

## THE METHOD OF QUASI-STATIONARY SENSITIVITY ANALYSIS

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### Abstract

A new sensitivity analysis technique is developed by utilizing Tihonov's singular perturbation theory. The described sensitivity analysis method deals with algebraic equations instead of solving the system of differential equations, which is the case in conventional sensitivity analysis. In the field of chemical kinetics, the proposed technique can supply information on the importance of elementary steps in complex reaction mechanisms. As examples, high-temperature propane pyrolysis and the chemistry of the "unpolluted" troposphere are studied.

### 1. Introduction

Mathematical models of reaction mechanisms are often used in the investigation of complex chemical systems. Sensitivity analysis of the models reveals the relationship between the model solutions and the input kinetic parameters, and also supplies information on the importance of the elementary reactions [1–3]. The basic quantity in conventional sensitivity analysis is the concentration sensitivity coefficient defined as the partial derivative of a species concentration  $c_i$  with respect to a kinetic parameter  $k_j$ :  $s_{ij} = \partial c_i / \partial k_j$ . It is a measure of the response of species concentration  $c_i$  at time  $t_2$  to the perturbation in the value of parameter  $k_j$  at time  $t_1$  (where  $t_2 > t_1$ ). Thus, the kinetic information derived by conventional sensitivity analysis belongs to a time interval  $(t_1, t_2)$  of the reaction course during which important reaction characteristics may change.

The kinetics and mechanism of a complex chemical reaction at a given stage of the process is determined unequivocally by the actual species concentrations and the rate coefficients. Consequently, kinetic and mechanistic problems should be studied by analysis techniques using quantities which only depend on the concentrations and the kinetic parameters. The recently suggested reaction rate analysis method [4], which uses sensitivity coefficients defined as the derivatives of the rates of species concentration changes with respect to the kinetic parameters, i.e.  $\varphi_{ij} = \partial f_i / \partial k_j$ , conforms to this type of treatment. These rate sensitivity coefficients rewritten in a log-normalized form,  $\tilde{\varphi}_{ij}(\mathbf{k}, \mathbf{c}) = \partial \ln f_i / \partial \ln k_j = \nu_{ij} R_j / f_i$ , represent the ratio of rate of formation or consumption of species  $i$  in reaction  $j$  and the net rate of concentration change of species  $i$ . They depend only on the species concentrations and kinetic parameters, and are particularly suitable for the investigation of mechanistic questions.

The method of quasi-stationary sensitivities described in this paper applies the concept of concentration sensitivities. An approximation allows us to replace the sensitivity differential equation by algebraic equations, and this considerably simplifies the analysis. In accordance with rate analysis, the sensitivities calculated by this method also depend only on actual concentration values.

A disadvantage of conventional sensitivity analysis is the significant computer time which is required in solving simultaneously both the kinetic and the sensitivity differential equation systems. However, in contrast to concentration sensitivity analysis, the use of the method presented in this work is inexpensive.

## 2. Sensitivity equations

The kinetic differential equations for a chemical system are given by the equations

$$\frac{d\mathbf{c}}{dt} = \mathbf{f}(\mathbf{c}, \mathbf{k}), \quad \mathbf{c}(0) = \mathbf{c}_0, \quad (1)$$

where  $\mathbf{c}(t)$  is the  $n$ -vector of species concentrations and  $\mathbf{k}$  is the  $m$ -vector of rate coefficients. Differential equations for local concentration sensitivity coefficients can be obtained by differentiation of the kinetic equations with respect to the parameters:

$$\frac{d}{dt} \frac{\partial \mathbf{c}}{\partial k_j} = \mathbf{J} \frac{\partial \mathbf{c}}{\partial k_j} + \mathbf{F}_j, \quad \frac{\partial \mathbf{c}}{\partial k_j}(0) = 0, \quad (2)$$

where  $\mathbf{J} = \partial \mathbf{f} / \partial \mathbf{c}$  and  $\mathbf{F}_j = \partial \mathbf{f} / \partial k_j$ , with  $j = 1, \dots, m$ .

### 3. Sensitivity in equilibrium and in stationary systems

In equilibrium and in stationary systems, the sensitivity coefficients may be regarded as dynamic quantities which are governed by eq. (2) [1]. The time profiles of the sensitivity coefficients give the dynamic response of the system to a differential change in  $k_j$  around the steady state (see the analytical expression in ref. [5]), and the stationary sensitivity coefficients are the limits in time of the dynamic quantities [6]. (Note that this latter statement is valid only if the steady state is stable.) Since at stationary conditions species concentrations as well as the matrices  $J$  and  $F$  are time invariant, the stationary sensitivity coefficients may be obtained from algebraic equations,

$$S_j^s = \left( \frac{\partial c}{\partial k_j} \right)^s = -J^{-1} F_j, \quad j = 1, \dots, m, \quad (3)$$

which follow from eq. (2) if the left-hand sides are taken to be zero.

The stationary sensitivity matrix which represents the change of stationary species concentrations to a differential change in parameters,

$$S_j^s = \frac{\partial c^s}{\partial k_j}, \quad (4)$$

carries valuable information on the reaction mechanism of the chemical process in equilibrium or in a stationary state [7]. The matrix  $S^s$  together with the principal component analysis (a powerful technique recently suggested [2,3] for handling sensitivity data) may be useful in, for instance, the study of chemical reactors operating in a stationary mode.

### 4. Quasi-stationary sensitivity analysis

In dynamic systems where species concentrations change with reaction time,  $J$  and  $F$  are time dependent. Thus, sensitivity equation (2) is a system of linear differential equations with variable coefficients. Therefore, calculation of the sensitivity coefficients is not as straightforward as in the case of equilibrium or stationary systems. We suggest, however, that by taking advantage of Tihonov's theorem [8] an approximation method may be developed for the calculation of sensitivities in dynamic systems which retains the simplicity of solving algebraic equations.

Tihonov's theorem can be presented in the interpretation of Klonowski [9] as follows.

Consider a system of  $p$  first-order ordinary differential equations. Let us assume that  $s$  of the  $p$  equations have a small parameter  $\mu$  multiplying the time derivatives:

$$d x_i / d t = f_i(x_1, \dots, x_n, z_1, \dots, z_s), \quad i = 1, \dots, n \quad (5a)$$

$$\mu d z_\ell / d t = g_\ell(x_1, \dots, x_n, z_1, \dots, z_s), \quad \ell = 1, \dots, s \quad (5b)$$

$$\mathbf{x}(0) = \mathbf{x}_0; \mathbf{z}(0) = \mathbf{z}_0.$$

where  $n + s = p$ . According to the theorem, when  $\mu \rightarrow 0$  the solution of the whole system (represented by eq. (5)) tends to the solution of the degenerate system (eq. (5) with  $\mu = 0$ ), if the following conditions are fulfilled:

(a) The solution  $\bar{z}_1 = \gamma_1(x_1, \dots, x_n), \dots, \bar{z}_s = \gamma_s(x_1, \dots, x_n)$  is an isolated root of the algebraic system

$$g_\ell(x_1, \dots, x_n, \bar{z}_1, \dots, \bar{z}_s) = 0, \quad \ell = 1, \dots, s; \quad (6)$$

(b) The solution  $\bar{z}_1, \dots, \bar{z}_s$  is a stable isolated singular point of system (5b) for all values of  $(x_1, \dots, x_n)$ :

(c) The initial value  $\mathbf{z}_0$  is in the domain of influence of the stable singular point of system (5b):

(d) The solutions of systems (5) and (5b) are unique and the right-hand sides ( $f_i$  and  $g_\ell$ ) are continuous functions.

In applying Tihonov's theorem to our problem in dynamic sensitivity analysis, eq. (5a) stands for the system of kinetic differential equations and eq. (5b) corresponds to the sensitivity equations with the left-hand side multiplied by parameter  $\mu$ :

$$\mu \frac{d}{dt} \frac{\partial \mathbf{c}}{\partial k_j} = J \frac{\partial \mathbf{c}}{\partial k_j} + F_j, \quad \frac{\partial \mathbf{c}}{\partial k_j}(0) = 0, \quad (7)$$

In our case, all four preconditions of application of Tihonov's theorem are fulfilled. In chemical kinetics,  $\mathbf{f}$  and  $\mathbf{g}$  are polynomials, which are continuously differentiable functions. Therefore, the solutions of systems (5) and (5a) are unique and consequently the solution of (5b) is also unique. Since (5b) is linear in our case, it has one singular point if  $J$  is regular (condition (a) is fulfilled). If it is stable (condition (b) is fulfilled), the whole variable space is in the domain of influence of the singular point. Furthermore, condition (b) and the regularity of matrix  $J$  are fulfilled if the real parts of the eigenvalues of the Jacobian of the sensitivity equation (2) are all negative at the concentrations obtained as the solution of eq. (1). The eigenvalues of the Jacobian are negative if the Jacobian is a diagonal matrix with negative elements. The eigenvalues are presumably also negative when the Jacobian is almost a diagonal

matrix. The Jacobian of eq. (2) is almost block diagonal with matrix  $J$  (i.e. the Jacobian of eq. (1)) in the blocks [10].  $J$  is a sparse matrix, and the negative diagonal elements represent consuming reactions of species.

The discussion presented above indicates that conditions (a)–(d) appear generally to be fulfilled; thus, one expects that – as an approximation – the left-hand side of the sensitivity equations (7) may be replaced by zero and the sensitivity coefficients can be derived by solving algebraic equations:

$$S_j^q = \left( \frac{\partial c}{\partial k_j} \right)^q = - J^{-1} F_j, \quad j = 1, \dots, m. \quad (8)$$

The sensitivity coefficients defined in eq. (8) and the corresponding matrix  $S^q$  will be referred to hereafter as quasi-stationary sensitivities. These depend on the actual species concentrations and are independent of the pre-history of the system, as it is required theoretically.

Use of eq. (8) presumes that the matrix  $J$  is invertible. If all species have at least one consuming reaction and if none of the species concentrations are zero, then all diagonal elements of matrix  $J$  are non-zero. Since  $J$  is a sparse matrix, it is usually invertible in this case.

If  $J$  is not invertible, a possibility is to use the generalized inverse of  $J$ . Furthermore, there is a computationally simple way of obtaining an approximate solution for eq. (8). Let us modify the original matrix  $J$ :

$$J' = J - I\lambda, \quad (9)$$

where  $I$  is the unit matrix and  $0 < \lambda \ll 1$ . The desired matrix can then be computed by

$$S^q = - (J')^{-1} F. \quad (10)$$

The method of quasi-stationary sensitivity analysis is an approximation method just like the quasi-steady-state assumption (QSSA) which is rather often applied in chemical kinetics. QSSA, also based on Tihonov's theorem [9], simplifies the treatment used in the solution of a number of kinetic problems by allowing to replace the kinetic differential equations for some short-lived species by algebraic equations. Both the quasi-steady-state assumption and the quasi-stationary sensitivity analysis break down when concentrations of some reactive species change very rapidly as, for instance, in the very early period of a complex chemical reaction. Near the lower time limit of the interval  $(t_1, t_2)$  in concentration sensitivity calculations, the sensitivity coefficients change remarkably (from zero at  $t = 0$ ), and consequently the quasi-stationary sensitivity analysis can not be applied.

Although the quasi-stationary sensitivity approach does not provide accurate values of concentration sensitivity coefficients, experiences in the use of quasi-

stationary analysis for reactions of different types indicate that the method may supply useful mechanistic information for a considerable number of reactions in various reaction conditions. Two examples are given in the next section.

## 5. Analysis of complex reaction mechanisms

In order to demonstrate the value of quasi-stationary sensitivity analysis, we shall briefly discuss the results obtained in the study of the  $S^q$  matrices computed for high temperature propane pyrolysis and for the chemistry of the "unpolluted" troposphere. A recently suggested technique [2,3] called principal component analysis is used for handling sensitivity data and for extracting kinetic information from the matrix. Conclusions drawn from quasi-stationary sensitivity analysis will be compared with the results of rate sensitivity analysis, which does not depend on assumptions and approximations like the former method.

### 5.1. HIGH TEMPERATURE PROPANE PYROLYSIS

The mechanism selected for analysis is based on the scheme published by Hautman et al. [11] which is supplemented by two further steps proposed by Bradley [12]. The whole 66-step mechanism, together with the kinetic parameters, is given in ref. [4].

Analysis of the mechanism has been carried out at temperature 1250 K,  $3.85 \times 10^{-5}$  mol dm<sup>-3</sup> propane concentration, and six different reaction times in the range of 0.0005 – 38% propane conversion. On the basis of the results of quasi-stationary sensitivity analysis, the original 66-step mechanism could be reduced to a 23-step scheme without significant loss in accuracy of species concentrations.

Quasi-stationary sensitivity results were compared with rate analysis results under identical conditions. Both methods selected the same steps as important processes.

Product concentrations calculated with the reduced scheme at 3% propane conversion agreed within one percent with the results derived from the full mechanism (see table VII in ref. [4]).

### 5.2. PHOTOCHEMISTRY OF THE "UNPOLLUTED" TROPOSPHERE

A mechanism was formulated by Bérces et al. [13] to describe the photochemistry of processes occurring in the slightly polluted troposphere. This mechanism, consisting of sixty elementary reactions of twenty-two reactive species, was used to calculate the diurnal variation of pollutants under typical meteorological conditions for a summer day at northern mid-latitudes of 45°. Sensitivity analysis was carried out with concentrations and rate parameters corresponding to each hour of the diurnal cycle.

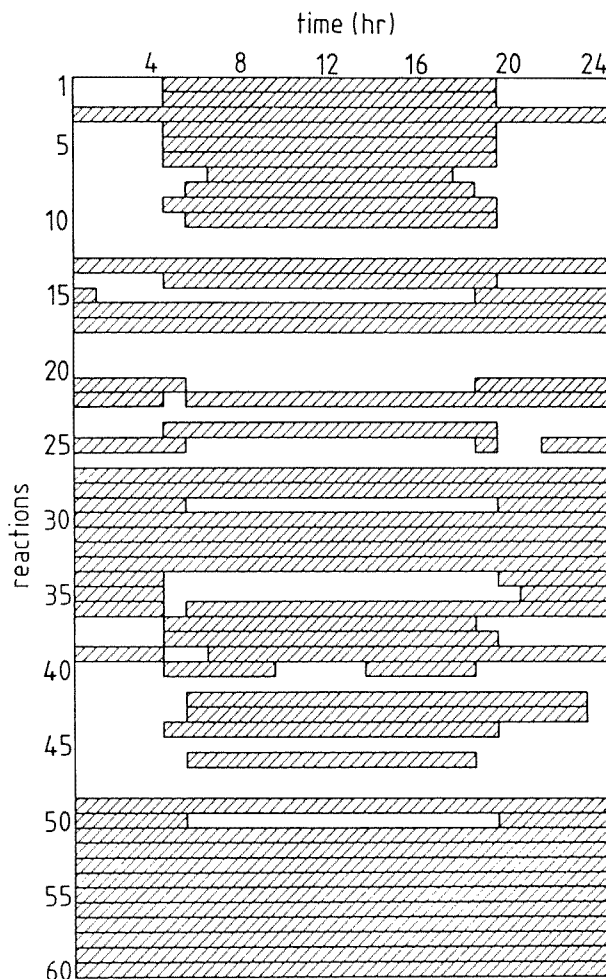


Fig. 1. Diurnal change of reaction importances in the model of unpolluted troposphere. Numbering of reactions refers to the mechanism in ref. [13].

The quasi-stationary sensitivity matrix was determined for each hour using the unmodified Jacobian. Principal component analysis was carried out and a reaction was considered important if it belonged to an eigenvector element greater than 0.1 and the eigenvector corresponded to an eigenvalue greater than 0.0001. The major results, which are very similar to the rate analysis outcomes, are presented in fig. 1. The time intervals indicated by shaded areas are those in which the particular reaction proved to be important. It can be seen that altogether there are forty-nine reaction steps which are important during the whole day or at least in one part of the day. The calculated diurnal concentration versus time profiles obtained from the 49-step

Table 1  
Comparison of the solutions at noon derived from the complete and the reduced models of unpolluted troposphere

Species	Concentrations at noon (mol cm <sup>-3</sup> )		Deviations <sup>a</sup> (%)
	66-step model		
NO	7.455 E + 08		- 2.54
NO <sub>2</sub>	5.661 E + 08		- 1.05
O <sub>3</sub>	1.432 E + 11		0.40
HCHO	5.037 E + 09		0.48
CH <sub>4</sub>	4.200 E + 13		0.00
CO	4.000 E + 12		- 0.03
SO <sub>2</sub>	8.054 E + 09		- 0.11
SO <sub>4</sub> <sup>2-</sup>	5.727 E + 08		1.44
CH <sub>3</sub> O <sub>2</sub> H	2.895 E + 09		7.95
H <sub>2</sub> O <sub>2</sub>	8.817 E + 09		7.59
HNO <sub>3</sub>	8.617 E + 08		2.10
HONO	4.231 E + 06		0.66
HO <sub>2</sub> NO <sub>2</sub>	2.697 E + 06		1.43
CH <sub>3</sub> O <sub>2</sub>	6.962 E + 07		3.15
HO <sub>2</sub>	2.573 E + 08		2.52
N <sub>2</sub> O <sub>5</sub>	1.732 E + 02		1.88
NO <sub>3</sub>	1.356 E + 04		3.01
OH	1.550 E + 06		3.27
CH <sub>3</sub> O	6.249 E + 01		0.89
O	4.754 E + 02		0.25
CH <sub>3</sub>	1.213 E - 01		3.33
O*	3.534 E - 03		0.41

<sup>a</sup> Deviations after 24 hours simulation time.

reduced mechanism are very close to the solution of the 66-step full mechanism. This is apparent from table 1, where concentrations for noon calculated from the two models are compared.

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## References

- [1] H. Rabitz, M.J. Kramer and D. Dacol, *Ann. Rev. Phys. Chem.* 34(1983)419.
- [2] S. Vajda, P. Valkó and T. Turányi, *Int. J. Chem. Kinet.* 17(1985)55.
- [3] S. Vajda and T. Turányi, *J. Phys. Chem.* 90(1986)1664.
- [4] T. Turányi, T. Bérces and S. Vajda, *Int. J. Chem. Kinet.* (in press).
- [5] M.J. Kramer, unpublished result cited in ref. [1], p. 426.
- [6] R.W. Atherton, R.B. Schainker and E.R. Dacot, *AIChE J.* 21(1975)441.
- [7] W. Schellong and C. Schuhler, *Z. phys. Chemie, Leipzig* 267(1986)15.
- [8] A.N. Tihonov, *Mat. Sb.N.S.* 31(1952)575, in Russian.
- [9] W. Klonowski, *Biophys. Chem.* 18(1983)73.
- [10] R.P. Dickinson and R.J. Gelinas, *J. Comput. Phys.* 21(1976)123.
- [11] D.J. Hautman, R.J. Santoro, F.L. Dryer and I. Glassman, *Int. J. Chem. Kinet.* 13(1981)149.
- [12] J.N. Bradley, *J.C.S. Faraday Trans. I* 75(1979)2819.
- [13] T. Bérces, T. Turányi and L. Haszpra, *Acta Chim. Hung.* 122(1986)147.