

Direct Monte Carlo simulation of chemical reaction systems: Dissociation and recombination

Shannon M. Dunn and James B. Anderson

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

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We report direct Monte Carlo simulations of a chemical reaction system with bimolecular and termolecular dissociation and recombination reactions of the type $M + AB \rightleftharpoons M + A + B$. The simulations are carried out at the molecular level using a simple flexible reaction model for termolecular reactions satisfying all the requirements of momentum and energy conservation, microscopic reversibility, and equilibrium. Energy transfer among reactants and products is included. The method is especially useful for treating reaction systems with nonequilibrium distributions and coupled gas dynamic-reaction effects. For systems with thermally equilibrated reactants the observed behavior is identical to that predicted by conventional methods. © 1995 American Institute of Physics.

I. INTRODUCTION

In earlier studies¹⁻⁵ we have found the direct Monte Carlo simulation method⁶⁻⁸ to be well suited for treating chemical reaction systems with nonequilibrium distributions, coupled gas dynamic-reaction effects, and many other effects difficult or impossible to treat in any other way. The systems examined thus far include simple bimolecular reactions, internal energy transfers and relaxation, a Lindemann-Christiansen unimolecular reaction, and an energy-dependent unimolecular reaction. Each of these prior studies was carried out with bimolecular collisions. The inclusion of termolecular collisions requires a somewhat different approach, and one method for including them has already been proposed.^{9,10}

We report here the development and testing of a new method for treating termolecular reactions in the direct Monte Carlo simulation of dissociation-recombination reactions of the type $M + AB \rightleftharpoons M + A + B$. These reactions are important in systems such as flames and explosions, shock waves and detonations, laser media, and the upper atmosphere—systems far from equilibrium for which direct simulations are most useful.

We have given a complete description of the direct Monte Carlo simulation technique in earlier work.¹⁻³ The usual differential equations of gas dynamics and chemical kinetics are eliminated and a real system is simulated by the motions and collisions of many fewer molecules in a scaled system having dynamic similarity with the real system. The method is exact in the limit of small time steps and small cell sizes. The combination of an efficient sampling technique introduced by Bird⁶ with high speed computers has made possible the simulation of a number of gas dynamic and chemical reaction systems previously impossible to analyze.

II. THEORETICAL BASIS

We consider the general dissociation-recombination reaction of the type $M + AB \rightleftharpoons M + A + B$ with the specific reactions of bimolecular dissociation



and of termolecular recombination



Reactions (1) and (2) are overall reactions which may occur as elementary steps exactly as written or may occur in a sequence of elementary steps, but they must be sufficiently fast to be completed in the time available before further encounters.

In addition we include the exchange of energy among the species A , B , AB , and M in bimolecular collisions according to the reactions



where $I = A, B, AB, M$ and $J = A, B, AB, M$.

Although complex molecular interactions might be readily utilized we treat the atoms A , B , and M as well as the molecule AB as hard elastic spheres in their nonreactive collisions with other. Each has a single state. The molecule AB is dissociated only in collisions with the atom M and the required dissociation energy E_{diss} is provided by translational energy. The reverse reaction of recombination of A and B occurs only with atom M as the third body.

Nonreactive bimolecular collisions are treated as in our earlier calculations. The cross section for collisions is $S_{I,J}$ and collision partners are selected with a probability proportional to the product of their collision cross section and relative velocity. In collisions their center-of-mass velocity is conserved and, as appropriate for hard spheres, the relative velocity is conserved in magnitude but randomized in direction. For thermal equilibrium the rate of bimolecular collisions is given by

$$R_C = \left(\frac{8kT}{\pi\mu_{I,J}} \right)^{1/2} S_{I,J} n_I n_J, \quad (4)$$

where $\mu_{I,J}$ is the reduced mass for the I - J pair and n_I and n_J are the number densities of species I and J .

Potentially reactive bimolecular collisions are selected as part of same procedure used to select nonreactive bimolecular collisions. Reaction (1) is treated with a line-of-centers model in which reaction occurs with probability P_1 for col-

lisions with a kinetic energy along the line-of-centers greater than an energy E^* . The reaction cross section, which might be obtained in other ways, is given by

$$S_1 = 0, \quad E_{\text{rel}} < E^*, \quad (5)$$

$$S_1 = P_1 S_{M,AB} (1 - E^*/E_{\text{rel}}), \quad E_{\text{rel}} \geq E^*, \quad (6)$$

where E_{rel} is the relative initial kinetic energy for M and AB . Under conditions of thermal equilibrium the rate constant for reaction (1) is given by

$$R_1 = \left(\frac{8kT}{\pi\mu_{M,AB}} \right)^{1/2} P_1 S_{M,AB} e^{-(E^*/kT)} n_M n_{AB}. \quad (7)$$

The termolecular recombination reaction, reaction (2), is treated in terms of a bimolecular collision of atom M with the center of mass of a pair of free A and B atoms, identified as $A-B$. Reaction occurs with probability P_2 for all collisions of M with $A-B$ in which the distance between A and B is less than a critical distance r_R . The probability of finding $A-B$ with a distance r_{A-B} less than r_R is given (approximately) by the ratio of the volume $\frac{4}{3}\pi r_R^3$ to the volume V_c of the cell containing A and B . Since A and B will normally have an attractive interaction the probability of finding $A-B$ within a distance r_R will normally be greater than that ratio, but one can simply adjust r_R to compensate. In effect, r_R is a free variable for fixing the reaction probability. The cross section for the reaction of M with $A-B$ pairs is given by

$$S_2 = 0, \quad r_{AB} \geq r_R, \quad (8)$$

$$S_2 = P_2 S_{M,A-B}, \quad r_{AB} < r_R. \quad (9)$$

Under conditions of thermal equilibrium the rate of reaction (2) is given by

$$R_2 = \left(\frac{8kT}{\pi\mu_{M,AB}} \right)^{1/2} P_2 S_{M,A-B} \frac{\frac{4}{3}\pi r_R^3}{V_c} n_M n_{A-B} \quad (10)$$

or

$$R_2 = \left(\frac{8kT}{\pi\mu_{M,AB}} \right)^{1/2} P_2 S_{M,A-B} \frac{4}{3}\pi r_R^3 n_M n_A n_B. \quad (11)$$

The rate constants and the equilibrium constant for reactions (1) and (2) are given by

$$k_1 = \left(\frac{8kT}{\pi\mu_{M,AB}} \right)^{1/2} P_1 S_{M,AB} e^{-(E^*/kT)}, \quad (12)$$

$$k_2 = \left(\frac{8kT}{\pi\mu_{M,AB}} \right)^{1/2} P_2 S_{M,A-B} \frac{4}{3}\pi r_R^3, \quad (13)$$

and

$$K_{\text{eq}} = \frac{P_1 S_{M,AB} e^{-(E^*/kT)}}{P_2 S_{M,A-B} \frac{4}{3}\pi r_R^3}. \quad (14)$$

The distribution of relative velocities for A and B which participate in reaction (2) is an unbiased distribution identical to that for $A-B$ pairs in the reaction cell. The distribution of relative velocities for M and $A-B$ participating in reac-

tion (2) is biased by the relative velocity $v_{M,A-B}$. For a thermal distribution of reactants the resulting distributions for molecules which react are

$$P(E_{A,B}, E_{M,A-B}) \sim e^{-(E_{A,B} + E_{M,A-B})/kT} v_{A,B}^2 v_{M,A-B}^3 dv_{A,B} dv_{M,A-B} \quad (15)$$

$$\sim e^{-(E_{A,B} + E_{M,A-B})/kT} E_{A,B}^{1/2} E_{M,A-B} dE_{A,B} dE_{M,A-B}, \quad (16)$$

where $v_{A,B}$ and $v_{M,A-B}$ are relative velocities and $E_{A,B}$ and $E_{M,A-B}$ are the corresponding kinetic energies. The two relative kinetic energies may be expressed as their sum, $E_t = E_{A,B} + E_{M,A-B}$, and the fraction f in $E_{A,B}$. In terms of the sum and the angle θ , defined by $f = \cos^2 \theta$, the distribution becomes

$$P(E_{A,B}, E_{M,A-B}) \sim e^{-(E_t/kT)} E_t^{5/2} \cos^3 \theta \sin^2 \theta dE_t d\theta. \quad (17)$$

In reaction (1) the energy available for distribution among the reaction products consists of the center-of-mass energy, which is fixed, and the relative initial kinetic energy for $M+AB$ less the dissociation energy, which is available to A , B , and M as kinetic energy relative to their center of mass. Equation (17) governs the distribution and it may be used as the basis for selecting these energies.

For reaction (2) the energy available to the reaction products M and AB is their center-of-mass energy, which is fixed, and the sum of the relative initial kinetic energies of A , B , and M and the dissociation energy, which becomes the kinetic energy of separation of the products M and AB .

The variations in cross sections for these reactions with reactant velocities and the distributions of reaction products are self-consistent. Momentum and energy are conserved and the reactions are microscopically reversible.

III. CALCULATION PROCEDURES

The calculation procedures described for previous work require only a few modifications. A termolecular collision clock is required in addition to the bimolecular collision and translational motion clocks used earlier. The translational time is advanced one step and each molecule is moved according to its velocity. Bimolecular collisions are then selected and the bimolecular clock is advanced for each collision until the bimolecular collision time passes the translation time. Termolecular collisions are then selected and the termolecular clock is advanced for each until the termolecular collision time passes the translation time. The process is repeated to continue the simulation.

The time advance Δt_B for bimolecular collisions (reactive or nonreactive) is calculated as in previous work according to

$$\Delta t_B = \frac{2V_c}{S_{I,J}} \frac{1}{v_{I,J} N^2}, \quad (18)$$

where V_c is the cell volume and N is the number of molecules in the cell.

The time advance Δt_T for termolecular collisions (reactive) is calculated in a similar manner using a rearrangement of Eq. (11),

$$\Delta t_T = \frac{V_c}{P_2 S_{M,A-B}} \frac{1}{v_{M,A-B}} \frac{1}{N_M} \frac{1}{N_{A-B}} \frac{V_c}{\frac{4}{3} \pi r_R^3} \quad (19)$$

or

$$= \frac{V_c^2}{P_2 S_{M,A-B}} \frac{1}{v_{M,A-B}} \frac{1}{N_M} \frac{1}{N_A} \frac{1}{N_B} \frac{1}{\frac{4}{3} \pi r_R^3} \quad (20)$$

The magnitudes of the relative velocities $v_{M,AB}$ for the products of reaction (2) and $v_{I,J}$ for the products of reaction (3) are fixed by the energy available. The directions of these relative velocities are taken as random.

The selections of the relative kinetic energies for M relative to $A-B$ and A relative to B for the products of reaction (1) are made according to Eq. (17). The sum of the energies E_t is distributed as $E_{A,B} = fE_t$ and $E_{M,A-B} = (1-f)E_t$, where $f = \cos^2 \theta$. The angle θ is selected at random in the interval $(0, \pi/2)$ and retained with a probability proportional to $\cos^3 \theta \sin^2 \theta$.

Our test calculations were carried out as simulations of homogeneous isotropic reactions using a single cell. The calculations were normally begun with the initial mixture of gases at thermal equilibrium. In the course of reaction non-equilibrium distributions of reactants and products may occur and the temperature (or its equivalent) of the system may change. In some cases it was useful to use an excess of inert gas and to scale the species velocities periodically in order to produce near-equilibrium distributions and fixed temperatures. This allowed direct comparisons with analytic solutions for isothermal systems with equilibrium distributions.

IV. TEST CALCULATIONS

We made a number of test calculations in order to explore the method. Some of the results are given here.

TABLE I. Reaction conditions.

Reactions: $M + AB \rightarrow M + A + B$ (1)
$M + A + B \rightarrow M + AB$ (2)
Molecular types: All hard spheres, single states
Dissociation energy of AB : 20 kcal/mol
Masses: $m_A = 50$, $m_B = 50$, $m_M = 50$ g/mol
Reaction: $M + AB$, dissociation with probability $P_1 = 0.1$ if line-of-centers $E > 20$ kcal/mol
$M + A + B$, see text, probability $P_2 = 0.1$ $\frac{4}{3} \pi r_R^3 = 1/4000$
Boundaries: Constant volume, isolation, except that constant temperature maintained by periodic adjustment of translational energies
Volume: $V = 1.0 \text{ cm}^3$
Bimolecular collision cross sections (simulation): 1.0 cm^3
Number of molecules (simulation): (initial $M + AB$) 8000 M , 4000 AB (initial $M + A + B$) 8000 M , 4000 A , 4000 B
Temperature: varied, 1500–3000 K
Rate constants (2000 K): $k_1 = 2.82 \text{ (molecule/cm}^3\text{)}^{-1} \text{ s}^{-1}$ $k_2 = 73.5 \text{ (molecule/cm}^3\text{)}^{-2} \text{ s}^{-1}$

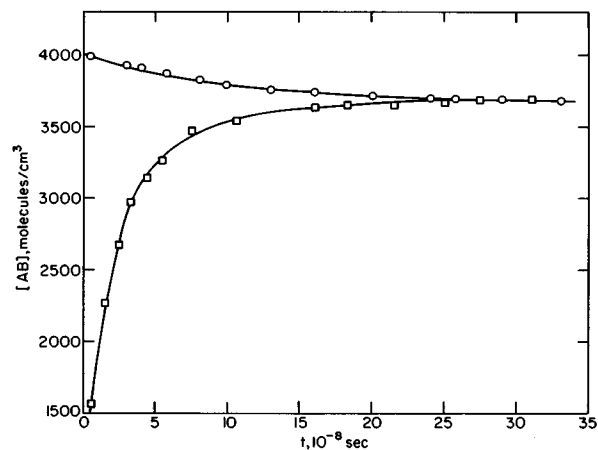


FIG. 1. Variation of concentration of AB with time for reaction at 2000 K as determined by direct Monte Carlo simulation. Squares, starting from mixture of M and AB . Circles, starting from mixture of M , A , and B . The solid lines are the corresponding analytic solutions. Conditions are listed in Table I.

The approaches to equilibrium from an excess of AB and from an excess of $A + B$ were investigated under conditions listed in Table I. For these conditions there was sufficient inert gas and the reaction probability was sufficiently low that near-equilibrium velocity distributions were observed and the temperature was maintained nearly constant.

The variations of concentration with time for species AB starting from a mixture of M and AB and starting from a mixture of M , A , and B are shown in Fig. 1. The analytic solutions for thermal distributions of reactants and products are also shown. The agreement between the Monte Carlo and the analytic results may be seen to be excellent. The equilibrium values attained in the simulations are equal to the independently calculated equilibrium value.

Similar sets of Monte Carlo calculations for near-equilibrium conditions were used to obtain rate constants for the dissociation and recombination reactions and equilibrium

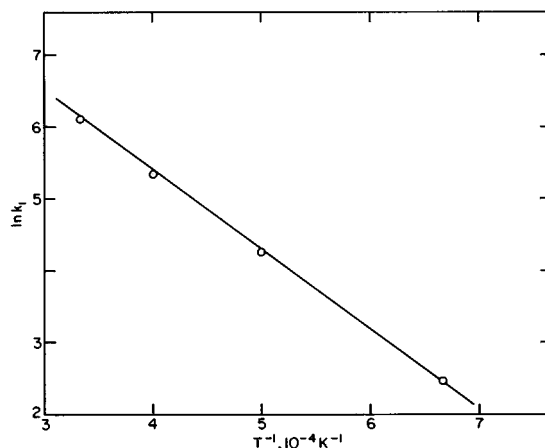


FIG. 2. Rate constants for dissociation reaction, $M + AB \rightarrow M + A + B$, at several temperatures. Circles, from direct simulation. Solid line, from analytic expression.

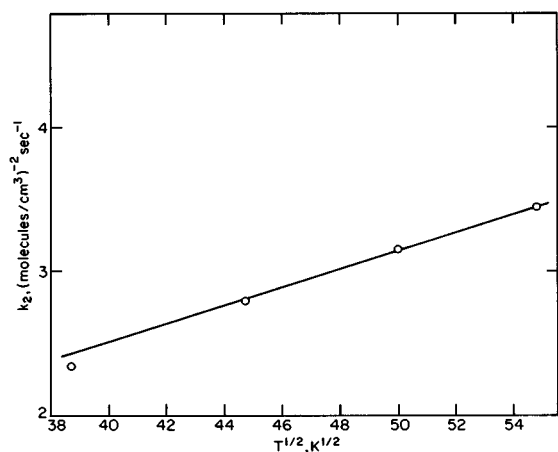


FIG. 3. Rate constants for recombination reaction, $M+A+B \rightarrow M+AB$, at several temperatures. Circles, from direct simulation. Solid line, from analytic expression.

constants at several different temperatures. The rate constants are shown in Figs. 2 and 3 along with the corresponding analytic values obtained from Eqs. (12) and (13). The agreement between the Monte Carlo results and the analytic results is essentially exact. Similar agreement was observed for the equilibrium constants.

We also explored reactions under conditions for which nonequilibrium distributions occurred and we observed the expected depletions of reacting species. Our observations were similar to those we made earlier for simple bimolecular reactions.¹

V. DISCUSSION

As in previous work we found the direct simulation Monte Carlo method to be simple, straightforward, easy to

program, and easy to execute. Our treatment of dissociation and recombination was limited to a single state for the molecule AB , but the inclusion of multiple states is not a particularly difficult or complex task. The flexibility of the method is such that can adapted to any real system for which detailed reaction rate information is available.

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