

**THE CALCULATION OF
HIGH-TEMPERATURE REACTION RATE CONSTANTS
USING AB INITIO POTENTIAL ENERGY SURFACES:
EXAMPLES FOR AIR AND HYDROGEN-AIR SYSTEMS**

Richard L. Jaffe
NASA Ames Research Center
Moffett Field, CA 94035

and
Ronald J. Duchovic and Stephen P. Walch
ELORET Institute
Sunnyvale, CA 94087

NASA has always been concerned with the development of new concepts for spacecraft and hypersonic aircraft. Vehicles and propulsion systems currently under investigation[1,2] would use novel combustion systems such as the air-breathing supersonic combustion ramjet engine (SCRAMjet) and fuels such as hydrogen. These vehicles would undergo prolonged operation in the low-density air regime where thermal and chemical equilibrium may not be maintained[3], both in the boundary layer outside the vehicle and inside the combustor. It is also not possible to completely duplicate these flight conditions in ground-based test facilities such as shock tunnels or arc-jets. As a result, extensive computer simulations of the air foil and engine performance are being used in the development and design of these vehicles. In order to properly account for the non-equilibrium effects, detailed chemical models must be incorporated into the computational fluid dynamics (CFD) equations.

One of the tasks undertaken by the Computational Chemistry Branch at NASA Ames Research Center is to provide critically needed chemical and physical data for the CFD models that are being used to simulate the performance of these hypersonic vehicles. In order to reliably predict cross sections and rate constants for the important high-temperature collisional processes we use a three-step approach[4] as outlined below.

First it is necessary to determine an accurate potential energy surface (PES) for the reaction system as described in a previous paper of this symposium by Walch *et al.* The PES gives a measure of the net interatomic forces between the colliding atomic and molecular species. It is usually determined, for a small set of selected atomic geometries, as discrete energies resulting from large-scale *ab initio* quantum chemical calculations. Often these data points are clustered around the saddle point or along the minimum energy path (MEP) connecting reactant and product geometries. The energy difference between the reactants and saddle point is generally comparable to the experimental activation energy.

Second, an interpolating function must be developed to provide values of the interaction energy at any atomic geometry required by the specific reaction dynam-

ics model being used. The determination of the interpolating function is not an easy task and depends, to a certain extent, on the amount of *ab initio* data available as well as the nature of the system studied. In the present study, we have used the valence-bond derived LEPS[5] and the Sorbie-Murrell (SM)[6] approach to represent global PES and piecewise polynomial fits to represent regions around the saddle point or along the MEP. In the LEPS method, electronically excited diatomic fragment potential energy curves are treated as adjustable fitting functions to control the topography of the PES. Their parameters are adjusted to reproduce the saddle point geometry and height, if it is known, and/or some experimental measure of the reaction dynamics such as a product scattering angle or product internal state distribution. The LEPS method is generally satisfactory for simple atom-diatom exchange reactions occurring on purely repulsive potential energy surfaces. However, if a collinear approach between reactants is not favored, or if intermediate complex formation is possible, the PES cannot usually be represented by the LEPS method. A more promising method for general systems is the SM method, which is based on the sum of an arbitrary series of terms describing all possible 2-body to *n*-body interactions. The increased flexibility of treating each term separately is a powerful feature of the method.

The final step in the procedure is the calculation of reaction dynamics and kinetics. In general, the reaction dynamics is treated using classical mechanics[7] which should not cause a significant error, especially for collisions well above threshold. Furthermore, in spite of the fact that systems containing hydrogen atoms may have important quantum effects, such as tunneling, we expect that the calculated rate constants should still be accurate at high temperatures. We also use statistical models such as canonical variational transition state theory (CVT)[8] to calculate rate constants. The statistical models allow for the inclusion of quantization of energy levels and corrections for tunneling in an approximate manner.

The classical trajectory method has been a standard approach for the calculation of the dynamics and kinetics of gas phase collisions of small molecules for more than 30 years. The calculations consist of integrating the classical equations of motion for an isolated collision between the reactant species. The propagation of these equations in time for a set of initial coordinates and momenta is called the calculation of a single trajectory and corresponds to the motion of the colliding species over a time period of ≈ 1 ps. Through the application of appropriate random sampling techniques, the behavior of an ensemble of molecules with a collision frequency of 10^{20} s^{-1} can be simulated by on the order of 10^4 trajectories.

Statistical models of chemical kinetics such as transition state theory have been in existence for more than 50 years. However, for the last 10 years, Truhlar and coworkers have systematized numerous models and concepts under the label of variational transition state theories (VTST)[8]. In this model, the optimal transition state is chosen to be the location along the intrinsic reaction path for which the free energy is minimized. Some versions of VTST use quantized anharmonic descriptions

of the transition state energy levels and include tunneling corrections. The VTST model has been thoroughly tested for elementary gas phase reactions and shown to be in agreement with experimental data and the results of classical and quantum scattering calculations.

In this presentation we first demonstrate the computational methods and give details of the calculations using the air exchange reaction

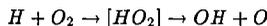


as an example. Walch and Jaffe[9] have completed *ab initio* calculations for this system of the two low-lying PES that connect the ground electronic states of reactants and products. These are the $^2A'$ and $^4A'$ surfaces with saddle point energies of 10.2 and 18.0 kcal/mol, respectively, referenced to the minimum in the $N + O_2$ asymptote (it was estimated that the calculated $^2A'$ saddle point energy is too high by ≈ 2 -3 kcal/mol). The MEP for both surfaces favored a 110° approach of the reactants. An additional complicating factor for the $^2A'$ PES is the presence of a deep potential well corresponding to the ground electronic state of the NO_2 molecule.

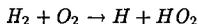
Fits to both $N-O-O$ surfaces were obtained using a modification[10] of the LEPS approach: an additional angle dependent term was added to shift the favored angle of approach from collinear to 110° . The resulting potential energy function provided a satisfactory representation of the PES for the $^4A'$ surface where only a small amount of *ab initio* data was available. It was not, however, satisfactory for the $^2A'$ PES. For that case, a more elaborate formulation based on the SM method has been developed[11]. As of this writing, the improved $N-O-O$ doublet potential energy function has not yet been used for trajectory calculations.

We have computed thermal rate constants for the $N + O_2$ reaction based on ensembles of 5000 trajectories at each temperature. The results shown in Figure 1 are the combined rate constants for exchange and dissociation. The rate constants for reaction occurring on the $^2A'$ and $^4A'$ surfaces have been combined with the proper degeneracy factors of 1/6 and 1/3, respectively. Below 2000 K reaction on the quartet surface makes little contribution to the overall rate constant because of the higher energy barrier. However, the larger degeneracy factor causes this process to become dominant at temperatures greater than 3000 K. Dissociation does not contribute significantly at temperatures below 5000 K. As can be seen from the figure, the agreement between the calculated and measured rate constants[12,13] is quite good. Calculations of VTST rate constants for this reaction are in progress.

In addition, statistical calculations of the rate constants for the reactions:



and



will be presented. The former is an important chain branching step in H_2/O_2 combustion. We have computed high-pressure limiting rate constants for HO_2

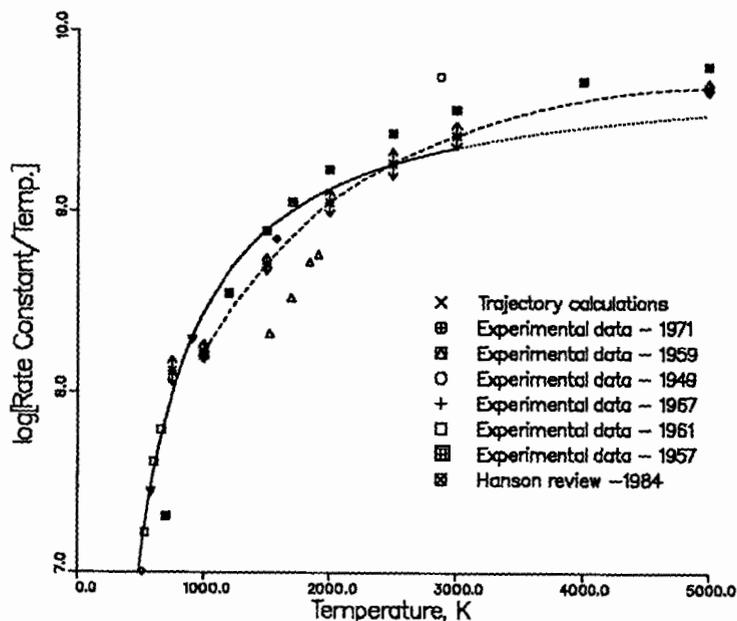


Figure 3. A comparison of the theoretical and experimental rate constants for $N + O_2 \rightarrow NO + O$.

formation using the MEP from *ab initio* PES calculations[14,15] and will also report VTST calculations for the exchange reaction. These results will be discussed in terms of the discrepancies in the measured high-temperature rate constants. The latter reaction has been suggested as the initiation step in the $H_2 + O_2$ reaction mechanism. However, no experimental data exist for this process.

REFERENCES:

1. "Pioneering the Space Frontier", Report of the National Commission on Space, (Bantam Books, New York, 1986).
2. G. Y. Anderson, "An Outlook on Hypersonic Flight", AIAA Paper 87-2074, AIAA/SAE/ASME/ASME 23rd Joint Propulsion Conference, San Diego, CA, June 1987.
3. D. M. Cooper, R. L. Jaffe and J. O. Arnold, *J. Spacecraft and Rockets* **22**, 60 (1985).
4. R. L. Jaffe, M. D. Pattengill, and D. W. Schwenke, to be published in the proceedings of the NATO Advanced Research Workshop *Supercomputer Algorithms on Reactivity, Dynamics and Kinetics of Small Molecules*, Colombella di Perugia, Italy, August 30-September 3, 1989, edited by A. Lagana (D. Reidel, Dordrecht, Holland).

5. J. C. Polanyi and J. L. Schreiber, "The dynamics of Bimolecular Reactions," in *Physical Chemistry - An Advanced Treatise, Vol. VI, Kinetics of Gas Reactions*, edited by H. Eyring, W. Jost and D. Henderson (Academic Press, New York, 1974), p. 383.
6. K. S. Sorbie and J. N. Murrell, *Mol. Phys.* **29**, 1387 (1975).
7. D. G. Truhlar and J. T. Muckerman, in "Atom-Molecule Collision Theory", ed. by R. B. Bernstein (Plenum Press, New York, 1979), chap. 16.
8. D. G. Truhlar, A. D. Isaacson, and B. C. Garrett, "Generalized Transition State Theory," in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC Press, Boca raton, FL, 1985), Vol 4, pp. 65-137.
9. S. P. Walch and R. L. Jaffe, *J. Chem. Phys.* **86**, 6946 (1987).
10. M. D. Pattengill, R. N. Zare and R. L. Jaffe, *J. Phys. Chem.* **91**, 5489 (1987).
11. R. L. Jaffe, M. D. Pattengill, T. Halicioglu, and S. P. Walch, manuscript in preparation.
12. D. L. Baulch, D. D. Drysdale, and D. G. Horne, "Evaluated Kinetic Data for High Temperature Reactions, Vol. II Homogeneous Gas Phase Reactions of the $H_2 - N_2 - O_2$ System" (Butterworth, London, 1973).
13. R. K. Hanson and S. Salimian, "Survey of Rate Constants in the $N/H/O$ System", in *Combustion Chemistry*, edited by W. C. Gardiner, Jr., (Springer-Verlag, New York, 1984), p. 361.
14. S. P. Walch, C. M. Rohlfling, C. F. Melius, and C. W. Bauschlicher, *J. Chem. Phys.* **88**, 6273 (1988).
15. R. J. Duchovic and S. P. Walch, unpublished results.