Princeton University
Department of Chemistry

SUMMARY REPORT

for the period of
February 1, 1990 - August 1, 1992

to the

Department of Energy

"ANALYSIS OF FORWARD AND INVERSE PROBLEMS IN CHEMICAL DYNAMICS AND SPECTROSCOPY"

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PROJECT SUMMARY

This document presents a concise overview of research carried out under Grant No. FG02-86ER13480, over a period of 2 1/2 years. In general, the research accomplished an interrelated set of objectives in the area of analyzing dynamics and kinetics phenomena, as described below.

The forward aspects of the research were concerned with mapping the relationship between input potential surface structure, and laboratory dynamical and kinetic observables. At the most detailed level, the influence of features in potential surfaces upon collision cross sections was explored for both reactive and non-reactive events. Considerable subtleties were uncovered, with the general conclusion that observable cross sections draw on potential features through a complex interference process. In some cases, the connection between the features in the cross sections may be interpreted intuitively, while in others, surprises arose. For example, although barriers on reactive surfaces were certainly identified as important for overall reaction rates, the region of highest sensitivity was not always at the barrier maximum; other regions may have nearly equal significance in a correlated fashion. The identification of correlation affects from one region to another on potential surfaces has important significance for guiding the improvement of potentials, and also for the inversion of laboratory data. In a parallel fashion, forward studies were also carried out by starting at the kinetic mechanism level, and proceeding to chemical species profiles, including for combustion systems. In this case, the role of particular mechanistic steps was explored, and a special point of interest was the examination of the role of strong (mechanistic, diffusive or thermal) coupling. It is found that under appropriate conditions, strong coupling can give rise to a type of dynamic system collapse, in that a small number of key dependent variables may have an overall dominant role in controlling the kinetic behavior of all of the other variables.

The second aspect of the research on inverse analysis represented a new direction complementing the forward analysis studies. In this case, the objective was the development of stable and reliable algorithms for inversion of quality laboratory data, back to underlying potential surfaces. Such surfaces, in turn, are valuable for once again proceeding in the forward direction and calculating new observables. The inverse tools being developed are intimately related to the former research, in that sensitivity analysis information is used to form the kernel of the inversion algorithm. Of special note here is the fact that the algorithms under development do not call for the imposition of any particular functional form for the sought-after potential surfaces. Rather, a stable algorithm is being developed based on the mild requirement that the resultant potential simply be smooth throughout configuration space. Initial applications of the algorithm on simulated systems, including up to three dimensions, are very promising. The main applications explored thus far involve collision cross sections as input data, although an initial study employing vibration-rotation spectral lines as input was also pursued.

Besides the overall themes of the research highlighted above, several supporting items of research in molecular dynamics and chemical kinetics were also explored. A synopsis of each research accomplishment is presented below.

RESEARCH HIGHLIGHTS

1. Quantum functional sensitivity analysis for the collinear $\text{H} + \text{H}_2$ reaction rate coefficient¹

The effects of features in the potential energy surface on the collinear $\text{H} + \text{H}_2$ reaction rate coefficient are investigated by the method of quantum functional sensitivity analysis (QFSA). The calculations use QFSA to connect features in the microscopic realm, with their response upon macroscopic quantities of chemical interest, via the intermediary sensitivities of the reactive transition probabilities. While the sensitivities of the individual transition probabilities show considerable structure, there is an attendant loss of structure in the rate coefficient sensitivities because of the thermal averaging. For the range of temperatures used in our study (200 - 400 K), the most important region of the potential energy surface is found to be not at the top of the barrier, but rather at the lower energy shoulders of the barrier. There are also regions near the barrier where an increase in the potential surface actually increases the reaction rate! The effects of using different underlying potentials [the Porter-Karplus (PK2), Liu-Siegbahn-Truhlar-Horowitz (LSTH), and double many-body expansion (DMBE) surfaces] on the nature of the results were also compared. The absolute sensitivity magnitudes on the PK2 surface vary considerably from the other two, but the relative change in the rate coefficient is about the same on all three surfaces. Furthermore, the identified regions of importance on the potential surfaces remain essentially the same. The reactive scattering calculations were performed with the log-derivative version of the Kohn variational principle.

2. The rotation-vibration potential of He-H₂ and its connection with physical phenomena²

This work examined the effect of infinitesimal functional variations in a three-dimensional vibration-rotation He-H₂ potential surface on several different levels of physical observables: inelastic cross sections, rate constants, and energy level populations. Earlier equations for a rigid-rotor system are extended, and a comparison of the current results with earlier rigid-rotor results is made. A significant difference in the sensitivity of observables to the potential components has been observed between those observables which are purely rotationally inelastic and those which are vibrationally inelastic. The region of highest sensitivity is dependent upon the energy or temperature, as well as the states related by the individual observable. Significant information loss has been observed in the transition from the microscopic observables to the macroscopic ones for those observables which are vibrationally inelastic.

3. Inversion of gas-surface scattering data for potential determination using functional sensitivity analysis. I. A case study for the He-Xe/C(0001) potential³

A general iterative inversion procedure based on functional sensitivity analysis is presented for determining the gas-surface interaction potential from low energy elastic scattering data. Formally, Tikhonov regularization, singular function analysis, and a recently developed exact transformation technique, are implemented to render the inversion stable and efficient. Specifically, the simulation of helium scattering from a rigid periodic xenon monolayer on the graphite (0001) face is considered. It is found that the functional sensitivity densities of the diffraction intensities, with respect to the He-Xe/C(0001) potential, contain profound information, and thus are invaluable in guiding the inversion of scattering data to yield the potential. Although

unequivocal determination of the full three-dimensional potential from the inevitably incomplete experimental data may be difficult, we demonstrate that simulated input data consisting of a finite number of polar scan specular intensities can be used to accurately recover the underlying He-Xe/C(001) potential. The recovered potential has been obtained without imposing any explicit functional form on the potential *per se*. The resulting procedure is quite promising for treating real laboratory data.

4. Inversion of gas-surface scattering data for potential determination using functional sensitivity analysis. II. Extraction of the full interaction potential from low energy diffraction data⁴

We demonstrate that the full gas-surface potential can be successfully recovered from low energy elastic scattering intensities within the framework of functional sensitivity analysis and Tikhonov regularization as formulated previously. Specifically, we consider an extensive, but finite, set of simulated discrete data from specular scattering and three in-plane diffraction orders over a wide range of incident polar angles for the rigid, periodic, and corrugated He-Xe/C(0001) system at fixed beam energy and fixed azimuthal angle. It is found that the potential extracted from these input data unambiguously resembles the intended model potential. The recovered potential is only slightly steeper in the upper portion of the repulsive wall, and its minima are slightly deeper. Moreover, the repulsive walls of the recovered and true potentials cross the zero at almost the same distances from the surfaces. Finally, all of the details of the input data, namely the positions and shapes of the bound-state resonance extrema for all scattering channels under study, are accurately reproduced by the recovered potential.

5. Regularized inversion of diatomic vibration-rotation spectral data: A functional sensitivity analysis approach⁵

We present a stable and accurate inversion method for extracting potentials from spectroscopic data of diatomic molecules. The method, which was developed previously for inverting scattering data, is based on first-order functional sensitivity analysis in conjunction with the Tikhonov regularization, singular system analysis, and an exact transformation technique. Besides being numerically stable, it requires neither explicit functional forms nor special basis function expansions for the potential corrections, when solving the corresponding linearized integral equation. Instead, we solve the linear equation directly in terms of the probability densities of the unperturbed vibrotation eigenstates. For illustrations, we consider the ground electronic state of the H_2 molecule. Inversions have been carried out for simulated data free of noise, and for those with noise of magnitude comparable to realistic experimental errors. It is found that in both cases, a relatively large deviation of the starting reference potential from the truth may be tolerated to still accurately recover the intended one. The propagation of the spectral errors is analyzed in detail based on the linearization assumption. The variance of the recovered potential reveals the reliability of various regions of the recovered potential.

6. The Calculation of Time-Correlation Functions for Molecular Collisions⁶

A general formalism relating cross sections to collisional time-correlation functions was applied to the calculation of energy transfer in molecular collisions. Basic aspects of the formalism are reviewed, followed by detailed description of methods suitable for the calculation of quantal state-to-state cross sections. These methods are particularly useful in the description of scattering by large systems, or of systems with high total energies where expansions in target basis sets are unsuitable.

We reviewed applications of quantal time-correlation functions (TCFs) to vibrational-rotational energy transfer in molecular collisions. Doubly differential cross sections (in scattering angles and transferred energy) are obtained from Fourier transforms of TCFs of the transition operator by means of two complementary treatments: multiple-scattering expansions for impulsive energy transfer, and a semiclassical limit for short translational wavelengths. The TCFs are evaluated by operator algebra, yielding efficient computational procedures that incorporate large numbers of vibrational-rotational transitions. The treatments are thus well-suited to scattering by complex polyatomic targets. Examples are given for inelastic scattering of atoms from diatomic and linear triatomic molecules by hyperthermal collision energies, and the calculated results are compared with experimental measurements. These methods are also applicable to scattering by solid surfaces and by adsorbates, and can include temperature effects. The review listed 140 references to related work on the formalism, methods of calculation, and applications.

7. Parametric Sensitivity and Self-Similarity in Thermal Explosion Theory⁷

This work studied the relations between thermal runaway (also called parametric sensitivity) and self-similarity, an interesting property of the sensitivity functions that has been numerically verified in many explosion and combustion systems. Both concepts are sensitivity-related but independent of the particular parameter being perturbed. This independence is emphasized by proposing a new generalized condition for parametric sensitivity. Criticality is defined as the point in the parameter space where the nominal trajectory exhibits maximum sensitivity to arbitrary, unstructured perturbations applied at the maximum temperature. The condition for criticality reduces to the analysis of the eigenvalues of the Jacobian matrix. In addition to its conceptual generality, the new condition shows that in certain cases

there exists no critical Semenov number. The sensitivity functions are shown to satisfy self-similarity relations if and only if the system exhibits critical or supercritical behavior. The onset of self-similarity is explained in terms of two properties of explosion systems, both related to parametric sensitivity. First, the temperature is a dominant variable, and any perturbation in the system affects the conversion mainly through the changes induced in the temperature. This strong coupling of the variables is shown by decomposing the sensitivity functions into direct and indirect terms. Second, the sensitivity equations are pseudo-homogeneous in a characteristic time window, in which the system becomes relatively insensitive to parameter perturbations applied within the same interval. The two properties are shown to imply self-similarity of the sensitivity functions. Relations to earlier parametric sensitivity and self-similarity conditions are discussed.

8. A Comprehensive Reaction Mechanism For Carbon Monoxide/Hydrogen/Oxygen Kinetics⁸

A comprehensive reaction mechanism for the oxidation of carbon monoxide in the presence of hydrogen is described in this work. Model predictions are compared with experimental data over wide ranges of physical conditions. The data, obtained from shock tube experiments and various types of reactor experiments, encompassed a combined temperature range of 823-2870 K, fuel-oxidizer equivalence ratios between 0.0005 and 6.0, C/H ratios between 0.005 and 128, and pressures between 0.3 and 2.2 atmospheres. Validation of the reaction mechanism is obtained with reproduction of the experimental results by model predictions and from sensitivity analysis calculations. Results from the latter calculations provided a quantitative measure of the sensitivity of the model predictions to the imposed input parameters over the complete range of experimental parameters noted above.

9. Flow Reactor Studies of Carbon Monoxide/Hydrogen/Oxygen Kinetics⁹

New data on the kinetics of $\text{CO}/\text{H}_2\text{O}/\text{O}_2$ and H_2/O_2 mixtures in the temperature range of 852-1138 K and at 1 atmosphere pressure are reported in this research. The data were obtained from adiabatic, constant pressure flow reactor experiments for variations in the initial carbon, hydrogen, and oxygen contents of the mixture, and also for variations in the initial temperature. In particular, the results define explosion limit temperatures for near stoichiometric mixtures of $\text{CO}/\text{H}_2\text{O}/\text{O}_2$ and H_2/O_2 systems at atmospheric pressure without the presence of surfaces, and also demonstrate the complex relationship between water vapor concentration and the carbon monoxide oxidation rate.

10. Convergence Properties of a Class of Boundary Element Approximations to Linear Diffusion Problems with Localized Nonlinear Reactions¹⁰

This work considered a boundary element (BE) algorithm for solving linear diffusion desorption problems with localized nonlinear reactions. The proposed BE algorithm provides an elegant representation of the effect of localized nonlinear reactions, which enables the effects of arbitrarily oriented defect structures to be incorporated into BE models without having to perform severe mesh deformations.

We propose a one-step recursion procedure to advance the BE solution of linear diffusion localized nonlinear reaction problems and investigate its convergence properties. The separation of the linear and nonlinear effects of the boundary integral formulation enables us to consider the convergence properties of approximations to the linear terms and nonlinear terms of the boundary integral equation separately.

For the linear terms, we investigate how the degree of piecewise polynomial collocation in space and the size of the spatial mesh relative to the time step affects the

accumulation of errors in the one-step recursion scheme. We develop a novel convergence analysis that combines asymptotic methods with Lax's Equivalence Theorem. We identify a dimensionless meshing parameter θ whose magnitude governs the performance of the one-step BE schemes. In particular, we show that piecewise constant (PWC) and piecewise linear (PWL) BE schemes are conditionally convergent, have lower asymptotic bounds placed on the size of time steps, and which display excess numerical diffusion when small time steps are used. There is no asymptotic bound on how large the time steps can be – this allows the solution to be advanced in fewer, larger time steps. The piecewise quadratic (PWQ) BE scheme is shown to be unconditionally convergent; there is no asymptotic restriction on the relative sizes of the time and spatial meshing, and no numerical diffusion. We verify the theoretical convergence properties in numerical examples. This analysis provides useful information about the appropriate degree of spatial piecewise polynomial and the meshing strategy for a given problem.

For the nonlinear terms, we investigate the convergence of an explicit algorithm to advance the solution at an active site forward in time by means of Caratheodory iteration combined with piecewise linear interpolation. We consider a model problem comprising a singular nonlinear Volterra equation that represents the effect of the term in the BE formulation that is due to a single defect. We prove the convergence of the piecewise linear Caratheodory iteration algorithm to a solution of the model problem for as long as such a solution can be shown to exist. This analysis provides a theoretical justification for the use of piecewise linear Caratheodory iterates for advancing the effects of localized reactions.

11. Factorization of Certain Evolution Operators Using Lie Algebra: Formulation of the Method¹¹

In this work, a new method to factorize certain evolution operators into an infinite product of simple evolution operators is presented. The method uses Lie operator algebra and the evolution operators are restricted to exponential form. The argument of these forms is a first-order linear partial differential operator. The method has broad application, including to the areas of sensitivity analysis, the solution of ordinary differential equations, and the solution of Liouville's equation. A sequence of defined ξ -approximants is generated to represent the Lie operators. Under certain conditions, the convergence rates of the ξ -approximants is remarkably high. This work presents the general formulation of the scheme and some simple illustrative examples. Investigation of convergence properties is given in a companion paper.

12. Factorization of Certain Evolution Operators Using Lie Algebra: Convergence Theorems¹²

This research concerns convergence theorems with a sequence of ξ -approximants for exponential evolution operators with Lie operator arguments. A companion paper presents the formulation of the ξ -approximants. The theorems presented in this research give the conditions which are sufficient for convergence of the sequences. Although the main emphasis will be on convergence properties of the one-dimensional case, the generalization to multidimensional cases is quite straightforward.

13. How do Different Regions of the Potential Surface Affect the Collision Dynamics of H_2 with HD ?¹³

The interrelationship between a set of dynamical observables, namely the relative translational energy and the rotational energies of the colliding H_2 and HD molecules, and their underlying potential surface is investigated by the methodology of classical functional sensitivity analysis (CFSA). The dynamical model of rotationally inelastic scattering is described quasiclassically by two coplanar rigid rotors with a given initial collision energy of 5 kcal/mol. Two aspects of the potential surface-to-dynamical observable mapping are investigated with CFSA. First, the importance of higher order terms in the potential expansion $V(R, \phi_1, \phi_2) = \sum_{m_1 m_2} v_{m_1, m_2}(R) \cos(m_1 \phi_1 + m_2 \phi_2)$ is investigated by examining, at the functional sensitivity derivatives $\delta O / \delta v_{m_1, m_2}(R)$, where O is one of the above-mentioned observables. The sensitivities for several of the higher order (m_1, m_2) combinations were found to be larger than many of the lower order (m_1, m_2) combinations. This means that a sizeable error introduced in fitting the higher order v_{m_1, m_2} terms can have a large effect on the calculated observables. Secondly, the full sensitivity functions, $\delta O / \delta V(R)$, were calculated to determine which regions of the potential surface were most important in controlling the dynamics. The sensitivities were found to be largest around the turning point region of the potential, with considerable structure present over a broadly identified region.

14. Quantum Functional Sensitivity Analysis within the Log-derivative Kohn Variational Method for Reactive Scattering¹⁴

We describe a new approach to calculating quantum functional sensitivity maps of transition probabilities. This approach is based on the log-derivative version of the Kohn variational principle and is applied here to the collinear $H + H_2$ hydrogen exchange reaction. The sensitivity maps provide detailed quantitative information

about how variations in the potential energy surface affect the state-to-state transition probabilities. The key issues investigated are: (i) the evolution of sensitivity structure in the 0.30 to 1.50 eV range of total energy; (ii) the comparison of sensitivity structure on the Porter-Karplus (PK2), the Liu-Siegbahn-Truhlar-Horowitz (LSTH), and the double-many-body-expansion (DMBE) potential energy surfaces; and (iii) the range of linearity for first order sensitivity predictions.

15. Predicting Observables on Different Potential Energy Surfaces using Feature Sensitivity Analysis: Application to the Collinear H + H₂ Exchange Reaction¹⁵

Two sensitivity analysis techniques are used to show how one can predict observables on new or perturbed potential energy surfaces (PES) without doing any additional dynamics calculations on the new PESs. Both techniques require the computation of the observable (O) and its sensitivity to variations in the potential ($\delta O/\delta V$) on just one surface. The first approach uses a simple first-order expansion of the observable with respect to δV . The second approach uses a nonlinear least-squares fit of particular features in the observable, and then uses the same functional form to predict the observable on a different PES, but with a modified set of fitting parameters. The new fitting parameters are related to the old via a functional Taylor expansion. Both approaches work well when variations in the potential are small. When the potential difference is large, the second approach gives reasonable results even in cases where the first approach is giving spurious predictions. These ideas are tested for the collinear H + H₂ reaction within the framework of quantum reactive scattering. The log-derivative version of the Kohn variational principle is used for the scattering calculations.

16. A method for inverting curvilinear transformations of relevance in the quantum mechanical Hamiltonian describing n-body systems¹⁶

A considerable practical barrier to the construction of the kinetic energy part of the quantum Hamiltonian describing systems executing large amplitude nuclear motion (curvilinear coordinates) involves analytic inversion of coordinate relationships between old and new coordinates. Direct inversion frequently provides extremely cumbersome expressions. A procedure satisfying the requirements of the metric tensors is proposed, which avoids the problems inherent in direct inversion.

17. On The Role of Potential Features in Fine-Structure Transitions with Applications to $H^+ + F(2P_{1/2}) \rightarrow H^+ + F(2P_{3/2})$ ¹⁷

The first order functional sensitivity densities $\delta \ln W_{|\Lambda|}(R)$ are employed to assess the role of structure in potential energy curves $W_0(R)$ and $W_1(R)$ involved in the fine-structure transition $H^+ + F(2P_{1/2}) \rightarrow H^+ + F(2P_{3/2})$. The results reveal that the fine-structure transition cross-section draws on the $W_0(2\Sigma)$ and $W_1(2\Pi)$ potentials in a highly correlated fashion, and a measurement of $\sigma_{1/2 \rightarrow 3/2}^{\pi}(E)$ for $H^+ + F$ will primarily allow information to be extracted only on the potential function difference $[W_0(R) - W_1(R)]$ for moderate to large internuclear distances ($R \gtrsim 3$ au). While there is a marginal preference for the π alignment in the region where splitting between the 2Π and 2Σ curves is equal to the fine-structure transition energy, the oscillatory nature of the sensitivity densities with respect to R indicates that the alignment effects may get scrambled upon averaging over many impact parameters.

18. On The Role of Potential Structure in Non-Adiabatic Collisions with Application to $He^+ + Ne(2p^6) \rightarrow He^+ + Ne(2p^53s)$ and $Na + I \rightarrow Na^+ + I^-$

The first order functional sensitivity densities $\delta\sigma_{12}(E)/\delta V_{ij}(R)$ from close coupling calculations are used for a quantitative probe of the role of structure in crossing diabatic curves used to model nonadiabatic collisions. Application to excitation of Ne by He^+ shows a region of significance for $\delta\sigma_{12}(E)/\delta V_{12}(R)$ as a prominent Gaussian-like profile around the crossing point (R^*) in accord with the $\delta(R - R^*)$ idealization of the Landau-Zener-Stueckelberg (LZS) theory. Similarly, the densities $\delta\sigma_{12}(E)/\delta V_{11}(R)$ and $\delta\sigma_{12}(E)/\delta V_{22}(R)$ mimic $d\delta(R - R^*)/dR$ -type behavior, with one being the negative of the other in the neighborhood of R^* in qualitative agreement with the LZS theory. However, all three sensitivity profiles identify a much broader area of importance for the potential curves than the loosely defined avoided crossing region. Also, although the sensitivities themselves decrease with increasing energy, the domain of importance of the curves increases. Examination of the functional sensitivity densities $\delta\sigma_{12}(E)/\delta V_{ij}(R)$ for the chemi-ionization collision $Na + I \rightarrow Na^+ + I^-$ reveals regions of potential function importance very different from that predicted by the LZS theory. The chemi-ionization cross-section is about ten times more sensitive to the ionic curve than the covalent curve. Also, the domain of sensitivity of the ionic curve is larger compared to that of the covalent curve. The density $\delta\sigma_{12}(E)/\delta V_{12}(R)$ for chemi-ionization shows that the area of maximum potential significance is not at the crossing point itself but the regions bracketing it on both sides. Also, the dominant sign dependence of the coupling sensitivity is unexpectedly negative. The results offer other new observations about the domain of validity of intuitive pictures rooted in the LZS theory. The significance of these results to the inversion of inelastic cross-section data is briefly discussed.

19. A Quantitative Technique for Evaluating the Usefulness of Experimental Data in Refining a Potential Surface¹⁹

A singular value decomposition is used to determine how much and what kind of information about a potential surface is available in a set of measurements. From the functional sensitivities which relate a set of observable cross sections to a potential, an orthogonal set of potential variations (a basis set) is produced. Corresponding to each basis vector is an image vector representing a linear combination of cross sections for which that particular potential variation is the effective observable response. Measurement errors and potential model errors are included in the analysis so as to identify those parts of the potential which the proposed measurements could detect as model errors. These tools are illustrated for the He-H₂ system, with observables taken as various field effect cross section measurements. The set of field effect measurements proposed here is found to provide five distinguishable pieces of information, primarily about the repulsive wall, which should be extremely useful, given actual quality laboratory data, for refining existing models of the anisotropy of the potential.

20. Sensitivity of the $F + H_2$ Reaction Probability to the Potential Surface²⁰

The method of functional sensitivity analysis is applied to the $F + H_2(j=1)$ reaction using the T5A potential. The influence of various regions of the potential upon the total integrated reaction probability for collision energies in the range of 0.032 to 0.066 eV for total angular momentum $J=5$ and $J=10$ is examined. Two regions are identified as having particularly strong influence on the reaction probability at these energies. One is, as expected, the saddle point and the

approaching slope. The other is the inner wall of the exit valley, which exerts a surprisingly large influence on the reaction probabilities. The implications of these results for refinement of the potential are discussed.

21. Sensitivity Analysis of a Steady-state, Premixed Laminar CO-H₂-O₂ Flame²¹

The direct and very efficient Newton method for obtaining sensitivities of two-point boundary value problems is utilized for detailed exploration of a reacting-diffusing CO+H₂+O₂ steady-state premixed laminar flame. Sensitivity coefficients and Green's functions calculated for this system offer exhaustive characterization and new insights into the role of diffusion and exothermicity in carbon monoxide oxidation kinetics. In particular, the reactions of the hydroperoxy radical with hydrogen, oxygen and hydroxyl radicals are found to be extremely important at all temperatures in the fuel lean (40 torr) flame studied here. The diffusive mixing of chemical species from the low and the high temperature portions of the flame and the large heats of reaction associated with the hydroperoxy radicals are found to be responsible for the increased importance of these reactions.

22. Generalized Parametric Sensitivity²²

We have recently introduced a generalized condition for thermal runaway or parametric sensitivity (see item 7. above). The condition defines criticality as the point in the parameter space at which the system's behavior exhibits maximum sensitivity to small, unstructured perturbations. Here we use the same concept to study the steady-state behavior of a single irreversible n th order exothermic reaction occurring in a nonadiabatic CSTR. Although the new condition provides critical parameter values in good agreement with the results of earlier methods, it reveals that the notion of parametric sensitivity in steady-state models considerably differs from

the notion of parametric sensitivity in dynamical systems. First, in the steady-state CSTR, criticality has its origin in the near singularity of the model equation. Second, unlike dynamical systems, there exists no well-defined boundary between subcritical and supercritical behavior. The close connections between thermal runaway and steady-state multiplicity, as well as thermal runaway and self-similarity of the sensitivity function, are discussed.

23. Determination of Constrained Lumping Schemes for Kinetic Models²³

The direct approach to determine the constrained lumping schemes presented previously is applied to a catalytic reforming model. The constant basis matrices of the transpose of the Jacobian matrix for the kinetic equations are replaced by a set of rate constant matrices at different temperatures, which properly cover the practical temperature region. The catalytic reforming model is used as an example, but this approach can be applied for other reforming models, as well as a wide variety of kinetic systems.

PUBLICATIONS RESULTING FROM THIS RESEARCH

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15. Predicting Observables on Different Potential Energy Surfaces using Feature Sensitivity Analysis: Application to the Collinear $H + H_2$ Exchange Reaction, J. Chang, N.J. Brown, M. D'Mello, R.E. Wyatt, and H. Rabitz, *J. Chem. Phys.*, in press.
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