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SEMI CLASSICAL THEORY OF ATOMIC AND MOLECULAR EXCITATION AND DISSOCIATION

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ABSTRACT

A semi classical theory for describing the thermal excitation and dissociation of a dilute mixture of diatomic molecules in an inert gas is reviewed. The statistical evolution of the system is assumed to be governed by a two dimensional master equation with the energy and angular momentum as the independent variables. The reduction of this equation to a simpler one dimensional master equation and Monte Carlo methods for obtaining the transition kernels and source terms required for its solution are also described. The general characteristics of the steady state solutions of these equations and the corresponding steady state rate constants are discussed. It is shown that although the latter are less than the equilibrium rate constants they still obey the usual detailed balancing condition. The comparison between theory and experiment is reviewed briefly.

I INTRODUCTION

The excitation and dissociation of a two body system in a collision with a third body and the inverse recombination and deexcitation processes are among the most basic reactions of interest in chemical kinetics. They are also of particular importance in reacting gas dynamics for two reasons. First, they involve large energy exchanges between the internal and translational degrees of freedom of the atoms and molecules and second, they provide a mechanism for changing the number of particles in a system. Both of these processes influence the pressure and temperature of the gas which in turn determine its dynamic and thermodynamic state.

The status of theoretical work on this problem has been reviewed previously by Keck [1] and a comparison between theory and experiment has been presented by Shui, Appleton and Keck [2].

In the present paper we shall be concerned primarily with the mathematical

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analysis of thermal excitation and dissociation for simple diatomic molecules. The treatment to be described is based largely on the work of Keck and Carrier [3] and divides naturally into three more or less separate and distinct parts involving: 1) the statistical mechanics of non-equilibrium gas mixtures, 2) the mechanics of three-body collisions and 3) the determination of the interaction potentials for the particles. The first two parts will be discussed in some detail in the next two sections. The last will be touched on only briefly in the final section.

II STATISTICAL MECHANICS OF EXCITATION AND DISSOCIATION

We shall consider a dilute mixture of molecules AB in a gas of inert atoms C. The reactions of interest are described by the chemical equations

$$AB(i) + C \rightleftarrows AB(j) + C \tag{1}$$

$$AB(i) + C \rightleftarrows A + B + C \tag{2}$$

and

$$AB(i) \rightleftarrows A + B \tag{3}$$

where i and j denote internal energy states of AB. Equation (1) represents collisional excitation and deexcitation, (2) represents collisional dissociation and recombination and (3) represents spontaneous decay and formation of metastable molecules.

A. MOLECULAR STATES

Given the interaction potential $V_{AB}(r)$ for the atoms A and B, the energy eigenvalues E_i for the molecules AB may be determined by solving the time independent radial Schrodinger Equation

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r} r^2 \frac{\partial \psi_i}{\partial r} + V_\ell(r)\psi_i = E_i\psi_i \tag{4}$$

where

$$V_\ell(r) = \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V_{AB}(r) \tag{5}$$

is the effective potential,

$$\mu = M_A M_B/(M_A+M_B)$$

is the reduced mass of A and B, r is the radial separation of A and B and ℓ is the total angular momentum quantum number.

The characteristics of the effective potential for typical molecules are shown in fig. 1). The lower curve shows the general form of the interaction potential V_{AB} corresponding to the case $\ell = 0$. It is assumed to have a single minimum of depth D_e at a radial separation $r = r_e$ and to approach zero more rapidly than r^{-2}. The upper curve shows the limiting case, corresponding to $\ell = \ell_m$, in which the effective potential has an horizontal inflection point of height B_m at $r = z_m$. The middle curve shows the effective potential for an intermediate value of ℓ. In this case, it has a relative minimum of depth D_ℓ

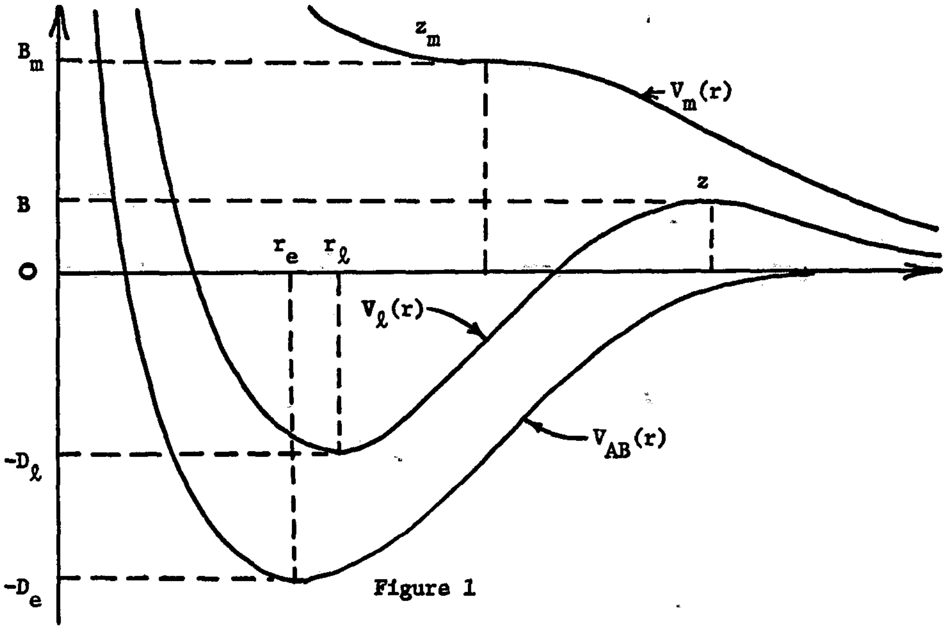

Figure 1

at $r = r_\ell$ and a relative maximum of height B at $r = z$. The loci of r_ℓ and z are given by the roots of the equation

$$\frac{\partial V_\ell(r)}{\partial r} = \frac{dV_{AB}(r)}{dr} - \frac{\hbar^2\ell(\ell+1)}{\mu r^3} = 0 \qquad (6)$$

For $0 \leq \ell \leq \ell_m$ equations (5) and (6) can be solved to obtain both ℓ and D_ℓ as functions of B and it follows that the chemical state of the molecules AB is completely determined by the two quantized parameters E_i and B_i both having the dimensions of energy. For $E_i \leq 0$ the molecules are unconditionally stable in the absence of an external perturbation, while for $0 \leq E_i \leq B_i$ the molecules are metastable due to the possibility of quantum mechanical penetration through the rotational barrier.

It can also be shown from equations (5) and (6) that if ℓ is regarded as a continuous function of B then

$$d\ell(\ell+1)/dB = 2\mu z^2/\hbar^2 \qquad (7)$$

This is an important relation which we shall use later.

B. MASTER EQUATION

We now consider the changes in the chemical state of the molecules AB produced by collisions with the third body C. We shall assume 1) that the collisions between AB and C are statistically independent and 2) that translational relaxation is sufficiently fast to maintain the translational degrees of freedom for all particles in an equilibrium Boltzmann distribution at a temperature T. Under these conditions, the evolution of the system of molecules can be described by a two dimensional Master Equation of the form

$$\partial N(i\ t)/\partial t = \sum_j [K(i\ j)N(j\ t) - K(j\ i)N(i\ t)] + S(i\ t) - [K_s(i) + K_c(i)]N(i\ t) \qquad (8)$$

where, $N(i\ t)$ is the concentration of molecules in the state i at time t, $K(j\ i)$ is the rate constant for transitions from i to j, $K_s(i)$ and $K_c(i)$ are the spontaneous and collision induced decay rate constants for the state i, and $S(i\ t)$ is the formation rate of molecules in the state i at time t.

A schematic representation of a transition from i to j in (E,B) space is shown in figure 2.

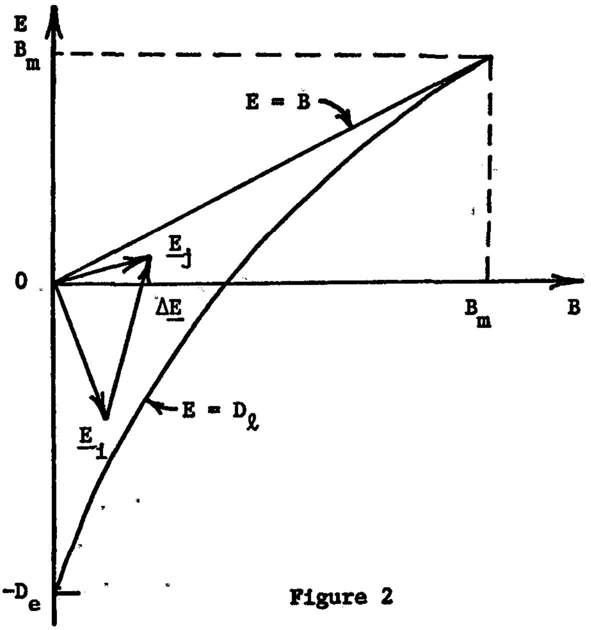

Figure 2

The allowed states of a molecule all lie within the region bounded by the curves $E = D_\ell$ and $E = B$ giving the loci of the minima and maxima of the effective potential.

At thermodynamic equilibrium the time derivative of $N(i\ t)$ must vanish and detailed balancing requires

$$K(i\ j)N_e(j) = K(j\ i)N_e(i) = R(i\ j) \qquad (9)$$

and

$$S_e(i) = [K_s(i) + K_c(i)]N_e(i) \qquad (10)$$

where

$$N_e(i) = C\ g_{AB}\ (2\ell+1)e^{-E_i/kT} \qquad (11)$$

is the equilibrium concentration of molecules in the state i. The normalizing constant C in equation (11) is related to the equilibrium concentrations $[AB]_e$, $[A]_e$ and $[B]_e$ and partition functions Q_{AB}, Q_A and Q_B of AB, A and B by either of the expressions

$$C = [AB]_e/Q_{AB} \qquad (12)$$

or

$$C = [A]_e[B_e]/Q_AQ_B. \tag{13}$$

It follows from equations (10), (11) and (13) and the assumption that the translational degrees of freedom of A and B are in equilibrium that the source term $S(i\ t)$ must be of the form

$$S(i\ t) = S_e(i)[A(t)][B(t)]/[A]_e[B]_e \tag{14}$$

Substituting this expression into equation (8) and using equation (9) we obtain the Master Equation in the more symmetrical form

$$\begin{aligned} N_e(i)\partial X(i\ t)/\partial t = \sum_j R(i\ j)[X(j\ t) - X(i\ t)] \\ + S_e(i)[X(\infty t) - X(i\ t)] \end{aligned} \tag{15}$$

where

$$X(i\ t) = N(i\ t)/N_e(i) \tag{16}$$

$$X(\infty\ t) = [A(t)][B(t)]/[A]_e[B]_e \tag{17}$$

are the "reduced" distributions for molecules and atoms.

C STEADY STATE SOLUTION OF MASTER EQUATION

As may be inferred from the work of Montroll and Shuller [4], the evolution of a system governed by equation (15) from any initial distribution to its final equilibrium distribution begins with a rapid relaxation of the initial distribution to a quasisteady distribution which is "almost Boltzmann" over most of the range $-D_\ell \leq E_i \leq B_i$. This initial transient, during which there is negligible dissociation or recombination, is followed by a much longer phase during which the shape of the "almost Boltzmann" distribution remains unchanged but its amplitude varies with time as dissociation or recombination proceeds. Throughout this second phase the left hand side of equation (15) is very small and may be set equal to zero for all energies $E_i > -D_e + kT$. Under these conditions the quasisteady distribution can be closely approximated by the expression [3]

$$X(i\ t) = X(\infty t) + [X(0\ t) - X(\infty t)]\chi(i) \tag{19}$$

where $\chi(i)$ satisfies the steady state Master Equation

$$0 = \sum_j R(i\ j)[\chi(j) - \chi(i)] - S_e(i)\chi(i) \tag{20}$$

and the normalization condition $\chi(0) = 1$.

RATE EQUATION AND RATE CONSTANTS

Substituting equation (19) into equation (15) and summing over i we obtain

$$\partial[AB]/\partial t = [X(\infty\ t) - X(0\ t)]\sum_i S_e(i)\chi(i). \tag{21}$$

In the usual range of interest $kT \ll D_e$ and $N_e(i)$ has a strong maximum at $i = 0$. Thus to an excellent approximation

$$[AB] = \sum_i N_e(i)X(i\ t) \approx [AB]_eX(o\ t) \tag{22}$$

and we obtain from equation (21) the well known phenomenalogical rate equation

$$\partial[AB]/\partial t = k_{rs}[A][B][C] - k_{ds}[AB][C] \quad (23)$$

where the steady state dissociation and recombination rate constants are defined by the equation

$$k_{ds}[AB]_e[C] = k_{rs}[A]_e[B]_e[C] = \sum_i S_e(i)\chi(i) \quad (24)$$

The corresponding "equilibrium" rate constants are defined by the equation

$$k_{de}[AB]_e[C] = k_{re}[A]_e[B]_e[C] = \sum_i S_e(i) \quad (25)$$

It follows from equations (24) and (25) that both the steady state and "equilibrium" rate constants obey detailed balancing condition

$$k_{ds}/k_{rs} = k_{de}/k_{re} = [A]_e[B]_e/[AB]_e \quad (26)$$

It can also be seen from equation (20) that $\chi(i) \leq 1$ over the range $E_i \leq B_i$ so that the steady state rate constants are in general less than the corresponding "equilibrium" rate constants.

It should be noted that it is the steady state, not the "equilibrium", rate constants which describe the approach of a system to final equilibrium. The "equilibrium" rate constants which are based on the assumption that $\chi(i) = 1$ over the entire range $E_i \leq B_i$ describe the "one way" dissociation or recombination rates in a system already in full equilibrium and are observable only under rather special circumstances. These points are illustrated qualitatively in figure 3 which shows the experimentally observable concentrations, rate constants and reduced distribution functions for two idealized cases:

In the first case which is shown on the left we assume that the translational temperature of the gas undergoes a step increase from a low value T_1 to an intermediate value T_2. As a result the system is left in a state where the total concentration of molecules far exceeds the equilibrium value and the reduced distribution function $X(i\ 0)$ has a sharp peak at $E_i = -D_e$. At this point the dissociation rate is very small due to the extremely low concentration of molecules in states of high energy from which the probability of dissociation is appreciable, and the observed rate constant will be correspondingly small. As previously mentioned, the relaxation to the new equilibrium begins with an initial transient having a duration of the order of the vibrational relaxation time τ_v during which the reduced distribution $X(i\ t)$ relaxes from its initial form to the quasi steady "almost Boltzmann" form $X(i\ t > \tau_v)$ and the observed rate constant rises assymptotically to its steady state value where it remains as dissociation proceeds and the new equilibrium is approached. It may be noted that the conditions just described can be closely approximated by shock heating a dilute mixture of diatomic molecules in an inert gas.

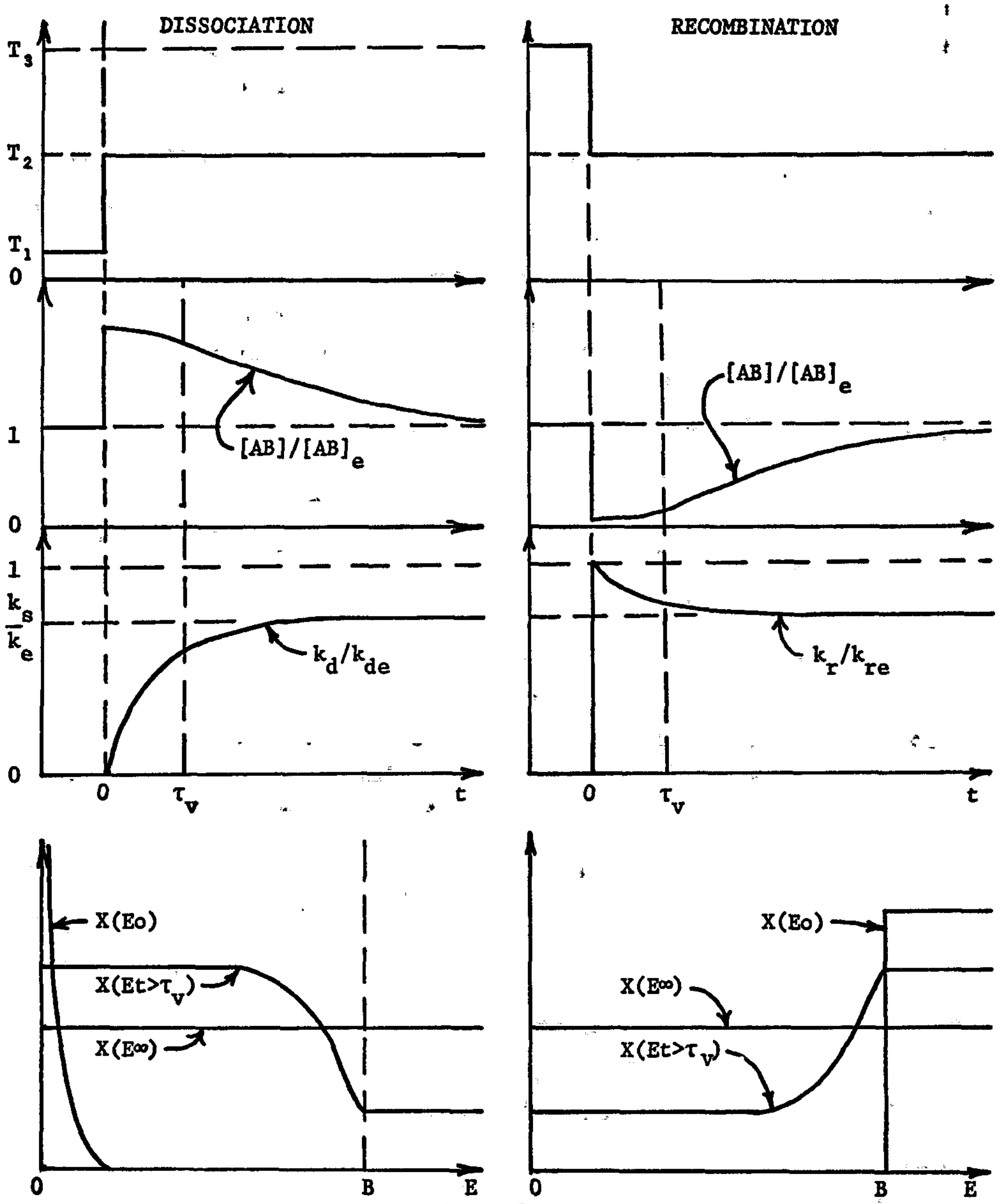

Figure 3

In the second case which is shown on the right side of fig. 3 we assume a step decrease in the translational temperature from a high value T_3 to the intermediate value T_2. Under these conditions the system is left in a state where the initial concentration of molecules is very much less than the new equilibrium concentration and the reduced distribution has a step discontinuity at the dissociation limit $E_i = B_i$. At this instant the observed recombination rate constant will be equal to the "equilibrium" value. During the transient phase which follows the initial distribution again relaxes to a quasi steady "almost Maxwellian" form as the high energy states are rapidly populated by recombination. This produces a back flux of dissociating molecules which causes the observed rate constant to fall toward the steady state value where it remains as the major part of the recombination is completed. While in principle this idealized recombination process provides a method by which the "equilibrium" rate constant could be observed on transient basis, in practice there appears to be no method for producing the required stepwise temperature decrease since expansion shocks do not exist.

In concluding this discussion we should like to emphasize again that no matter how closely a dissociating or recombining system approaches equilibrium the observed rate constant will always be the steady state value and a transition to the "equilibrium" value can not be observed in this manner. This is a point which is frequently misunderstood.

APPROXIMATE ONE DIMENSIONAL MASTER EQUATION

To date no solutions of the two dimensional master equation (15) have been obtained. This is due in part to the complexity of the equation and in part to a lack of information about the transition kernel $R(i\ j)$. Both of these difficulties may be overcome, however, by the reduction of the two dimensional equation to an approximate one dimensional equation.

To accomplish this reduction we first observe that in the vicinity of the dissociation limit the density of states $\eta(i)$ will be sufficiently high to permit the discrete master equation (15) to be approximated by the continuous master equation

$$N_e(\underline{E}_i)\partial X(\underline{E}_i t)/\partial t = \int R(\underline{E}_i\underline{E}_j)[X(\underline{E}_j t) - X(\underline{E}_i t)]d\underline{E}_j + S_e(\underline{E}_i)[X(\infty t) - X(\underline{E}_i t)] \qquad (27)$$

where

$$N_e(\underline{E}_i) = N_e(i)\eta(i)$$

$$S_e(\underline{E}_i) = S_e(i)\eta(i)$$

$$R(\underline{E}_i\underline{E}_j) = R(i\ j)\eta(i)\eta(j)$$

and $\underline{E}_i$ is a two dimensional vector having components E_i and B_i. We further anticipate that in general the transition rate constants $K(i\ j)$ and $K(j\ i)$ and decay constant $K_s(i)$ will be rapidly increasing functions of the energy E_i for a fixed rotational barrier height B_i but relatively slowly varying functions of B_i for a fixed energy difference $U_i = E_i - B_i$. Under these conditions we may also expect that, for a fixed value of U_i, the reduced distribution function $X(i\ t)$ will be a slowly varying function of B_i.

If we now use the new variable U_i to replace E_i in equation (27) and integrate both sides over B_i keeping U_i fixed we obtain

$$\partial N(U_i t)/\partial t = \iiint R(\underline{E}_i \underline{E}_j)[X(\underline{E}_j t) - X(\underline{E}_i t)]dB_i dB_j dU_j$$

$$+ \int S_e(\underline{E}_i)[X(\infty t) - X(\underline{E}_i t)]dB_i \qquad (28)$$

where

$$N(U_i t) = \int N_e(\underline{E}_i)X(\underline{E}_i t)dB_i \qquad (29)$$

Using equation (7), (11) and (28) and approximating the density of states $\eta(i)$ by the semiclassical expression

$$\eta(i) = [\hbar\omega(i)]^{-1}d\ell/dB,$$

where $\omega(i)$ is the classical angular frequency for a molecule in the state i we obtain from equation (29) the expression

$$N(U_i t) = Cg_{AB}\left(\frac{2\mu}{\hbar^3}\right) e^{-U_i/kT}\int X(B_i U_i t)\ \Phi\ (z)dz \qquad (30)$$

where

$$\Phi\ (z) = z^2|dB/dz|e^{-B/kT} \qquad (31)$$

The general dependence of B and the function Φ (B) on the position z of the rotational maximum is shown in fig. 4

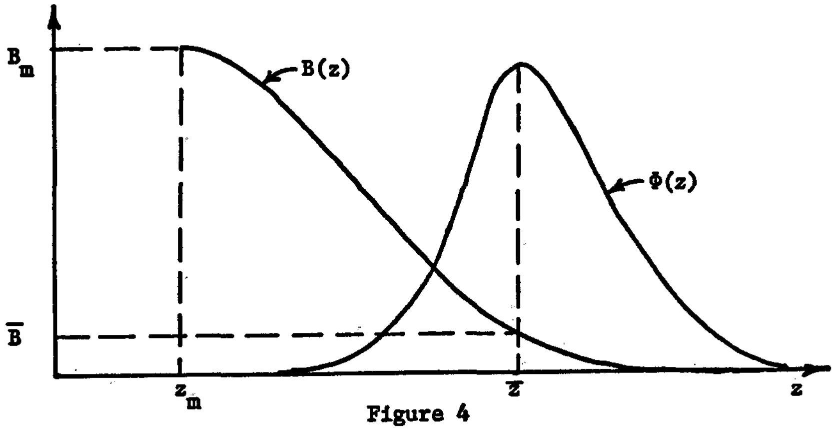

Figure 4

It can be seen that Φ (B_i) has a relatively sharp maximum at a value of $z = \overline{z}$ where $d\Phi/dz = 0$. In this connection it is of interest to note that, for $kT << B_m$, the value $\overline{B} = B(\overline{z})$ is in general very close to kT. This implies that for fixed U_i, the most probable value of the angular momentum for a molecule at equilibrium is that for which the corresponding rotational barrier height is equal to the characteristic thermal energy in rotation.

We may now evaluate the integral in equation (30) approximately by setting

$$X(B_i U_i t) = X(\overline{B}\ U_i t).$$

this gives

$$N(U_i t) \approx N_e(U_i)X(\overline{B}\ U_i t) \equiv N_e(U_i)X(U_i t) \qquad (32)$$

where

$$N_e(U_i) = \int N_e(i)dB_i \tag{33}$$

Thus the left hand side of the master equation (28) can be written

$$\partial N(U_i t)/\partial t = N_e(U_i)\partial X(U_i t)/\partial t \tag{34}$$

The terms on the right hand side may also be approximated using the same technique and this leads to the one dimensional master equation

$$N_e(U_i)\partial X(U_i t) = \int R(U_i U_j)[X(U_j t) - X(U_i t)]dU_j + S_e(U_i)[X(\infty t) - X(U_i t)] \tag{35}$$

where

$$R(U_i U_j) = \int R(\underline{E}_i \underline{E}_j)dB_i dB_j \tag{36}$$

and

$$S_e(U_i) = \int S_e(\underline{E}_i)dB_i \tag{37}$$

The transient solutions of equation (35) have been investigated by Brau, Keck and Carrier [5]. Their results confirm the general description of the evolution of the system presented earlier.

As in the case of the two dimensional master equation (28) the steady state solution of equation (35) may be obtained in the form

$$X(U_i t) = X(\infty t) + [X(-\bar{D}\ t) - X(\infty t)]\chi(U_i) \tag{38}$$

where $\bar{D} = D_e(\bar{B}) + \bar{B}$ and $\chi(U_i)$ satisfies the equation

$$0 = \int R(U_i U_j)[\chi(U_j) - \chi(U_i)]dU_j - S_e(U_i)\chi(U_i) \tag{39}$$

and the normalization $\chi(-\bar{D}) = 1$

SOLUTION OF STEADY STATE MASTER EQUATION

A variety of techniques may be used for solving equation (39) depending on the character of the transition kernel $R(U_i U_j)$. In general, if the root mean square energy transfer per collision $< \Delta U^2 >^{\frac{1}{2}}$ is large compared to kT, equation (39) may be conveniently solved by iteration using the recursion relation

$$\chi^{(n+1)}(U_i) = [\mathcal{Z}(U_i) + S_e(U_i)]^{-1}\int R(U_i U_j)\chi(U_j)dU_j \tag{40}$$

where

$$\mathcal{Z}(U_i) = \int R(U_i U_j)dU_j \tag{41}$$

On the other hand if $< \Delta U^2 >^{\frac{1}{2}}$ is small compared to kT equation (39) may be transformed to an equivalent diffusion equation

$$0 = \frac{1}{2}\frac{d}{dU} < \Delta U^2 > \mathcal{Z}(U)\frac{d\chi(U)}{dU} - S_e(U)\chi(U) \tag{42}$$

where

$$< \Delta U^2 > = [\mathcal{Z}(U)]^{-1}\int R(U'U)(U'-U)^2 dU' \tag{43}$$

and $\chi(U)$ satisfies the boundary condition $\chi(0) = 0$.

III COLLISION MECHANICS

To solve the equations set forth in the previous section requires a knowledge of the spontaneous decay rate $K_s(i)$, the collision induced decay rate $K_c(i)$ and the transition rate constant $K(i\ j)$. The first of these rates may be approximated by the well known expression

$$K_s(i) = \frac{\omega(i)}{2\pi} \exp \quad - \frac{2}{\hbar}\int [2m(V_\ell - E_i)]^{\frac{1}{2}} dr \tag{44}$$

obtained from a WKB solution of the radial Schrodinger Equation (4) for a slowly varying effective potential $V_\ell(r)$. The most reliable information about the latter two at the present time comes from classical Monte Carlo trajectory calculations.

A. VARIATIONAL THEORY OF REACTION RATES

The variational theory [6] reaction rates provides a convenient starting point for the classical study of collision processes using Monte Carlo methods [1]. We assume that the classical Hamiltonian $H(\underline{p}\ \underline{q})$ of the system and the density of representative points in phase space $\rho(\underline{p}\ \underline{q})$ are known and depend only on the magnitude of $\underline{p}$. Then under steady state conditions the one way flux of points across a hypersurface S dividing any two states i and j of the system is given by the variational rate

$$R_v = \frac{1}{2}\int_s \rho|\underline{v}\cdot\underline{n}|dS \tag{45}$$

where $\underline{v}$ is the generalized velocity of a point in phase space and $\underline{n}$ is the unit normal to the surface element dS. If the equation of the dividing surface S is expressed in the form $\phi(\underline{p}\ \underline{q}\ \underline{\beta}) = 0$, then the unit normal can be written

$$\underline{n} = (\underline{\nabla}\phi)dh/d\phi \tag{46}$$

where dh is the element of length perpendicular to dS. Substituting equation (46) into (45) and using Hamiltons equation

$$\dot{p}_i = -\partial H/\partial q_i, \ \dot{q}_i = \partial H/\partial p_i \tag{47}$$

to obtain the components of $\underline{v}$ we obtain

$$R_v = \frac{1}{2}\int_{\phi=0} \rho|\underline{v}\cdot\underline{\nabla}\phi|d\Omega/d\phi \tag{48}$$

where

$$d\Omega = \prod_{i=1}^{3n} dp_i dq_i \tag{49}$$

is the volume element in phase space and n is the number of particles in the system.

We now observe that, since every trajectory connecting the two states i and j of the system must cross the dividing surface S one or more times, the variational rate R_v gives an upper bound the true reaction rate. Thus for any assumed functional form of the dividing surface a least upper bound can be obtained by minimizing R'_v with respect to all allowed variations of S. In this connection it should be noted that the only constraint on the variations of S is that the resulting division of phase space be acceptable for the calculation of partition functions for the two states which it separates.

These points are illustrated in figure 5

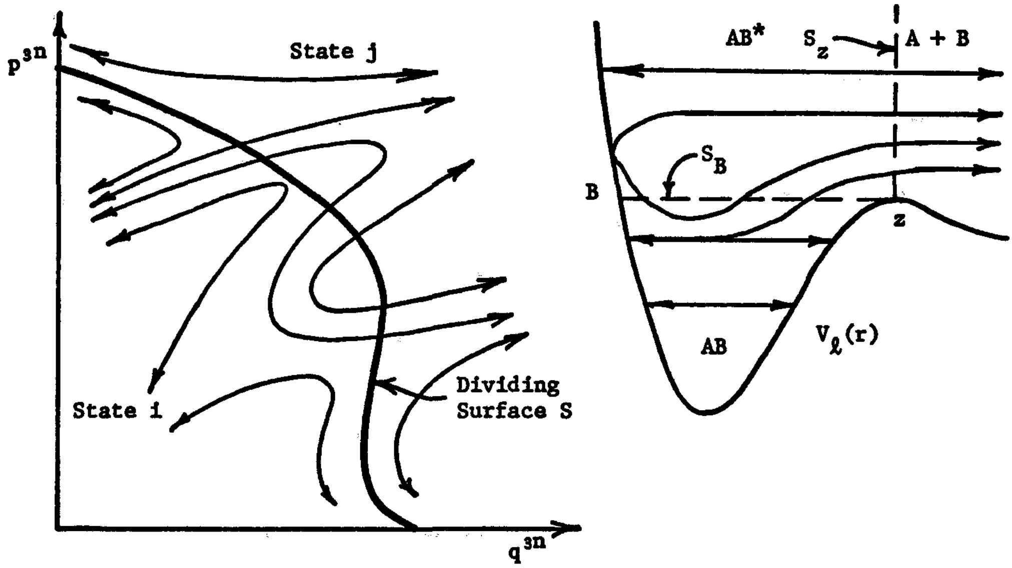

Figure 5

On the left is a schematic representation of the phase space of an n particle system showing a dividing surface S and some of the simpler types of trajectories which occur. On the right is a sketch of the effective potential curve for a diatomic molecule showing two surfaces S_B and S_z separating molecules AB from free atoms A + B. For temperatures such that $kT \ll D$ and atom concentrations such that $[A] \sim [B] \ll z^{-3}$ either of these surfaces would be acceptable for the calculation of partition functions for AB or A + B since the partition function for unstable molecules AB* is completely neglibible under the specified conditions. Also shown in this figure are several trajectories of the type which can occur during threebody collisions of A, B and C. It is of interest to note at this point that in the absence of a third body C the relative energy of A and B is a constant of the motion and the surface S_B can never be crossed while the surface S_z is still crossed in every binary encounter of A and B. It follows that for purposes of estimating the dissociation or recombination rate of AB the surface S_B is a much better apriori choice than S_z. In fact it is a general rule that the best dividing surfaces are those which are functions only of the constants of motion in the absence of the perturbations which cause the transitions.

Although in principle it is possible to find dividing surfaces for which the variational rate would equal the true reaction rate, in practice this can not usually be done and the variational rate must therefore be corrected for recrossings.

B MONTE CARLO CALCULATIONS

It follows from the preceding discussion that the one way equilibrium reaction rate $R(U_iU_j)$ can be expressed

$$R(U_iU_f) = \lim_{\Delta U\to 0} (2\Delta U^2)^{-1} \int_{\phi=0} m^{-1} I(ij)\rho_e |\underline{v}\cdot\nabla\phi| d\Omega/d\phi \ , \tag{50}$$

Where

$$\rho_e = Cg_{AB}e^{-E_i/kT}, \tag{51}$$

m is the number of times a given trajectory crosses the surface S and I (i j) is a characteristic function to which we assign the value 1 for a trajectory with terminals in the energy intervals $U_i \pm \frac{1}{2}\Delta U$ and $U_j \pm \frac{1}{2}\Delta U$ and the value 0 otherwise.

To determine the functions m and I(i j), the equations of motion (47) must be solved for our threebody system and this can only be done numerically. Under these conditions the multidimensional integral (50) must also be evaluated numerically and the Monte Carlo method is ideally suited for the problem. To apply the method a suitable dividing surface S for which the equilibrium variational rate R_{ve} can be evaluated analytically is chosen. Initial conditions for the trajectory calculations are generated by random sampling of points on S with a weight function w, and the equations of motion are integrated backward and forward in time to determine the character of the trajectories. Finally, equation (50) is evaluated using the Monte Carlo approximation

$$R(U_iU_j) = \lim_{\Delta U\to 0} (2\Delta U^2 N)^{-1} \sum_{k=1}^{N} [\rho_e |\underline{v}\cdot\underline{\nabla}\phi| I(i\ j)/wm]_k \tag{52}$$

when N is the number of trajectories sampled. In the absence of any information about the functions m and I(i j) the best choice of the wright function is

$$w = \rho_e|\underline{v}\cdot\underline{\nabla}\phi|/2R_{ve} \tag{53}$$

and equation (52) reduces to

$$R(U_iU_j) = R_{ve} \lim_{\Delta U\to 0} (\Delta U^2 N)^{-1} \sum_{k=1}^{N} [I(i\ j)/m]_k \tag{54}$$

The efficiency of the Monte Carlo calculations just outlined depends critically on the choice of the dividing surfaces used for sampling. In the calculations made to date two surfaces have been employed:

1) IMPACT PARAMETER SAMPLING

The most familiar and commonly used method of sampling involves what may be called "impact parameter surfaces" [7]. For two particles with a relative separation $\underline{r}$ these surfaces are defined by

$$\phi(\underline{p}\ \underline{r}\ \underline{a}) = a + (\underline{r}\cdot\underline{p})/|\underline{p}| = 0 \tag{55}$$

where a is a "stand-off" distance slightly greater than the range of the interaction potential. The variational rate for the impact parameter surface is

$$R_v(a) = \int_{\phi=0} \rho|\dot{\underline{r}}|\,2\pi b\,db\,d\underline{p}\,d\underline{P}\,d\underline{R} \tag{56}$$

where $b = |\underline{r} \times \underline{p}|/|\underline{p}|$ is the impact parameter, $\underline{p}$ is the relative momentum and $\underline{P}$ and $\underline{R}$ are the momentum and position of the center of mass of the colliding particles. As is well known this rate diverges and convergence of the transition rate $R(U_iU_j)$ is obtained only if the factor $[I(i\ j)/m]$ in equation (50) goes to zero more rapidly than b^{-2} for large values of b. When impact parameter sampling is used the divergence is usually handled by introducing a cutoff on b. This must be done with care, however. If the cut-off is too large the calculations become inefficient; if it is too small an artificial bias may be introduced.

2) CONSTANT ENERGY SAMPLING

For calculations involving thermal dissociation and recombination it is usually far more efficient to sample on the so called "barrier surfaces" [1]. The "barrier surfaces" are surfaces of constant energy lying a fixed distance $-U_o$ below the top of the rotational barrier and are defined by

$$\phi(U\ U_o) = U_o - U = 0,\ r \leq z \tag{57}$$

For short range potentials characteristic of interactions between neutral particles, the variational expressions for the barrier rate

$$R_v(U_o) = \tfrac{1}{2}\int_{U=U_o} \rho|\underline{v}\cdot\underline{\nabla}\phi|\,d\Omega/d\phi \tag{58}$$

is finite. For coulomb interactions $R_v(U_o)$ diverges linearly and a cut-off must be introduced. Even so the calculations are significantly more efficient than those carried out using impact parameter sampling.

IV CONCLUDING REMARKS

At the present time calculations of the type reviewed above are limited in their accuracy primarily by a lack of knowledge of the required threebody potentials necessary to specify the Hamiltonian for the systems. In only one case, that of pure coulomb interactions, is the exact potential known and calculations of dissociation and recombination rates for the system $H^+ + e^- + e^-$ are in reasonably good agreement with experiment [7,8]. There is some question however about the validity of the classical approximation as applied to the electrons in this case. In a second case, that of H + H + H, fairly accurate semiempirical potentials have been developed and calculations of dissociation and recombination rates are again in reasonable agreement with experiment [9]. Unfortunately the experiments in this case are not very accurate and do not cover a very wide range of conditons. In all other cases, it has been necessary to approximate the threebody potentials assuming pairwise superposition in the form

$$V_{ABC} = V_{AB} + V_{AC} + V_{BC} \ . \tag{58}$$

In general the interaction potential V_{AB} for the dissociating or recombining molecules is reasonably well known from spectroscopic data. The interaction potentials V_{AC} and V_{BC} for the third body on the other hand are rather poorly known and must be estimated from emperical correlation rules. Calculations covering a fairly wide range of systems have been made with potentials of the form (58) and once again reasonable agreement with experiment has been found [2,10,11]. In these cases, however, virtually perfect agreement can be achieved by small adjustments of the uncertain potential parameters and this suggests that the theory may provide a useful tool for obtaining at least some insight into the characteristics of threebody potentials.

In summary, it seems reasonable to conclude that the general mathematical description of atomic and molecular excitation and dissociation reviewed in this paper is basically correct. However, the calculations are still rather limited in accuracy and restricted to fairly simple systems. To overcome both of these limitations significant improvements in the analytical and numerical methods for calculating the required transition rates and solving the appropriate master equations are needed.

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