ is sufficiently steep. The connection with stationary-state calculations are also illustrated through eq 8, since if $f_i = 0$, eq 4 can always be applied.

The solution of eqs 7 and 8 gives not only the magnitude of the instantaneous error but also its sign, which is most easily demonstrated through eq 8 for a single species. The diagonal elements of the sub-Jacobian $J_{ii}^{(22)}$, are invariably negative. It is possible to construct a Jacobian having a positive diagonal element (e.g., when the mechanism contains an autocatalytic, $\mathcal{X} + \mathcal{A} = 2\mathcal{X} + \mathcal{B}$, type reaction), but such reactions are not found in mechanisms constructed from elementary reactions. J_{ii} is zero only if species c_i has no consuming reactions. A QSSA species will always have at least one consuming reaction which is first or higher order in c_i for a mechanism composed of elementary reactions. Thus Δc_i^s takes a sign opposite to that of f_i so that if c_i is increasing, then the QSSA concentration, C_i , is greater than c_i . Only if f_i is identically zero is $c_i = C_i$. Unfortunately in the case of several QSSA species a similarly clear interpretation of the sign of the instantaneous error cannot be given.

Equations 7 and 8 give a means of estimating the absolute instantaneous error. The comparison of different species from the point-of-view of QSSA behavior requires the calculation of the fractional or percentage instantaneous error of quasi-steady-

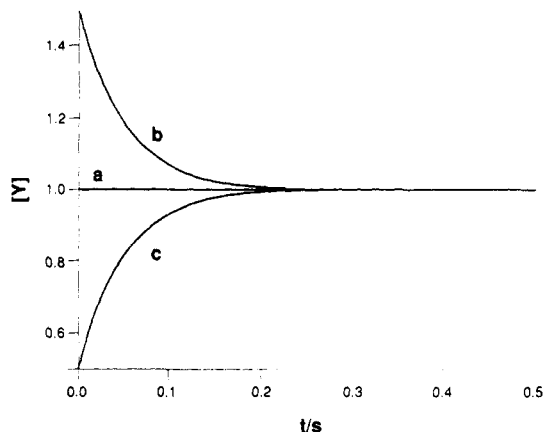


Figure 2. Relaxation to a steady-state, $X \rightleftharpoons Y$, $k_f = k_b = 10 \text{ s}^{-1}$: (a) A steady-state solution $X = Y = 1$, (b) $X_0 = 0.5$, $Y_0 = 1.5$, (c) $X_0 = 1.5$, $Y_0 = 0.5$.

state approximation. The fractional error is given by

$$e_i = \Delta c_i / c_i \quad (9)$$

4. Instantaneous Error: A Dynamic Approach

The derivation of the error equations in the previous section is based on a static approach. Now a second, dynamic approach is also presented, which gives more insight into the physical background of the QSSA.

An important feature of QSSA species is that their concentrations are completely determined by the concentration of other species through eq 4. If the concentrations of the QSSA species calculated by eq 1 are perturbed slightly, this perturbation must vanish within a short time. This property of QSSA species has been noted previously, by Klonowski for example (ref 38, p 83), who stated that "the fast components 'forget' their initial values". Thus a perturbation analysis can also be used as a probe of the QSSA behavior.

On the basis of a linear approach, the history of any perturbation in a dynamic system can be described by the equation

$$\Delta \mathbf{c}(t) = e^{\mathbf{J}(t)t} \Delta \mathbf{c}_0 \quad (10)$$

where $\Delta \mathbf{c}_0$ is the perturbation at $t = 0$, $\Delta \mathbf{c}(t)$ is the deviation at time t , and $\mathbf{J}(t)$ is the Jacobian of the system.

The corresponding initial value problem

$$d\Delta \mathbf{c}/dt = \mathbf{J}\Delta \mathbf{c}, \quad \Delta \mathbf{c}(0) = \Delta \mathbf{c}_0 \quad (11)$$

can be expanded using the partitioned Jacobian introduced in eq 2 to give

$$\begin{aligned} d\Delta \mathbf{c}^{(1)}/dt &= \mathbf{J}^{(11)}\Delta \mathbf{c}^{(1)} + \mathbf{J}^{(12)}\Delta \mathbf{c}^{(2)} \\ d\Delta \mathbf{c}^{(2)}/dt &= \mathbf{J}^{(21)}\Delta \mathbf{c}^{(1)} + \mathbf{J}^{(22)}\Delta \mathbf{c}^{(2)} \end{aligned} \quad (12)$$

If the perturbation is limited to the QSSA species over a very short time period, then the concentration of the non-QSSA species can be assumed to be unchanged. We also assume in this case that no error is induced in the non-QSSA species and so $\Delta \mathbf{c}^{(1)}$ is zero, i.e. we consider, in effect only the instantaneous error.

Equation 12 then reduces to a single equation in $\Delta \mathbf{c}^{(2)}$:

$$\frac{d\Delta \mathbf{c}^{(2)}}{dt} = \mathbf{J}^{(22)}\Delta \mathbf{c}^{(2)}, \quad \Delta \mathbf{c}^{(2)}(0) = \Delta \mathbf{c}_0^{(2)} \quad (13)$$

The rate of relaxation of a perturbation therefore depends on the distance of the perturbed solution from the fixed point, and on the magnitude of the Jacobian. If the fixed point is stationary then the perturbed solution tends exactly to the fixed point. This case is illustrated via the reaction $X \rightleftharpoons Y$ with $k_f = k_b = 10 \text{ s}^{-1}$ (Figure 2), which has a simple steady state for $X = Y = 1$. Solutions

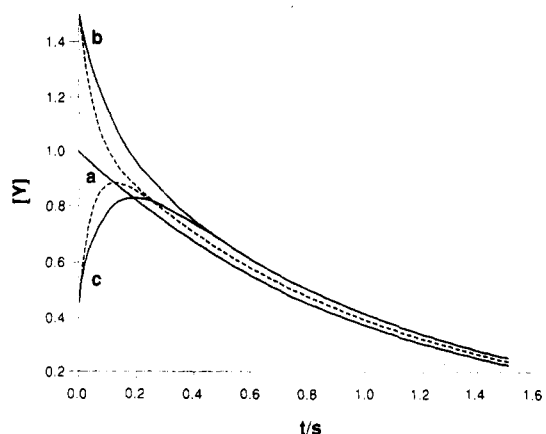
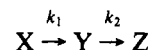


Figure 3. Relaxation to a quasi steady-state, $X \xrightarrow{k_1} Y \xrightarrow{k_2} Z$ for $k_1 = 1 \text{ s}^{-1}$ and $k_2 = 10 \text{ s}^{-1}$ (---) and $k_2 = 20 \text{ s}^{-1}$ (—). (a) real solution, $X_0 = 10$ (---), 20 (—), $Y_0 = 1.0$, (b) perturbed solution, $X_0 = 10$ (---), 20 (—), $Y_0 = 1.5$, (c) perturbed solution, $X_0 = 10$ (---), 20 (—), $Y_0 = 0.5$. The perturbation of a shorter lifetime species relaxes more quickly and its trajectory becomes closer to the real solution.

with initial conditions away from the steady state eventually relax to the steady state.

If we consider a quasi stationary system then the fixed point moves with a speed $dc^{(2)}/dt$. The Jacobian elements for the QSSA species will be large as discussed in section 3, and so the initial approach will be fast. However, since the fixed point is moving in time, the perturbed solution will never exactly reach it but will remain at a distance $\Delta c^{(2)}$. The scheme



in Figure 3 illustrates this case. Y can be considered a QSSA species whose quasi-steady-state concentration decays with time. The real concentration therefore never reaches the QSSA concentration but remains above it since dy/dt is negative. The final distance depends on the size of k_2 and hence on the lifetime of Y. This distance is the error induced by the application of the QSSA and is governed by the speed of the quasi stationary point. Since we use the quasi-stationary point as our reference system $dc^{(2)}/dt = 0$ and

$$\frac{d\Delta \mathbf{c}^{(2)}}{dt} = \frac{d\mathbf{c}^{(2)}}{dt} - \frac{d\mathbf{c}^{(2)}}{dt} = \frac{d\mathbf{c}^{(2)}}{dt} \quad (14)$$

Hence

$$d\mathbf{c}^{(2)}/dt = \mathbf{J}^{(22)}\Delta \mathbf{c}^{(2)} \quad (15)$$

and we again arrive at eq 7.

If there is a single QSSA species and the effect of the perturbation of its concentration on the concentration of any other species can be neglected, the corresponding equations are

$$\Delta c_i(t) = \Delta c_i^0 e^{J_{ii}t} \quad (16)$$

$$\frac{d\Delta c_i}{dt} = J_{ii}\Delta c_i, \quad \Delta c_i(0) = \Delta c_i^0 \quad (17)$$

$$dc_i/dt = J_{ii}\Delta c_i \quad (18)$$

where eq 18 is identical to eq 8. As before, this equation can also be considered as a first approximation in the case of several QSSA species.

The induction period can also be interpreted in terms of a perturbation analysis. Let us assume that the concentrations of QSSA species are zero at $t=0$ and the concentrations of non-QSSA species do not change significantly during the induction period. The non-QSSA species concentrations determine a quasi-stationary point for the QSSA species and the real concentrations of QSSA species approach this point from zero. So here the

perturbation is the difference between the real initial concentrations and those calculated using the QSSA. This is not an infinitesimal perturbation but equations 10 and 16 can be applied as a rough estimation. For simplicity consider this relaxation for each species separately. Let the fractional error of the QSSA species be not more than r_i at the end of the induction period t_i^{ind} . $r_i = \Delta c_i(t_{\text{ind}})/C_i^0$ since the QSSA concentration is assumed not to change with time. The real concentration is zero at the initial time, hence $C_i^0 = \Delta c_i^0$ and $r_i = \Delta c_i(t_{\text{ind}})/\Delta c_i^0$. Substituting for $\Delta c_i(t_{\text{ind}})$ in eq 16, the induction period for a QSSA species i is given approximately by

$$r_i \Delta c_i^0 \approx \Delta c_i^0 e^{J_{ii} t_i^{\text{ind}}} \quad (19)$$

$$t_i^{\text{ind}} \approx (\ln r_i)/J_{ii} \quad (20)$$

Thus a rough estimate can be given for the length of the induction period of QSSA species i which depends only on the accuracy limit required and the corresponding diagonal element of the Jacobian. If $r_i = 5 \times 10^{-5}$, then $t_i^{\text{ind}} \approx -10/J_{ii}$. Note that t_i^{ind} depends only logarithmically on r_i .

If there are several QSSA species, the quasi-steady-state approximation can be applied only after passing the induction period for each QSSA species. Therefore

$$t^{\text{ind}} = \max_i t_i^{\text{ind}} \quad (21)$$

where i runs over the indexes of the QSSA species.

The length of induction period can be determined exactly by calculating the instantaneous error at several times, but eq 20 provides a guideline.

5. Propagation of Instantaneous Errors

Small instantaneous errors of QSSA species forecast but do not justify small overall errors of important species. The error of QSSA species implies a continuous perturbation of concentration trajectories and therefore the overall error can be assessed by studying the effect of the growth or decay of this perturbation in time. For non-QSSA species this overall error $\Delta_{\text{ov}}c$ can be calculated by the solution of eq 1, giving the Jacobian elements along with the following equation:

$$d\Delta_{\text{ov}}c^{(1)}/dt = J^{(1)}\Delta_{\text{ov}}c^{(1)} + J^{(12)}\Delta_{\text{ov}}c^{(2)}, \quad \Delta_{\text{ov}}c^{(1)}(t_0) = 0 \quad (22)$$

Although this equation indicates how the errors of the QSSA and non-QSSA species are coupled it is difficult to calculate since we now only the instantaneous errors of the QSSA species and not the overall errors. For small $\Delta_{\text{ov}}c^{(1)}$ however these two errors should be similar and we can substitute the instantaneous error $\Delta c_i^{(2)}$ for $\Delta_{\text{ov}}c^{(2)}$ in eq 22.

In most cases it is enough to calculate the instantaneous error for the QSSA species and to check whether they cause large errors in important species, either directly or indirectly through another species. These "problematic" QSSA species can be detected in both cases by the calculation of the initial concentration sensitivities.

The initial concentration sensitivities can be calculated by the following equation:

$$\frac{d\mathbf{K}(t, t_1)}{dt} = \mathbf{J}(t)\mathbf{K}(t, t_1), \quad \mathbf{K}(t_1, t_1) = \mathbf{I}, \quad t > t_1 \quad (23)$$

where \mathbf{J} is the Jacobian and \mathbf{K} is the initial concentration sensitivity matrix (see e.g. ref 63), $\mathbf{K}(t, t_1) = \{\partial c_i(t)/\partial c_j^0(t_1)\}$.

Let j be the index of an important species, i the index of a QSSA species and $\Delta c_i(t_1)$ the instantaneous error at time t_1 . A deviation of Δc_i at time t_1 causes a deviation Δc_j^i of species j at time t_2 , and this deviation can be approximately calculated from

the following equation:

$$\Delta c_j^i(t_2) = \frac{\partial c_j(t_2)}{\partial c_i^0(t_1)} \Delta c_i(t_1) \quad (24)$$

Here, Δc_j^i is not the real overall error, as the overall error is the result of a continuous perturbation, but eq 24 shows that the initial concentration sensitivities $\partial c_j(t_2)/\partial c_i^0(t_1)$ can indicate whether the small errors of QSSA species are increased or decreased when propagated to the important species.

6. Algorithm for the Proper Application of QSSA

The following algorithm is suggested for the selection of the QSSA species. Following an integration of eq 1, the individual fractional instantaneous QSSA error $\Delta c_i^s/c_i$ of each species should be calculated by eqs 8 and 9. Those having a small fractional error are potential QSSA species, and the interaction of their errors has to be calculated using eqs 7 and 9. If the errors $\Delta c_i^s/c_i$ remain small, these species can be considered as QSSA species. A trial calculation using eqs 3 and 4 can prove if the small instantaneous errors of QSSA species cause small overall errors in important species. If small instantaneous errors result in large overall errors of important species, then the "problematic" QSSA species can be pinpointed on the basis of the calculation of the initial concentration sensitivity matrix. It is thus possible to estimate the errors induced by the application of the QSSA to various groups of species with only one simulation of the full model and in this way to choose the optimum group.

Equations 7 and 8 are applicable not only for the selection of QSSA species but also for the determination of the time interval over which the QSSA is valid. If the QSSA species concentrations are initially zero and the instantaneous error is calculated at several times, a sudden decrease in the instantaneous error is observed and the induction period has been passed. Clearly the length of the induction period depends on the QSSA species selected. This method is an exact way of the determination of induction period t_{ind} , while rough approximation can be based on eq 20.

In some cases the QSSA has been found to be invalid at very high conversions,³⁰ and so its validity must be checked over the whole time interval of intended application.

7. Lifetime of Species

The lifetime of a species is an important quantity in photochemistry. Since most photochemical processes are first order, the photochemical lifetime is usually defined⁶⁴ as the reciprocal of the sum of the pseudo-first-order rate coefficients of the consuming reactions of species i , i.e., $\tau_i = 1/\sum k_j$.

Lifetimes are also frequently calculated in atmospheric chemistry. The rate of change of species i can be written as $dc_i/dt = P - Lc_i$, where P and Lc_i are the production and loss terms, so that $\tau_i = 1/L$.²⁴ L depends on the concentration of other species, but it is independent of c_i provided there are no loss terms which are second order in c_i . This requirement is fulfilled in atmospheric chemistry for many radical species but implies a loss of generality. In laboratory photochemical studies, conditions can usually be arranged such that the concentrations of other species reacting with c_i are invariant, so that τ_i is constant and proportional to the half-life. The atmospheric lifetime, on the other hand, can be time and space dependent and is based on the current, local concentrations.

A generalized interpretation of the lifetime can be based on the Jacobian. Using our present notation $\tau_i = -J_{ii}^{-1}$ for any mechanism. It is easy to show that this is equivalent to the photochemical lifetime if there are only first order reactions in the mechanism. It is also equal to the atmospheric chemistry lifetime providing there are no quadratic consuming reactions of species i (i.e., L does not contain any c_i terms).

The concept of a species lifetime may be used to amplify our earlier discussions. Equation 8 implies that the absolute instantaneous error of a single QSSA species is equal to the product of its lifetime and of its net production rate. Equation 20 implies that the induction period is expected to be several times the lifetime of the longest lived QSSA species.

Conclusions differing from those presented here have been reached in earlier studies. Frank-Kamenetskii⁶² compares the lifetime of the QSSA species with the normalized rate of the fastest changing species concentration, which he calls the characteristic time of the course of the reaction. Rice,⁶⁵ continuing Frank-Kamenetskii's argument, stated that, for the successful application of the QSSA, the lifetime of QSSA species has to be much less than the lifetime of non-QSSA species and that the induction period has to be small compared with the time for the overall reaction. In the present paper, the lifetime of a QSSA species is compared with the rate of change of concentration of the same species. It is also clear from the error equations derived here that the error and the lifetime of each species are independent of the length of the simulation time scale. Clearly the overall simulation time should be greater than the induction period for a successful application of the QSSA, but is not related to the instantaneous error of the QSSA species.

Hesstvedt et al.²⁴ have applied the lifetime as a criterion for the selection of QSSA species. Our error formulas, however, do not justify their assumption that the selection of the QSSA species depends on the step size of the integration.

8. Stiffness of Kinetic Equations and the QSSA

An important practical feature of chemical kinetic differential equations is that they are almost always stiff. Special programs have to be used for their numerical solution, and the solution requires much more computer time than is required for nonstiff equations.

Many practical applications require the simulation of spatially inhomogeneous systems. The operator splitting method is frequently applied for the numerical solution of such systems, where the kinetic equations have to be solved at each grid point. Having solved the kinetic equations, the transport equation is solved over the same time interval. This time interval Δt is determined by the stability and/or the accuracy of the transport equation and is usually short, while stiff ODE solvers require time to "start up" and are therefore not very efficient over a short time interval. Hence any method, which decreases the stiffness of kinetic equations, may result in considerable savings of computer time in the modeling of spatially inhomogeneous systems.

The stiffness of a system of differential equations can be characterized by the stiffness ratio, which depends linearly on the largest absolute eigenvalues of the Jacobian (see ref 66, p 165). Stiffness relates to the eigenvalues of the Jacobian while the QSSA was related to the diagonal elements. To relate stiffness to the QSSA, a relation has to be found between the eigenvalues and the diagonal elements of the Jacobian. A series of mechanisms have been investigated in the fields of atmospheric, combustion, and pyrolysis chemistry, and good agreement has been found between the diagonal elements and the eigenvalues of the Jacobian. This agreement is even better for the $J^{(22)}$ submatrix of QSSA species. Coincidence of eigenvalues and diagonal elements is good in the case of nearly diagonal or nearly triangular matrices.⁶⁷ The Jacobian is in many cases nearly triangular, and this feature becomes apparent if the rows and columns of the matrix are arranged in the order of increasing diagonal elements. Figure 4 represents an example from propane pyrolysis which will be discussed in more detail in section 10. The height of a column indicates the log of the Jacobian element divided by the corresponding diagonal element in the same row. There are few significant elements in the upper triangle.

For a triangular matrix the eigenvalues λ_i are equal to the diagonal elements. For a nearly lower triangular matrix, the

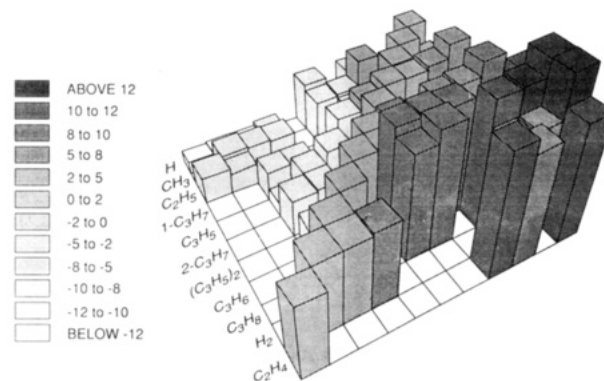


Figure 4. Illustration of a nearly triangular Jacobian for the propane scheme at $t = 10^{-2}$ s. The height of the columns represents the log of the absolute value of the Jacobian element relative to the diagonal element and species are ordered in terms of increasing lifetime.

TABLE I: Comparison of the Eigenvalues with the Diagonal Jacobian Elements for Each Species of the Propane Pyrolysis Mechanism at $t = 10^{-2}$ s^a

species i	eigenvalue λ_i	diagonal element J_{ii}
H	-0.2165×10^{10}	-0.2165×10^{10}
CH ₃	-0.2265×10^7	-0.2072×10^7
C ₂ H ₅	-0.6111×10^6	-0.6111×10^6
1-C ₃ H ₇	-0.2164×10^6	-0.4099×10^6
C ₃ H ₅	-0.2561×10^5	-0.2561×10^5
2-C ₃ H ₇	-0.6179×10^3	-0.9349×10^4
(C ₃ H ₅) ₂	-0.9168×10^{-3}	-0.9168×10^{-1}
C ₃ H ₆	-0.4043×10^{-3}	-0.8818×10^{-3}
C ₃ H ₈	-0.1226×10^{-3}	-0.1904×10^{-3}
H ₂	-0.2292×10^{-5}	-0.1434×10^{-3}
C ₂ H ₄	0.2174×10^{-4}	-0.1205×10^{-3}

^a Reaction conditions are as in ref 6 i.e., at a reaction temperature of 817.16 K and an initial propane concentration of 1.912×10^{-3} mol dm⁻³. The initial concentrations of all other species are zero.

diagonals provide an approximation to the eigenvalues, the deviations depending on the magnitude of the upper triangular elements.⁶⁷ Let A be a lower triangular matrix and E an upper triangular matrix with small elements. The nearly triangular matrix is given by $A + E$. If λ is an eigenvalue of A and x and y satisfy $Ax = \lambda x$ and $y^T A = \lambda y^T$ with $\|x\|_2 = \|y\|_2 = 1$, then a bound on the deviations of the eigenvalues of $A + E$ from those of A is given by $\|E\|/s(\lambda)$, where s is the condition of the eigenvalue:

$$s(\lambda) \equiv \|y^T x\|_2 \quad (25)$$

Practically $s(\lambda)$ is small only if A is close to a matrix having multiple eigenvalues, and so if this ill-conditioning is avoided a small perturbation from the triangular matrix implies a small perturbation of the eigenvalues. This deviation will therefore be much smaller for large diagonal elements where the upper matrix elements are less significant and the differences between the absolute values of the eigenvalues are bigger. Large diagonal elements correspond, therefore, to large eigenvalues. (A comparison is made in Table I for the propane example at the same conditions as for Figure 4.) Removing species with large J_{ii} values therefore reduces the stiffness of the system.

9. Practical Application

The algorithm presented in section 6 enables the selection of QSSA species and of the time interval for application of the QSSA. On the basis of the discussion in section 8, it is evident that, in most cases, the more species to which the QSSA is applied, the greater the reduction in the stiffness of the problem. There are however, some practical aspects which may limit the number of QSSA species.

In most cases the aim of the application of QSSA is to save computer simulation time. There are several possible strategies for the application of QSSA, some may improve efficiency more

than others. If eq 4 has at least one real positive root, this root can always be calculated numerically. However, numerical solution of a nonlinear system of algebraic equations is based on iteration, while the solution of a linear system can be obtained by Gauss elimination. It may be more efficient to limit the application of the QSSA to a subset of the QSSA species which results in a set of linear algebraic eqs 4.

Some recent programs for the solution of differential equations have also been designed to handle differential-algebraic systems (see, e.g., DASSL,⁶⁸ SPRINT⁶⁹). The simultaneous solution of differential-algebraic equations seems to be the most efficient way for the numerical solution of eqs 3 and 4. Some of these programs have a choice of integration routines depending on the stiffness of the system which may further increase the numerical efficiency. However, we have found that the application of the QSSA using a numerical solution, even with the use of an efficient differential-algebraic equation solver, does not significantly reduce simulation time. A possible reason for this unexpected result is that the recent stiff ODE solvers are very efficient, and it is not easy to improve the efficiency further by a purely numerical approach. Of course, the savings depend on the problem and it is possible that for some specific problems considerable savings can be achieved. However, in our opinion to produce a significant increase of computational efficiency, the practical application of the QSSA must involve the analytical solution of the QSSA equations, which requires the conversion of eq 4 into an explicit form. If this equation is linear, such an explicit form can always be found although the algebra may be difficult. The analytical solution of eq 4 is still possible if the system contains second order terms in one of the species, but it becomes impossible even in the case of second-order terms for two species. The requirement of finding an explicit solution of eq 4 may therefore exclude the application of the QSSA to some species even if the algorithm given in section 6 indicates that they are potential QSSA species.

If there are many QSSA species the explicit solution is not easily found and can rarely be achieved by hand. Algebraic manipulation packages such as REDUCE⁷⁰ and MATHEMATICA⁷¹ can be used. Both are able to produce the resulting expressions in the form of a Fortran code which can immediately be used with an ODE solver. The major problem with such packages is that they cannot yet be used to solve automatically nonlinear sets of equations. Another possible solution is to approximate the solution of the QSSA equations by a set of polynomials, or to truncate²² the QSSA expressions to some linear form.

The explicit solution for the concentration of QSSA species, obtained by hand, by an algebraic manipulation program or by a polynomial fit, is then inserted into the function calculation subroutine of the differential equation solver. In this case, considerable savings can be expected compared with the solution of the original kinetic differential equations. If an analytical expression has been found for the calculation of the concentrations of all short lifetime species, the resulting problem will not be stiff and longer time steps and/or a more efficient integrator can be chosen. The number of variables also decreases and, according to theoretical predictions, the simulation time is proportional to the second or third power of the number of variables, depending on the algorithm applied. On the other hand, calculation of the concentrations of QSSA species itself consumes computer time.

Having recognized the stiff variables, a saving of computer time can also be achieved without the application of the QSSA. A well-established technique for the efficient solution of stiff differential equations is partitioning of the system into transient and smooth parts (see references in ref 66, pp 240–243). The differential equations are separated into two sets which are solved by different methods (i.e., the nonstiff equations are solved by a nonstiff ODE solver and the stiff ("transient") equations by a stiff ODE solver). Partitioning is usually based on the eigenvalues of the Jacobian. As the partitioning is time dependent, it has to be checked several times, reducing the effectiveness of the method.

TABLE II: Lifetimes and Approximated and Real Instantaneous Fractional ($\Delta c_i/c_i$) Errors for Single Species of the Propane Pyrolysis Mechanism at $t = 10^{-2}$ s^a

order	species	$\Delta c_i^2/c_i$		species	lifetime τ/s
		approx	real		
1	C ₂ H ₄	-1.052 × 10 ⁶	-1.052 × 10 ⁶	C ₂ H ₄	0.8298 × 10 ⁴
2	H ₂	-8.937 × 10 ⁵	-8.937 × 10 ⁵	H ₂	0.6971 × 10 ⁴
3	C ₃ H ₆	-1.455 × 10 ⁵	-1.455 × 10 ⁵	C ₃ H ₆	0.5252 × 10 ⁴
4	(C ₃ H ₅) ₂	-4.303 × 10 ³	-4.303 × 10 ³	C ₃ H ₆	0.1134 × 10 ⁴
5	C ₃ H ₈	9.961 × 10 ⁻¹	9.961 × 10 ⁻¹	(C ₃ H ₅) ₂	0.1091 × 10 ²
6	C ₃ H ₅	-5.194 × 10 ⁻³	-5.194 × 10 ⁻³	2-C ₃ H ₇	0.1070 × 10 ⁻³
7	2-C ₃ H ₇	-4.476 × 10 ⁻⁴	-4.476 × 10 ⁻⁴	C ₃ H ₅	0.3904 × 10 ⁻⁴
8	C ₂ H ₅	2.812 × 10 ⁻⁴	2.812 × 10 ⁻⁴	1-C ₃ H ₇	0.2440 × 10 ⁻⁵
9	H	1.430 × 10 ⁻⁴	1.430 × 10 ⁻⁴	C ₂ H ₅	0.1636 × 10 ⁻⁵
10	1-C ₃ H ₇	4.315 × 10 ⁻⁵	4.315 × 10 ⁻⁵	CH ₃	0.4825 × 10 ⁻⁶
11	CH ₃	2.789 × 10 ⁻⁵	2.789 × 10 ⁻⁵	H	0.4618 × 10 ⁻⁹

^a Conditions are the same as for Table I.

By basing the separation of stiff and nonstiff variables on eq 8, the effectiveness of the usual partitioning methods is enhanced.

10. Examples: Propane Pyrolysis and Hydrogen Oxidation

Pyrolysis models are conventional fields for the application of QSSA. The first detailed low-temperature alkane pyrolysis model was presented by Edelson and Allara and a refined version was investigated⁷² by concentration sensitivity analysis. As it is a widely known mechanism, it was chosen as a basis of our numerical example without updating the rate coefficients.

This 98-step alkane pyrolysis model of 36 species has been reduced by Turányi⁶¹ to a 38-step propane pyrolysis model of 13 species. The deviation between the two models is of the order of 0.5% for each important species. This reduced model was employed in our investigations and the following results serve to illustrate the theoretical points made above. The model and the circumstances of investigation are reproduced from refs 72 and 61.

10.1. Calculation of Instantaneous Errors. 10.1.1. Single Species: The instantaneous errors for each individual species are presented in Table II at $t = 10^{-2}$ s. The errors are presented as fractional errors, i.e., $\Delta c_i/c_i$. The second column shows the estimated instantaneous error $\Delta c_i^2/c_i$ calculated from eq 8. In column 3 the errors are calculated from the difference between the real concentrations and the concentrations calculated from algebraic eqs 4, where the concentrations of the non-QSSA species are their real concentrations. The agreement is excellent and extends to six significant figures. Table II also presents the instantaneous lifetimes, τ_i , of all the species. The six species with the shortest lifetimes also have the smallest instantaneous errors, although their ordering is slightly different. The results suggest that these six species are practical QSSA candidates.

10.1.2. Groups of Species: To study the interaction of the instantaneous errors, the approximate and real instantaneous errors Δc_i^2 and Δc_i were compared for groups of QSSA species. The groups were formed in such a way that the first two, three, four, etc. species were considered together in the order of the increasing instantaneous errors for single species. Table III compares $\Delta c_i/c_i$ and $\Delta c_i^2/c_i$ with $\Delta c_i^2/c_i$ calculated from eq 7, which includes contributions to the error from other QSSA species. The results are presented with increasing numbers in the QSSA group. The agreement is good up to four QSSA species but with five species the group error estimates differ significantly from the individual errors; indeed in some cases the sign is even wrong. The interactions between QSSA species are therefore very significant.

The agreement of the group estimated instantaneous error $\Delta c_i^2/c_i$ with the real instantaneous error $\Delta c_i/c_i$ is always very good provided only those species with small Δc_i^2 are included in the group. Deviations are below 1%. Inspection of the six species group indicates that these six species (CH₃, 1-C₃H₇, H, C₂H₅, 2-C₃H₇, and C₃H₅) are good QSSA candidates, as the interaction

TABLE III: Comparison of Approximated and Real Instantaneous ($\Delta c_i/c_i$) Fractional Errors Calculated for Single Species ($\Delta c_i^s/c_i$) and for Groups of Species (c_i^g/c_i) of the Propane Pyrolysis Mechanism at $t = 10^{-2}$ s^a

no. of species	species	$\Delta c_i^s/c_i$	$\Delta c_i^g/c_i$	$\Delta c_i/c_i$
2	CH ₃	2.789×10^{-5}	1.211×10^{-4}	1.211×10^{-4}
	1-C ₃ H ₇	4.315×10^{-5}	9.582×10^{-5}	9.582×10^{-5}
3	CH ₃	2.789×10^{-5}	2.518×10^{-4}	2.518×10^{-4}
	1-C ₃ H ₇	4.315×10^{-5}	4.315×10^{-5}	2.301×10^{-4}
	H	1.430×10^{-4}	1.430×10^{-4}	1.430×10^{-4}
4	C ₂ H ₅	2.812×10^{-4}	2.812×10^{-4}	2.812×10^{-4}
	CH ₃	2.789×10^{-5}	2.574×10^{-4}	2.574×10^{-4}
	1-C ₃ H ₇	4.315×10^{-5}	2.359×10^{-4}	2.359×10^{-4}
	H	1.430×10^{-4}	1.431×10^{-4}	1.431×10^{-4}
5	2-C ₃ H ₇	-4.476×10^{-4}	-3.975×10^{-3}	-3.967×10^{-3}
	H	1.430×10^{-4}	-3.828×10^{-3}	-3.820×10^{-3}
	1-C ₃ H ₇	2.301×10^{-4}	-3.573×10^{-3}	-3.566×10^{-3}
	CH ₃	2.789×10^{-5}	-3.448×10^{-3}	-3.441×10^{-3}
	C ₂ H ₅	2.812×10^{-4}	2.810×10^{-4}	2.810×10^{-4}
6	C ₃ H ₅	-5.194×10^{-3}	-9.012×10^{-3}	-9.004×10^{-3}
	2-C ₃ H ₇	-4.476×10^{-4}	-3.975×10^{-3}	-3.967×10^{-3}
	H	1.430×10^{-4}	-3.829×10^{-3}	-3.821×10^{-3}
	1-C ₃ H ₇	4.315×10^{-5}	-3.574×10^{-3}	-3.566×10^{-3}
	CH ₃	2.789×10^{-5}	-3.449×10^{-3}	-3.442×10^{-3}
	C ₂ H ₅	2.812×10^{-4}	2.812×10^{-4}	2.810×10^{-4}
7	(C ₃ H ₅) ₂	-4.303×10^3	-4.381×10^3	-4.381×10^3
	C ₃ H ₅	-5.194×10^{-3}	-9.012×10^{-3}	-9.004×10^{-3}
	2-C ₃ H ₇	-4.476×10^{-4}	-3.975×10^{-3}	-3.967×10^{-3}
	H	1.430×10^{-4}	-3.829×10^{-3}	-3.821×10^{-3}
	1-C ₃ H ₇	4.315×10^{-5}	-3.574×10^{-3}	-3.566×10^{-3}
	CH ₃	2.789×10^{-5}	-3.449×10^{-3}	-3.442×10^{-3}
	C ₂ H ₅	2.812×10^{-4}	2.812×10^{-4}	2.810×10^{-4}
8	(C ₃ H ₅) ₂	-4.303×10^3	-3.708×10^9	-1.123×10^{14}
	C ₃ H ₆	-1.455×10^5	-4.285×10^5	-1.212×10^7
	C ₃ H ₅	-5.194×10^{-3}	-4.307×10^5	-1.415×10^5
	H	1.430×10^{-4}	2.834	9.880×10^{-1}
	CH ₃	2.789×10^{-5}	1.468	9.472×10^{-1}
	1-C ₃ H ₇	4.315×10^{-5}	1.268	6.156×10^{-1}
	2-C ₃ H ₇	-4.476×10^{-4}	6.618×10^{-3}	1.713×10^{-1}
	C ₂ H ₅	2.812×10^{-4}	2.466×10^{-3}	1.375×10^{-2}

^a Conditions are the same as for Table I.

of the individual errors does not increase the total error, when they are treated as QSSA species simultaneously.

Admitting long-lifetime species into the groups causes the estimated error to deviate from the real error emphasizing the point that only species with small individual errors should be included in the group calculation and that it is worthwhile using eq 8 as a first guide.

10.2. Induction Period. According to the algorithm given in section 6, the next step is the determination of time domain over which the QSSA is applicable. In this case it means the determination of the length of the induction period. The group instantaneous error of the six QSSA species was calculated by eq 7 at several times over the time interval 0–0.1 s. The instantaneous error for all the species becomes sufficiently small after about 0.01 s and therefore the QSSA is applicable from this time for the whole group. At 10^{-3} s the group fractional errors are >1 for most of the six species although the individual errors for some are small. If a smaller group is chosen including only 1-C₃H₇, CH₃, C₂H₅, and H the group errors are sufficiently small at 10^{-3} s for the application of the QSSA.

Equations 20 and 21 provide order-of-magnitude estimates of the length of the induction period. As the lifetime of the longest lifetime species (2-C₃H₇) is greater than 1×10^{-4} s, the length of the induction period must be at least $t = 10^{-3}$ s.

10.3. Comparison of Instantaneous and Overall Errors. The QSSA was then applied from 0.01 s for the six species and the (real) overall error of each species calculated. The overall error is simply the difference in concentrations calculated from a full solution (via eq 1) and a QSSA solution (via eqs 3 and 4). As

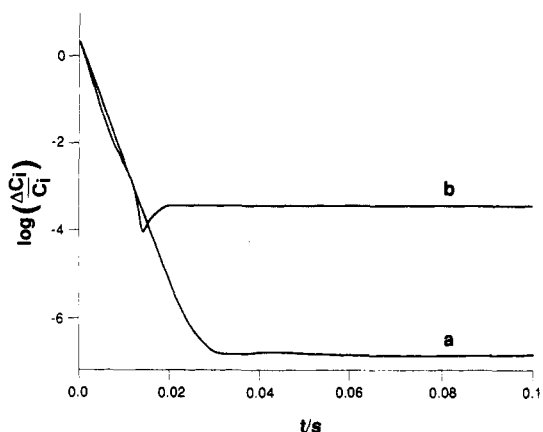


Figure 5. Log of fractional overall and instantaneous errors for CH₃, the QSSA species with the lowest individual instantaneous error: (a) overall; (b) instantaneous.

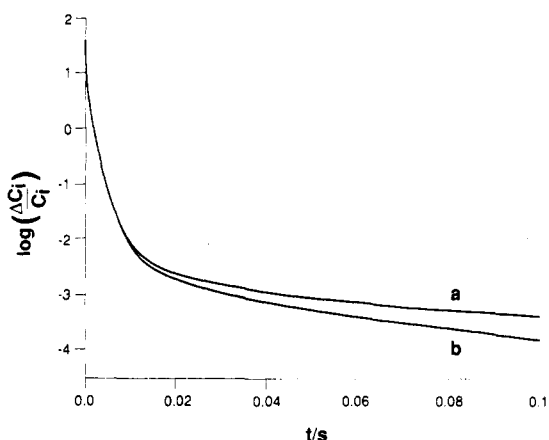


Figure 6. Log of fractional overall and instantaneous errors for C₃H₅, the QSSA species with the highest individual instantaneous error: (a) overall; (b) instantaneous.

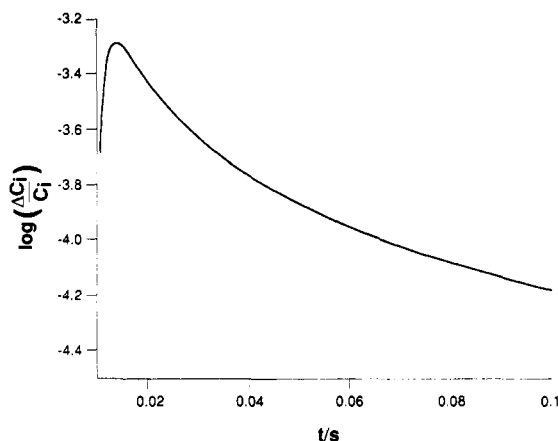


Figure 7. Log of fractional overall error for C₃H₆, the major product.

an example, the fractional overall error of C₃H₅ and CH₃, i.e., the species with the highest and lowest individual instantaneous errors of the six QSSA species, respectively, are plotted in Figures 5 and 6.

For a comparison, the estimated instantaneous error $\Delta c_i^s/c_i$ (calculated by eq 7) is also given in the figures.

The real test of the application of the QSSA is the error induced in the important species. Figure 7 shows the real overall error of C₃H₆, which is a main product of the pyrolysis. The error remains small showing that the propagation of errors is low for all QSSA species.

10.4. Initial Concentration Sensitivities. The above results are confirmed by the calculation of initial concentration sensitivities, showing the effect of a perturbation in any of the QSSA

TABLE IV: Example Fractional Error Calculation ($\Delta c_i^s/c_i$, Approximate Error for Single Species; $\Delta c_i/c_i$, Real Instantaneous Error) from a Model Describing the Oscillatory Oxidation of Hydrogen in a Flow Reactor under Stoichiometric Conditions^a

order	species	$\Delta c_i^s/c_i$	$\Delta c_i/c_i$	species	lifetime/ τ /s
1	H ₂	-9.507	-9.507	H ₂	0.8000 × 10
2	O ₂	-7.030	-7.030	O ₂	0.8000 × 10
3	H ₂ O	1.000	1.000	H ₂ O	0.8000 × 10
4	H ₂ O ₂	9.999 × 10 ⁻¹	9.999 × 10 ⁻¹	H ₂ O ₂	0.6405 × 10
5	O ₃	9.952 × 10 ⁻¹	9.952 × 10 ⁻¹	O ₃	0.1642
6	HO ₂	3.804 × 10 ⁻²	3.804 × 10 ⁻²	HO ₂	0.1331 × 10 ⁻¹
7	H	8.679 × 10 ⁻³	8.679 × 10 ⁻³	H	0.2369 × 10 ⁻²
8	O	3.115 × 10 ⁻³	3.115 × 10 ⁻³	O	0.6545 × 10 ⁻³
9	OH	3.207 × 10 ⁻⁴	3.207 × 10 ⁻⁴	OH	0.7049 × 10 ⁻⁴

^a Pressure = 20 Torr, temperature = 790K, residence time = 8s and $t = 0.1s$.

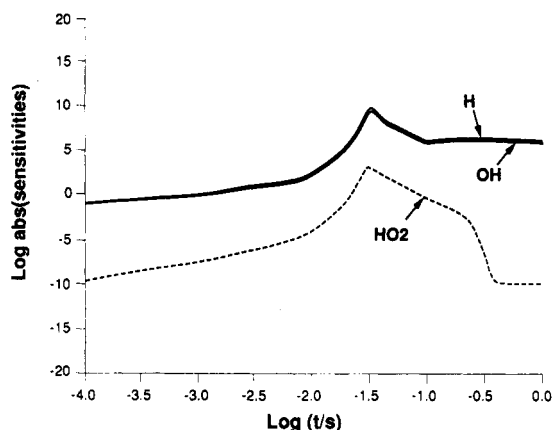


Figure 8. Initial concentration sensitivities $\partial c_i(t_2)/\partial c_i(t_1)$ for radicals H, OH, and HO₂ during the first ignition stages of the reaction under stoichiometric conditions, showing that the system is far more sensitive to initial errors in H concentration than to errors in the concentration of HO₂. Pressure = 20 Torr, temperature = 790 K, residence time = 8 s.

species concentrations on the important species C₃H₈, H₂, CH₄, C₃H₆, C₂H₄, C₂H₆. The result of this calculation is that the perturbation of each QSSA species produced approximately the same effect on the non-QSSA species. This means that the interconversion of radicals is fast and the spread of errors to the important species is much the same for each QSSA species.

There are certain situations where the sensitivity to radical perturbations is very different for each radical species. A good example is the hydrogen oxidation reaction in a flow reactor as discussed in an earlier article.⁵⁷ Under certain conditions the radicals O, OH, H, and also HO₂ have a short lifetime and a low instantaneous error as shown in Table IV and so are chosen as the group of QSSA species. An initial QSSA calculation shows however that such an approximation leads to negative radical concentrations and so at least one of this group is not a good QSSA species. Calculation of initial concentration sensitivities of H₂ to the radicals shows (Figure 8) that the sensitivity to H and OH is many orders of magnitude higher than to HO₂, and so any errors in their concentrations spread much more quickly to the important species than for HO₂. H is suspected as the "pathological" species since it has a much higher instantaneous error and a longer lifetime than OH, and when H is removed from the group the agreement between the QSSA calculation and the full calculation is good. Thus the unsuitability of H as a QSSA species can be demonstrated by supplementing the instantaneous error tests with a calculation of the initial concentration sensitivities.

11. Conclusions

For a single QSSA species at a specific time, the deviation between the exact solution and the quasi-steady-state approximation (the instantaneous error) can be interpreted as the product

of the lifetime and the net production rate of this species. The lifetime of a species, according to a general interpretation, is equal to the negative reciprocal of the corresponding diagonal element of the Jacobian of the system of kinetic differential equations. In the case of several QSSA species, the instantaneous errors of individual QSSA species interact, but the resulting instantaneous errors can be obtained by the solution of a simple system of algebraic equations which contains the corresponding block of the Jacobian and the reaction rate of QSSA species only. The error formulas derived provide a simple guideline for the selection of QSSA species and the exact determination of the time period when the QSSA approximation is valid for the QSSA species chosen.

The error in the concentration of QSSA species causes an error in the concentration of important species. The overall error of important species is the most significant measure of the applicability of QSSA for a particular problem, but low instantaneous QSSA errors usually imply low overall errors. The calculation of the initial concentration sensitivity matrix can be used to investigate "pathological" cases since it indicates if the kinetic system investigated increases or decreases the instantaneous errors causing a large or small overall error, respectively. In the former case the QSSA is applicable even in case of large instantaneous errors. The simplest way to calculate the overall errors is to compare results from a full and a QSSA calculation and in this respect it is not possible to predict a priori the exact error induced by the application of the QSSA. However, the instantaneous error which can be calculated via a simple expression involving only one simulation of the full model, provides a reasonable method of estimating possible errors. A selection of QSSA species can therefore be made without preparing and testing numerous QSSA calculations involving different numbers of QSSA species.

Two physical pictures are provided for the interpretation of the QSSA, and both exclude the simplistic idea that the overall production rate of QSSA species must be close to zero. According to the first, static picture, the difference between the actual concentration of a species and the quasi-stationary concentration, depends on the steepness of the net production rate surface in the space of species concentrations. This steepness is characterized by the Jacobian. According to the second, dynamic picture, the concentrations of the QSSA species follow the quasi-stationary concentrations and the difference between the two concentrations depends on the lifetime of species and the rate of change of the species. On the basis of the dynamic approach, an estimation is given for the length of the induction period which is of the order of 10 times the lifetime of the longest lifetime QSSA species.

A technique for the separation of stiff and nonstiff variables has previously been discussed by Miranker.⁷³ The technique uses the fact that the solution of stiff systems can be characterized in terms of boundary layers. Singular perturbation theory can then be used to separate the variables and find inner and outer solutions. Such methods normally apply in systems where a small parameter ϵ can be identified. Miranker has extended the techniques to systems where the small parameter remains hidden, by dividing the system into regular and singular parts. This technique for the separation of variables does not require the use of a stiff ODE solver. Miranker, however, makes no estimation of the length of the boundary layer (or induction period using the present terminology), nor an estimation of the accuracy of the outer solution once the induction period has passed.

Côme⁴⁵ extended Miranker's work by defining criteria for the application of the QSSA. These criteria relate to the time period over which the QSSA can be applied. Again Côme's method does not require a stiff solver but requires an a priori selection of QSSA species, which he assumes to be radicals. His work does not provide a method for predicting the error during the period over which the QSSA is a valid approximation. The present work has provided a method for the selection of QSSA variables regardless of their status as chemical species. Our method is based on the investigation of simple, physically interpretable

quantities such as lifetimes and production rates. We have shown that even for valid QSSA species, an error is still induced after the boundary layer has passed and have provided a method for calculating this error.

There have been several empirical observations or conclusions based on the investigation of small model reaction systems which showed that the rates of consuming reactions of QSSA species are usually high,^{23,74} that the concentrations,^{7,23,29,30,75} and the net rates of reaction¹¹ of QSSA species are usually low, that the induction period is usually short,^{23,30,74,75} and that most QSSA species are radicals. These observations are simple consequences of the physical pictures presented above and the error formulas derived from them.

The quasi-steady-state approximation is frequently applied in chemical kinetics both for kinetic modeling and for the derivation of theoretical formulas in several fields (e.g., enzyme kinetics, theory of unimolecular reactions). The error formulas here derived are directly applicable in both cases. In the theory of numerical methods for the solution of stiff differential equations, the error formulas may be applied without any physical background for the improvement of the numerical procedure as a part of the partition process.

Practically a very important application of the QSSA is in the simulation of spatially inhomogeneous combustion processes. The derivation of error formulas which consider not only spatially homogeneous kinetics but also the effect of diffusion, the spatial stiffness, and the damping of the instantaneous errors in spatial simulations is a task for the future.

12. Computations

The numerical solution of the differential and coupled differential-algebraic equations was calculated using the program package SPRINT.⁶⁹ The initial concentration sensitivities and species lifetimes were calculated by KINAL.⁷⁶ The NAG routine f02Abf was used for eigenvalue, eigenvector calculations, and REDUCE⁷⁰ for the explicit solution of the algebraic QSSA equations.

Acknowledgment. The authors are indebted to Dr. J. Tóth, Dr. S. Vajda, Dr. D. A. Goussis, Dr. B. J. Whitaker, Prof. J. Merkin, and Dr. J. Brindley for very helpful discussions. We thank the Royal Society for a visiting fellowship for T.T. and ICI plc. for funding for A.S.T.

References and Notes

- (1) Bodenstein, M. Z. *Phys. Chem.* **1913**, *85*, 329.
- (2) Underhill, L. K.; Chapman, D. L. *J. Chem. Soc. Trans.* **1913**, *103*, 496.
- (3) Lutkemeyer, H.; Bodenstein, M. Z. *Phys. Chem.* **1924**, *114*, 208.
- (4) Semenov, N. N. *J. Chem. Phys.* **1939**, *7*, 683.
- (5) Semenov, N. N. *Zh. Fiz. Him.* **1943**, *17*, 187.
- (6) Semenov, N. N. *Acta Physicochim. USSR* **1943**, *18*, 433.
- (7) Snow, R. H. *J. Phys. Chem.* **1966**, *70*, 2780.
- (8) Keneshea, T. J. *Report No. 67-0221, Env. Res. Paper: US Air Force Cambridge Res. Lab.* **1967**.
- (9) Gelinis, R. J. *J. Comput. Phys.* **1972**, *9*, 222.
- (10) Edelson, D. J. *Comput. Phys.* **1973**, *11*, 455.
- (11) Edelson, D.; Farrow, L. A. *Int. J. Chem. Kinet.* **1974**, *6*, 787.
- (12) Graedel, T. E.; Farrow, L. A. *J. Phys. Chem.* **1977**, *81*, 2480.
- (13) Edelson, D. *Int. J. Chem. Kinet.* **1979**, *11*, 687.
- (14) Côme, G. M. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1983; Vol. 24, p 297.
- (15) Peters, N. *Lect. Notes Phys.* **1985**, *241*, 90.
- (16) Paczko, G.; Lefdal, P. M.; Peters, N. *21st Int. Symp. Combust.* **1988**, *739*.
- (17) Kee, R. J.; Peters, N. *Combust. Flame* **1987**, *68*, 17.
- (18) Peters, N.; Williams, F. A. *Combust. Flame* **1987**, *68*, 185.
- (19) Peters, N.; Seshadri, K. *Combust. Flame* **1988**, *187*, 197.
- (20) Peters, N. *Prog. Astron. Aeron.* **1988**, *113*, 67.
- (21) Smooke, M. D., Ed. *Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*; Springer-Verlag: Berlin, 1992.
- (22) Peters, N.; Rogg, B., Eds. *Reduced kinetic mechanisms for applications in combustion systems*; Springer-Verlag: Berlin, 1993.
- (23) Corcoran, W. H.; Blakemore, J. E. *Ind. Eng. Chem., Process Des. Dev.* **1969**, *8*, 206.
- (24) Hesstvedt, E.; Hov, O.; Isaksen, I. S. A. *Int. J. Chem. Kinet.* **1978**, *10*, 971.
- (25) Rubajlo, V. G.; Vidóczy, T.; Nemes, I.; Strehó, M.; Emanuel, N. M.; Gál, D. *Magy. Kém. Foly.* **1975**, *81*, 75.
- (26) Nicholson, A. J. C. *Can. J. Chem.* **1983**, *61*, 1831.
- (27) Savage, P. A. *Chem. Eng. Sci.* **1990**, *45*, 859.
- (28) Froment, G. F.; Sundaram, K. M. *Int. J. Chem. Kinet.* **1978**, *10*, 1189.
- (29) Benson, S. W. *J. Chem. Phys.* **1952**, *20*, 1605.
- (30) Oppenheim, A. K.; Bowen, J. R.; Acrivos, A. *Chem. Eng. Sci.* **1963**, *18*, 177.
- (31) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 143.
- (32) Volk, L.; Richardson, W.; Lau, K. H.; Hall, M.; Lin, S. H. *J. Chem. Educ.* **1977**, *54*, 95.
- (33) Mayer, I. *Magy. Kém. Foly.* **1971**, *77*, 302.
- (34) Shin, H. K.; Giddings, J. C. *Trans. Faraday Soc.* **1961**, *57*, 468.
- (35) Heineken, F. G.; Tsuchiya, H. M.; Aris, R. *Math. Biosci.* **1967**, *1*, 95.
- (36) Aris, R.; Georgakis, C. *Math. Biosci.* **1975**, *25*, 237.
- (37) Fraser, S. J.; Nguyen, A. H. *J. Chem. Phys.* **1989**, *91*, 186.
- (38) Klonowski, W. *Biophys. Chem.* **1983**, *18*, 73.
- (39) Siemrod, M.; Segel, L. A. *SIAM J. Sci. Stat. Comput.* **1988**, *8*, 1.
- (40) Segel, L. A. *Bull. Math. Biol.* **1988**, *50*, 579.
- (41) Côme, G. M. *J. Phys. Chem.* **1977**, *81*, 2560.
- (42) Vasil'eva, A. B.; Sayasov, Yu. S. *Zh. Fiz. Him.* **1955**, *29*, 802.
- (43) Hudjaev, S. I.; Vasil'ev, V. M.; Vol'pert, A. I. *Zh. Vichisl. Mat. Mat. Fiz.* **1973**, *13*, 683.
- (44) Miller, J. J. H.; Côme, G. M.; Hemker, P. W., Eds. *Numerical analysis of singular perturbation problems*; Academic Press: New York, 1979.
- (45) Côme, G. M. *Comput. Chem. Eng.* **1979**, *3*, 603.
- (46) Lapidus, L.; Aiken, R. C. *AIChE J.* **1975**, *21*, 817.
- (47) Liu, Y. A.; Lapidus, L.; Aiken, R. C. *Stiff Differential Systems*; Plenum Press: New York, 1974; pp 187-200.
- (48) Tihonov, A. N. *Mat. Sbornik.* **1952**, *31*, 575.
- (49) Vajda, S.; Valkó, P.; Turányi, T. *Int. J. Chem. Kinet.* **1985**, *17*, 55.
- (50) Turányi, T.; Bérces, T.; Vajda, S. *Int. J. Chem. Kinet.* **1989**, *21*, 83.
- (51) Fraser, S. J. *J. Chem. Phys.* **1988**, *88*, 4732.
- (52) Fraser, S. J.; Roussel, M. R. *J. Chem. Phys.* **1990**, *93*, 1072.
- (53) Fraser, S. J.; Roussel, M. R. *J. Chem. Phys.* **1991**, *94*, 7106.
- (54) Williams, F. A. *Combustion Theory*, 2nd ed.; Benjamin/Cummings: Menlo Park, CA, 1985.
- (55) Dixon-Lewis, G. *Philos. Trans. R. Soc. London* **1979**, *292*, 45.
- (56) Vajda, S.; Rabitz, H.; Yetter, R. A. *Combust. Flame* **1990**, *82*, 270.
- (57) Tomlin, A. S.; Pilling, M. J.; Turányi, T.; Merkin, J. H.; Brindley, J. *Combust. Flame* **1992**, *91*, 107.
- (58) Tomlin, A. S., et al., to be published.
- (59) Erdi, P.; Tóth, J. *Mathematical models of chemical reactions*; Princeton University Press: Princeton, NJ, 1989.
- (60) Maas, U.; Pope, S. B. *Combust. Flame* **1992**, *88*, 239.
- (61) Turányi, T. *New J. Chem.* **1990**, *14*, 795.
- (62) Frank-Kamenetskii, D. A. *Zh. Fiz. Him.* **1940**, *14*, 695. A commented English translation is also available: Turányi, T.; Tóth, J. *Acta Chim. Hung.-Models Chem.*, in press.
- (63) Turányi, T. *Math. Chem.* **1990**, *5*, 203.
- (64) Wayne, R. P. *Principles and applications of photochemistry*; Oxford Science Publications: Oxford, 1988.
- (65) Rice, O. K. *J. Phys. Chem.* **1960**, *64*, 1851.
- (66) Fatunla, S. O. *Numerical methods for initial value problems in ordinary differential equations*; Academic: Boston, 1988.
- (67) Golub, G. H.; vanLoan, C. F. *Matrix computations*; North Oxford Academic: New York, 1983.
- (68) Petzold, L. R. *SAND82-8637, Applied Maths Div.* **1982**, 8331.
- (69) Berzins, M.; Furlzland, R. M. *Shell Res. Ltd.* **1985**, TNER 85058.
- (70) Hearn, A. C. *RAND Publication CP78* **1987**, 7.
- (71) Wolfram, S. *Mathematica: a system for doing maths by computer*; Addison-Wesley: CA, 1988.
- (72) Edelson, D.; Allara, D. L. *Int. J. Chem. Kinet.* **1980**, *12*, 605.
- (73) Miranker, W. L. *Computing* **1973**, *11*, 221.
- (74) Hirschfelder, J. O. *J. Chem. Phys.* **1957**, *26*, 271.
- (75) Skinner, G. B.; Porter, M. D. *J. Chem. Educ.* **1976**, *53*, 366.
- (76) Turányi, T. *Comput. Chem.* **1990**, *14*, 253.