Principal Component Analysis of Kinetic Models

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Abstract

An eigenvalue–eigenvector analysis is used to extract meaningful kinetic information from linear sensitivity coefficients computed for several species of a reacting system at several time points. The main advantage of this method lies in its ability to reveal those parts of the mechanism which consist of strongly interacting reactions, and to indicate their importance within the mechanism. Results can be used to solve three general kinetic problems. Firstly, an objective condition for constructing a minimal reaction set is presented. Secondly, the uncovered dependencies among the parameters are shown to confirm or deny validity of quasi-steady-state assumptions under the considered experimental conditions. Thirdly, taking into account only sensitivities of observed species, the analysis is used to yield error estimates on unknown parameters determined from the experimental observations, and to suggest the parameters that should be kept fixed in the estimation procedure. To illustrate we chose the well-known hydrogen–bromine reaction and the kinetics of formaldehyde oxidation in the presence of CO.

Introduction

Detailed kinetic models involving elementary reactions are primarily used to gain insight into mechanism of the kinetic process. As suggested by Allara and Edelson [1,2], at the first stages of a fundamental kinetic analysis it is advisable to consider a large family of relevant elementary reactions in order to reduce the possibility of something important being left out. However, the more complex the model becomes the more difficult it is to see the relative importance of its parts or to explain certain features of the kinetic behavior. To solve such problems some sort of sensitivity analysis is usually required [1–5].

In most cases the results of sensitivity analysis are expressed in terms of normalized sensitivity coefficients $\partial \ln[A]/\partial \ln k_j$, where $[A]$ denotes the concentration of the species A and k_j is the rate coefficient of the reaction j. Sensitivities are evaluated at some nominal parameter

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International Journal of Chemical Kinetics, Vol. 17, 55–81 (1985)
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value k^0 and are functions of time. Several efficient numerical methods have been proposed for computing these coefficients [3–6], thereby bringing extensive sensitivity analysis within range of practical computation. It should be, however, emphasized that for complex models the array of sensitivity coefficients at each time point contains a large number of elements and hence, it is far from simple to obtain the meaningful kinetic information from such a mass of numerical information. A method proposed in the literature [7] is to rank the reactions according to the absolute values of their normalized sensitivities for each species at each time point and then to cumulate these ratings for the entire calculation. Though the approach offers a convenient measure for relative reaction significance, the ratings can no longer be used to predict concentration changes brought about by a variation in rate constants. Furthermore, as it will be shown, the information on parameter interactions, originally contained in the array of sensitivity coefficients, is also lost in the rank-ordering procedure.

The objective of the present paper is to propose a less heuristic and more informative summary of the sensitivity results in terms of eigenvalues and eigenvectors of the matrix S^TS, where S denotes the array of normalized sensitivity coefficients. Eigenvalues will be shown to provide an absolute measure of significance for some parts of the mechanism, consisting of closely interacting elementary reactions. This information then offers an objective criterion for selecting a minimal reaction set. The second and perhaps even more important advantage of the eigenvalue–eigenvector analysis is that it reveals the possible dependencies among the parameters in the model and can confirm or deny the validity of simplifying kinetic assumptions (such as quasi steady-state hypothesis) under the considered experimental conditions.

Response Surface and Sensitivities

Let $y_i(t, k)$ denote the concentration of the ith species at time t and parameters k. To simplify the presentation we will restrict our consideration to isothermal processes and the components of the p-vector k will be taken as rate constants. Assume that sensitivities are of interest for species concentrations $y_i(t, k), \ldots, y_m(t, k)$ at selected time points $t_1, t_2, \ldots, t_q$. As usual, we introduce the normalized parameters

$$\alpha_i = \ln k_i, \; i = 1, 2, \ldots, p \tag{1}$$

Let k^0 denote nominal parameter values, then $\alpha_i^0 = \ln k_i^0$. The effect on the calculated behavior of a reaction mechanism brought about by a variation in the rate coefficients may be quite naturally expressed in terms of a function defined by

$$Q(\alpha) = \sum_{j=1}^{q} \sum_{i=1}^{m} \left[\frac{y_{i,j}(\alpha) - y_{i,j}(\alpha^0)}{y_{i,j}(\alpha^0)} \right]^2 \tag{2}$$

where $y_{i,j}(\alpha) = y_i(t_j, \alpha)$, $i = 1, 2, \ldots, m$, denote concentrations of "observed" species. Since $Q(\alpha)$ is the sum of squared relative deviations of these "observed" concentrations, it gives a clear picture of the effect of a particular change in the parameter values (see Fig. 1). Expanding (2) about the point α° into its Taylor series gives us

$$Q(\alpha) \approx Q(\alpha^0) + G^T(\alpha^0)\,\Delta\alpha + \frac{1}{2}(\Delta\alpha)^T H(\alpha^0)\Delta\alpha \tag{3}$$

where $\Delta\alpha = \alpha - \alpha^0$, G is the gradient vector and H is the Hessian matrix of Q, defined by $[G]_i = \partial Q/\partial\alpha_i$ and $[H]_{i,j} = \partial^2 Q/\partial\alpha_i\partial\alpha_j$, respectively. Both G and H are evaluated at α^0. Since α^0 is a minimum of Q, $Q(\alpha^0) = 0$ and $G(\alpha^0) = 0$, thus

$$Q(\alpha) \approx \frac{1}{2}(\Delta\alpha)^T H(\alpha^0)\Delta\alpha \tag{4}$$

Furthermore

$$H = \left[\frac{\partial^2 Q}{\partial\alpha_i\,\partial\alpha_j} \right]_{\substack{i=1,\ldots,p \\ j=1,\ldots,p}} = 2\,S^T S + R \tag{5}$$

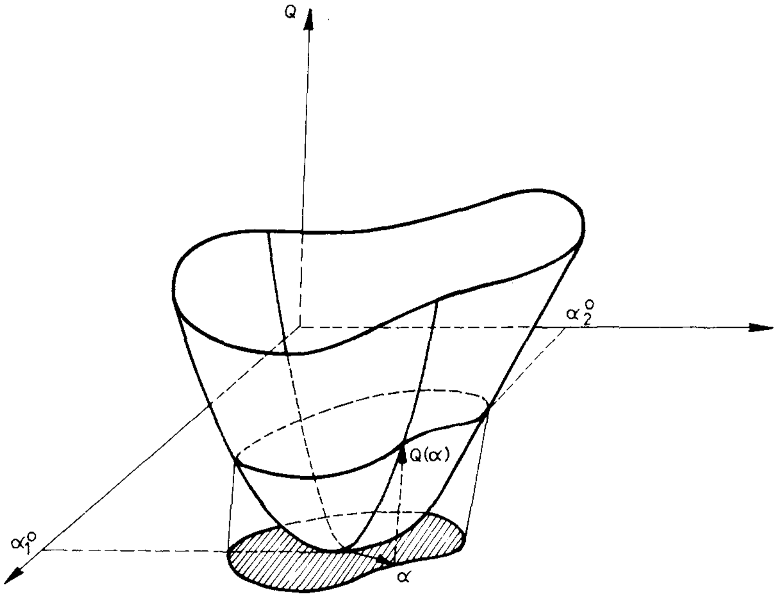

Figure 1. The response surface.

where

$$S = \begin{bmatrix} S_1 \\ S_2 \\ \vdots \\ S_q \end{bmatrix} \tag{6}$$

is the array of normalized sensitivities according to the time points $t_1, \ldots, t_q$, thus

$$S_i = \begin{bmatrix} \frac{\partial \ln y_{1,i}}{\partial \ln k_1} & \frac{\partial \ln y_{1,i}}{\partial \ln k_2} & \cdots & \frac{\partial \ln y_{1,i}}{\partial \ln k_p} \\ \frac{\partial \ln y_{2,i}}{\partial \ln k_1} & \frac{\partial \ln y_{2,i}}{\partial \ln k_2} & \cdots & \frac{\partial \ln y_{2,i}}{\partial \ln k_p} \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ \frac{\partial \ln y_{m,i}}{\partial \ln k_1} & \frac{\partial \ln y_{m,i}}{\partial \ln k_2} & \cdots & \frac{\partial \ln y_{m,i}}{\partial \ln k_p} \end{bmatrix} \tag{7}$$

In eq. (5) only the term R involves second derivatives of concentrations (see, e.g., Bard [8], p. 97). According to the well-known Gauss approximation [8], this term can be neglected and hence we can use the approximate response function

$$Q(\alpha) \approx \tilde{Q}(\alpha) = (\Delta\alpha)^T S^T S \, (\Delta\alpha) \tag{8}$$

to study the effect of parameter variations.

Principal Components

Expression (8) is a quadratic function of the variation $\Delta\alpha_i$, $i = 1,2, \ldots, p$. At any fixed ε the inequality $\tilde{Q}(\alpha) \leq \varepsilon$ defines an ellipsoid in the parameter space with principal axes in general not along the components of α (see Fig. 2). To see how $\tilde{Q}$ changes with α we need to examine the eigenvalues of $S^T S$. The function $\tilde{Q}$ is most sensitive to change in α along the principal axis corresponding to the largest eigenvalue and is least sensitive to change in α along the principal axis corresponding to the smallest eigenvalue of $S^T S$.

The full picture is obtained by diagonalization (eigenvalue–eigenvector decomposition) of the matrix $S^T S$, say

$$S^T S = U \Lambda U^T \tag{9}$$

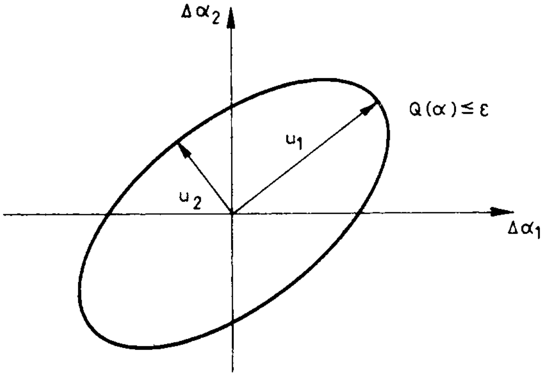

Figure 2. An approximate region defined by $Q(\alpha) \leq \varepsilon$.

where Λ is a diagonal matrix formed by the eigenvalues of $S^T S$ and U denotes the matrix of normed eigenvectors u_i, $i = 1, 2, \ldots, p$ such that $u_i^T u_i = 1$ for each i. Define the new set of the parameters

$$\Psi = U^T \alpha \tag{10}$$

called principal components (see Bard [8], p. 184), then $\Delta\Psi = U^T \Delta\alpha$. In their terms

$$\tilde{Q}(\Psi) = \sum_{i=1}^{p} \lambda_i \|\Delta\Psi_i\|^2 \tag{11}$$

where $\lambda_1 > \lambda_2 \ldots > \lambda_p$ are the eigenvalues of $S^T S$ and $\|\Delta\Psi_i\|^2 = (\Delta\Psi_i)^T(\Delta\Psi_i)$.

Let $u_1 = (u_{1,1}, u_{1,2}, \ldots, u_{1,p})^T$ denote the eigenvector corresponding to the largest eigenvalue λ_1, thus $\Psi_1 = (u_{1,1}\alpha_1, \ldots, u_{1,p}\alpha_p)^T$. Selecting $\Delta\alpha_i = \ln(k_i/k_i^0) = u_{1,i}$, $i = 1, 2, \ldots, p$, we move along the vector u_1 in the space of parameters α. Then $\|\Delta\Psi_1\| = 1$ and by orthogonality of the eigenvectors $\tilde{Q}(\Psi) = \lambda_1$. If $u_{1,j} \leq 0.2$, then $\Delta\alpha_j$ contributes less than 4% to this effect and hence for an approximate analysis such components of u_1 can be excluded from consideration. Assume that dropping its small entries, u_1 takes on the form $\tilde{u} = (u_{1,1}, u_{1,2}, \ldots, u_{1,r}, 0, 0, \ldots, 0)$. Then the largest effect on concentrations is brought about by a simultaneous change in the rate coefficients $k_1, \ldots, k_r$ along the vector $\tilde{u}_1$. Therefore, the corresponding elementary reactions form the most influential part of the mechanism. This analysis emphasizes that such a "mechanism kernel" is not simply a set of separate significant steps, but a closely interacting reaction sequence.

Useful kinetic information can be gained also from the existence of small eigenvalues. The following section presents this result.

Dependencies among the Parameters and the Quasi-Steady-State Approximation

Consider first the particular case in which the eigenvector corresponding to a small eigenvalue $\lambda_i \approx 0$ possesses two nonzero components, say, $u_i = (u_{i,1}, u_{i,2}, 0, \ldots, 0)$ and let $c = u_{i,1}/u_{i,2}$ be constant. Then $\bar{Q}(\alpha) \approx$ const along the line $\Delta\alpha_2 = \Delta\alpha_1/c$, which defines the curve $k_1/k_2^c =$ const in the space of the original parameters. Therefore, the response function $\tilde{Q}(\alpha)$ depends only upon the parameter combination k_1/k_2^c and does not depend upon the parameters k_1 and k_2 separately.

From a practical point of view the most important particular cases are $c = 1$ and $c = -1$. Since u_i is normed (i.e., $\|u_i\| = 1$), at $c = 1$ we obtain $u_i = (0.707, 0.707, 0, 0, \ldots, 0)$, and this specific form of the eigenvector reveals that the response function (8) depends only upon the ratio k_1/k_2 of the two involved parameters. Similarly, at $c = -1$ the normed eigenvector is $u_i = (0.707, -0.707, 0., \ldots, 0.)$ and then the response function depends only upon the product k_1k_2.

Consider now the more general case $u_i = (u, u/c_2, u/c_3, \ldots, u/c_p)$, where $c_2, \ldots, c_p$ are constants. Returning to the original parameters shows that now the response function (8) depends on the nonlinear parameter combination $k_1/k_2^{c2}, k_1/k_3^{c3}, \ldots, k_1/k_p^{c_p}$. These parameter combinations are obviously not unique, since, e.g., k_1/k_3^{c3} can be replaced by k_2^{c2}/k_3^{c3}. It should be, however, emphasized that the case of several interconnected parameters in the principal component Ψ_i can always be reduced to the more simple situation already discussed. Indeed, evaluating the sensitivity matrix S only with respect to a pair of the parameters, say k_1 and k_2, while keeping the others fixed, we obtain $u_i = (u, u/c)$ and the analysis enables us to determine the exact form of dependency among the parameters.

As it is well known, application of the quasi-steady-state hypothesis to some of the species in the reacting system usually leads to nonlinear parameter combinations of the form k_i/k_j^c appearing in the kinetic differential equations and hence in the response function (2). Therefore, as our first example shows, the presence or lack of such parameter interactions can confirm or deny, respectively, the validity of the hypothesis.

Example 1: Hydrogen–Bromine Reaction

The well-known reaction mechanism

$$\begin{array}{lll} & 1\text{–}2 & Br_2 + X \rightleftharpoons 2\,Br + X \\ (13) & 3\text{–}4 & Br + H_2 \rightleftharpoons H + HBr \\ & 5 & H + Br_2 \rightleftharpoons Br + HBr \end{array}$$

was chosen to give a first insight into the proposed analysis method. Expressing concentrations in mol/cm^3, the rate constants are $k_1 = 6.26 \times 10^5$, $k_2 = 1.56 \times 10^{15}$, $k_3 = 2.61 \times 10^9$, $k_4 = 1.39 \times 10^{13}$, and $k_5 = 1.17 \times 10^{14}$. The constants and the initial conditions $[Br_2]_0 = [H_2]_0 = 1 \times 10^{-8}$, $[X]_0 = [X] = 1 \times 10^{-5}$ were taken from Snow [9], where X represents the "third body" and $[X]$ is kept constant.

Let the "observed" components be Br_2, H_2, and HBr. Selecting ten time points within the interval 0.01–1 s we obtain eigenvalues and eigenvectors shown in Table I. The principal component Ψ_5, corresponding to the small eigenvalue λ_5 clearly reveals that the response function depends only upon the ratio k_4/k_5 and does not depend on k_4 and k_5 separately. To prove this the kinetic equations were solved at $k_i = k_i^0$, $i = 1, 2, 3$, $k_4 = 10k_4^0$, and $k_5 = 10\,k_5^0$, (i.e., keeping k_4/k_5 fixed). As shown in Table II, even at the end point of the considered time interval concentrations of the molecular species are only slightly changed in spite of the considerable changes in [Br] and [H]. On the other hand, setting $k_4 = 10\,k_4^0$ while keeping $k_5 = k_5^0$ fixed results in rather different solutions for the molecular species as well (see column 3 of Table II).

To show that the relationship between k_4 and k_5 stems from the validity of a quasi-steady-state assumption (QSSA), we first consider [Br] and [H] as also "observed" components. Then the small eigenvalue is removed (see Table III, where according to Ψ_2, the parameter k_5

TABLE I. Eigenvalues and eigenvectors in the hydrogen–bromine system if all molecular species are "observed."

	λ^b	k_1	k_2	k_3	k_4	k_5
1	1.68(1)	.441	-.354	.789	-.169	.169
2	5.66(-1)	.550	.454	.105	.490	-.490
3	1.13(-1)	-.276	-.692	-.045	.470	-.470
4	5.21(-2)	.653	-.436	-.603	-.099	.099
5	2.25(-10)	.00	.00	.00	.707	.707

[a] Time points are 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.8, and 1.0 s.

[b] Numbers in parentheses denote powers of ten.

TABLE II. Computed concentrations in the hydrogen–bromine system at $t = 1$ s with nominal and perturbed rate coefficients.

	$k=k^o$	$k_4=10k_4^o, k_5=10k_5^o$		$k_4=10k_4^o$	
Species	moles/cm^3 x 10^8	moles/cm^3 x 10^8	deviations %	moles/cm^3 x 10^8	deviations %
Br_2	.12878(0)	.13384(0)	6.9	.28828(0)	123.8
HBr	.16699(1)	.16506(1)	-0.6	.13155(1)	-21.2
H_2	.16506(0)	.16809(0)	3.4	.34225(0)	107.3
Br	.72568(-1)	.51447(-1)	-29.1	.10795(0)	48.8
H	.81599(-6)	.95377(-7)	-88.3	.48416(-6)	-40.7

has a significant and independent effect on concentrations). On the other hand, the partial QSSA $d[H]/dt = 0$ leads to rate equations

$$\frac{d}{dt}[Br_2] = -r_1 - r_2; \quad \frac{d}{dt}[HBr] = 2r_2 \tag{14}$$

$$\frac{d}{dt}[H_2] = -r_2; \quad \frac{d}{dt}[Br] = 2r_1$$

TABLE III. Eigenvalues and eigenvectors in the hydrogen–bromine system if all species are "observed."

	λ	k_1	k_2	k_3	k_4	k_5
1	2.21(1)	.476	-.352	.771	-.164	-.167
2	7.31(0)	-.033	.007	.234	-.003	.971
3	3.05(0)	.628	-.502	-.549	-.161	.157
4	9.81(-1)	.528	.705	.093	.464	-.008
5	2.98(-1)	-.313	-.355	.201	.855	-.054

with

$$r_1 = k_1[\mathrm{Br}_2][X] - k_2[\mathrm{Br}]^2[X]; \quad r_2 = \frac{k_3[\mathrm{Br}][\mathrm{H}_2]}{\dfrac{k_4}{k_5}\dfrac{[\mathrm{HBr}]}{[\mathrm{Br}_2]} + 1} \tag{15}$$

depending on k_1, k_2, k_3, and k_4/k_5.

The principal component analysis, however, denies the validity of the additional QSSA $d[\mathrm{Br}]/dt = 0$ under the considered experimental conditions. Indeed, together with the already justified assumption on the stationarity of [H], this QSSA would imply

$$\frac{d}{dt}[\mathrm{Br}_2] = -r, \quad \frac{d}{dt}[\mathrm{HBr}] = 2r, \quad \frac{d}{dt}[H_2] = -r \tag{16}$$

with the well-known rate expression

$$r = \frac{k_i[\mathrm{H}_2][\mathrm{Br}_2]^{1/2}}{k_t\dfrac{[\mathrm{HBr}]}{[\mathrm{Br}_2]} + 1} \tag{17}$$

depending only upon the parameter combinations $k_i = (k_1/k_2)^{1/2}k_3$ and $k_t = k_4/k_5$. Since Table I does not reveal any dependency among k_1, k_2, and k_3 (i.e., there are no further small eigenvalues), the existence of parameter k_i is excluded. This result is obvious, for the concentration of atomic bromine reaches the same magnitude as the concentration of the molecular species (see Table II).

Since the hydrogen-bromine reaction played a key role in the development of the steady-state approximation theory, it is interesting to find the experimental conditions under which rate expression (17) applies. Consider the time interval 1–10 s and evaluate S^TS for the molecular species. Then we still have only two small eigenvalues, indicating the parameter groups k_4/k_5 and k_1/k_2, parameter k_3 being independent. Both QSS assumptions apply, however, if the only observed component is HBr. Then we obtain three small eigenvalues ($\leq 10^{-8}$). To identify the exact form of the relationship among k_1, k_2, and k_3, we evaluated partial S^TS matrices from the columns (1,2), (1,3), and (2,3), respectively, of the sensitivity matrix S. Table IV shows the eigenvector $u_{\min}$ corresponding to the smallest eigenvalue $\lambda_{\min}$ for each of these cases. The derived relationships clearly reveal that the underlying parameter group is $(k_1/k_2)\ k_3^2$. Applicability of the quasi steady-state approximation to describe the [HBr] time pattern is proved by solving eqs. (16) and (17). Calculated concentrations for HBr are close to the original ones (the mean absolute deviation is 3.5%), while concentrations of other species, including Br_2 and H_2, are considerably changed.

TABLE IV. Eigenvectors corresponding to smallest eigenvalues of partial S^TS matrices if only [HBr] is "observed."[a]

Free parameters	u_{min}		relationship
k_1, k_2	.707	.707	k_1/k_2
k_1,k_3	.893	-.450	$k_1\ k_3^2$
k_2,k_3	.893	.450	k_2/k_3^2

[a] Time points are 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 s.

Remark 1: Though our analysis is completely deterministic, it is obviously rooted in the nonlinear parameter estimation theory. Indeed, the response function (2) may be regarded as the least-squares objective function. If we want to estimate the parameters of the model by minimizing this function, then linear combinations (principal components) of the parameters α that correspond to small eigenvalues are poorly determined (large variance), whereas principal components corresponding to large eigenvalues are well determined (small variance). Since near singularity of the matrix S^TS is one of most frequent causes of failure in nonlinear parameter estimation, its eigenvalue-eigenvector decomposition is a well-established step of the estimation procedure. The really new contribution of this paper is, however, demonstrating the advantages stemming from the use of normalized sensitivities $\partial \ln y_j/\partial \ln k_i$ (i.e., the introduction of the parameter transformations $\alpha_i = \ln k_i$, i = 1, 2, . . . , p). As it has been shown, the linear dependencies among the transformed parameters α, uncovered by the principal component analysis, correspond to nonlinear dependencies of the form k_i/k_j^c = const among the original parameters and these latter relationships are usually connected with the validity of some kind of quasi steady-state assumption.

Remark 2: The method extracts information from the response function (2) and is a compact way of exhibiting relative importance of system parameters. However, the response function measures only total sensitivity of the system over arbitrarily selected time points, whereas the importance of certain reactions can be different at different stages of the process. Similarly, the analysis does not necessarily uncover parameter dependencies existing only for a certain period of time but not over the entire time domain of interest. One way to avoid these difficulties is to look at the plots of the temporal behavior of sensitivity coefficients for the proper selection of time points [10,11]. If necessary, one can also select several time intervals and apply the principal component analysis separately.

As a matter of fact, the sensitivity plots can be directly used for unraveling parameter dependencies (see [11]). Such an analysis is, however, quite tedious in complex mechanisms and some relationships may be overlooked. Therefore, principal components with properly selected time points and/or subintervals offer a useful summary and provide quantitative characterization of all dependencies among the parameters.

Remark 3: To obtain the very small eigenvalues (e.g., $\lambda_5 = 2.25 \times 10^{-10}$ in Table I) accurate sensitivity coefficients are required. In this paper we used the decomposed direct (DD) method [3], recently implemented as the compact FORTRAN subroutine ROW4S [12] in conjunction with a semi-implicit Runge-Kutta algorithm [13] for solving the differential equations.

As shown in [12], the DD method provides highly accurate sensitivities and for kinetic problems of moderate complexity is competitive with the well-known Green's function (GF) approach [4,5] also in terms of computer time requirements. To analyze highly complex mechanisms it is, however, advisable to use the GF or the polynomial approximations (PA) methods [11] for their economic advantages with possible sacrifice of accuracy in the results. Then the smallest eigenvalues can be increased, whereas the eigenvectors are generally quite invariant. For the principal component analysis it is sufficient to keep the "small" eigenvalues below certain limits (usually 10^{-4}, see also the next section). A proper selection of the grid points in GF and PA methods to satisfy this condition offers a tradeoff between computational cost and reliability. Choosing a particular method and a rule for selecting the grid points, it is useful to solve example 1 and observe the eigenvalue λ_5 in order to see whether or not the obtained sensitivities are sufficiently accurate for computing the eigenvalues.

We note that the listing of the ROW4S procedure is available by request [12].

Mechanism Reduction

As it has already been noted, the fundamental kinetic approach of including a large number of elementary reactions to reduce the possibility of something important being left out results in a complex reaction mechanism. Selecting the most important part of this reaction set is then desirable both for kinetic analysis and practical applications.

Though sensitivity is a measure of reaction significance, the possibility of eliminating reactions with small sensitivities is far from obvious (see [1 and 2]). Now we will show that the principal component analysis offers an effective means for the solution of this problem.

Since the transformations (1) are not defined at $k_i = 0$, we introduce another parameter transformation given by

$$\tilde{\alpha}_i = k_i/k^0_i,\ i = 1, 2, \ldots, p \tag{18}$$

It should be emphasized that at $k_i = k_i^0$ *we obtain*

$$\frac{\partial \ln y_r}{\partial \tilde{\alpha}_i} = \frac{\partial \ln y_r}{\partial \ln k_i} \tag{19}$$

thus both transformations (1) and (18) yield the same normalized sensitivities. Therefore, the properties of S^TS can also be studied in terms of the parameters $\tilde{\alpha}$.

Let λ_i and u_i denote a small eigenvalue and the corresponding eigenvector, respectively. As shown in the previous section, several significant (i.e., $\geqslant 0.2$) entries in u_i reveal dependencies among the parameters and hence we here restrict our consideration to the case $u_i = (0, 0, \ldots, 1, 0, \ldots, 0)$, thus $\Psi_i = \tilde{\alpha}_j$ for some j.

Since $\tilde{\alpha}_j^0 = k_j^0/k_j^0 = 1$, $k_j = 0$ implies $\|\Delta\Psi_i\| = \|\Delta\tilde{\alpha}_j\| = \|\tilde{\alpha}_j - 1\| = 1$. Setting $k_j = 0$ we move along u_i, hence $Q(\tilde{\alpha}) = \lambda_i$. Therefore, λ_i is a measure of the effect brought about by setting $k_j = 0$, thus eliminating the jth reaction. Then the change in the concentration of the species i at the time point t_r can be characterized by the relative deviation

$$\frac{|\Delta y_{i,r}|}{y_{i,r}} = \frac{|y_{i,r}(k_1^0, \ldots, k_j^0, \ldots, k_p^0) - y_{i,r}(k_1^0, \ldots, k_{j-1}^0, 0, k_{j+1}^0, \ldots, k_p^0)|}{y_{i,r}(k_1^0, \ldots, k_j^0, \ldots, k_p^0)} \tag{20}$$

If we require $|\Delta y_{i,r}|/y_{i,r} \leqslant 0.01$ for each i and r, then approximately $Q\ (\tilde{\alpha}) \leqslant mq \times 10^{-4}$. Since $Q(\tilde{\alpha}) = \lambda_i$, eliminating a reaction which is a dominant element of a principal component corresponding to an eigenvalue $\lambda_i \leqslant mq \times 10^{-4}$ we may expect small ($\leqslant$1%) changes in each of the observed concentrations.

Example 2: Formaldehyde Oxidation Kinetics

To show an application of the proposed procedure we chose the moderately complex mechanism given by Vardanyan, Sachyan, and Nalbandyan [14] for the kinetics of formaldehyde oxidation in the presence of CO. Note that detailed sensitivity results are available for this model [5].

The reaction set, rate constants, and initial species concentrations are listed in Table V. We calculated normalized sensitivities for all species dt the time points 1×10^{-5}, 5×10^{-5}, 1×10^{-4}, 1×10^{-3}, 2×10^{-3}, 3×10^{-3}, and 5×10^{-3} s, i.e., up to the time point considered in [5]. Eigenvalues of S^TS and significant entries ($\geqslant 0{,}2$) of the corresponding eigenvectors are shown in Table VI. According to the magnitude of eigenvalues, the reactions can be divided into three classes as follows:

(i) Eigenvalues λ_1–λ_9 are much larger than the remaining ones ($\Sigma_{i=1}^{9} \lambda_i / \Sigma_{j=1}^{25} \lambda_j = 0.999$). Principal components Ψ_1–Ψ_9 contain steps 1, 2, 3, 4, 9, 10, 11, 12, 16, and 22, forming the "basic" part of the mechanism. (Though step 8 is present in Ψ_9, its contribution is small and hence is moved to the next group.) According to Ψ_1, the most influential reaction sequence is formed by (22), (10), (4), and (9). This "reaction kernel" emphasizes that the largest effect is brought about by setting $k_j = k_j^0 e^{u_{1,j}}$ (i.e., $k_{22} = 0.55\, k_{22}^0$, $k_{10} = 0.59\, k_{10}^0$, $k_9 = 0.73\, k_9^0$, and $k_4 = 1.51\, k_4^0$) and not by perturbing a single parameter.

(ii) In this example $m = 12$, $q = 7$, and $mq \times 10^{-4} = 8.4 \times 10^{-3}$. According to Ψ_{10}–Ψ_{13}, reactions (8), (13), and (6) are of "transitional" importance: As it will be shown, in spite of their small contributions they can not be removed from the mechanism.

(iii) Finally, reactions (5), (7), (14), (15), (17), (18), (19), (20), (21), (23), (24), and (25) contained in Ψ_{14}–Ψ_{25} with eigenvalues below 8.4×10^{-3} are unimportant and can be eliminated. Notice that the simplification condition proposed in this section may immediately only apply to Ψ_{22}–Ψ_{25} and Ψ_{14} [i.e., to reactions (21), (19), (15), (20), and (24)]. According to Ψ_{19}–Ψ_{21} steps 17, 5, and 23 are not independent, but all combinations are eliminable. Similarly, Ψ_{16} and Ψ_{18} indicate that the solution depends on k_{14}/k_7 and $k_7 \times k_{14}$, both being unimportant. Finally, we drop steps 25 and 18 according to Ψ_{15} and Ψ_{17}.

Weeding out the class (iii), the obtained minimal mechanism consists of thirteen reactions (1), (2), (3), (4), (6), (8), (9), (10), (11), (12), (13), (16), and (22). As it has been expected, the mean change in the concentrations is less then 1% and even the maximum deviations, obtained at the end point 5×10^{-3} s are small. Column A of Table VII shows relative deviations of the product concentrations from the "true" ones, computed by the complete model and listed in column 1 of the same table. Notice that the product distribution is even less affected by the reduction of the model and the relative deviations remain below 0.5% for each species and time point. Thus the proposed rule for selecting a minimal reaction set is completely justified.

TABLE V. Formaldehyde oxidation in the presence of CO.[a]

	Reaction	Rate constant
1.	$HCO+O_2 \rightarrow HO_2+CO$	1.0(-13)
2.	$HO_2+CH_2O \rightarrow H_2O_2+HCO$	5.7(-14)
3.	$H_2O_2+M \rightarrow 2OH+M$	6.66(-18)
4.	$OH + CH_2O \rightarrow H_2O+HCO$	1.6(-10)
5.	$OH+H_2O_2 \rightarrow H_2O+HO_2$	5.1(-12)
6.	$H_2O_2 \xrightarrow{wall}$ destruction	1.05(+2)
7.	$HO_2 \xrightarrow{wall}$ destruction	1.05(+1)
8.	$HO_2+HO_2 \rightarrow H_2O_2+O_2$	3.00(-12)
9.	$OH+CO \rightarrow CO_2+H$	3.3(-13)
10.	$HO_2+CO \rightarrow CO_2+OH$	1.2(-15)
11.	$H+CH_2O \rightarrow H_2+HCO$	2.7(-12)
12.	$H+O_2 \rightarrow OH+O$	5.51(-14)
13.	$H+O_2+M \rightarrow HO_2+M$	1.0(-32)
14.	$HO_2+M \rightarrow H+O_2+M$	4.7(-19)
15.	$O+H_2 \rightarrow OH+H$	3.02(-13)
16.	$O+CH_2O \rightarrow OH+HCO$	1.0(-10)
17.	$H+H_2O_2 \rightarrow HO_2+H_2$	1.3(-12)
18.	$H+H_2O_2 \rightarrow H_2O+OH$	5.9(-12)
19.	$O+H_2O_2 \rightarrow OH+HO_2$	1.0(-13)
20.	$HCO \rightarrow H+CO$	4.6(-12)
21.	$OH+H_2 \rightarrow H_2O+H$	1.0(-11)
22.	$CH_2O+O_2 \rightarrow HCO+HO_2$	2.9(-20)

TABLE V. *(Continued from previous page.)*

	Reaction	Rate constant
23.	$H+HO_2 \rightarrow 2OH$	5.0(-12)
24.	$H+HO_2 \rightarrow H_2O+O$	5.0(-11)
25.	$H+HO_2 \rightarrow H_2+O_2$	4.5(-11)

[a] Units: molecules, cm^2, s. Initial concentrations: $[CH_2O]^{(0)}$ = 6.77(16); $[O_2]^{(0)}$ = 1.27(18); $[CO]^{(0)}$ = 2.83(18); [M] = 7.09(18). The remaining initial species concentrations are zero.

We show that no further reduction of the mechanism is possible if all concentration changes should be small. Indeed, according to Ψ_{12} the next reaction of low significance is step 6. Dropping this step, all concentrations are significantly changed (see column B in Table VII). As shown in column C of Table VII, elimination of step 13, the dominant element of Ψ_{10} gives a similar effect. Finally, dropping the set {8,13,6} (i.e., all reactions of "transitional" importance) quite large concentration deviations occur (see column D in Table VII).

Remark 4: According to our result, reactions in principal components with small eigenvalues can be dropped. It should be, however, carefully checked that the effects of such steps through other principal components also be small, e.g., $\tilde{\alpha}_{12}$ is a significant entry in Ψ_{13} with $\lambda_{13} = 4.06 \times 10^{-3}$. Step 12 is, however, also present in the important principal components Ψ_3, Ψ_4, and Ψ_7 and hence can not be eliminated.

Remark 5: As reported by Dougherty, Hwang, and Rabitz [5], the most important rate constants at $t = 5 \times 10^{-3}$ s are 10, 22, 3, 2, 9, 4, and 8, roughly in order of decreasing sensitivity, whereas we obtained 22, 10, 4, 9, 2, and 16. The difference clearly stems from the fact that we selected several time points. Indeed, reactions (2) and (3) are relatively unimportant at the beginning of the reaction and increase their importance as the overall reaction proceeds. It was also shown by Dougherty, Hwang, and Rabitz [5] that reactions (14)–(25) (with the exception of step 22) are unimportant, at least at the considered stage of the reaction. Our analysis shows, however, that reaction (16) is also definitely important (it is present in the important principal components Ψ_2, Ψ_3, Ψ_4, and Ψ_7, see Table VI). Indeed, dropping step 16 from the minimal mechanism, all concentrations are altered and a dramatic increase in [0] occurs (column E in Table VII). The source

TABLE VI. Eigenvalues and principal components for the formaldehyde oxidation kinetics.

	λ	Dominant elements of the principal components [a]							
1	1.38(2)	22 -.60	10 -.52	4 .41	9 -.32				
2	2.12(1)	22 .51	2 .48	9 -.42	4 .40	16 .26	1 -.21		
3	1.45(1)	2 -.60	10 .36	12 -.34	11 .31	16 .30	3 -.29	22 .21	
4	8.90(0)	16 .49	12 -.48	4 -.36	2 .31	11 .31	9 .28	22 -.27	3 .22
5	5.43(0)	10 .62	9 -.43	22 -.42	3 .41				
6	4.96(0)	1 .95	2 .22						
7	3.08(0)	11 .85	12 .35	16 -.31					
8	2.71(0)	4 .73	9 .55	10 .29					
9	1.15(0)	3 .72	2 -.46	10 -.31	8 -.26	22 .26			
10	3.85(-2)	13 .71	8 -.61	3 -.22					
11	3.17(-2)	8 .59	16 .46	12 .46	13 .42				
12	1.52(-2)	6 .94	13 .26						
13	4.06(-3)	12 -.47	16 -.47	13 .43	8 .41	3 .27	6 -.26		
14	6.53(-4)	24 .96							

TABLE VI. *(Continued from previous page.)*

	λ	Dominant elements of the principal components [a]		
15	7.30(-5)	25 .86	18 .44	
16	3.75(-5)	7 .73	14 .64	
17	1.35(-5)	18 .86	25 -.42	7 -.26
18	1.61(-6)	14 .76	7 -.61	
19	4.21(-8)	17 .88	23 -.39	
20	1.38(-8)	5 -.82	23 .43	17 .32
21	3.78(-9)	23 .80	5 .53	17 .25
22	4.48(-12)	21 .98		
23	2.12(-13)	19 .98		
24	1.33(-17)	15 .98		
25	3.27(-29)	20 1.00		

[a] Top line refers to the rate constant for the reaction listed in Table V. The bottom line lists eigenvector components of magnitude $\geqslant 0.20$.

of this contradiction is that step 16 is particularly important by virtue of interactions with other important steps, as Ψ_2, Ψ_3, Ψ_4, and Ψ_7 show. Further discussion will be given in Remark 8.

TABLE VII. Product concentrations in formaldehyde oxidation, computed from the complete and different partial models at $t = 5.(-3) \cdot$ s.

Species	Concentrations from the complete model [a]	% deviations					
		A	B	C	D	E	F
HCO	3.5910(12)	2.3	11.2	12.9	87.5	-20.0	-11.4
HO_2	5.8197(13)	2.4	10.6	11.3	87.5	-19.0	-11.8
H_2O_2	3.4201(14)	1.9	22.1	9.5	47.1	-16.2	1.1
OH	2.0453(10)	2.3	12.2	12.5	90.0	-20.1	-11.2
H_2O	3.8696(14)	1.6	7.4	9.8	44.7	-16.5	-11.1
CO_2	3.9331(14)	1.7	6.5	8.9	43.9	-15.4	-11.3
H	5.5287(10)	3.6	13.8	55.1	158.3	-19.7	22.2
H_2	1.7924(13)	1.0	6.8	48.2	95.5	-17.4	19.9
O	6.0204(8)	-0.4	9.4	49.2	149.2	9653.3	13741.2

[a] Units: molecules/cm^3.

A: reactions (1), (2), (3), (4), (6), (8), (9), (10), (11), (12), (13), (16), and (22); B: reactions (1), (2), (3), (4), (8), (9), (10), (11), (12), (13), (16), and (22); C: reactions (1), (2), (3), (4), (6), (8), (9), (10), (11), (12), (16), and (22); D: reactions (1), (2), (3), (4), (9), (10), (11), (12), (16), and (22); E: reactions (1), (2), (3), (4), (6), (8), (9), (10), (11), (12), (13), and (22); F: reactions (1), (2), (3), (4), (8), (9), (10), (11), (12), and (22).

Remark 6: Eigenvalues and eigenvectors are based on sensitivities computed for several components and several time points. A similar summary of this kind is the "overall" sensitivity coefficient defined by

$$B_r = \sum_{j=1}^{q} \sum_{i=1}^{m} \left[\frac{\partial \ln y_{i,j}(k)}{\partial \ln k_r} \right]^2 \tag{21}$$

i.e., the sum of squared sensitivities for all observed components and time points. Notice that the B's are the diagonal entries of S^TS, and $B_r = \Sigma_{j=1}^{p} \lambda_j u_{j,r}^2$. Though B_r is a convenient measure of the significance of reaction (r), its application for mechanism reduction can lead to erroneous conclusions, e.g., in order of decreasing overall sensitivity the reactions of Table V are (22), (10), (4), (9), (2), (16), (12), (11), (1), (13), (14), (3), (6), (7), (24), (8), (25), (23), (18), (17), (5), (21), (19), (15), and (20). The most important steps [i.e., (22), (10), (4), (9), (2), (16), (12), (11), and (1)] and the most unimportant ones [i.e., (25), (23), (18), (17), (5), (21), (19), (15), and (20)] are those also revealed by the principal component analysis. As shown in column A of Table VII, eliminating the latter set of reactions implies small changes in concentrations. Additional elimination of step 8, as suggested by the overall sensitivities leads, however, to large deviations (e.g., at $t = 5 \times 10^{-3}$ s the relative difference for $[HO_2]$ is 51%). On the other hand, some reactions [e.g., (14) and (7)] with much larger overall sensitivities can be dropped. To explain this result notice that the relative importance of step 8 is in its interactions with other important reactions (see Ψ_9–Ψ_{11}) and such secondary effects are not shown by the "overall" sensitivity coefficients.

Remark 7: We may ask whether or not the reduced mechanism, consisting of thirteen reactions can be further simplified if small changes are required only in $[HO_2]$ and $[CO_2]$, the other concentrations being unobserved [14]. Eigenvalues and eigenvectors for the two observed species shown in Table VIII, suggest that reactions (16), (13), and (6) can also be dropped, according to Ψ_{13}, Ψ_{12}, and Ψ_9, respectively. This choice, however, results in large deviations also for $[HO_2]$ and $[CO_2]$, as shown in column F of Table VII.

We show that the above contradiction stems from a general problem of sensitivity analysis. Consider the simple sequence

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{21}$$

of first-order reactions, assume that $k_2 >> k_1$ (say, $k_2/k_1 = 100$) and the observed species are A and C. Then, as discussed by Boudart [15], step 1 is rate determining, the QSSA $d[B]/dt = 0$ applies, and $d[C]/dt \approx k_1[A]$. Since $\partial[A]/\partial k_2 = 0$, sensitivities with respect to k_2 are very small in spite of obvious significance of step 2 in the simple mechanism. Decreasing k_2 the sensitivity will be increased. However, with $k_2 >> k_1$ the situation is changed if and only if $[B]$ is also observed, since the normalized sensitivity $\partial \ln[B]/\partial \ln k_2$ is large in spite of small $[B]$ values.

It may be easily shown that observing only $[HO_2]$ and $[CO_2]$, the insensitivity of reaction (16) in the formaldehyde system stems from the source just discussed. Indeed, the slow reactions (15), (19), and (24) have already been eliminated, hence the atomic O is produced only in step 12 and will react in 16. Since $[CH_2O]$ and $[O_2]$ are almost

TABLE VIII. Eigenvalues and eigenvectors for the reduced formaldehyde oxidation mechanism, observing [HO_2] and [CO_2].

	λ	Dominant elements of the principal component [a]					
1	1.87(1)	10 .55	22 .79				
2	2.47(0)	10 .83	22 -.54				
3	1.67(0)	2 .61	3 .61	8 -.24	22 -.25		
4	3.57(-2)	1 .76	4 .30	8 -.29	9 -.30	12 -.25	
5	7.21(-3)	1 .59	4 -.28	8 .59	9 .29	12 .25	
6	5.31(-4)	2 .25	3 .33	4 .30	8 .69	9 -.29	12 -.29
7	5.06(-5)	2 .20	4 .47	9 -.37	11 -.38	12 .60	
8	1.73(-5)	2 .68	3 -.66				
9	6.06(-7)	6 .97					
10	5.84(-8)	4 .68	9 .72				
11	1.86(-8)	11 -.82	12 -.55				

TABLE VIII. *(Continued from previous page.)*

	λ	Dominant elements of the principal component [a]
12	2.55(-9)	12 13 .20 .97
13	2.25(-10)	16 1.00

[a] Top line refers to the rate constant for the reactions listed in Table V. The bottom line lists eigenvector components of magnitude $\geqslant 0.20$.

unchanged at the considered stage of the reaction, the involved reaction rates are approximately given by $r_{12} = \tilde{k}_{12}[\mathrm{H}]$ and $r_{16} = \tilde{k}_{16}[\mathrm{O}]$ with rate coefficients $\tilde{k}_{12} = k_{12}\,[\mathrm{O_2}] \approx 6 \times 10^4$ and $\tilde{k}_{16} = k_{16}\,[\mathrm{CH_2O}] \approx 6 \times 10^6$, respectively. Therefore, we obtain the sequence (21) just discussed and $k_{16}/k_{12} \approx 100$. As expected from this analysis, a decrease on the value of k_{16} increased its sensitivity even by an order of magnitude. In view of the above examples it should be emphasized that considering only "observed" species very low sensitivities can be obtained both for relatively slow as well as relatively fast and hence quite important reaction steps. This intrinsic ambiguity is somewhat overlooked in the literature (see, e.g., [2 and 6]), where computing sensitivities for the observable species is usually considered as the source of complete and useful sensitivity information. To avoid erroneous conclusions, reduction of the mechanism clearly requires performing sensitivity analysis for all species. It should be, however, noted that the reduced mechanism obtained this way will retain all species present in the original system and hence the rule here proposed can be considered only as a first and quite conservative step toward a systematic model reduction methodology.

Remark 8: Table VIII reveals further useful kinetic information. According to Ψ_{10}, concentrations of observed species depend only on the ratio k_4/k_9. Notice that in the reduced mechanism the OH radical reacts only in steps 4 and 9 and hence the QSSA $d[\mathrm{OH}]/dt = 0$ yields the steady-state concentration

$$[\mathrm{OH}]_s = \frac{2r_3 + r_{10} + r_{12} + r_{16}}{k_4[\mathrm{CH_2O}] + k_9\,[\mathrm{CO}]} \tag{22}$$

where r_i denotes the rate of the reaction (i). Setting (22) into the set of kinetic equations, it will depend only upon the ratio k_4/k_9.

A similar explanation applies also to the dependence between k_{11} and k_{12}, revealed by Ψ_{11} in Table VIII. Indeed, the QSSA $d[\mathrm{H}]/dt = 0$ yields the steady-state concentration

$$[\mathrm{H}]_s = \frac{r_9}{k_{11}[\mathrm{CH_2O}] + k_{12}[\mathrm{O_2}] + k_{13}[\mathrm{M}]\,[\mathrm{O_2}]} \tag{23}$$

for atomic H. Since step 13 is relatively unimportant, the ratio k_{11}/k_{12} will appear in the kinetic equation, somewhat corrupted by the presence of reaction (13).

We note that applicability of these two QSSA assumptions differs considerably. Considering all molecular components (i.e., H_2O_2, H_2O, CO_2, H_2, CH_2O, O_2, and CO) and HO_2 as "observed" species, the resulting eigenvectors still reveal the relationship between k_4 and k_9, whereas k_{11} and k_{12} become independent. Indeed, setting $k_4 = 100\ k_4^0$ and $k_9 = 100\ k_9^0$ all the obtained concentrations (including radicals) differ less than 0.1% from those of the reduced (13-parameter) model. On the other hand, $k_{11} = 100\ k_{11}^0$ and $k_{12} = 100\ k_{12}^0$ give only slight changes in $[HO_2]$ and $[CO_2]$ while considerably changing the concentration patterns of other species. We note that there exists a further dependency among the parameters, i.e., according to Ψ_8 in Table VIII, $[HO_2]$ and $[CO_2]$ depend only on the product k_2k_3. This relationship is, however, eliminated if all molecular species are observed.

Practical Identifiability of the Parameters

Studying formaldehyde oxidation kinetics the main interest of Vardanyan, Sachyan, and Nalbandyan [14] was in determining the rate constant k_{10} from $[CO_2]$ and $[HO_2]$ measured at a single point. The approach they used relies on a number of assumptions and does not yield any error estimates. As outlined Dougherty, Hwang, and Rabitz [5], a more fundamental parameter estimation procedure should have utilized the computer model. We will now show that the principal component analysis can be then used to yield the expected error estimates on the parameters.

Assume that $[CO_2]$ and $[HO_2]$ are measured at several time points such that the method of least squares applies. Using sensitivity information for error bound estimation has been discussed in [16]. Furthermore, as shown in Remark 1, eigenvalues and eigenvectors offer a natural characterization of the expected variances. It should be emphasized that the presence of small eigenvalues reveals large variances and hence practical unidentifiability of some parameters. In the estimation literature this situation is described by saying the model is poorly parametrized [17] or the parameter estimation problem is nearly singular [18]. Numerous efficient minimization methods have been proposed for the solution of such problems [19], usually resulting in a reasonable fit to the data. The estimates of ill-conditioned parameters are, however, frequently at variance with the best experimental and theoretical values available [20]. Therefore, many chemists feel it is advisable to estimate only some of the parameters while keeping the others fixed at values obtained from the relevant literature (see, e.g., [21]). We show that the principal component analysis offers a justification for this "partial estimation" approach.

To answer the question whether or not the parameter estimation problem is nearly singular let $\tilde{\alpha}$ and $\hat{\tilde{\alpha}}$ denote the unknown true value and its least-square estimate, respectively, of the transformed parametrization vector (18). Since we can choose $k_i^0 = \hat{k}_i$, $\hat{\tilde{\alpha}} = 1$. As shown in [23], using the usual linearization approach the average value of the squared distance $\tilde{\alpha}$ from $\hat{\tilde{\alpha}} = 1$ is given by

$$E\{|\tilde{\alpha} - 1|^2\} = \sum_{i=1}^{p} \frac{\sigma^2}{\lambda_i} > \frac{\sigma^2}{\lambda_{\min}} \tag{24}$$

where σ^2 denotes the variance of relative measurement errors. Thus, in case of small eigenvalues the least-squares estimates of the parameters will be pulled away from their true values. It is reasonable to require 10% relative error margin in each of the estimated parameters, thus $E\{|\tilde{\alpha} - 1|^2\} \leqslant 0.01$ and $> \sigma^2/0.01$. Assuming, e.g., 1% relative measurement errors we have $\sigma^2 = 10^{-4}$ and the bound $\lambda_{\min} \geqslant 0.01$ on the eigenvalues.

Remark 9: Expression (24) assumes $\lambda_i > 0$ for each i, $i = 1, 2, \ldots, p$. In fact, the matrix $S^T S$ is positive semidefinite by definition, thus $\lambda_i \geqslant 0$. The totally singular (i.e., $\lambda_{\min} = 0$) case means exact linear dependencies among the sensitivities. Detection of such models is the objective of the numerous studies on deterministic (structural) identifiability [23,24]. Structurally unidentifiable models are rare in reaction kinetics and hence we may assume $\lambda_{\min} > 0$.

According to Table VIII, measurements of $[HO_2]$ and $[CO_2]$ at the selected time points do not allow one for estimating all parameters simultaneously. To formulate a sensible (i.e., well conditioned) estimation problem the following decisions should be taken.

(i) Fix parameters k_{16}, k_{13}, and k_6 at their nominal values to eliminate the small eigenvalues λ_{13}, λ_{12}, and λ_9. Notice that these selected values will practically not affect the response function and the estimates of the other parameters.

(ii) Since we can estimate the parameter combinations k_4/k_9,

> k_{11}/k_{12}, and k_2k_3, fix k_9, k_{12}, and k_3 to eliminate the eigenvalues λ_{10}, λ_{11}, and λ_8. It should be emphasized that the estimates $\hat{k}_4$, $\hat{k}_{11}$, and $\hat{k}_2$ will then heavily depend on the selected nominal values k_9^0, k_{12}^0, and k_3^0, respectively.

To see the sources of further small eigenvalues, at this point we performed an additional principal component analysis with respect to the remaining "free" parameters k_1, k_2, k_4, k_8, k_{10}, k_{11}, and k_{22}. According to its result, there exists a relationship between k_4 and k_{11}, leading to an eigenvalue $\lambda_{\min} = 1.66 \times 10^{-5}$. Therefore

(iii) fix $k_{11} = k_{11}^0$, thereby influencing $\hat{k}_4$

A further principal component analysis with respect to k_1, k_2, k_4, k_8, k_{10}, and k_{22} shows that the parameter k_4 is also connected with k_2 and k_8. Since this parameter combination results in an eigenvalue $\lambda_{\min} = 2.8 \times 10^{-4}$.,

(iv) set $k_4 = k_4^0$, thereby influencing the estimates $\hat{k}_2$ and $\hat{k}_8$

According to the decisions (i)–(iv), the parameters to be estimated are k_1, k_2, k_8, k_{10}, and k_{22}. The corresponding eigenvalues and eigenvectors shown in Table IX are then used to predict the expected parameter variances. According to Ψ_1 and Ψ_2, the parameters k_{10} and k_{22}, though correlated, can be determined with small (ca. 1%) variances. Notice that $\hat{k}_{10}$ and $\hat{k}_{22}$ will not depend on the estimates of the other parameters, since Ψ_1 and Ψ_2 are orthogonal to the corresponding coordinate axes. Small variance ($\leq 10\%$) is expected also for $\hat{k}_2$, it is, however, slightly correlated with $\hat{k}_8$ and depends on the selected values k_3^0, k_4^0, and k_9^0. According to Ψ_4, the expected variance of $\hat{k}_1$ is about 10% and this parameter is independent of the others. Finally, only an "order of magnitude" estimate can be obtained for k_8 (see Ψ_5) and this value depends on $\hat{k}_2$, k_4^0, and k_9^0. This detailed analysis shows that in spite of difficulties, observations of $[HO_2]$ and $[CO_2]$ at several sample points allow one to obtain a reliable estimate for k_{10} without the assumptions used by Vardanyan, Sachyan, and Nalbandyan [14]. Though some parameters should be kept fixed during the estimation procedure, their values will not influence the derived parameter $\hat{k}_{10}$. However, k_{22} should be estimated simultaneously, since its selected value k_{22}^0 would heavily influence $\hat{k}_{10}$. Furthermore, to obtain a good fit it is advisable to estimate also k_2, k_1, and k_8, though $\hat{k}_2$ will depend on a number of assumptions, whereas $\hat{k}_1$ and $\hat{k}_8$ will have considerable variances. It should be emphasized that such a preliminary analysis is absolutely necessary to obtain relaible estimates for some of the parameters at the least, since otherwise the poor parametrization of the model will lead to serious numerical difficulties in the estimation process and to meaningless estimates.

TABLE IX. Eigenvalues and eigenvectors for the reduced formaldehyde oxidation kinetics with respect to the parameters k_1, k_2, k_8, k_{10}, and k_{22}, observing $[HO_2]$ and $[CO_2]$.

	λ	Dominant elements of the principal component [a]	
1	1.81(1)	22	10
		.81	.57
2	2.45(0)	10	22
		.82	.56
3	7.99(-1)	2	8
		.92	.37
4	2.46(-2)	1	
		.98	
5	3.50(-3)	8	2
		.91	.37

[a] Top line refers to the rate constant for the reactions listed in Table V. The bottom line lists eigenvector components of magnitude ≥ 0.20.

Conclusions

The main objectives of kinetic analysis are usually the identification of the most important elementary reactions in a mechanism and elimination of the least important ones in order to obtain a tractable kinetic model. A generally accepted method of solving such problems is sensitivity analysis. Sensitivity studies, however, produce a mass of numerical information, rather difficult to deal with. As shown in the present paper, principal component analysis offers an effective means for extracting useful kinetic information from the derived sensitivity tables. Eigenvectors reveal strongly interacting reaction sequences and the corresponding eigenvalues measure the significance of these separate parts of the mechanism. Three application areas have been briefly discussed.

Firstly, considering sensitivities for all species present in the system, results can be used to select a minimal reaction set. This step is particularly useful when a large number of elementary processes is to be investigated, say in detailed atmospheric and combustion models. Secondly, evaluating principal components only from sensitivities of molecular components, some dependencies among the parameters are assessed which can confirm or deny the validity of quasi-steady-state assumptions under the considered experimental conditions. Thirdly, taking into account only observed species, the identified parameter–parameter interactions provide answers as to how errors on known parameters affected the ability to use the mechanism for determining unknown parameters and how large variances can be expected for parameter estimates.

As noted by Dougherty, Hwang, and Rabitz [5], in kinetic analysis one should always be alert for possible secondary nonlinear effects in the mechanism leading to parameter interactions. Using principal components forgotten or unknown relationships can be made manifest. When dependencies are found, it is up to the kineticist to uncover their causes on the basis of available chemical knowledge.

Finally, we emphasize that having computed the sensitivity coefficients, little effort need be expended for evaluating also the principal components. From the same sensitivity table eigenvalues and eigenvectors can be computed with respect to different sets of observed species and parameters. The entire time interval of interest can also be divided into subintervals. The relatively simple examples of this paper are presented to illustrate the method of analysis. More complex mechanisms (e.g., pyrolysis of simple hydrocarbons) have also been studied, including estimation of the parameters. Other problems (e.g., mechanisms for oscillating reactions) required separate principal component analysis over several short time intervals. These applications will be described in forthcoming papers and support that principal components provide a way of gaining considerable insight into chemical mechanism.

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Received March 1, 1984
Accepted July 31, 1984