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SOFTWARE NOTE

KINAL—A PROGRAM PACKAGE FOR KINETIC ANALYSIS OF REACTION MECHANISMS

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Abstract—A program package is provided for analysis of kinetic mechanisms on personal computers. KINAL consists of four programs called DIFF, SENS, PROC and YRED. These require similar input data and use common subroutines. DIFF solves stiff differential equations and SENS computes the local concentration sensitivity matrix. PROC generates the rate sensitivity matrix or the quasi-stationary sensitivity matrix from concentration data or uses a matrix computed by SENS and extracts the kinetic information inherent in sensitivity matrices by principal component analysis. Finally, YRED provides suggestions for the elimination of species from the reaction mechanism.

INTRODUCTION

Simulation of complex reaction mechanisms play an important role in chemical kinetics. Investigation of mechanisms under spatially homogeneous isotherm conditions includes the solution of kinetic differential equations, the study of the effect of parameter changes on the solution (sensitivity analysis) and the identification of redundant species and unimportant reactions. The aim of the development of package KINAL was to provide a solution of all of these problems by using the same code and the same input data file.

In the input file of KINAL the mechanism is described by chemical equations (in a coded form) and by rate coefficients. In atmospheric chemistry and in condensed phase kinetics these are usually the common informations which are available for the mechanisms to be investigated. In these cases KINAL can be applied without any modification. In combustion chemistry, however, very often further informations are also needed in detailed modeling, e.g. third-body efficiencies, pressure dependency of the reactions, thermodynamic properties for the calculation of temperature changes in nonisothermal systems, etc. There are several programs available for such calculations and some of them can also be used for the calculation of reaction sensitivities (e.g. Lutz *et al.*, 1988). Another field of kinetic modeling where sophisticated methods are required is the description of spatially inhomogeneous systems. KINAL can also be applied to the modeling of nonisothermal and inhomogeneous systems, by coupling it to the special programs. The concentrations and/or sensitivities are supplied by these special programs and then redundant species and redundant reactions of the utilized mechanism are identified by slightly modified versions of YRED and PROC.

The KINAL program package

There are four programs in program package KINAL called DIFF, SENS, PROC and YRED. KINAL is written in Fortran 77 language and includes four main programs and 20 subroutines. Most of the subroutines are used by at least two main programs. KINAL has been developed on an IBM PC compatible personal computer, but the package does not utilize any special service of PCs (like, for instance, graphics) and therefore it is transferable to other computers.

DIFF: solution of ODEs

The solution of kinetic differential equations in KINAL is based on a fourth-order semi-implicit Runge–Kutta method (Gottwald & Wanner, 1981). The right-hand sides of kinetic ODEs and their derivatives with respect to concentrations and rate coefficients are generated automatically in an algebraic way. The number of species are not limited on either side of the chemical equations and stoichiometric numbers of products may be real numbers as well.

The program has three operation modes. In mode zero it only solves the differential equations, while in mode one DIFF also writes the computed concentrations into the input data file. In mode two the program reads the previously computed concentrations, performs the calculations of a reduced reaction system and compares the solutions of the full and reduced mechanisms.

SENS: computation of local concentration sensitivities

In a kinetic problem, rate coefficients and initial concentrations are considered as parameters. Several algorithms were elaborated for the numerical calculation of parametric sensitivities. Computation of sensitivities in SENS is based on the Decomposed Direct Method (Valkó & Vajda, 1984). This is a member of a group of similar algorithms which are improved versions of the Direct Method (see also Dunker, 1984; Caracotsios & Stewart, 1985; Leis & Kramer, 1985).

SENS computes the local concentration sensitivities according to both reaction rates and initial concentrations. It calculates sensitivities either for all parameters or only for a selected group of them. The latter enables the investigation of a large model in parts when using a computer of very limited memory. SENS can also continue the computation of sensitivities by reading the previously calculated sensitivity matrix.

PROC: processing of sensitivity matrices

The local concentration sensitivity matrix has been applied in chemical kinetics for more than a decade for the investigation of reaction mechanisms. Recently it was shown that there are other sensitivity-type matrices, which can also be used for the study of mechanisms. These are the algebraic rate sensitivity matrix **F** (Turányi *et al.*, 1989) and the quasi-stationary sensitivity matrix (Turányi *et al.*, 1988). Principal component analysis (Vajda *et al.*, 1985) is an efficient method for the interpretation of sensitivity results.

PROC carries out a principal component analysis of sensitivity matrices and provides a list of overall sensitivities and reaction rates. Sensitivity matrices belonging to different reaction times can be investigated by PROC either separately or simultaneously. Principal component analysis incorporates eigenvalue–eigenvector decomposition of the cross-product of normed sensitivity matrices. In KINAL, eigenvalues and eigenvectors are computed by a QR algorithm, which is sufficiently stable and provides suitably accurate eigenvectors.

PROC proposes a reduced mechanism by identifying reactions which belong to large elements in eigenvectors corresponding to large eigenvalues. The best threshold values may be different at different problems and PROC provides the opportunity to try several limits in an interactive way.

YRED: identification of redundant species

In a recent article (Turányi, 1990a), two methods were proposed for the identification of redundant species in a mechanism. According to the first one, a species is redundant if the elimination of its consuming reactions does not cause significant deviation from the solution of the full model, regarding important species and/or features. In some cases, forming reactions of the species considered have to be investigated as well. DIFF (mode two) is a software support for such investigations.

The second method is based on the investigation of the Jacobian and is supported by program YRED. This program estimates the effect of change of concentrations of each species upon the concentrations of a selected group of species. A species is considered to be redundant if both its direct and indirect effects on important species are small. (Species A effects directly the concentration of species B, if A is consumed in a reaction in which B is consumed or produced.) Direct effects are estimated by the sum of squares of normalized Jacobian elements. Indirect effects are taken into account by an iteration procedure.

Getting started in the use of KINAL

A users manual, sample data files and sample output files are provided with the program. Moreover, results of the investigation of large mechanisms by principal component analysis were published by Vajda *et al.* (1985), Vajda & Turányi (1986), Turányi *et al.* (1988), Turányi *et al.* (1989), Turányi (1990a), Turányi (1990b) and Turányi & Bérces (1990). These papers contain practical hints for mechanism investigation and reduction by the principal component analysis of sensitivity matrices. The last five articles were produced by the assistance of KINAL.

Program package KINAL is available from the author. Those who are interested in receiving the programs are requested to send a blank $5\frac{1}{4}''$ floppy disk.

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