The Calculation of Reaction Cross Sections from Rate Constant Data

Undergraduate Research Thesis

Chemistry 80

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Work Done under

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CHECK ONE

____ I enthusiastically approve this thesis and recommend its author receive a Nobel Prize.

_____ I approve this thesis; it is acceptable.

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ABSTRACT

Starting with the theoretical expressions of Eliason and Hirshfelder relating rate constants and reaction cross sections for bimolecular gas phase reactions, selected numerical calculations were made to estimate the experimental accuracies required in the concentration and temperature measurements to estimate the cross section. These calculations indicate that the accuracies required are far beyond those presently attainable.

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1. Introduction

The experimental determination of reaction cross sections in important because of the fundamental role which reaction cross sections play in the understanding of chemical reactions. Just as the potential energy as a function of internuclear distance is essential to the understanding of vibration and rotation of diatomic molecules, the reaction cross section as a function of the relative kinetic energy of the reactant molecules is a fundamental description of the chemical reaction. The cross section describes not only equilibrium processes, but also the chemistry of flames, shock tubes, and detonations.

Eliason and Hirshfelder[1] have developed the formalism relating the reaction cross section to the rate constant for bimolecular gas phase reactions. Can experimental rate constant data be used in conjunction with this formalism to calculate the reaction cross section? This research indicates that the experimental accuracy required is not technologically feasible.

2. Reaction Cross Section Formalism of Rate Constants

In the formalism of Eliason and Hirshfelder[2] the rate of a bimolecular reaction of the form

$$A + B \longrightarrow C + D$$

ought to be considered as the sum of the rates of reactions of the form

$$A_i + B_j \longrightarrow C_k + D_l$$

where the subscript denotes the entire set of quantum numbers for a particular internal state. The detailed rate equation is then

$$-(dn_{ai}/dt)_{j,kl} = K_{ij}^{kl} n_{ai} n_{bj}$$

where n_{ai} and n_{bj} are the number densities of A_i and B_j, and K_{ij}^{kl} is the detailed rate constant. The overall rate is given by

$$-(dn_a/dt) = \sum_{ij} \sum_{kl} K_{ij}^{kl} n_{ai} n_{bj}$$

The kinetic theory of gases predcicts that the number of collisions in unit volume and unit time in which a molecule A_i collides with another molecule Bj to give product molecules C_k and D_l is

$$-(dn_{ai}/dt) = n_{ai} n_{bj} \iint f_{ai} f_{bj} C_{ij}^{kl}(E) g_{ij} d\vec{v}_{ai} d\vec{v}_{bj}$$

f_{ai} and f_{bj} are the normalized distribution functions for the molecular species A_i and B_j. ${C_{ij}}^{kl}(E)$ is the reaction cross section referring to collisions between molecules in states i and j, with initial asymptotic relative kinetic energy E, in which the resultant molecules are in states k and l. ${C_{ij}}^{kl}(E)$ contains no angular dependence. The quantity g_{ij} is the magnitude of the initial relative velocity, while $\vec{V}_{ai}$ and $\vec{V}_{bj}$ represent the velocity vectors of the molecules A_i and B_j in the laboratory system.

The detailed rate constant is then given by

$$K_{ij}^{kl} = \int\int f_{ai} f_{bj} \, {C_{ij}}^{kl}(E) \, g_{ij} \, d\vec{V}_{ai} \, d\vec{V}_{bj}$$

The rate equation becomes

$$-\left(dn_a/dt\right) = \sum_{ij} \sum_{kl} \left\{ \int\int f_{ai} f_{bj} \, {C_{ij}}^{kl}(E) \, g_{ij} \, d\vec{V}_{ai} \, d\vec{V}_{bj} \right\} n_{ai} n_{bj} \qquad (1)$$

If the velocities obey a Boltzmann distribution, eq. (1) can be specialized. The normalized Maxwell-Boltzmann velocity vector distribution is

$$f(\vec{r}, \vec{V}, t) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-m\vec{V}^2/2kT\right)$$

Substituting this distribution and tranforming to the center-of-mass system of the reactants yields

$$K_{ij}^{kl}(T) = 4\pi \left(\mu/2\pi kT\right)^{3/2} \int_0^\infty \exp\left(-\mu g_{ij}^2/2kT\right) {C_{ij}}^{kl}(E) \, g_{ij}^3 \, dg_{ij}$$

The integrals over the velocity of the center of mass and the angular portions of g_{ij} have been carried out since the reaction cross section is a function only of the relative kinetic energy. μ is the reduced mass of the reactants. In terms of an integral over relative kinetic energies, the detailed rate constant becomes

$$K_{ij}^{kl}(T) = (\pi\mu)^{-\frac{1}{2}} (2/kT)^{3/2} \int_0^\infty C_{ij}^{kl}(E)\, E \exp(-E/kT)\, dE$$

Finally, the rate equation has the form

$$-(dn_a/dt) = \sum_{ij} \sum_{kl} \frac{n_{ai} n_{bj}}{(\pi\mu)^{\frac{1}{2}}} (2/kT)^{3/2} \int_0^\infty C_{ij}^{kl}(E)\, E \exp(-E/kT)\, dE \qquad (2)$$

If the distribution among internal states of the reactant molecules is determined by thermal equilibrium, the internal partition function is

$$Z_a^{INT} = \sum_i \exp(-\epsilon_{ai}/kT)$$

$$n_{ai} = (n_a/Z_a^{INT}) \exp(-\epsilon_{ai}/kT)$$

With this substitution, eq. (2) becomes

$$-(dn_a/dt) = \left\{ \frac{(2/kT)^{3/2}}{(\pi\mu)^{\frac{1}{2}} Z_a^{INT} Z_b^{INT}} \sum_{ij} \sum_{kl} \exp\left[-(\epsilon_{ai} + \epsilon_{bj})/kT\right] \right.$$

$$\left. \times \int_0^\infty C_{ij}^{kl}(E)\, E \exp(-E/kT)\, dE \right\} n_a n_b$$

Comparison of this expression with the usual form of the rate equation

$$-(dn_a/dt) = k n_a n_b$$

leads to the identification

$$K(T) = \frac{(2/kT)^{3/2}}{(\pi\mu)^{\frac{1}{2}} Z_a^{INT} Z_b^{INT}} \sum_{ij} \sum_{kl} \exp\left[-(\epsilon_{ai} + \epsilon_{bj})/kT\right]$$

$$\times \int_0^\infty C_{ij}^{kl}(E)\, E \exp(-E/kT)\, dE$$

$$= \frac{(2/kT)^{3/2}}{(\pi\mu)^{\frac{1}{2}} Z_a^{INT} Z_b^{INT}} \sum_{ij} \exp\left[-(\epsilon_{ai} + \epsilon_{bj})/kT\right]$$

$$\times \int_0^\infty \left(\sum_{kl} C_{ij}^{kl}(E)\right) E \exp(-E/kT)\, dE \qquad (3)$$

$C_{ij}(E) = \sum_{kl} C_{ij}^{kl}(E)$ is the total reaction cross section for reactant molecules A_i and B_j reacting to give product molecules C and D. Eq. (3) may be further simplified if only one quantum state of each of the reactant molecules is significantly populated. This would be true in the case of low temperatures and large spacing between low-lying energy levels. The simplified result is

$$K(T) = (\pi\mu)^{\frac{1}{2}} (2/kT)^{3/2} \int_0^\infty C(E)\, E \exp(-E/kT)\, dE \qquad (4)$$

This simplified expression was used in the actual calculations. The experimental accuracy required to determine even this structureless cross section C(E) cannot be attained. A more complicated calculation involving partition functions can only lead to worse results.

3. Calculation of Reaction Cross Sections from Rate Constants

3.1. Estimation of Relative Error in C(E) for Specific Models

3.1.1. General Formalism

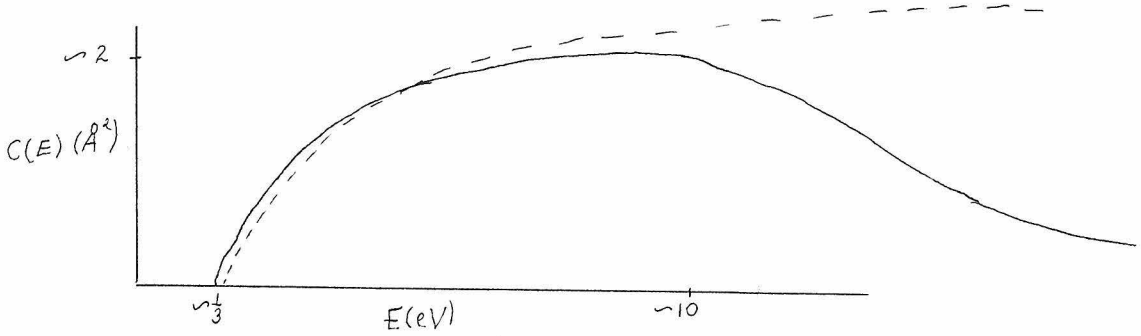
The first method is based on the statistical estimation of the relative error in the reaction cross section C(E) as a function of the relative error in K(T) due to concentration errors and as a function of the absolute error in temperature measurements for K(T). The relative error in K(T) due to errors in the concentration measurements, $\triangle K_{rc}$, and the absolute error in the temperature measurements, $\triangle T$, were determined subject to two criteria:

1) In order to present accurately the relative error in C(E), it should be estimated at an energy for which C(E) is neither very small nor large. The result is reported at an energy $E_{\frac{1}{2}}$, defined by the following relation

$$C(E_{\frac{1}{2}}) = \tfrac{1}{2} C_{max}$$

2) The contributions to $\frac{\Delta C}{C}(E_{\frac{1}{2}})$ from $\triangle K_{rc}$ and $\triangle T$ should be approximately equal. Experimentally, it is superfluous to make one source of error much smaller than another since the larger error will then dominate the result.

A qualitative sketch of the reaction cross section for a bimolecular reaction such as $H_2 + H \rightarrow H + H_2$ is shown by the solid line in the following graph.



The cross section C(E) is zero below the threshold energy Eo, rises to a maximum, and decreases to zero as E becomes large.

On the basis of these features, a rather general function was chosen.

$$C(E) = \begin{cases} 0 & E \le E_o \\ \sum_{i=1}^{N} D_i \left(1 - \left(\frac{E_o}{E}\right)^i\right) & E_o \le E \le \bar{E} \\ D_o \left(1 - \frac{E_o}{E}\right) & \bar{E} \le E \end{cases} \qquad (5)$$

Do is chosen so that C(E) is continuous at $\bar{E}$.

The behavior of this functionC(E) is sketched by the dotted line in the above graph. The discrepency at energies of several electron volts and larger in not important. The exponential in the integral of eq. (4) is such that the contribution to the integral from energies greater than three electron volts is numerically negligible compared

to the total integral.

Using eq. (5) for C(E) and statistical error formulae, the absolute error in C(E), $\triangle C(E)$, and hence the relative error, $\frac{\triangle C}{C}(E)$, may be estimated.

The expression for the root mean square statistical error in an experimental quantity G as a function of several independent experimental variables $x_1, x_2, \ldots, x_n$ was used to estimate the error.

$$\triangle G = \left[\sum_{i=1}^{n} \left(\frac{\partial G}{\partial x_i} \triangle x_i \right)^2 \right]^{\frac{1}{2}} \qquad (6)$$

where $\triangle x_i$ is the absolute error in the quantity x_i.[3]

Define the following:

$\triangle K_{jrc}$ = relative error in $K(T_j)$ due to error in concentration measurements

$\triangle K_{jc}$ = absolute error in $K(T_j)$ due to error in concentration measurements

$= K(T_j) \times \triangle K_{jrc}$

$\triangle T_j$ = absolute error in measurement of temperature T_j

$\triangle K_{jt}$ = absolute error in $K(T_j)$ due to error in temperature measurements

$= \frac{\partial K}{\partial T}(T_j) \times \triangle T_j$

$\triangle K_j$ = maximum($\triangle K_{jc}$, $\triangle K_{jt}$)

These quantities will be used equations of the general form of eq. (6).

Consider now the rate constant as a function of the temperature and the several cross section parameters Eo, D1, D_2,..., D_n. The temperature dependence may be removed by labeling the rate constants at a series of temperatures as distinct quantities.

$$K_j = K(E_o, D_1, \ldots, D_N, T_j)$$

Taking a series of temperatures T_1, T_2,..., T_{n+1}, these equations for K_j 1(1)n+1 may be solved implicitly, if not explicitly, for the cross section parameters.

$$E_o = E_o(K_1, K_2, \ldots, K_{N+1}) \tag{7a}$$

$$D_i = D_i(K_1, K_2, \ldots, K_{N+1}) \qquad i = 1(1)N \tag{7b}$$

Formula (6) may then be applied to eqs. (5), (7a), and (7b).

$$\Delta C(E) = \left[\left(\frac{\partial C(E)}{\partial E_o}\Delta E_o\right)^2 + \sum_{i=1}^{N}\left(\frac{\partial C(E)}{\partial D_i}\Delta D_i\right)^2\right]^{\frac{1}{2}} \tag{8a}$$

$$\Delta E_o = \left[\sum_{j=1}^{N+1}\left(\frac{\partial E_o}{\partial K_j}\Delta K_j\right)^2\right]^{\frac{1}{2}} \tag{8b}$$

$$\Delta D_i = \left[\sum_{j=1}^{N+1}\left(\frac{\partial D_i}{\partial K_j}\Delta K_j\right)^2\right]^{\frac{1}{2}} \qquad i = 1(1)N \tag{8c}$$

where the ΔK_j are defined as before.

From these formulae, $\frac{\Delta c}{c}(E_{\frac{1}{2}})$ may be estimated for a given set of ΔK_{jrc} and ΔT_j. These values of ΔK_{rc} and ΔT may not, however, be the values for which the

contribution to the error from temperature and concentration measurements are approximately equal. Such values of ΔK_{rc} and ΔT may be determined by noting that

$$\Delta K_j = \max(\Delta K_{jc}, \Delta K_{jt})$$

If $\Delta K_{jc} > \Delta K_{jt}$, then ΔK_{jt} may be increased until $\Delta K_{jt} = \Delta K_{jc}$ without altering the calculated results for $\frac{\Delta C}{C}(E_{\frac{1}{2}})$. This basic idea is utilized in the following algorithm:

1) An initial choice of ΔK_{rc} and ΔT is made and $\frac{\Delta C}{C}(E_{\frac{1}{2}})$ is estimated.

2) $\frac{\Delta C}{C}(E_{\frac{1}{2}})$ is homogenous of first order in the ΔK_j, i.e., if the ΔK_j are divided by a factor a, then $\frac{\Delta C}{C}(E_{\frac{1}{2}})$ is divided by the same factor a. If it is desired that $\frac{\Delta C}{C}(E_{\frac{1}{2}})$ equal a particular value f, then it may be scaled to the desired value. ΔK_{rc} and ΔT must be scaled by the same factor.

$$\frac{\Delta C}{C}/a = f = \left(\frac{\Delta C}{C}\right)'$$

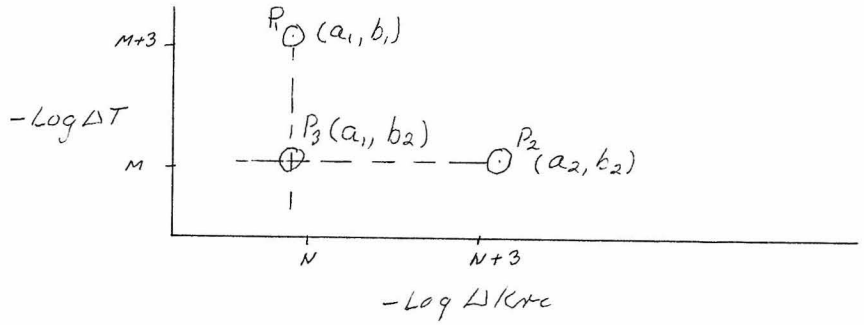
$$\Delta K_{rc} \longrightarrow \Delta K_{rc}' = \Delta K_{rc}/a$$

$$\Delta T \longrightarrow \Delta T' = \Delta T/a$$

3) On a graph of (-Log ΔT) versus (-Log ΔK_{rc}), the point (-Log $\Delta K_{rc}'$, -Log $\Delta T'$) is plotted and labeled by its f value.

4) The procedure above is repeated for different initial values of ΔK_{rc} and ΔT. If the first set of values was such that $\Delta K_{jc} > \Delta K_{jt}$, then the second set of values of ΔK_{rc} and ΔT should be chosen so that $\Delta K_{jc} < \Delta K_{jt}$, and vice versa.

5) A third point is now determined for the two already plotted. Consider the following example. Let P_1 be such that $\Delta K_{jc} > \Delta K_{jt}$ and have coordinates (a_1, b_1). Let P_2 be such that $\Delta K_{jt} > \Delta K_{jc}$ and have coordinates (a_2, b_2).



For point P_1, ΔK_{jt} can be increased until $\Delta K_{jt} = \Delta K_{jc}$ without altering the calculated result $\frac{\Delta C}{C}(E_{\frac{1}{2}})$. This corresponds to moving P_1 downward on the graph. Similarly, P_2 may be moved to the left until $\Delta K_{jc} = \Delta K_{jt}$. The intersection of these two lines, $P_3 = (a_1, b_2)$, is the point at which ΔK_{jc} is approximately equal to ΔK_{jt}.

The method is only approximate since ΔK_{jc} and ΔK_{jt} should both contribute to the error when they are approximately equal. The result of the method is an average ΔK_{rc}

and an average ΔT. Since only an order of magnitude estimate of these quantities is required, the approximate method is acceptable.

3.1.2. Hard Sphere Line of Centers Model

In the particular case of the line of centers model,[4]

$$C(E) = \begin{cases} 0 & E < E_o \\ \pi b^2 \left(1 - \frac{E_o}{E}\right) & E \geq E_o \end{cases}$$

For this function, the rate constant can be evaluated in closed form to obtain

$$K(T) = \pi b^2 \left(\frac{8k}{\pi\mu}\right)^{\frac{1}{2}} T^{\frac{1}{2}} \exp(-E_o/kT)$$

Taking the rate constant at two temperatures, T_1 and T_2, this expression may be inverted to obtain Eo and πb^2 as explicit functions of $K(T_1)$ and $K(T_2)$.

$$E_o = \frac{-k}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \left[\ln \frac{K(T_1)}{K(T_2)} - \frac{1}{2} \ln \frac{T_1}{T_2} \right]$$

$$\pi b^2 = \left(\frac{\pi\mu}{8k}\right)^{\frac{1}{2}} \exp\left[\frac{T_1 \ln K(T_1) - T_2 \ln K(T_2) - \frac{1}{2} T_1 \ln T_1 + \frac{1}{2} T_2 \ln T_2}{T_1 - T_2} \right]$$

The following values were chosen for the calculations: Eo = 1/3 eV; $\pi b^2 = 1.0$ Å^2. These values are a reasonable approximation for the bimolecular reaction $H_2 + D \rightarrow H + HD$.

Using formulae (8abc), $\frac{\Delta C}{C}(E_{\frac{1}{2}})$ may be estimated. The results are summarized in table I.

TABLE I

Accuracies Required

	$T_1=200^\circ K$ $T_2=300^\circ K$		$T_1=800^\circ K$ $T_2=900^\circ K$	
$\frac{\Delta C}{C}(E_{\frac{1}{2}})$	$\Delta T(^\circ K)$	ΔK_{rc}	$\Delta T(^\circ K)$	ΔK_{rc}
0.50	6.5	4×10^{-2}	2.0	1×10^{-1}
0.10	1.3	8×10^{-3}	0.4	3×10^{-2}
0.01	0.13	8×10^{-4}	0.04	3×10^{-3}
0.001	0.013	8×10^{-5}	0.004	3×10^{-4}

To obtain C(E) to an accuracy of 1-10% the temperature must be known and homogeneous to a few tenths of a degree and the rate constant itself must be known to three significant digits. These accuracies are attainable with present experimental technology.

3.1.3. Trajectory Calculation Model

The constraints implicit in the line of centers model cannot be justified physically. The model requires that the curve C(E) have a monotonically decreasing first derivative, i.e., no quantum effects, and that the reactant molecules interact as hard spheres. If the second constraint is relaxed and the more general cross section of eq. (5) is assumed, the likelihood that the model is physically

acceptable is increased.

Karplus, Porter, and Sharma have estimated a five term reaction cross section from trajectory calculations for the exchange reaction $H_2 + H \longrightarrow H + H_2$.[5] Physically reasonable data for the calculations may be obtained by using a particular set of these values for the hydrogen molecule in the state (v=0, J=2).

In the case of the more general cross section, the functions required can no longer be obtained explicitly, and consequently numerical methods are required. The mathematics supporting these methods is detailed in the following paragraphs.

Again the temperature dependence of the rate constant may be removed mathematically by considering the rate constant at different temperatures as separate functions, i.e.,

$$K_j = K(E_o, D_1, \ldots, D_5, T_j) \qquad j = 1(1)6 \qquad (9)$$

The K_j were calculated from the parameters given by Karplus, Porter and Sharma and then were regarded as experimental data for the calculation of ΔE_o, ΔD_i i=1(1)5. To obtain the errors given by eqs. (8bc), the derivatives

$$\frac{\partial E_o}{\partial K_j}, \quad \frac{\partial D_i}{\partial K_j} \qquad i = 1(1)5 \quad j = 1(1)6$$

are required.

Consider the inverse expressions for Eo and D_i i=1(1)5, which cannot be obtained explicitly.

$$E_o = E_o(K_1, K_2, \ldots, K_6)$$

$$D_i = D_i(K_1, K_2, \ldots, K_6) \qquad i = 1(1)5$$

Because of the previous indexing of the rate constant by temperature, there is no explicit temperature dependence in these formulae. Taking the total differential of these formulae yields the following expressions:

$$dE_o = \sum_{j=1}^{6} \frac{\partial E_o}{\partial K_j} dK_j \qquad (10a)$$

$$dD_i = \sum_{j=1}^{6} \frac{\partial D_i}{\partial K_j} dK_j \qquad i = 1(1)5 \qquad (10b)$$

Return now to eq. (9),

$$K_j = K(E_o, D_1, \ldots, D_5, T_j) \qquad j = 1(1)6 \qquad (9)$$

and take its total differential.

$$dK_j = \frac{\partial K_j}{\partial E_o} dE_o + \sum_{i=1}^{5} \frac{\partial K_j}{\partial D_i} dD_i \qquad j = 1(1)6 \qquad (11)$$

Eq. (11) yields six linear equations in the six unknowns dEo, dD_1, ..., dD_5. Define the matrix of the coefficients of these equations to be $\tilde{A}$. Define the minor of the ij element of $\tilde{A}$ to be $\tilde{A}_{ij}$. Cramer's rule gives the following result:

$$dE_o = \frac{1}{DET(\tilde{A})} \sum_{j=1}^{6} (-1)^{j+1} DET(\tilde{A}_{j,1})\, dK_j \qquad (12a)$$

$$dD_i = \frac{1}{DET(\tilde{A})} \sum_{j=1}^{6} (-1)^{j+i+1} DET(\tilde{A}_{j,i+1})\, dK_j \qquad i = 1(1)5 \qquad (12b)$$

Comparing the individual terms in eqs. (10) and (12), the desired derivatives are obtained.

$$\frac{\partial E_0}{\partial k_j} = (-1)^{j+1} \frac{DET(\check{A}_{j1})}{DET(\check{A})}$$

$$\frac{\partial D_i}{\partial k_j} = (-1)^{j+i+1} \frac{DET(\check{A}_{ji+1})}{DET(\check{A})} \qquad i = 1(1)5 \quad j = 1(1)6$$

Using formulae (8abc), $\frac{\Delta c}{c}(E_{\frac{1}{2}})$ may now be estimated. The results are summarized in table II.

TABLE II

Accuracies Required

	200°K-300°K		800°K-900°K	
$\frac{\Delta c}{c}(E_{\frac{1}{2}})$	$\Delta T(^{\circ}K)$	ΔK_{rc}	$\Delta T(^{\circ}K)$	ΔK_{rc}
0.50	1×10^{-7}	1×10^{-6}	5×10^{-6}	4×10^{-8}
0.10	1×10^{-8}	2×10^{-7}	1×10^{-6}	8×10^{-9}
0.01	1×10^{-9}	2×10^{-8}	1×10^{-7}	8×10^{-10}

In order to obtain an accuracy of 1-10% in the reaction cross section at 200-300°K, the temperature must be known and homogeneous to one one-hundred millionth of a degree, and the rate constant must be measured to seven significant digits. At 800-900°K, an accuracy of 1-10% can be obtained if the temperature is known and homogeneous to one millionth of a degree and if the rate constant is known to eight significant digits. These accuracies are far beyond the capabilities or expectations of experimental technology.

3.2. No Restrictions on Form of Reaction Cross Section

In the second method, all constraints are relaxed. However, the input data from Karplus, Porter, and Sharma previously described are initially used to estimate "correct" rate constants. These constants are then regarded as experimental data and direct calculation of C(E) at several energies is attempted.

$$K(T) = A(T) \int_0^\infty C(E)\, E \exp(-E/kT)\, dE$$

where $A(T) = (\pi\mu)^{-\frac{1}{2}} (2/kT)^{3/2}$

Since computers can perform integration only over finite intervals, the integral above must be truncated at an energy F. The condition for F is that

$$\int_F^\infty C(E)\, E \exp(-E/kT)\, dE < 10^{-9} \int_0^F C(E)\, E \exp(-E/kT)\, dE$$

Since Caltech's IBM 7090-7094 system normally carries only eight significant digits, the integration from 0 to F instead of 0 to ∞ causes negligible error.

$$K(T)/A(T) \cong \int_0^F C(E)\, E \exp(-E/kT)\, dE$$

The truncated integral may be approximated by a sum over a finite number of points by repeated use of Simpson's rule,[6] in which the integrand over each successive set of three points is approximated by a parabola, and the

integral over each parabolic arc is performed analytically.

$$K(T)/A(T) \cong \frac{1}{3}\sum_{i=1}^{N}\left[h_i E_{2i-2}\exp(-E_{2i-2}/kT)C(E_{2i-2}) + 4h_i E_{2i-1}\exp(-E_{2i-1}/kT)C(E_{2i-1}) + h_i E_{2i}\exp(-E_{2i}/kT)C(E_{2i})\right]$$

where $E_{2i} = 2\sum_{j=1}^{i} h_j$; $E_{2i-1} = E_{2i-2} + h_i$

If the above expression is evaluated at a series of 2n temperatures T_1, T_2, ..., T_{2n}, 2n linear equations in the 2n unknowns $C(E_1)$, $C(E_2)$, ..., $C(E_{2n})$ are obtained. These equations may be solved on the computer. The matrix of the coefficients is quite unstable, and meaningful solutions are difficult to obtain. Tables III and IV illustrate the instability.

Comparison of the results in tables III and IV show that a tiny change in the step length, h_i, produces large changes in the calculated solution. This instability may be inherent in the problem since an oscillatory function of the form shown the the next graph could still give the same value for the integral, and consequently for K(T), as a smooth function.

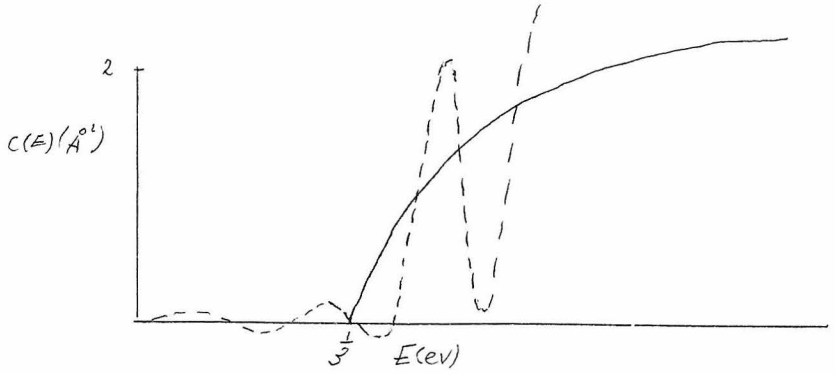


TABLE III

Direct Calculation of C(E)

E(eV)	C(E) ($\AA^2$)		ERROR (absolute)
	Calculated	Correct	
0.2220	0.453×10^{-3}	0.	0.453×10^{-3}
0.4440	0.389	0.329	0.600×10^{-1}
0.6660	0.161×10^{1}	1.030	0.580
0.8880	-0.494×10^{2}	1.278	-0.506×10^{2}
1.1100	0.414×10^{3}	1.395	0.413×10^{3}
1.3320	-0.791×10^{4}	1.473	-0.791×10^{4}
1.5540	0.752×10^{5}	1.529	0.752×10^{5}
1.7760	-0.362×10^{7}	1.571	-0.362×10^{7}
1.9980	0.210×10^{8}	1.603	0.210×10^{8}
2.2200	-0.357×10^{9}	1.629	-0.357×10^{9}

T = 800(10)890°K

TABLE IV

Direct Calculation of C(E)

E(eV)	C(E) (Å^2)		ERROR (absolute)
	Calculated	Correct	
0.2217	-0.120×10^{-3}	0.	-0.120×10^{-3}
0.4433	0.473	0.327	0.136
0.6650	-0.311	1.028	-0.134×10^{1}
0.8866	0.533×10^{2}	1.277	0.520×10^{2}
1.1083	-0.462×10^{3}	1.394	0.461×10^{3}
1.3299	0.128×10^{5}	1.472	0.128×10^{5}
1.5516	-0.333×10^{5}	1.528	-0.333×10^{5}
1.7732	-0.120×10^{7}	1.570	-0.120×10^{7}
1.9949	0.108×10^{8}	1.603	0.108×10^{8}
2.2165	-0.204×10^{9}	1.629	-0.204×10^{9}

$T = 800(10)890^{\circ}K$

If the true solution is oscillatory, then the large change in the calculated C(E) resulting from small variation in the step length corresponds to changes along the quickly varying oscillatory curve rather than the slowly varying average curve.

The appearance of an oscillatory solution is not unique to this problem of calculating reaction cross sections. The integral expression

$$K(T)/A(T) = \int_0^\infty C(E)\, E\, \exp(-E/kT)\, dE$$

defines G(1/kT) = K(T)/A(T) as the LaPlace transform of E x C(E).

The numerical inversion of LaPlace transforms has been treated by Lanczos[7], who examined four numerical methods and concluded that no method was generally applicable. The problem has been treated for specific types of functions in RAND reports[8] and reports of the Argonne National Laboratory.[9]

Using other methods, it may be possible to calculate C(E) more accurately. Assuming that this can be done, the sensitivity of the method to the accuracy of K(T) will be determined by systematically varying K(T) from its "correct" value. This procedure will not, however, distinguish between error in K(T) due to inaccuracy in temperature measurements and error from inaccuracy in concentration measurements.

4. Conclusions

The method of calculation of section 3.1. demonstrates conclusively that rate constant data cannot be used to obtain the cross section over a large energy range. The results in tables III and IV indicate that useful information might be obtained for a small energy range immediately above the threhold energy. This last statement cannot be presently confirmed, because more work would be required to reach a firm conclusion.

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