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Application of Stochastic Theory to Dilute Gas Reactions

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The stochastic approach to chemical kinetics discussed previously is specialized to dilute gas reactions. In this limit the stochastic master equations are Boltzmann equations for which collision theory is used. Internal rearrangement reactions, both in the presence and absence of inert diluent, and bimolecular reactions, in the absence of inert diluent, are discussed in some detail. In the latter case the "reservoir" role must be played by translational and internal degrees of freedom of the reactants (and products) themselves. The rate constants for the reaction can be explicitly calculated in terms of cross sections in both the limit of long-lived (i.e., internally equilibrated) and that of short-lived (decomposing before exchanging energy with other molecules) "activated complexes." It is found that the Arrhenius temperature factors are identical in these two limits. In addition the "frequency" factors are similar but involve slightly different averages (over energy) of the same cross sections.

KEY WORDS: Chemical kinetics; Boltzmann equation; transition state theory; gas phase.

1. INTRODUCTION

In a previous paper⁽¹⁾ (II) we have elaborated the application to chemical reactions of a stochastic approach to multiparticle kinetics illustrated in an

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earlier article$^{(2)}$ (I). In I and II it has been assumed that the rates of change of populations of molecular microstates in a system undergoing a rate process could be described by a stochastic "master equation" in which account is taken not only of reactive events in the "system" of interest but also of the coupled events among those degrees of freedom (serving as "heat bath" or "reservoir") that supply the activation energy required by the reactive transitions. This detailed bookkeeping permitted application of both the law of energy conservation and that of microscopic reversibility to transitions in the system–reservoir combination. With only the further assumption that nonreactive events are much more frequent than reactive ones it was possible to deduce the familiar proposition that a reaction rate depends on the product of a "frequency factor" and the exponential of a "free energy of activation" divided by the absolute temperature. However, the "frequency" factor was intimately related to the dynamics of the reaction and was not given simply by a kinematical factor such as kT/h. Furthermore, a dependence of the frequency factor on an effective "number of states" was identified.

The analysis in I and II did not require the familiar assumption of equilibrium between reactant molecules and "activated complex" or "transition state" species. The physical basis for the appearance in I and II of the exponential dependence on a free energy of activation is entirely different from that associated with the conventional treatment, in which this equilibrium assumption is made.

Even though this equilibrium assumption has often been severely questioned, the transition state theory has been widely used in organic and inorganic chemistry and biochemistry. The alternatives, the so-called "collision theory"$^{(3,4)}$ and "phase space trajectory theory,"$^{(5)}$ have been restricted in their applicability to reactions in dilute gases. Since in the stochastic treatment the degrees of freedom that serve as the "reservoir" are not restricted to nonreacting degrees of freedom of the reacting molecules themselves but may also be those of solvent molecules, and also since the master equation of the stochastic treatment is not obviously restricted to low-density application as is the Boltzmann equation of collision theory, the possibility exists that the stochastic treatment may provide that generalization of collision theory which can encompass reactions in liquids and liquid solution as well as those in gases.

It remains to be shown, however, that the stochastic treatment, or at least one of its cases (that of "short-lived activated complex" in II), does indeed reduce in the low-density limit to conformity with one of the more sophisticated treatments$^{(3,4)}$ of collision theory. To this end we here explore, more fully than in II, the consequences of the stochastic treatment in this limit.

Collision theory has been applied to calculation of the temperature dependence of rate constants for gas-phase chemical reactions by Ross and Mazur⁽³⁾ and Eu and Ross.⁽⁴⁾ Ross and Mazur showed that an energy threshold in the reactive cross section for a molecular gas-phase reaction is sufficient to yield a rate constant for the reaction which depends upon a "free energy of activation" in the familiar exponential fashion. In II this kind of temperature dependence was obtained for arbitrary density, with the condition that the generalized transition probability for the chemical reaction shows an energy threshold. Eu and Ross showed that a sufficient condition for an energy threshold is the formation of a collision complex or resonance during the reaction. It is the relationship among these particular treatments that will be explored here. We shall expand upon the existing collision theory to consider in some detail limiting cases of both "long"- and "short-lived activated complexes" (as defined in II) for a bimolecular gas-phase reaction. In the case of "short-lived" activated complexes the results to be obtained here may be identified, as expected, with those of Ross and Mazur⁽³⁾ and Eu and Ross,⁽⁴⁾ as well as with those of II for this case. In the case of "long-lived" activated complexes the results obtained here are rigorously identified with a low-density form of the corresponding results in I and II.

The advantage of treating the limiting cases of both short- and long-lived activated complexes in more detail than was possible for arbitrary density in II is that we are thus able to compare the rate expressions in the two limits. We shall find that the two expressions are very similar. The consequence of this similarity is that a calculation of the rate coefficient using either assumption as to which limit is applicable should yield an accurate value for the coefficient (regardless of which limit is actually applicable and, indeed, of the possibility that neither one is !).

In II we defined a "long-lived" activated complex as one which persists sufficiently long to suffer collisions adequate to equilibrate the ratio of the populations of its (internal) microstates. We defined a "short-lived" activated complex as one which decomposes to form products (or reform reactants) before undergoing equilibrating collisions. Here we find it convenient to break the latter category into two subcategories. One is an activated complex which really has identifiable microstates (called a collision complex by Eu and Ross⁽⁴⁾) but is nevertheless "short lived." The other is an activated complex which is not actually an identifiable intermediate in this sense but is defined by the existence of an energy threshold in the cross section for the reaction (a consequence of a potential barrier which, in this case, would not possess even a shallow minimum in the neighborhood of maxima).

In Section 2 we consider an isomerization reaction in the gas phase both in the presence of inert diluent (serving as reservoir) and in the absence of inert diluent (when other degrees of freedom of reactants and products play the reservoir role). We consider there only the case of "long-lived" activated complex. We shall see that the results of our earlier treatments (in I and II) for this case are rigorous in the low-density limit. We shall also see that the possibility, noted earlier, of a dependence of the frequency factor on an "effective number of states" applies only to those of internal (as opposed to translational) degrees of freedom. This result is easily seen to be general in the low-density limit and can be assumed for the cases treated in Sections 3 and 4, although it is not explicitly stated there. In Section 3 we discuss bimolecular reactions in the low-density limit for the case in which the activated complex appears only via a threshold in the reaction cross section. There we make contact with the results of Ross and Mazur.(3) In Section 4 we consider bimolecular reactions in cases where "microstates" of the activated complex can be identified and compare there the cases of long- and short-lived activated complexes. This comparison, though confined here to the low-density limit, sheds some light on the differences between these cases in condensed media as well.

2. ISOMERIZATION REACTION IN THE GAS PHASE

Here we discuss the low-density limit, where all but binary collision events can be ignored, for the isomerization process discussed in I,

$$\mathrm{A} + \mathrm{R} \rightleftarrows B + R \rightleftarrows C + R \tag{1}$$

which occurs in the presence of inert diluent.

For sufficiently low densities it is well known that the rate of change of the phase space distribution for A molecules is governed by a Boltzmann equation[3]

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_A}{m_A}\cdot\nabla\right) f_a(\mathbf{r}\mathbf{p}_A t) = E_a(\mathbf{r}\mathbf{p}_A t) + R_a(\mathbf{r}\mathbf{p}_A t) \tag{2}$$

in which $f_a(\mathbf{r}\mathbf{p}_A t)$ is the density in phase space of molecules of species A in internal state a at position $\mathbf{r}$ with momentum $\mathbf{p}_A$ at time t. Here $E_a(\mathbf{r}\mathbf{p}_A t)$ and $R_a(\mathbf{r}\mathbf{p}_A t)$ represent the change in f due to nonreactive and reactive collisions, respectively. In particular

$$\begin{aligned} E_a(\mathbf{r}\mathbf{p}_\mathrm{A} t) = {} & -\sum_{rr'a'} \int d\mathbf{p}_\mathrm{A}'\, d\mathbf{p}_\mathrm{R}\, d\mathbf{p}_\mathrm{R}'\, \frac{1}{\mu^2}\, \sigma_{NR}(a\mathbf{p}_\mathrm{A} r\mathbf{p}_\mathrm{R} | a'\mathbf{p}_\mathrm{A}' r'\mathbf{p}_\mathrm{R}') \\ & \times [f_r(\mathbf{r}\mathbf{p}_\mathrm{R} t) f_a(\mathbf{r}\mathbf{p}_\mathrm{A} t) - f_{r'}(\mathbf{r}\mathbf{p}_\mathrm{R}' t) f_{a'}(\mathbf{r}\mathbf{p}_\mathrm{A}' t)] \\ & \times \delta(\mathbf{p}_\mathrm{A} + \mathbf{p}_\mathrm{R} - \mathbf{p}_\mathrm{A}' - \mathbf{p}_\mathrm{R}')\, \delta(E_a(\mathbf{p}_\mathrm{A}) + E_r(\mathbf{p}_\mathrm{R}) \\ & - E_a(\mathbf{p}_\mathrm{A}') - E_{r'}(\mathbf{p}_\mathrm{R}')) \end{aligned} \tag{3}$$

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[3] See Ref. 3 and the references therein.

and

$$
\begin{aligned}
R_a(\mathbf{r}\mathbf{p}_{\mathrm{A}}t) = -\sum_{rr'b}\int & d\mathbf{p}_{\mathrm{B}}\, d\mathbf{p}_{\mathrm{R}}\, d\mathbf{p}_{\mathrm{R}}'\, \frac{1}{\mu^2}\, \sigma_{\mathrm{R}}(a\mathbf{p}_{\mathrm{A}}r'\mathbf{p}_{\mathrm{R}}'|b\mathbf{p}_{\mathrm{B}}r\mathbf{p}_{\mathrm{R}}) \\
& \times [f_{r'}(\mathbf{r}\mathbf{p}_{\mathrm{R}}'t)f_a(\mathbf{r}\mathbf{p}_{\mathrm{A}}t) - f_r(\mathbf{r}\mathbf{p}_{\mathrm{R}}t)f_b(\mathbf{r}\mathbf{p}_{\mathrm{B}}t)] \\
& \times \delta(\mathbf{p}_{\mathrm{A}} + \mathbf{p}_{\mathrm{R}}' - \mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{R}})\, \delta(E_a(\mathbf{p}_{\mathrm{A}}) + E_{r'}(\mathbf{p}_{\mathrm{R}}') \\
& - E_b(\mathbf{p}_{\mathrm{B}}) - E_r(\mathbf{p}_{\mathrm{R}}))
\end{aligned}
\tag{4}
$$

where f_r and f_b are defined similarly to f_a; σ_{NR} and σ_R are, respectively, the nonreacting and reacting differential cross sections for the indicated processes; and μ is the effective mass of a colliding (A–R or B–R) pair

$$(1/\mu = 1/m_{\mathrm{A}} + 1/m_{\mathrm{R}} = 1/m_{\mathrm{B}} + 1/m_{\mathrm{R}}).$$

The single-particle energies are assumed to be of the form

$$E_x(\mathbf{p}_{\mathrm{X}}) = (p_{\mathrm{X}}^2/2m_{\mathrm{X}}) + \epsilon_x \tag{5}$$

where X $=$ A, B, R (later also C) and $x = a, b, r$ (later c), and ϵ_x is an internal energy.

Clearly $f_b(\mathbf{r}, \mathbf{p}_{\mathrm{B}}, t)$ and $f_c(\mathbf{r}, \mathbf{p}_{\mathrm{C}}, t)$ (similarly defined) satisfy equations similar to (2).

For the purpose of discussing homogeneous chemical reactions in the gas phase it is sufficient to seek a solution which is spatially uniform.[4] Thus we can assume that

$$f_x(\mathbf{r}\mathbf{p}_{\mathrm{X}}t) \equiv f_x(\mathbf{p}_{\mathrm{X}}t) \tag{6}$$

The (time-varying) density of the Xth species is related to f_x by

$$n_{\mathrm{X}}(t) = \sum_x \int d\mathbf{p}_{\mathrm{X}} f_x(\mathbf{p}_{\mathrm{X}}t) \tag{7}$$

To obtain the analog of (5) of II for this case we can sum (2) over a and integrate over $\mathbf{p}_{\mathrm{A}}$ to obtain

$$
\begin{aligned}
q_{\mathrm{AB}}(t) = -\frac{dn_{\mathrm{A}}(t)}{dt} = \sum_{\substack{a,b\\ r,r'}} \int & d\mathbf{p}_{\mathrm{A}}\, d\mathbf{p}_{\mathrm{B}}\, d\mathbf{p}_{\mathrm{R}}\, d\mathbf{p}_{\mathrm{R}}' \\
& \times \frac{1}{\mu^2}\, \sigma_{\mathrm{R}}(a\mathbf{p}_{\mathrm{A}}r'\mathbf{p}_{\mathrm{R}}'|b\mathbf{p}_{\mathrm{B}}r\mathbf{p}_{\mathrm{R}})[f_a(\mathbf{p}_{\mathrm{A}}t)f_{r'}(\mathbf{p}_{\mathrm{R}}'t) \\
& - f_b(\mathbf{p}_{\mathrm{B}}t)f_r(\mathbf{p}_{\mathrm{R}}t)]\, \delta(\mathbf{p}_{\mathrm{A}} + \mathbf{p}_{\mathrm{R}}' - \mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{R}}) \\
& \times \delta(E_a(\mathbf{p}_{\mathrm{A}}) + E_{r'}(\mathbf{p}_{\mathrm{R}}') - E_b(\mathbf{p}_{\mathrm{B}}) - E_r(\mathbf{p}_{\mathrm{R}}))
\end{aligned}
\tag{8}
$$

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[4] This assumption is certainly valid for the discussion of ordinary chemical reactions. However, when light scattering experiments from reacting mixtures are being discussed, it is necessary to keep the spatial dependence of F. See, for example, Simons.(6)

The dependence on σ_{NR} drops out because the total number of A's $[\sim n_{\mathrm{A}}(t)V$, where V is the volume$]$ is conserved by σ_{NR}.

Equation (8) is of the form of the "master equation" of II,

$$q_{\mathrm{AB}}(t) = \sum_{\substack{\{a\mathbf{p}_{\mathrm{A}}\}\{b\mathbf{p}_{\mathrm{B}}\}\\ \{r\mathbf{p}_{\mathrm{R}}\}\{r'\mathbf{p}_{\mathrm{R}}'\}}} W(a\mathbf{p}_{\mathrm{A}}r'\mathbf{p}_{\mathrm{R}}'|b\mathbf{p}_{\mathrm{B}}r\mathbf{p}_{\mathrm{R}})[\bar{n}_a(\mathbf{p}_{\mathrm{A}}t)\bar{n}_r(\mathbf{p}_{\mathrm{R}}t) - \bar{n}_b(\mathbf{p}_{\mathrm{B}}t)\bar{n}_{r'}(\mathbf{p}_{\mathrm{R}}'t)] \tag{9}$$

if we make the identifications[5]

$$\sum_{\{x\mathbf{p}_{\mathrm{X}}\}} = \sum_{x} \int \frac{d\mathbf{p}_{\mathrm{X}}\lambda_{\mathrm{X}}^3}{h^3}$$

$$\bar{n}_x(\mathbf{p}_{\mathrm{X}}t) = h^3 f_x(\mathbf{p}_{\mathrm{X}}t), \qquad x = a, b, c, r, \quad \mathrm{X} = \mathrm{A, B, C, R}$$

and

$$\begin{aligned} W(a\mathbf{p}_{\mathrm{A}}r'\mathbf{p}_{\mathrm{R}}'|b\mathbf{p}_{\mathrm{B}}r\mathbf{p}_{\mathrm{R}}) = h^6\, & \frac{\sigma_{\mathrm{R}}(a\mathbf{p}_{\mathrm{A}}r'\mathbf{p}_{\mathrm{R}}'|b\mathbf{p}_{\mathrm{B}}r\mathbf{p}_{\mathrm{R}})}{\mu^2\lambda_{\mathrm{A}}^3\lambda_{\mathrm{R}}^6\lambda_{\mathrm{B}}^3} \\ & \times \delta(\mathbf{p}_{\mathrm{A}} + \mathbf{p}_{\mathrm{R}}' - \mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{R}}) \\ & \times \delta(E_a(\mathbf{p}_{\mathrm{A}}) + E_{r'}(\mathbf{p}_{\mathrm{R}}') - E_b(\mathbf{p}_{\mathrm{B}}) - E_r(\mathbf{p}_{\mathrm{R}})) \end{aligned}$$

Here $\lambda_{\mathrm{X}} = (h^2\beta/2\pi m_{\mathrm{X}})^{1/2}$ (X = A, B, C, R) is the thermal wavelength of the Xth species (h and β have their usual meanings).

The density of molecules of species X in internal state x having momentum $\mathbf{p}_{\mathrm{X}}$ is related to $\bar{n}_x$ by

$$n_x(\mathbf{p}_{\mathrm{X}}t) = \frac{\bar{n}_x(\mathbf{p}_{\mathrm{X}}t)}{\lambda_{\mathrm{X}}^3} = \left(\frac{h}{\lambda_{\mathrm{X}}}\right)^3 f_x(\mathbf{p}_{\mathrm{X}}t) \tag{10}$$

Thus in this limit we identify $\gamma_{\mathrm{X}} = \lambda_{\mathrm{X}}^3$.

For this case the internal equilibrium assumption (8) of II takes the form

$$\begin{aligned} f_x(\mathbf{p}_{\mathrm{X}}t) &= n_{\mathrm{X}}(t)\left(\frac{\lambda_{\mathrm{X}}}{h}\right)^3 \exp\left[-\beta\left(\frac{\mathbf{p}_{\mathrm{X}}^2}{2m_{\mathrm{X}}} + \epsilon_x - f_{\mathrm{X}}\right)\right] \\ &\equiv n_{\mathrm{X}}(t)P_x(\mathbf{p}_{\mathrm{X}}). \end{aligned} \tag{11}$$

where

$$\exp(-\beta f_{\mathrm{X}}) = \sum_x \exp(-\beta\epsilon_x)$$

is the internal partition function. We expect (11) to be valid when reactive collisions are infrequent relative to nonreactive collisions,[6] i.e., $\sigma_{NR} \gg \sigma_R$.

[5] This differs from the choice of summation index for momentum states, which is $\sum'_{\mathbf{p}_{\mathrm{X}}} = (V/h^3)\, d\mathbf{p}_{\mathrm{X}}$. This measure is obtained, for example, when the molecules are confined to a "spherical" box of volume V. We chose instead to employ the thermal wavelength λ_{X} (cubed) to make the momentum summation dimensionless. The advantage of this is that the transition probabilities are intensive. Otherwise they would contain factors $1/V^4$.

[6] This has been shown to be true by explicit expansion of the exact solution of a certain model kinetic equation in powers of σ_R/σ_{NR} in Ref. 6.

When (11) is substituted into (8) and the energy conservation implied by the δ function is observed, we obtain, as in I and II,

$$q_{\mathrm{AB}}(t) = \bar{n}_{\mathrm{R}} W_{\mathrm{AB}}^{1}\{\bar{n}_{\mathrm{A}}(t) \exp[-\beta(f_{\mathrm{B}} - f_{\mathrm{A}})] - \bar{n}_{\mathrm{B}}(t)\} \tag{12}$$

where

$$\begin{aligned} W_{\mathrm{AB}} &= \sum_{\substack{ab\\rr'}} \int \frac{d\mathbf{p}_{\mathrm{A}}\, d\mathbf{p}_{\mathrm{B}}\, d\mathbf{p}_{\mathrm{R}}\, d\mathbf{p}_{\mathrm{R}}'}{\lambda_{\mathrm{B}}{}^{3}\lambda_{\mathrm{R}}{}^{3}} \frac{1}{\mu^{2}}\, \sigma_{\mathrm{R}}(a\mathbf{p}_{\mathrm{A}} r' \mathbf{p}_{\mathrm{R}}' | b\mathbf{p}_{\mathrm{B}} r\mathbf{p}_{\mathrm{R}}) Pb(\mathbf{p}_{\mathrm{B}}) P_{r}(\mathbf{p}_{\mathrm{R}}) \\ &\quad \times\ \delta(\mathbf{p}_{\mathrm{A}} + \mathbf{p}_{\mathrm{R}}' - \mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{R}}) \\ &\quad \times\ \delta(E_{a}(\mathbf{p}_{\mathrm{A}}) + E_{r'}(\mathbf{p}_{\mathrm{R}}') - E_{b}(\mathbf{p}_{\mathrm{B}}) - E_{r}(\mathbf{p}_{\mathrm{R}})) \\ &= \sum_{\substack{ab\\rr'}} \int \frac{d\Omega_{\mathrm{AR}}\, d\mathbf{p}_{\mathrm{B}}\, d\mathbf{p}_{\mathrm{R}}}{\lambda_{\mathrm{B}}{}^{3}\lambda_{\mathrm{R}}{}^{3}}\, v_{ar'br}(\mathbf{p}_{\mathrm{B}}\mathbf{p}_{\mathrm{R}}) \\ &\quad \times\ \sigma_{\mathrm{R}}(a\mathbf{p}_{\mathrm{A}} r' \mathbf{p}_{\mathrm{B}} + \mathbf{p}_{\mathrm{R}}' - \mathbf{p}_{\mathrm{A}} | b\mathbf{p}_{\mathrm{B}} r\mathbf{p}_{\mathrm{R}}) P_{b}(\mathbf{p}_{\mathrm{B}}) P_{r}(\mathbf{p}_{\mathrm{R}}) \end{aligned}$$

and

$$\bar{n}_{\mathrm{X}}(t) = \lambda_{\mathrm{X}}{}^{3} n_{\mathrm{X}}(t)$$

$\int d\Omega_{\mathrm{AR}}$ denotes integration over the initial (A–R) relative solid angle and

$$v_{ar'br}(\mathbf{p}_{\mathrm{B}}\mathbf{p}_{\mathrm{R}}) = |\mathbf{v}_{\mathrm{A}} - \mathbf{v}_{\mathrm{R}}| = \frac{1}{\mu}\left[\left(\frac{\mu}{m_{\mathrm{B}}}\mathbf{p}_{\mathrm{B}} - \frac{\mu}{m_{\mathrm{R}}}\mathbf{p}_{\mathrm{R}}\right)^{2} + 2\mu(\epsilon_{a} + \epsilon_{r'} - \epsilon_{b} - \epsilon_{r}\right]^{1/2} \tag{13}$$

is the relative speed of the colliding A and R molecules. We have assumed, as in Section 2 of II, that the reservoir concentration is constant.

Thus we have, in (12), the manifestation at low densities of the "free energy of activation" for the processes of "climbing" to B previously obtained in I and II.

The expression for W_{AB}^{1} also allows us to make an identification of the "number-of-states" dependence of W_{AB}^{1}. We see that W_{AB}^{1} can be expressed as

$$W_{\mathrm{AB}}^{1} = \sum_{a,r} \int d\Omega_{\mathrm{A}}\, W_{ar}(\Omega_{\mathrm{AR}}) \tag{14}$$

where

$$\begin{aligned} W_{ar}(\Omega_{\mathrm{AR}}) &= \sum_{r',b} \int \frac{d\mathbf{p}_{\mathrm{B}}\, d\mathbf{p}_{\mathrm{R}}}{\lambda_{\mathrm{B}}{}^{3}\lambda_{\mathrm{R}}{}^{3}}\, v_{ar'br'}(\mathbf{p}_{\mathrm{B}}\mathbf{p}_{\mathrm{R}}) \\ &\quad \times\ \sigma(a\mathbf{p}_{\mathrm{A}} r\mathbf{p}_{\mathrm{B}} + \mathbf{p}_{\mathrm{R}} - \mathbf{p}_{\mathrm{A}} | b\mathbf{p}_{\mathrm{B}} r\mathbf{p}_{\mathrm{R}}) P_{b}(\mathbf{p}_{\mathrm{B}}) P_{r}(\mathbf{p}_{\mathrm{R}}) \end{aligned}$$

in which $\mathbf{p}_{\mathrm{A}}$ is chosen to be consistent with energy conservation (i.e., only its angle can be independently specified). We see that the contribution of the translational degrees of freedom is a trivial one, arising only through the dependence on the relative solid angle of the velocities of the molecules A and R.

By the procedures outlined in II, we can write W_{AB}^1 in the form

$$W_{\mathrm{AB}}^1 = 4\pi\omega_{\mathrm{AR}}\overline{W}_{\mathrm{AB}}^1 \tag{15}$$

where

$$\omega_{\mathrm{AR}} = \frac{\delta\epsilon_{\mathrm{AR}}^W}{\delta\epsilon_{\mathrm{AR}}(T_W)} \exp \frac{S_{\mathrm{A}}(T_W) + S_{\mathrm{R}}(T_W)}{k} \tag{16}$$

T_W is defined by

$$\epsilon_{\mathrm{AR}}(T_W) \equiv \sum_{a,r} (\epsilon_a + \epsilon_r) P_a(T_W) P_r(T_W) = \sum_{a,r} (\epsilon_a + \epsilon_r) w_{ar} \tag{17}$$

where

$$P_x(T) = \int d\mathbf{p}_{\mathrm{X}}\, P_x(\mathbf{p}_{\mathrm{X}})|_{\beta = 1/kT}$$

and

$$w_{ar} = \left[\int d\Omega_{\mathrm{AR}}\; W_{ar}(\Omega_{\mathrm{AR}})\right] / W_{\mathrm{AB}}^1$$

The variances $\delta\epsilon_{\mathrm{AR}}^W$ and $\delta\epsilon_{\mathrm{AR}}(T)$ are defined by

$$[\delta\epsilon_{\mathrm{AR}}^W]^2 = \sum_{a,r} [\epsilon_a + \epsilon_r - \epsilon_{\mathrm{AR}}(T_W)]^2 w_{a,r} \tag{18a}$$

and

$$[\delta\epsilon_{\mathrm{AR}}(T)^2] = \sum_{a,r} [\epsilon_a + \epsilon_r - \epsilon_{\mathrm{AR}}(T)]^2 P_a(T) P_r(T) \tag{18b}$$

We note in (15) that only the trivial factor 4π appears as the contribution of the translational degrees of freedom. Since the kinetic energies are independent of solid angle, only the internal states contribute to the definition of T_W. This is consistent with the idea that a chemical reaction primarily involves the internal degrees of freedom of the reacting molecules.

We also note that W_{AB}^1 is of the suggestive form

$$W_{\mathrm{AB}}^1 = (1/\lambda_{\mathrm{B}}^3) \sum_a \int d\Omega_{\mathrm{AR}}\; \bar{v}\sigma_a(\Omega_{\mathrm{AR}}) \tag{19}$$

where

$$\sigma_a(\Omega_{\mathrm{AR}}) = \sum_{b,r,r'} \int d\mathbf{p}_{\mathrm{B}}\, d\mathbf{p}_{\mathrm{R}}{}'\, \frac{v_{ar'br}(\mathbf{p}_{\mathrm{B}}\mathbf{p}_{\mathrm{R}})}{\bar{v}}$$
$$\times\; \sigma_{\mathrm{R}}(ap_{\mathrm{A}}r'\mathbf{p}_{\mathrm{A}} + \mathbf{p}_{\mathrm{R}}{}' - \mathbf{p}_{\mathrm{B}}|b\mathbf{p}_{\mathrm{B}}r\mathbf{p}_{\mathrm{R}}) P_b(\mathbf{p}_{\mathrm{B}}) P_r(\mathbf{p}_{\mathrm{R}})$$

and where

$$\bar{v} = (3/2\beta\mu)^{1/2}$$

is the rms Maxwellian relative speed. In terms of (19) it is convenient to write (12) in a form reminiscent of kinetic theory,

$$q_{\mathrm{AB}}(t) = n_{\mathrm{R}}\sigma_{\mathrm{AB}}\bar{v}\{n_{\mathrm{A}}(t)\exp[-\beta(f_{\mathrm{B}}-f_{\mathrm{A}})] - n_{\mathrm{B}}(t)\} \tag{20}$$

where

$$\sigma_{\mathrm{AB}} = \sum_{a} \int d\Omega_{\mathrm{AR}}\, \sigma_a(\Omega_{\mathrm{AR}})$$

and where we have used $\lambda_{\mathrm{B}} = \lambda_{\mathrm{A}}$.

The elimination of B can be accomplished, as in I and II, via a steady-state assumption. This yields the rate equation for the overall reaction,

$$\begin{aligned} q(t) &= q_{\mathrm{AB}}(t) = -q_{\mathrm{CB}}(t) \\ &= n_{\mathrm{R}}\bar{v}\, \frac{\sigma_{\mathrm{AB}}\sigma_{\mathrm{CB}}}{\sigma_{\mathrm{AB}}+\sigma_{\mathrm{CB}}} \\ &\qquad \times \{n_{\mathrm{A}}(t)\exp[-\beta(f_{\mathrm{B}}-f_{\mathrm{A}})] - n_{\mathrm{C}}(t)\exp[-\beta(f_{\mathrm{B}}-f_{\mathrm{C}})]\} \end{aligned} \tag{21}$$

where σ_{CB} is defined analogously to σ_{AB}.

It is interesting to consider the case in which there is no inert species present so that reactants themselves must play the role of reservoir. Thus we consider in the low-density limit the internal rearrangement reaction

$$\mathrm{A} + \mathrm{X} \rightleftarrows \mathrm{B} + \mathrm{X} \rightleftarrows \mathrm{C} + \mathrm{X}, \qquad \mathrm{X} = \mathrm{A}, \mathrm{C} \tag{22}$$

By an analysis similar to the above we can show that

$$q_{\mathrm{AB}}(t) = -\frac{dn_{\mathrm{A}}(t)}{dt} = \bar{v} \sum_{\mathrm{X}=\mathrm{A},\mathrm{C}} \sigma_{\mathrm{AB}}^{\mathrm{X}} n_{\mathrm{X}}(t)\{n_{\mathrm{A}}(t)\exp[-\beta(f_{\mathrm{B}}-f_{\mathrm{A}})] - n_{\mathrm{B}}(t)\}$$

where

$$\begin{aligned} \sigma_{\mathrm{AB}}^{\mathrm{X}} &= \sum_{\substack{a,b\\ x,x'}} \int d\Omega_{\mathrm{AX}}\, d\mathbf{p}_{\mathrm{B}}\, d\mathbf{p}_{\mathrm{X}} \\ &\qquad \times \frac{v_{ax'bx}(\mathbf{p}_{\mathrm{B}}\mathbf{p}_{x})}{\bar{v}}\, \sigma_{\mathrm{R}}(a\mathbf{p}_{\mathrm{A}}x'\mathbf{p}_{\mathrm{X}} + \mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{A}} | b\mathbf{p}_{\mathrm{B}}x\mathbf{p}_{\mathrm{X}}) P_b(\mathbf{p}_{\mathrm{B}}) P_x(\mathbf{p}_{\mathrm{X}}) \\ &\qquad \mathrm{X} = \mathrm{A}, \mathrm{C} \end{aligned} \tag{23}$$

Elimination of n_{B} via a steady-state approximation yields

$$\begin{aligned} q(t) &= \bar{v}\, \frac{[\sum_{\mathrm{X}=\mathrm{A},\mathrm{C}} \sigma_{\mathrm{AB}}^{\mathrm{X}} n_{\mathrm{X}}(t)][\sum_{\mathrm{X}=\mathrm{A},\mathrm{C}} \sigma^{\mathrm{X}} n_{\mathrm{X}}(t)]}{\sum_{\mathrm{X}=\mathrm{AC},} (\sigma_{\mathrm{AB}}^{\mathrm{X}} + \sigma_{\mathrm{AB}}^{\mathrm{X}}) n_{\mathrm{X}}(t)} \\ &\qquad \times \{n_{\mathrm{A}}(t)\exp[-\beta(f_{\mathrm{B}}-f_{\mathrm{A}})] - n_{\mathrm{C}}(t)\exp[-\beta(f_{\mathrm{B}}-f_{\mathrm{C}})]\} \end{aligned} \tag{24}$$

In the discussion following (16) of II the possibility of a significant time dependence in the average transition probabilities comprising the "frequency factor" was noted for cases in which the reacting species themselves must play the reservoir role. Equation (24) shows this dependence for reaction (22).

3. RELATION TO THE TREATMENT BY ROSS AND MAZUR

In this section we briefly consider the bimolecular reaction

$$A_1 + A_2 \rightleftarrows \mathrm{C}_1 + \mathrm{C}_2 \tag{25}$$

We do not assume that any complex B (i.e., with corresponding microstates) is formed in this reaction. Cases involving both long- and short-lived complexes B will be treated in the next section. Using identifications analagous to those utilized in Section 2 for reaction (25), we readily see that the stochastic equation which describes the rate of (25) reduces in the low-density limit to the Boltzmann equation

$$\begin{aligned} q_{\mathrm{AC}}(t) = -\frac{dn_{\mathrm{A}_1}}{dt} = \sum_{\substack{a_1a_2\\c_1c_2}} \int & d\mathbf{p}_{\mathrm{A}_1}\, d\mathbf{p}_{\mathrm{A}_2}\, d\mathbf{p}_{\mathrm{C}_1}\, d\mathbf{p}_{\mathrm{C}_2} \\ & \times \frac{1}{\mu^2}\, \sigma_{\mathrm{R}}(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{C}_2})[f_{a_1}(\mathbf{p}_{\mathrm{A}_1}t)f_{a_2}(\mathbf{p}_{\mathrm{A}_2}t) \\ & - f_{c_1}(\mathbf{p}_{\mathrm{C}_1}t)f_{c_2}(\mathbf{p}_{\mathrm{C}_2}t)]\, \delta(\mathbf{p}_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2} - \mathbf{p}_{\mathrm{C}_1} - \mathbf{p}_{\mathrm{C}_2}) \\ & \times\, \delta(E_{a_1}(\mathbf{p}_{\mathrm{A}_1}) + E_{a_2}(\mathbf{p}_{\mathrm{A}_2}) - E_{c_1}(\mathbf{p}_{\mathrm{C}_1}) - E_{c_2}(\mathbf{p}_{\mathrm{C}_2})) \end{aligned} \tag{26}$$

Equation (26) is identical (with appropriate identification of labels) with that employed by Ross and Mazur.(3) If σ_{R} is assumed to have a threshold energy for reaction, we obtain their result of rate constants depending exponentially on "free energies of activation" (with preexponentials not necessarily equal to kT/h) by methods identical to theirs [or by the methods employed by us to obtain (24) of II].

4. DETAILED TREATMENT OF BIMOLECULAR REACTION WHEN MICROSTATES OF THE ACTIVATED COMPLEX CAN BE IDENTIFIED

Here we consider in detail the bimolecular reaction discussed in Section 3 of II and show explicitly the close relationship between the limits of "long"- and "short"-lived "activated complexes." We assume that the microscopic dynamics involves events consistent with processes of the form

$$\mathrm{A}_1 + \mathrm{A}_2 \rightleftarrows \mathrm{B} \rightleftarrows \mathrm{C}_1 + \mathrm{C}_2 \tag{27}$$

When B is short-lived, its existence will be manifest theoretically if there is a threshold in the reactive cross sections. This threshold constitutes, in fact, the definition of "short-lived activated complex."

In the low-density limit the widths (inverse lifetimes) of the microstates of A and C are of the first order in the density [because (27) is bimolecular in A and C] and therefore may be made arbitrarily small. However, to the widths of the states of B there must be a contribution which is of zeroth order in the density (since the reaction is unimolecular in B). Since this persists at all densities, even a kinetic equation for low-density behavior must explicitly involve the widths of the states of B. Inclusion of these will permit explicit consideration of the distinction between "long"- and "short"-lived "activated complexes." We have seen in Sections 2 and 3 of II that the Arrhenius temperature dependence appears in the same way regardless of the lifetime of the "activated complex." Here we shall see that the forms of the pre-exponential factors are only slightly different for the two cases.

When the lifetime of the activated complex B cannot be neglected, the rate equations are no longer of the usual Boltzmann type.[7] It can be shown[8] that the rate equation for the species A_1, modified to include the lifetime of B, is

$$\begin{aligned} q_{\mathrm{AB}} &= -\frac{dn_{\mathrm{A}_1}(t)}{dt} = -\frac{dn_{\mathrm{A}_2}(t)}{dt} \\ &= \sum_{a_1 a_2 b} \int \frac{d\mathbf{p}_{\mathrm{A}_1}\, d\mathbf{p}_{\mathrm{A}_2}\, d\mathbf{p}_{\mathrm{B}}\, d\omega_{\mathrm{B}}}{2\pi\bar{\lambda}^3} \frac{1}{\mu^2}\, \sigma(a_1\mathbf{p}_{\mathrm{A}_1} a_2\mathbf{p}_{\mathrm{A}_2} | b\mathbf{p}_{\mathrm{B}}) \\ &\quad \times [h^3 f_{a_1}(\mathbf{p}_{\mathrm{A}_1} t) f_{a_2}(\mathbf{p}_{\mathrm{A}_2} t) - f_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}} t)] \\ &\quad \times A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\, \delta(\mathbf{p}_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2} - \mathbf{p}_{\mathrm{B}})\, \delta(\hbar\omega_{\mathrm{B}} - E_{a_1}(\mathbf{p}_{\mathrm{A}}) - E_{a_2}(\mathbf{p}_{\mathrm{A}_2}) \end{aligned} \tag{28}$$

Here $\bar{\lambda} = (\beta h^2/2\pi\mu)^{1/2} = \lambda_{\mathrm{A}_1}\lambda_{\mathrm{A}_2}/\lambda_{\mathrm{B}}$ is the relative thermal wavelength; $f_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}} t)$ is the phase space density (here assumed uniform in space) of molecules B which are in internal state b and which have momentum $\mathbf{p}_{\mathrm{B}}$ and energy $\hbar\omega_{\mathrm{B}}$ at time t; and $A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})$ is the spectral function[9] which describes the widths of the microstates of B. It is related to the "linewidth function" $\Gamma_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})$ by the Lorentzian-like expression

$$A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}) = \frac{\Gamma_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})}{\{\omega - [E_b(\mathbf{p}_{\mathrm{B}})/\hbar]\}^2 + [\frac{1}{2}\Gamma_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})^2]^2} \tag{29}$$

$[\Gamma_b(\mathbf{p}_{\mathrm{B}} E_b(\mathbf{p}_{\mathrm{B}})/\hbar)]^{-1}$ is essentially the lifetime of a B molecule in internal state b having momentum $\mathbf{p}_{\mathrm{B}}$ and $\sigma(a_1\mathbf{p}_{\mathrm{A}_1} a_2\mathbf{p}_{\mathrm{A}_2} | b\mathbf{p}_{\mathrm{B}})$ is the cross section for the indicated process. In the low-density limit it is simply related to the

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[7] However, Boltzmann-like equations for "quasiparticles" are well known in solid state and nuclear physics when level widths are in some sense small. The first discussion of quasiparticle Boltzmann equations is due to Landau.(7) A modern derivation of such equations from the point of view of quantum field theory is given by Kadanoff and Baym.(8)

[8] This equation has been derived by application of the methods of Kadanoff and Baym,(8) Chapters 3 and 9, by Fleming.(9)

[9] Notation and nomenclature of Kadanoff and Baym(8) and of Martin and Schwinger.(10)

corresponding off-diagonal matrix element of the total Hamiltonian of the system⁽⁹⁾ by

$$\sigma(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|b\mathbf{p}_{\mathrm{B}}) = \frac{\bar{\lambda}^3\mu^2}{(2\pi)^2\hbar^4}\,|\langle a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|H|b\mathbf{p}_{\mathrm{B}}\rangle|^2 \tag{30}$$

$q_{\mathrm{CB}}(t)$ is given by an equation analogous to (28) with C's substituted for A's.

The width function $\Gamma_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})$ must be related to the rate of decay of the state $\{b, \mathbf{p}_{\mathrm{B}}\}$ into states of A_1 and A_2 or states of C_1 and C_2. In particular⁽⁹⁾

$$\begin{aligned}\Gamma_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}) = {} & \sum_{a_1a_2}\int\frac{d\Omega_{\mathrm{C}}}{\bar{\lambda}^3}\,v_{a_1a_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\sigma(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{A}_1}|b\mathbf{p}_{\mathrm{B}}) \\ & + \sum_{c_1c_2}\int\frac{d\Omega_{\mathrm{A}}}{\bar{\lambda}^3}\,v_{c_1c_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\sigma(c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{C}_1}|b\mathbf{p}_{\mathrm{B}})\end{aligned} \tag{31}$$

where

$$v_{a_1a_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}) = |\mathbf{v}_{\mathrm{A}_1} - \mathbf{v}_{\mathrm{A}_2}| = \{2\mu[\hbar\omega_{\mathrm{B}} - E_b(\mathbf{p}_{\mathrm{B}})] + \epsilon_b - \epsilon_{a_1} - \epsilon_{a_2}\}^{1/2}$$

and

$$v_{c_1c_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}) = |\mathbf{v}_{c_1} - \mathbf{v}_{c_2}| = \{2\mu[\hbar\omega_{\mathrm{B}} - E_b(\mathbf{p}_{\mathrm{B}})] + \epsilon_b - \epsilon_{c_1} - \epsilon_{a_2}\}^{1/2}$$

are the relative speeds of the indicated colliding molecules and where $d\Omega_{\mathrm{X}}$ denotes integration over the corresponding relative solid angles.

The usual phase space distribution function for the states of B is related to $f_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}t)$ by[10]

$$f_b(\mathbf{p}_{\mathrm{B}}t) = \int\frac{d\omega_{\mathrm{B}}}{2\pi}\,f_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}t)A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}) \tag{32}$$

The spectral function A is normalized[11] such that

$$\int\frac{d\omega_{\mathrm{B}}}{2\pi}\,A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}) = 1 \tag{33}$$

Thus $f_b(\mathbf{p}_{\mathrm{B}}t)$ may be regarded as an average of $f_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}t)$ over energy.

When the B states are sufficiently long-lived, i.e., $\beta\hbar\Gamma_b \ll 1$, the spectral function A_b can be effectively replaced by a δ function

$$A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}}) = 2\pi\delta\left(\omega_{\mathrm{B}} - \frac{E_b(\mathbf{p}_{\mathrm{B}})}{\hbar}\right) \tag{34}$$

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[10] See Chapters 6, 8, and 9 of Kadanoff and Baym.⁽⁸⁾

[11] Kadanoff and Baym,⁽⁸⁾ Chapter 1.

When this approximation is valid, (28) may be replaced by the Boltzmann equation

$$q_{\mathrm{AB}}(t) = \sum_{a_1 a_2 b} \int \frac{d\mathbf{p}_{\mathrm{A}_1}\, d\mathbf{p}_{\mathrm{A}_2}\, d\mathbf{p}_{\mathrm{B}}}{2\pi \bar{\lambda}^3} \times \frac{1}{\mu^2}\, \sigma(a_1 \mathbf{p}_{\mathrm{A}_1} a_2 \mathbf{p}_{\mathrm{A}_2} | b \mathbf{p}_{\mathrm{B}})[h^3 f_{a_1}(\mathbf{p}_{\mathrm{A}_1} t) f_{a_2}(\mathbf{p}_{\mathrm{A}_2} t) - f_b(\mathbf{p}_{\mathrm{B}} t)] \tag{35}$$

However, for the purpose of elucidating the relationship between long- and short-lived "activated complexes" it is crucial to retain the dependence on Γ_b.

When the species B are in equilibrium with the species A and C we have for low B densities[12]

$$f_b(\mathbf{p}_{\mathrm{B}} \omega_{\mathrm{B}} t) = f_b(\omega_{\mathrm{B}}) = \{\exp[-\beta(\hbar\omega_{\mathrm{B}} - \mu_{\mathrm{B}})]\}/h^3 \tag{36}$$

where μ_{B} is the chemical potential of species B. The equilibrium phase space density consistent with μ_{B} is

$$f_b(\mathbf{p}_{\mathrm{B}}) = \int \frac{d\omega_{\mathrm{B}}}{2\pi} \frac{\exp[-\beta(\hbar\omega_{\mathrm{B}} - \mu_{\mathrm{B}})]}{h^3} A_b(\mathbf{p}_{\mathrm{B}} \omega_{\mathrm{B}}) = \frac{\exp\{-\beta[E_b(\mathbf{p}_{\mathrm{B}}) + \Delta_b(\mathbf{p}_{\mathrm{B}}) - \mu_{\mathrm{B}}]\}}{h^3} \tag{37}$$

where

$$\exp[-\beta\, \Delta_b(\mathbf{p}_{\mathrm{B}})] = \int \frac{d\omega}{2\pi} [\exp(-\beta\hbar\omega)] A_b\left(\mathbf{p}_{\mathrm{B}} \omega + \frac{E_b(\mathbf{p}_{\mathrm{B}})}{\hbar}\right)$$

Clearly $\Delta_b(\mathbf{p}_{\mathrm{A}})$ is at least of order $\hbar\beta\Gamma$.[13]

In equilibrium the total density of species B is given by

$$n_{\mathrm{B}} = \sum_b \int d\mathbf{p}_{\mathrm{B}} \frac{\exp\{-\beta[E_b(\mathbf{p}_{\mathrm{B}}) + \Delta_b(\mathbf{p}_{\mathrm{B}}) - \mu_{\mathrm{B}}]\}}{h^3} = \frac{\exp[-\beta(\bar{f}_{\mathrm{B}} - \mu_{\mathrm{B}})]}{\bar{\lambda}_{\mathrm{B}}^{\,3}} \tag{38}$$

where

$$\exp(-\beta \bar{f}_{\mathrm{B}}) = \sum_b \exp(-\beta \bar{\epsilon}_b)$$

and

$$\frac{1}{\bar{\lambda}_{\mathrm{B}}^{\,3}} = \int \frac{d\mathbf{p}_{\mathrm{B}}}{h^3} \exp[-\beta \bar{E}_{\mathrm{B}}(\mathbf{p}_{\mathrm{B}})]$$

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[12] Kadanoff and Baym,(8) Chapter 1. There (36) is obtained in the limit $\beta\mu_{\mathrm{B}} \to -\infty$.

[13] Actually it can be shown to be of order $(\hbar\beta\Gamma)^2$.

with $\bar{\epsilon}_b = \epsilon_b + \Delta_b(0)$ and

$$\exp[-\beta\bar{E}_B(\mathbf{p}_B)] = \sum_b \exp[-\beta\bar{E}_b(\mathbf{p}_B)] \exp[-\beta(\bar{\epsilon}_b - \bar{f}_B)]$$

in which $\bar{E}_b(\mathbf{p}_B) = (\mathbf{p}_B{}^2/2m_B) + \Delta_b(\mathbf{p}_B) - \Delta_b(0)$.

This enables us to eliminate the chemical potential in favor of the density. Thus (36) and (37) respectively, become

$$f_b(\mathbf{p}_B) = n_B(\bar{\lambda}_B/h)^3 \exp\{-\beta[\bar{E}_b(\mathbf{p}_B) + \bar{\epsilon}_b - \bar{f}_B]\} \equiv n_B\bar{P}_b(\mathbf{p}_B) \tag{39}$$

and

$$f_B(\omega_B) = n_B(\bar{\lambda}_B/h)^3 \exp[-\beta(\hbar\omega_B - \bar{f}_B)] \equiv n_B P_B(\omega_B) \tag{40}$$

Thus, when lifetimes cannot be neglected, the equilibrium assumption [cf. (7) of II or (11) of this paper] is

$$f_B(\mathbf{p}_B\omega_B t) = n_B(t)P_B(\omega_B) \tag{41}$$

By integration we have

$$f_b(\mathbf{p}_B t) = n_B(t)\bar{P}_b(\mathbf{p}_B) \tag{42}$$

Note that when $\beta\hbar\Gamma_b \ll 1$, $\bar{\lambda}_B \to \lambda_B$, $\bar{\epsilon}_b \to \epsilon_b$, $\bar{E}_b(\mathbf{p}_B) \to \mathbf{p}_B{}^2/2m_B$, and (42) reduces to (11) with X = B.

When (41) is substituted into (28), we obtain

$$q_{AB}(t) = \frac{\bar{v}\sigma_{AB}}{\bar{\lambda}^3}\left(n_{A_1}(t)n_{A_2}(t)\{\exp[-\beta(\bar{f}_B - f_{A_1} - f_{A_2})]\}\left(\frac{\lambda_{A_1}\lambda_{A_2}}{\bar{\lambda}_B}\right)^3 - n_B(t)\right) \tag{43}$$

where

$$\begin{aligned}\sigma_{AB} = \sum_{a_1a_2}\int \frac{d\Omega_A\, d\mathbf{p}_B\, d\omega_B}{2\pi}\, \frac{v_{a_1a_2b}(\mathbf{p}_B\omega_B)}{\bar{v}}\, \sigma(a_1\mathbf{p}_{A_1}a_2\mathbf{p}_B - \mathbf{p}_{A_1}|b\mathbf{p}_B)\bar{P}_b(\mathbf{p}_B)\\ \times \exp\{-\beta[\hbar\omega_B + E_b(\mathbf{p}_B) - \Delta_b(\mathbf{p}_B)]\}A_B(\mathbf{p}_B\omega_B)\end{aligned}$$

When $\beta\hbar\Gamma_B \ll 1$, (43) remains unchanged, except that $\bar{\lambda}_B \to \lambda_B$, $\bar{f}_B \to f_B$, and the expression for σ_{AB} becomes

$$\sigma_{AB} = \sum_{a_1a_2b}\int d\Omega_A\, d\mathbf{p}_B\, \frac{v_{a_1a_2b}}{\bar{v}}\, \sigma(a_1\mathbf{p}_{A_1}a_2\mathbf{p}_B - \mathbf{p}_{A_1}|b\mathbf{p}_B)P_b(\mathbf{p}_B) \tag{44}$$

where $v_{a_1a_2b} = [2\mu(\epsilon_b - \epsilon_{a_1} - \epsilon_{a_2})]^{1/2}$.

When we eliminate $n_B(t)$ from the pair of equations for $q_{AB}(t)$ [Eq. (43)] and $q_{CB}(t)$ [equation analogous to (43)] via a steady-state approximation, we obtain

$$\begin{aligned}q(t) &= q_{AB}(t) = -q_{CB}(t)\\ &= \bar{v}\,\frac{\sigma_{AB}\sigma_{CB}}{\sigma_{AB} + \sigma_{CB}}\left(\frac{\lambda_B}{\bar{\lambda}_B}\right)^3 (\{\exp[-\beta(\bar{f}_B - f_{A_1} - f_{A_2})]\}n_{A_1}(t)n_{A_2}(t)\\ &\quad -\{\exp[-\beta(\bar{f}_B - f_{C_1} - f_{C_2})]\}n_{C_1}(t)n_{C_2}(t))\end{aligned} \tag{45}$$

Equation (45) differs from the result we would obtain when $\beta\hbar\Gamma_b \ll 1$ by the trivial factor $(\lambda_B/\bar{\lambda}_B)^3$ and the substitution $\bar{f}_B$ for f_B. The point to notice is that the assumption of sharply well-defined energies for the B states is not crucial to the appearance of the Arrhenius type of temperature factor. Equation (45) is valid for B state widths which are sufficiently small that the corresponding lifetimes are long compared to nonreactive collision times. This case can be imagined even though the nonreactive collisions are bimolecular and the B decay is unimolecular.

However, it is possible to reduce the pressure so that no collisions occur prior to decay. For this case (45) is no longer a good approximation. Thus the validity of (45) is restricted to "high" gas pressures.[14] For the "low"-pressure case (28) remains valid, but (42) is no longer a good approximation. Therefore we must employ a rate equation which involves a cross section for the direct reaction. It is possible to show$^{(9)}$ that Eq. (28) can be transformed into

$$\begin{aligned} q_{\mathrm{AC}}(t) &= -\frac{dn_{\mathrm{A}_1}(t)}{dt} \\ &= \sum_{\substack{a_1a_2\\c_1c_2}} \int d\mathbf{p}_{\mathrm{A}_1}\, d\mathbf{p}_{\mathrm{A}_2}\, d\mathbf{p}_{\mathrm{C}_1}\, d\mathbf{p}_{\mathrm{C}_2} \frac{1}{\mu^2}\, \sigma_{\mathrm{R}}(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{C}_2}) \\ &\quad \times [f_{a_1}(\mathbf{p}_{\mathrm{A}_1}t)f_{a_2}(\mathbf{p}_{\mathrm{A}_2}t) - f_{\mathrm{C}_1}(\mathbf{p}_{\mathrm{C}_1}t)f_{\mathrm{C}_2}(\mathbf{p}_{\mathrm{C}_2}t)] \\ &\quad \times \cdot\delta(\mathbf{p}_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2} - \mathbf{p}_{\mathrm{C}_1} - \mathbf{p}_{\mathrm{C}_2})\, \delta(E_{a_1}(\mathbf{p}_{\mathrm{A}_1}) + E_{a_2}(\mathbf{p}_{\mathrm{A}_2}) \\ &\quad - E_{\mathrm{C}_1}(\mathbf{p}_{\mathrm{C}_1}) - E_{\mathrm{C}_2}(\mathbf{p}_{\mathrm{C}_2})) \end{aligned} \tag{46}$$

where

$$\begin{aligned} &\sigma_{\mathrm{R}}(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{C}_2}) \\ &\quad = \sum_b (2\pi)^2\hbar^4(\bar{\lambda}^6\mu^2)^{-1}\sigma(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|b_1\mathbf{p}_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2}) \\ &\qquad \times \sigma(c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{C}_2}|b_1\mathbf{p}_{\mathrm{C}_1} + \mathbf{p}_{\mathrm{C}_2}) \\ &\qquad \times ([E_{a_1}(\mathbf{p}_{\mathrm{A}_1}) + E_{a_2}(\mathbf{p}_{\mathrm{A}_2}) - E_b(\mathbf{p}_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2})]^2 \\ &\qquad + \{\tfrac{1}{2}\hbar\Gamma_b(p_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2}[E_{a_1}(\mathbf{p}_{\mathrm{A}_1}) + E_{\mathrm{A}_2}(\mathbf{p}_{\mathrm{A}_2})]/\hbar)\}^2)^{-1} \end{aligned}$$

The equilibrium assumption (11) should be valid for the A's and C's for all reasonable gas pressures provided the cross section σ_{R} is smaller than the corresponding nonreactive cross section σ_{NR}, since both the reactive and

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[14] Of course, the terms "high" and "low" pressure are only relative. Where the transition between the two limits occurs is very sensitive to the relative magnitudes of reactive and nonreactive cross sections.

nonreactive processes are bimolecular. Then application of the now familiar procedure to (46) gives

$$q_{\mathrm{AC}}(t) = \sigma_{\mathrm{AC}}\bar{v}(\{\exp[-\beta(f_{\mathrm{C}_1} + f_{\mathrm{C}_2} - f_{\mathrm{A}_1} - f_{\mathrm{A}_2})]\}n_{\mathrm{A}_1}(t)n_{\mathrm{A}_2}(t) - n_{\mathrm{C}_1}(t)n_{\mathrm{C}_2}(t)]) \tag{47}$$

where

$$\begin{aligned}\sigma_{\mathrm{AC}} = \frac{1}{\bar{v}} \sum_{\substack{a_1a_2\\c_1c_2}} \int & d\mathbf{p}_{\mathrm{A}_1}\, d\mathbf{p}_{\mathrm{A}_2}\, d\mathbf{p}_{\mathrm{C}_1}\, d\mathbf{p}_{\mathrm{C}_2} \\ & \times \frac{1}{\mu^2}\, \sigma_{\mathrm{R}}(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{C}_2})\, \delta(\mathbf{p}_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2} - \mathbf{p}_{\mathrm{C}_1} - \mathbf{p}_{\mathrm{C}_2}) \\ & \times \delta(E_{a_1}(\mathbf{p}_{\mathrm{A}_1}) + E_{a_2}(\mathbf{p}_{\mathrm{A}_2}) - E_{\mathrm{C}_1}(\mathbf{p}_{\mathrm{C}_1}) - E_{\mathrm{C}_2}(\mathbf{p}_{\mathrm{C}_2}))P_{\mathrm{C}_1}(\mathbf{p}_{\mathrm{C}_1})P_{\mathrm{C}_2}(\mathbf{p}_{\mathrm{C}_2})\end{aligned}$$

We notice from (46) that for each pair of colliding molecules the cross section σ_R has a threshold. As observed by Ross and Mazur,(3) this is a sufficient condition for the appearance of a "free energy of activation." We can see how this comes about in this case by inserting integration over δ functions of $\mathbf{p}_{\mathrm{B}}$ and ω_{B} into the definition of σ_{AC}. This yields

$$\begin{aligned}\sigma_{\mathrm{AC}} = \sum_{\substack{a_1a_2\\c_1c_2\\b}} \int & d\mathbf{p}_{\mathrm{A}_1}\, d\mathbf{p}_{\mathrm{A}_2}\, d\mathbf{p}_{\mathrm{C}_1}\, d\mathbf{p}_{\mathrm{C}_2}\, d\mathbf{p}_{\mathrm{B}} \\ & \times \frac{d\omega_{\mathrm{B}}}{2\pi}\, \frac{(2\pi)^3\hbar^3}{\bar{\lambda}^6\mu^2\bar{v}}\, \sigma(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{A}_2}|b\mathbf{p}_{\mathrm{A}_1} + \mathbf{p}_{\mathrm{A}_2}) \\ & \times \delta(\hbar\omega_{\mathrm{B}} - E_{a_1}(\mathbf{p}_{\mathrm{A}_1}) - E_{a_2}(\mathbf{p}_{\mathrm{A}_2}))\, \delta(\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{A}_1} - \mathbf{p}_{\mathrm{A}_2}) \\ & \times \sigma(c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{C}_2}|b\mathbf{p}_{\mathrm{C}_1} + \mathbf{p}_{\mathrm{C}_2})\, \delta(\hbar\omega_{\mathrm{B}} - E_{\mathrm{C}_1}(\mathbf{p}_{\mathrm{C}_1}) - E_{\mathrm{C}_2}(\mathbf{p}_{\mathrm{C}_2})) \\ & \times \delta(\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{C}_1} - \mathbf{p}_{\mathrm{C}_2})\{\exp[-\beta(\hbar\omega_{\mathrm{B}} - E_b(\mathbf{p}_{\mathrm{B}}) - \Delta_b(\mathbf{p}_{\mathrm{B}})]\} \\ & \times \frac{A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})}{\Gamma_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})}\, \bar{P}_b(\mathbf{p}_{\mathrm{B}}) \exp[-\beta(\bar{f}_{\mathrm{B}} - f_{\mathrm{C}_1} - f_{\mathrm{C}_2})] \\ = \sum_{\substack{a_1a_2\\c_1c_2\\b}} \int & d\mathbf{p}_{\mathrm{B}}\, \frac{d\omega_{\mathrm{B}}}{2\pi}\, \{\exp[-\beta(\hbar\omega_{\mathrm{B}} - E_b(\mathbf{p}_{\mathrm{B}}) - \Delta_b(\mathbf{p}_{\mathrm{B}}))]\}A_b(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\bar{P}_b(\mathbf{p}_{\mathrm{B}}) \\ & \times \frac{1}{\bar{v}}\Bigg[\int d\Omega_{\mathrm{A}} v_{a_1a_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\sigma(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{A}_1}|b\mathbf{p}_{\mathrm{B}}) \\ & \times \int d\Omega_{\mathrm{C}}\, v_{c_1c_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\sigma(c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{C}_1}|b\mathbf{p}_{\mathrm{B}})\Bigg] \\ & \times \Bigg[\sum_{a_1a_2} \int d\Omega_{\mathrm{A}}\, v_{a_1a_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\sigma(a_1\mathbf{p}_{\mathrm{A}_1}a_2\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{A}_1}|b\mathbf{p}_{\mathrm{B}}) \\ & + \sum_{c_1c_2} \int d\Omega_{\mathrm{C}}\, v_{c_1c_2b}(\mathbf{p}_{\mathrm{B}}\omega_{\mathrm{B}})\sigma(c_1\mathbf{p}_{\mathrm{C}_1}c_2\mathbf{p}_{\mathrm{B}} - \mathbf{p}_{\mathrm{C}_1}|b\mathbf{p}_{\mathrm{B}})\Bigg]^{-1}\end{aligned}$$

$$\times \left(\frac{\lambda_{\mathrm{B}}}{\bar{\lambda}_{\mathrm{B}}}\right)^3 \exp[-\beta(\bar{f}_{\mathrm{B}} - f_{\mathrm{C}_1} - f_{\mathrm{C}_2})]$$

$$\equiv \left\langle \frac{\sigma_{\mathrm{AB}}\sigma_{\mathrm{CB}}}{\sigma_{\mathrm{AB}} + \sigma_{\mathrm{CB}}} \right\rangle \left(\frac{\lambda_{\mathrm{B}}}{\bar{\lambda}_{\mathrm{B}}}\right)^3 \exp[-\beta(\bar{f}_{\mathrm{B}} - f_{\mathrm{C}_1} - f_{\mathrm{C}_2})] \tag{48}$$

Thus, upon substitution into (47), we obtain

$$\begin{aligned} q(t) &= q_{\mathrm{AC}}(t) \\ &= \bar{v} \left\langle \frac{\sigma_{\mathrm{AB}}\sigma_{\mathrm{CB}}}{\sigma_{\mathrm{AB}} + \sigma_{\mathrm{CB}}} \right\rangle \left(\frac{\lambda_{\mathrm{B}}}{\bar{\lambda}_{\mathrm{B}}}\right)^3 (\{\exp[-\beta(\bar{f}_{\mathrm{B}} - f_{\mathrm{A}_1} - f_{\mathrm{A}_2})]\} n_{\mathrm{A}_1}(t) n_{\mathrm{A}_2}(t) \\ &\quad - \{\exp[-\beta(\bar{f}_{\mathrm{B}} - f_{\mathrm{C}_1} - f_{\mathrm{C}_2})]\} n_{\mathrm{C}_1}(t) n_{\mathrm{C}_2}(t)) \end{aligned} \tag{49}$$

Equations (45) and (49) are very similar. The only difference is an interchange in the order of the averaging over B states and the multiplication of the cross sections. It is hard to imagine pathological cross sections for which the two different preexponential factors would differ by more than a few percent.

We note that our results in the "low-pressure" regime are not only in agreement with those of Ross and Mazur$^{(3)}$ but are also similar to those of Eu and Ross,$^{(4)}$ who considered the consequences of resonant reactive scattering on the temperature dependence of chemical reactions. As we see, the cross section σ_R in (46) is a resonant reaction cross section for the indicated scattering process.

The explicit forms of (45) and (49) allow us to compare their preexponential factors with the Eyring value kT/h. For simplicity in estimating this factor, we assume that $A_1 = A_2$, $C_1 = C_2$, and $\sigma_{\mathrm{AB}} = \sigma_{\mathrm{CB}} = \sigma$ is constant. Then the rate equations (45) and (49) are identical and can be written in terms of the dimensionless concentrations $\bar{n}_{\mathrm{A}}$ and $\bar{n}_{\mathrm{C}}$ as

$$\begin{aligned} -\frac{d\bar{n}_{\mathrm{A}}(t)}{dt} &= \frac{\sigma\bar{v}}{2\lambda^3} (\{\exp[-\beta(f_{\mathrm{B}} - 2f_{\mathrm{A}})]\} \bar{n}_{\mathrm{A}}(t)^2 \\ &\quad - \{\exp[-\beta(f_{\mathrm{B}} - 2f_{\mathrm{C}})]\} \bar{n}_{\mathrm{C}}(t)^2) \end{aligned} \tag{50}$$

where $\lambda = \lambda_{\mathrm{A}} = \lambda_{\mathrm{C}} = (\beta/2\pi m)^{1/2}$ is the common thermal wavelength. The width Γ [Eq. (31)] is given by

$$\Gamma = 2(\bar{v}\sigma/\bar{\lambda}^3) = \bar{v}\sigma/(\sqrt{2}\lambda^3) \tag{51}$$

Thus, the preexponential factor is related to the level width of the activated complex by

$$k_0 = \bar{v}\sigma/2\lambda^3 = (1/\sqrt{2})\Gamma \tag{52}$$

Thus, k_0 is kT/h if $\Gamma = \sqrt{2}(kT/h)$. This corresponds to a level width (uncertainty in energy) of order of the width of the Maxwellian distribution.

The activated complex lifetime corresponding to this width is of the order of 10^{-13} sec at room temperature.

For the "long-lived activated complex," we must have $\Gamma \ll kT/h$ and, hence, $k_0 \ll kT/h$. For the "short-lived activated complex," Γ may be of order $\sqrt{2}\, kT/h$, but not necessarily equal to it. Thus, we conclude that k_0 may be equal to kT/h, but this factor does not emerge from our analysis in any natural way.

5. DISCUSSION

We have here explored the implications of the stochastic approach to chemical reaction rates in the limit of low densities. It has been shown that the analysis given in I and II conforms with that of collision theory in this limit and that insights which penetrate further than existing collision theory can be obtained even in this well-understood limit.

The expressions for the rate constants [either (45) or (49)] obtained here should have (to a good approximation, at least at low densities) wide applicability regardless of the lifetime of the activated complexes. The results certainly suggest that the main determinant of the temperature dependence of the rate of a chemical reaction is the magnitude of the energy necessary to surmount its potential barrier, regardless of the time spent in the neighborhood of the top of the barrier. In addition it is suggested that the value of the preexponential factor is also fairly insensitive to the lifetime of the "activated" state (although not necessarily equal to the putatively universal kT/h). Although the expressions obtained here for the rate constants do possess simplicity, they allow for a dependence on the fundamental probabilities (here cross sections) for the processes involved in the reaction. Indeed we must expect differences in reaction rates between systems which are weakly coupled and those which are strongly coupled, even when the activation energies (or free energies) involved are the same.

It appears that the stochastic approach, now seemingly certified in the low-density limit, provides the basis for a general theory of chemical reaction rates, applicable to condensed media as well as to the gas phase.

We may expect that further progress toward an understanding of the stochastic approach may be obtained with use of the methods of quantum field theory,(7–10) some results of which have been utilized here. This formalism, which was constructed for the study of elementary particle reactions,[15] would appear to be particularly useful in the study of chemical reactions, since it carries a natural allowance for matrix elements which are off-diagonal in particle number.

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[15] See, for example, Schweber.(11)

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