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Generalized Diffusion Theory of Nonequilibrium Reaction Rates

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A simple expansion procedure is used in conjunction with the detailed balancing condition to show that the linear master equation describing the relaxation of an atomic system in a background of inert atoms can be approximated by an equivalent diffusion equation with appropriate boundary conditions. This equation has the form of the ordinary heat-conduction equation for a medium of variable heat capacity and thermal conductivity and is simplier than the commonly used Fokker–Planck equation. It is expected to be a reasonable approximation under conditions where the changes in the constants of the motion are small in a single collision. A similar equation has been derived by Van Kampen who showed that it implies the phenomenological equations of nonequilibrium thermodynamics. However, he did not consider the boundary conditions necessary to deal with chemical reactions or phase changes.

I. INTRODUCTION

IN a previous paper[1] Keck and Carrier showed that the one-dimensional integrodifferential master equation describing the vibrational relaxation and dissociation of a molecule in a background of inert atoms could be approximated by an equivalent one-dimensional diffusion equation with appropriate boundary conditions. In the present paper a similar approach is employed to obtain the corresponding generalized diffusion equation and its boundary conditions. This equation has the form of the ordinary heat-conduction equation for a medium of variable heat capacity and thermal conductivity and is simplier than the Fokker–Planck equation sometimes used to describe chemical reactions.[2]

The reduction of the Fokker–Planck equation to the diffusion equation is based on the symmetry of the transition kernel implied by the detailed balancing condition and has previously been accomplished by Van Kampen[3] using a somewhat more complicated technique. Van Kampen also showed that the diffusion equation could be used to derive the phenomenological equations of nonequilibrium thermodynamics and the Onsager reciprocal relations, but he did not consider the boundary condition necessary to describe chemical reactions or phase changes. The consistent use of the detailed balancing condition to obtain such boundary conditions is the principle new feature of the present work.

II. GENERALIZED DIFFUSION EQUATION

We consider an ensemble of atomic or molecular systems interacting with a background of inert atoms at constant temperature and density. The evolution of such an ensemble as it approaches thermodynamic equilibrium can be described by a master equation of the form

$$\frac{\partial N(\mathbf{x},t)}{\partial t}=\int[K(\mathbf{x},\mathbf{x}')N(\mathbf{x}',t)-K(\mathbf{x}',\mathbf{x})N(\mathbf{x},t)]d\mathbf{x}', \tag{1}$$

where $\mathbf{x}$ is a vector whose components are the constants of motion describing the state of a system between collisions with a background atom, t is the time, $N(\mathbf{x},t)d\mathbf{x}$ is the number of systems in the volume element $d\mathbf{x}$ at $\mathbf{x}$, and $K(\mathbf{x}',\mathbf{x})N(\mathbf{x},t)d\mathbf{x}'d\mathbf{x}$ is the rate of collision-induced transitions from $d\mathbf{x}$ at $\mathbf{x}$ to $d\mathbf{x}'$ at $\mathbf{x}'$.

Following Keck and Carrier we first introduce the specific distribution

$$X(\mathbf{x},t)\equiv N(\mathbf{x},t)/N_e(\mathbf{x}), \tag{2}$$

which is defined as the ratio of the actual distribution to the equilibrium distribution $N_e(\mathbf{x})$. Substituting (2) into (1) we obtain

$$N_e(\mathbf{x})\,\frac{X(\mathbf{x},t)}{\partial t}=\int R(\mathbf{x}',\mathbf{x})[X(\mathbf{x}',t)-X(\mathbf{x},t)]d\mathbf{x}', \tag{3}$$

where, by detailed balancing,

$$R(\mathbf{x}',\mathbf{x})\equiv K(\mathbf{x}',\mathbf{x})N_e(\mathbf{x})=K(\mathbf{x},\mathbf{x}')N_e(\mathbf{x}')\equiv R(\mathbf{x},\mathbf{x}'). \tag{4}$$

If we assume that the transition kernel $R(\mathbf{x}',\mathbf{x})$ is such that the changes in $\mathbf{x}$ in a single collision are small, then we can anticipate that, sufficiently close to equilibrium, it should be a reasonable approximation to expand $X(\mathbf{x}',t)$ in (3) in a Taylor series about $\mathbf{x}$. This leads to the partial differential equation

$$\begin{aligned}N_e\frac{\partial X}{\partial t}&=\sum_i\langle\Delta_i\rangle_R\frac{\partial X}{\partial x_i}+\tfrac{1}{2}\sum_{ij}\langle\Delta_i\Delta_j\rangle_R\frac{\partial^2 X}{\partial x_i\partial x_j}+\cdots\\&=\langle\mathbf{\Delta}\rangle_R\cdot\nabla X+\tfrac{1}{2}\langle\mathbf{\Delta\Delta}\rangle_R:\nabla\nabla X+\cdots,\end{aligned} \tag{5}$$

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[1] J. Keck and G. Carrier, J. Chem. Phys. **43**, 2284 (1965).

[2] See, e.g., H. A. Kramers, Physica **7**, 284 (1940); H. C. Brinkman *ibid.* **22**, 29, 149 (1956); T. A. Bak and J. L. Lebowitz, Phys. Rev. **131**, 1138 (1963).

[3] N. G. Van Kampen, Physica **23**, 707, 816 (1957).

where $\mathbf{\Delta}=\mathbf{x}'-\mathbf{x}$ is the change of $\mathbf{x}$ in a collision and

$$\langle\phi\rangle_R(\mathbf{x})\equiv\int R(\mathbf{x}',\mathbf{x})\phi d\mathbf{x}'. \tag{6}$$

We now observe that the symmetry of $R(\mathbf{x}',\mathbf{x})$ with respect to interchange of $\mathbf{x}'$ and $\mathbf{x}$ requires

$$R(\mathbf{x}',\mathbf{x})\equiv S(\bar{\mathbf{x}},\mathbf{\Delta})=S(\bar{\mathbf{x}},-\mathbf{\Delta}), \tag{7}$$

where $\bar{\mathbf{x}}=\frac{1}{2}(\mathbf{x}'+\mathbf{x})$ is the mean value of $\mathbf{x}$ for a collision. If we further assume that $S(\bar{\mathbf{x}},\mathbf{\Delta})$ is large only for small values of $\mathbf{\Delta}$ and varies slowly with $\bar{\mathbf{x}}$, then we can expand about $\mathbf{x}$, so that

$$S(\bar{\mathbf{x}},\mathbf{\Delta})=S(\mathbf{x},\mathbf{\Delta})+(\bar{\mathbf{x}}-\mathbf{x})\cdot\nabla S(\mathbf{x},\mathbf{\Delta})+\cdots. \tag{8}$$

Substituting (8) into (6) we obtain

$$\langle\mathbf{\Delta}\rangle_R=\tfrac{1}{2}\nabla\cdot\langle\mathbf{\Delta\Delta}\rangle_R+\cdots. \tag{9}$$

This approximate relation between the first and second moments of the transition kernel $R(\mathbf{x}',\mathbf{x})$ permits us to reduce (5) to the equivalent diffusion equation

$$N_e(\partial X/\partial t)=\tfrac{1}{2}\nabla\cdot\langle\mathbf{\Delta\Delta}\rangle_R\nabla X+\cdots. \tag{10}$$

Equation (10) has the form of the generalized heat-conduction equation with variable conductivity and specific heat and is equivalent to the result obtained by Van Kampen. It may be noted that the analogy with heat flow can be quite helpful for obtaining a physical insight into the character of the nonequilibrium distribution occurring during a reaction.

The diffusion current obtained from (10) is

$$\mathbf{j}=-\tfrac{1}{2}\langle\mathbf{\Delta\Delta}\rangle_R\nabla X, \tag{11}$$

which has the form of the phenomenological equation of nonequilibrium thermodynamics.[3] Equation (11) is a direct result of the expansion procedure and the symmetry of the kernel $R(\mathbf{x}',\mathbf{x})$ which follows from detailed balancing. The Onsager reciprocal relations for this case are automatically satisfied by the symmetry of the conductivity tensor $\langle\mathbf{\Delta\Delta}\rangle$.

III. BOUNDARY EQUATIONS

In developing the above diffusion equation, we have tacitly assumed that $R(\mathbf{x}',\mathbf{x})$ was continuous for all values of $\mathbf{x}$ and $\mathbf{x}'$. In general, this will not be the case and $R(\mathbf{x}',\mathbf{x})$ will be continuous in finite domains bounded by reflecting or absorbing barriers or surfaces across which a phase change occurs. To obtain the boundary conditions at such surfaces, we equate the diffusion current toward the surface given by (11) to the current across the surface obtained from the integral equation (3). For an element of area δA at a point $\mathbf{a}$ on the surface, this leads to the condition

$$-\tfrac{1}{2}\mathbf{n}\cdot\langle\mathbf{\Delta\Delta}\rangle_R(\mathbf{a}^-)\nabla X(\mathbf{a}^-,t)\delta A$$
$$=\int_{\delta V}\int_{\delta V'}R(\mathbf{x}',\mathbf{x})[X(\mathbf{x},t)-X(\mathbf{x}',t)]d\mathbf{x}'d\mathbf{x}, \tag{12}$$

where $\mathbf{n}$ is the unit outward normal to δA, $\mathbf{a}^-$ is a point just inside the surface at $\mathbf{a}$, and the volume elements δV and $\delta V'$ are determined by δA and the conditions $\mathbf{n}\cdot(\mathbf{x}-\mathbf{a})\leq 0$ and $\mathbf{n}\cdot(\mathbf{x}'-\mathbf{a})\geq 0$ which imply that a system has crossed the surface in the neighborhood of $\mathbf{a}$. Substituting (7) into (12) and noting that the Jacobian of the transformation $(\mathbf{x}',\mathbf{x})$ to $(\bar{\mathbf{x}},\mathbf{\Delta})$ is unity, we find

$$-\tfrac{1}{2}\mathbf{n}\cdot\langle\mathbf{\Delta\Delta}\rangle_R(\mathbf{a}^-)\nabla X(\mathbf{a}^-,t)\delta A$$
$$=\int_{\delta V}\int_{\delta V'}S(\bar{\mathbf{x}},\mathbf{\Delta})[X(\mathbf{x},t)-X(\mathbf{x}',t)]d\bar{\mathbf{x}}d\mathbf{\Delta}. \tag{13}$$

We now assume that the discontinuities in $S(\bar{\mathbf{x}},\mathbf{\Delta})$ are confined to the boundaries of the domain of integration in (13) and that in the interior $S(\bar{\mathbf{x}},\mathbf{\Delta})$ varies sufficiently slowly with $\bar{\mathbf{x}}$ so that we can expand about $\mathbf{a}$. Thus

$$S(\bar{\mathbf{x}},\mathbf{\Delta})=S(\mathbf{a},\mathbf{\Delta})+(\bar{\mathbf{x}}-\mathbf{a})\cdot\nabla S(\mathbf{a},\mathbf{\Delta})+\cdots. \tag{14}$$

We further assume that sufficiently close to equilibrium we can expand the specific distributions about points $\mathbf{a}^-$ and $\mathbf{a}^+$ just inside and outside the surface at $\mathbf{a}$ so that

$$X(\mathbf{x}',t)=X(\mathbf{a}^+,t)+(\mathbf{x}'-\mathbf{a}^+)\cdot\nabla X(\mathbf{a}^+,t)+\cdots \tag{15a}$$

and

$$X(\mathbf{x},t)=X(\mathbf{a}^-,t)+(\mathbf{x}-\mathbf{a}^-)\cdot\nabla X(\mathbf{a}^-,t)+\cdots. \tag{15b}$$

Substituting (14) and (15) into (13) and integrating over $\bar{\mathbf{x}}$, we obtain, to terms of order ∇X,

$$-\tfrac{1}{2}\mathbf{n}\cdot\langle\mathbf{\Delta\Delta}\rangle_R(\mathbf{a}^-)\nabla X(\mathbf{a}^-,t)$$
$$\approx\tfrac{1}{2}\langle|\,\mathbf{n}\cdot\mathbf{\Delta}\,|\rangle_S(\mathbf{a})[X(\mathbf{a}^-,t)-X(\mathbf{a}^+,t)]$$
$$+\tfrac{1}{4}\mathbf{n}\cdot\langle\mathbf{\Delta\Delta}\rangle_S(\mathbf{a})[\nabla X(\mathbf{a}^-,t)-\nabla X(\mathbf{a}^+,t)], \tag{16}$$

where

$$\langle\phi\rangle_S(\mathbf{a})=\int S(\mathbf{a},\mathbf{\Delta})\phi d\mathbf{\Delta}. \tag{17}$$

For a reflecting barrier at $\mathbf{a}$, $S(\mathbf{a},\mathbf{\Delta})=0$ and the boundary condition (16) becomes simply

$$n\cdot\langle\mathbf{\Delta\Delta}\rangle_R(\mathbf{a}^-,t)\nabla X(\mathbf{a}^-,t)=0. \tag{18}$$

For an absorbing barrier across which $R(\mathbf{x}',\mathbf{a}^-)$ is continuous, $X(\mathbf{a}^+,t)=\nabla X(\mathbf{a}^+,t)=0$ and $\langle\phi\rangle_R(\mathbf{a}^-)\approx\langle\phi\rangle_S(\mathbf{a})$, so that (16) becomes

$$-\tfrac{1}{2}\mathbf{n}\cdot\langle\mathbf{\Delta\Delta}\rangle_R(\mathbf{a}^-)\nabla X(\mathbf{a}^-,t)=\langle|\,\mathbf{n}\cdot\mathbf{\Delta}\,|\rangle_R(\mathbf{a}^-)X(\mathbf{a}^-,t). \tag{19}$$

This would be the appropriate boundary condition for diatomic molecules dissociating under conditions where the atom concentration $\mathrm{A}(t)=0$. A more realistic boundary condition for this case, which is also applicable when $\mathrm{A}(t)\neq 0$, can be obtained by assuming that $\langle\mathbf{\Delta\Delta}\rangle_R(\mathbf{a}^+)$ is essentially infinite due to the very fast relaxation rate of the translational degrees of freedom of the atoms. This implies that $\nabla X(\mathbf{a}^+, t)=0$ and $X(\mathbf{a}^+, t)=[A(t)/A_e]^2$, so that (16) becomes

$$-\tfrac{1}{2}\mathbf{n}\cdot\langle\boldsymbol{\Delta\Delta}\rangle_R(\mathbf{a}^-)\nabla X(\mathbf{a}^-, t) = \langle|\,\mathbf{n}\cdot\boldsymbol{\Delta}\,|\rangle_R(\mathbf{a}^-)\{X(\mathbf{a}^-, t)-[A(t)/A_e]^2\}. \quad (20)$$

In the one-dimensional case, (20) reduces to the boundary condition used by Keck and Carrier.

IV. REMARKS

It is difficult to give a rigorous mathematical justification of the truncation procedures used in the derivation of the diffusion equation (10) and its boundary condition (16) from the integrodifferential master equation (1). The validity of the approach depends both on the properties of the transition kernel $R(\mathbf{x}', \mathbf{x})$ and the character of the problem under investigation. In general, however, it is anticipated that the diffusion theory should be a reasonable approximation for describing the approach to equilibrium of systems for which the changes in a single collision are small. In particular applications it should be possible to obtain some idea of the validity of the theory by estimating the magnitude of the terms which have been neglected and by comparison with experiments. For a more detailed discussion of the mathematical aspects of this problem, the reader is referred to Van Kampen.[4]

An important advantage of the diffusion equation over the master equation is that the moments of the kernel $R(\mathbf{x}', \mathbf{x})$ are in general very much more accessible than the kernel itself. It is anticipated that, in certain simple cases, analytic expressions for the moments can be obtained. In more complicated cases, statistical or numerical methods can be employed. All these approaches are currently being investigated in connection with a variety of rate processes and will be reported later.

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[4] N. G. Van Kampen, *Fluctuation Phenomena in Solids* (Academic Press Inc., New York, 1965), p. 139.

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Acetylene–Oxygen Reaction in Shock Waves. Origin of CO_2

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The ir emissions from CO and CO_2, formed in the C_2H_2–O_2 reaction in a shock tube, have been observed as a function of time. By calibrating these emissions in terms of concentrations and by comparing them with the emission of CH* ($A\ {}^2\Delta\rightarrow X\ {}^2\pi$), produced in the same reaction, it has been possible to confirm that CO_2 is formed in the early stages by a reaction other than $CO+OH\rightarrow CO_2+H$. This reaction involves a primary carbon-containing radical and an O_2 molecule, and its rate at 1800°K is 5% of the rate of formation of CO, produced by a similar reaction.

The importance of the reaction $CO+OH\rightarrow CO_2+H$ in the later stages of oxidation has been examined as a function of the initial O_2/C_2H_2 ratio, and the growth of OH concentration during the reaction elucidated.

More decisive proof is given that CH* is produced by a reaction which is second order in reaction intermediates.

INTRODUCTION

The production of CO_2 from the oxidation of acetylene has been ascribed generally to the reaction

$$CO+OH\rightarrow CO_2+H. \quad (1)$$

This is known[1] to be a fast reaction and to occur in hydrocarbon oxidations.

Glass *et al.*[2] presented controversial evidence that this reaction could not account for the appearance of CO_2 in the initial stages of the C_2H_2–O_2 reaction. Their conclusions depended on a comparison of the time constants of exponential rise for CO and CO_2 and were not completely convincing since the statistical scatter of the mass spectra was large and the actual values of the time constants were much greater than would be expected.

The known rate of Reaction (1), together with a determined rate of production of CO_2 and the concentration of CO, has previously been used[3] to calculate the concentration of OH in acetylene flames. If CO_2 were produced to a significant extent by any other reaction, this method would be in error. Furthermore, proposals[2,4] as to the reaction mechanisms leading to the minor products $C_3H_3^+$, CO*, and CH* depend on

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[1] A. A. Westenberg and R. M. Fristrom, Symp. Combust. 10th, Cambridge Univ. 1964, 473 (1965).

[2] G. P. Glass, G. B. Kistiakowsky, J. V. Michael, and H. Niki, J. Chem. Phys. **42**, 608 (1965).

[3] C. P. Fenimore and G. W. Jones, J. Chem. Phys. **39**, 1514 (1963).

[4] J. B. Homer and G. B. Kistiakowsky, J. Chem. Phys. **45**, 1359 (1966).