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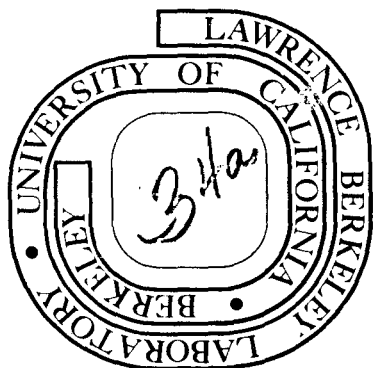
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ACTIVATED COMPLEX THEORY OF BIMOLECULAR REACTIONS

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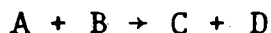
It has been 40 years since absolute rate theory (ART) was formulated (1-3). In its early years, the theory was controversial, and even the many applications provided (4) by its progenitors did not dispell a general skepticism concerning its merits. However, beginning (5) in the 1950's, a number of comparisons of the predictions of ART with reputable experimental data were made with quite satisfactory results. An important aspect of these comparisons is that they involved the use of our modern understanding of molecular structure to estimate the necessary parameters of the theory (6). That is, predictions about kinetic phenomena were made successfully with ART, using data from non-kinetic experiments. The result has been a rather firm confidence of most workers in chemical kinetics that, provided the necessary molecular structure parameters are available, absolute rate theory is in most (fairly well defined) cases an adequate way to estimate the pre-exponential factors of thermal bimolecular reactions.

In view of this success, it is unfortunate that the theory does not enjoy better understanding and confidence among non-specialists. Some of this difficulty can be traced to the rather unconvincing derivations of the ART expression for the rate constant which are found in many physical chemistry texts and monographs on chemical kinetics. Satisfactory and

edifying derivations exist (6-8), but do not seem to be very well-known. In a recent article in this Journal (9), it has even been suggested that the standard ART expression is in error by a factor of two. It is the purpose of this paper to present a detailed but simple derivation of the ART expression for a bimolecular reaction which avoids certain of the difficulties in the common treatments, and exposes the assumptions involved in a clear fashion. The procedure is based on an early paper by Horiuti (10), which was virtually totally ignored for 20 years.

The Bimolecular Rate Constant

We consider the bimolecular gas phase reaction



and assume that classical mechanics provides an adequate description of the system. We imagine that in the phase (coordinate and momentum) space of the system, perpendicular to the coordinate q_1 there is a surface S which has the property that well to one side of the surface there exist molecular conformations that we recognize as reactants, while the products lie on the other side. The reaction rate will be calculated as the rate at which systems cross the surface S in the direction leading from reactants to products. The exact location of the surface is somewhat at our disposal, and for the present will be left unspecified.

An important step in the derivation is the calculation of the concentration of systems which lie on the critical surface S . By "system" we mean an A-B molecular pair, which has a total of n atoms. We make the assumption that for the fraction of systems $d^{6n}N/N$ which lie in a volume element of phase space $dp_1 \dots dp_{3n} dq_1 \dots dq_{3n}$ we can use the standard expression (11) from equilibrium statistical mechanics

$$\frac{d^{6n}N}{N} = \frac{e^{-H/kT} dp_1 \dots dq_{3n} / h^{3n}}{\int e^{-H/kT} dp_1 \dots dq_{3n} / h^{3n}} \quad (1)$$

The dimensionality of the differential $d^{6n}N$ is indicated to remind us that the mechanical state of all n atoms of the system A+B can be specified by a point in a $6n$ -dimensional phase space. In eqn. (1), $H = H(p,q)$ is the classical Hamiltonian of the system; i.e., the total energy expressed in terms of the coordinates and momenta. Use of eqn. (1) is of course equivalent to assuming that the regions of phase space important to us are populated in the reacting system just as if complete equilibrium existed. That is, we have just made the equilibrium assumption of chemical kinetics (12). This assumption is made implicitly or explicitly in every common treatment of thermal bimolecular reaction rate constants by ART or by collision theory. Expressions in which partition functions or Boltzmann factors appear have this assumption somewhere in their derivation. Claims to the contrary are delusions.

Is the equilibrium assumption of chemical kinetics valid? We shall delay a detailed discussion of this point until the derivation is completed. For the moment, it is fair to say that there will be regions of phase space for which the assumption is in substantial error, and other regions where it will be very accurate. We must keep the critical surface S in the regions where eqn. (1) is valid.

To obtain the rate of reaction, we imagine that the volume element of eqn. (1) is just on the product side of the surface S . Then we divide both sides of eqn. (1) by the differential of time dt , and get

$$-\frac{d^{6n}N}{dt} = N \frac{dq_1}{dt} \frac{e^{-H/kT} dq_2 \dots dp_{3n}/h^{3n}}{\int e^{-H/kT} dq_1 \dots dp_{3n}/h^{3n}} \quad (2)$$

The minus sign appears because there is a net loss of reactant pairs by passage through the surface into the product region. The expression now gives the contribution to the rate from one particular volume element. To get the full rate of reaction, we must sum (integrate) this expression over all values of $q_2 \dots q_{3n}$, and $p_2 \dots p_{3n}$, since all these coordinates and momenta lie on the surface S , and we are claiming that passage anywhere through the surface leads to products. Also, we must integrate over all positive values of p_1 , since only this motion (along the reaction coordinate q_1) takes systems from the reactant to the product region of phase space.

To carry out the integration, we write

$$H = \frac{p_1^2}{2m_1} + H'$$

where m_1 is the mass associated with motion along the q_1 direction, and H' is the part of the classical Hamiltonian that remains after the kinetic energy term $p_1^2/2m_1$ is separated out. Recognizing that $p_1 = m_1 dq_1/dt$, we get

$$-\frac{dN}{dt} = N \frac{\frac{1}{m_1 h} \int_0^\infty p_1 e^{-\frac{p_1^2}{2m_1 kT}} dp_1 \int^S e^{-H'/kT} dq_2 \dots dq_{3n} dp_2 \dots dp_{3n} / h^{3n-1}}{\int^\Gamma e^{-H/kT} dq_1 \dots dp_{3n} / h^{3n}} \quad (3)$$

for the full rate. Note that on the left, integration over $6n-1$ coordinates and momenta $q_2 \dots q_{3n}, p_1 \dots p_{3n}$ has reduced the dimensionality of the differential to one. On the right hand side, the integration over p_1 can be carried out in an elementary fashion, and when combined with $1/m_1 h$, gives the familiar factor of kT/h . In the denominator, the integral is to be carried out over the full volume Γ of phase space that corresponds to all values of the coordinates and momenta which we recognize as describing the reactant molecules A and B. Thus this multiple integral is just the phase integral (partition function) of the reactants. We can write it as $Q_A V Q_B V$, the product of the partition functions per unit volume for the individual molecules A and B, and two factors of the volume V of the containing flask. The quantity N is the total number of A-B pairs, and so can be replaced on the right side of eqn. (3) by $N_A N_B$, the product of numbers of individual A and B molecules. The result of all these integrations and substitutions is then

$$-\frac{dN}{dt} \frac{1}{[A][B]} = \frac{kT}{h} \frac{\int^S e^{-H'/kT} dq_2 \dots dq_{3n} dp_2 \dots dp_{3n}}{Q_A Q_B} \quad (4)$$

where the concentrations on the left have appeared as a result of dividing the numbers of molecules N_A and N_B by the volume factors from the reactant partition functions.

It is now only a short distance to the final expression for the rate constant. Imagine that there is a saddle point in the potential energy surface such that the potential energy profile along q_1 reaches a maximum value while the potential energy along all other coordinates reaches a minimum value. We choose to have the surface S pass through this saddle point, perpendicular to q_1 , for two reasons. First, experience with detailed molecular mechanics suggests to us that most systems which cross such a saddle point with relatively low velocities along q_1 will remain on the product side of the saddle. To the extent that this is not true, the theory will overestimate the reaction rate. The second reason for this choice is that near an extremum in the potential energy surface, the Hamiltonian becomes expressible as the sum of squares of coordinates and momenta, and the multi-dimensional phase integral factors into a simple product of elementary one-dimension integrals. This is a great convenience, but by no means necessary nor fundamental to the theory.

If the potential energy at the saddle point is V_0 , we can write

$$H' = V_0 + H''$$

and make this substitution in eqn. (4). Also, choose $q_2, q_3,$ and q_4 to be the coordinates which locate the center-of-mass of the A-B pairs that are at the surface S. Integration over these coordinates merely gives V , the total volume of the container. This factor can be brought to the denominator on the left side, and there combined with N to give the rate of disappearance of reactant pairs expressed in terms of concentration units. The result is

$$\frac{\text{Rate}}{[A][B]} = \frac{kT}{h} \frac{e^{-V_0/kT}}{Q_A Q_B} \int^S e^{-H''/kT} dq_5 \dots dq_{3n} dp_2 \dots dp_{3n} / h^{3n-1}.$$

The remaining integral is the phase integral per unit volume for reactant pairs which have conformations which place them on the surface S, with their zero of energy taken at the saddle point potential energy V_0 . Since the coordinate q_1 and momentum p_1 have been dealt with separately, this phase integral is just the partition function per unit volume of the activated complex, or Q^\ddagger . Thus we get

$$\frac{\text{Rate}}{[A][B]} = \tilde{k} = \frac{kT}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-V_0/kT} \quad (5)$$

for the rate constant, which is the conventional ART expression.

The basic assumptions of absolute rate theory enter this derivation in a particularly clear manner. Classical mechanics must provide an adequate description of the system, the phase space of reactants must be populated according to the equilibrium

(Boltzmann) distribution law, and systems which cross the critical surface become products. Each one of these assumptions is subject to scrutiny and may be found unsatisfactory to some degree in a given situation. However, within these basic assumptions, the conventional formulation of ART is correct. There are no missing factors of 2. The contribution to the rate of only those activated complexes which are moving toward the product region is included correctly by integrating over positive values only of the momentum p_1 along the reaction coordinate.

The Validity of the Assumptions

What can be said concerning the validity of the assumptions made in the derivation of the ART expression? It is well-known that at and above room temperature, the classical expressions for the translational and (with the exception of H_2 , D_2 , and HD) rotational partition functions are very accurate, provided the proper symmetry numbers are used. For most vibrational motions, this is not true, and accordingly, the classical phase integrals for the vibrational motions in both the numerator and denominator of eqn. (5) should be replaced with the corresponding quantum partition functions. Quantum correction factors which accomplish just this have been tabulated (6). Corrections for quantum mechanical effects on motion along the reaction coordinate are another matter, however. A rigorous, fully quantum mechanical version of ART has never been formulated, and it is therefore not clear what

the correct treatment of the reaction coordinate should be. Factors which attempt to correct the classical expression for tunnel effects have been employed with some success(6), but these still remain ex post facto modifications, rather than consequences of the fundamental formulation.

To assess the validity of the assumption of an equilibrium population in the reactant portion of phase space, consider the following argument. The parts of phase space which represent large separations of reactant molecules correspond to the independent internal and relative motions of independent A and B molecules. The states of A and B are kept filled at very near their equilibrium populations by the very large numbers of A-A, B-B, and A-B collisions that are non-reactive. The populations of these states of A and B tend to be depleted by the A-B collisions that lead to reaction. At complete chemical equilibrium, this depletion does not occur, since reactive collisions of C with D just balance the loss in the population of A and B states due to A-B reactive collisions. When C and D are not present, or are in very small concentration, the states of A and B must be depleted from their equilibrium population.

Is this population depletion important? This matter has been investigated (13) by advanced methods of kinetic theory (the Boltzmann transport equation modified to include chemical reaction). The conclusion is that if the reaction is sufficiently slow, the population of the states of the individual reactants will differ from equilibrium values by negligible amounts. The rate constant will be within 8% of the value

calculated by equilibrium theory if $E_a/RT > 5$, where E_a is the Arrhenius activation energy. Even smaller ratios of E_a/RT can be tolerated if substantial amounts of inert gas are present.

If the states of the separated reactant molecules have very close to their equilibrium population, then any state of the reactant pairs that can be reached by binary A-B collisions alone has close to its equilibrium population. This includes conformations of the reactant pairs that lie close to the critical surface S ; i.e., activated complexes. It does not apply to states which we recognize as the products C and D, since equilibrium among all the states of C and D is maintained by mechanisms other than A-B reactive collisions. Therefore we reach the conclusion that the equilibrium assumption involved in ART is in fact a good approximation in most common experimental situations. It is worth emphasizing that this equilibrium assumption is not unique to ART. It is also made in standard collision theory when one converts an exact collision cross section to a rate constant by averaging over a Boltzmann distribution of relative speeds.

The assumption that all systems which cross the critical surface separate to form products can be tested for individual potential surfaces by examining the results of exact classical trajectory calculations. In a strict sense, the assumption is always violated, since some systems which pass the critical surface at the potential energy saddlepoint are reflected back into the reactant channel. This occurs most frequently, but not

exclusively, in high energy collisions. Fortunately, when the reactants have a Boltzmann energy distribution, high energy collisions make only a very small contribution to the reaction rate. In most of the reactive collisions, the total energy in the reaction coordinate exceeds the minimum value of V_0 by no more than $2 kT$. In these cases, the drop in potential energy which almost always occurs on the product side of the saddle point promotes the separation of the collision complex to products. Of course, pathological surfaces for which this is not true do exist (14), and in these situations the rate calculated by ART will exceed the true experimental value by substantial factors. Thus it appears that we can rely on the simplest version of ART to provide an upper limit to the reaction rate, and this limit may frequently be close to the true value.

Short Derivations of the ART Expression

Frequently, derivations of the ART expression start with an assertion of equilibrium between reactants and activated complexes. Then the rate constant is formulated as

$$k = \nu K = \nu \frac{Q}{Q_A Q_B} e^{-V_0/kT} \quad (6)$$

where K and Q are the complete equilibrium constant and partition function for the activated complex, and ν is the frequency with which activated complexes decay to products. Then some method of handling the contribution of the reaction

coordinate is employed. The simplest, and by far the least convincing, is to treat the reaction coordinate as a classical vibration which has a partition function $kT/h\nu$. Then the frequency factor ν in eqn. (6) is unquestionably the oscillator frequency, and multiplication of ν by $kT/h\nu$ gives the familiar kT/h factor, and leaves Q^\ddagger , the partition function of activated complexes less the reaction coordinate, in the numerator.

A more satisfactory procedure is to treat the reaction coordinate as a translation, but care is required. If the usual one-dimensional partition function $(2\pi m_1 kT)^{1/2} \delta/h$ is employed, motion of activated complexes in both directions along the reaction coordinate is included. In that case ν must be calculated as $\nu = \bar{v}/\delta$, where

$$\bar{v} = \frac{\int_0^{\infty} v e^{-\frac{m_1 v^2}{2kT}} dv}{\int_{-\infty}^{\infty} e^{-\frac{m_1 v^2}{2kT}} dv}$$

$$= \frac{kT/m_1}{\left(\frac{2\pi kT}{m_1}\right)^{1/2}} = \left(\frac{kT}{2\pi m_1}\right)^{1/2}$$

That is, the normalizing factor in the calculation of \bar{v} must include motion in both directions, if the corresponding partition function does. The integral in the numerator must be carried out over positive velocities only, in order to pick out only

activated complexes moving toward products. Of course, one can use $1/2 (2\pi m_1 kT)^{1/2} \delta/h$ for the partition function of activated complexes moving only in the product direction (15), and then the normalizing integral in the calculation of \bar{v} must be carried out only over positive velocities, since now this is the type of activated complex whose concentration we have computed with the modified partition function. The result of multiplying the average velocity $(2 kT/\pi m_1)^{1/2}$ by the modified partition function is of course again kT/h . Mixing these procedures (9) gives extraneous and erroneous factors of 2 in the expression for the rate constant.

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