THE EFFECTS OF THERMAL ENERGY AND ION–REMOVAL TIME ON THE "PULSED SOURCE" METHOD FOR MASS SPECTROMETER INVESTIGATIONS OF ION–MOLECULE REACTIONS

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Summary

This paper examines two aspects of an experimental technique designed to investigate the dependence of ion–molecule specific reaction rates on primary ion energy. In this experiment the reaction proceeds in a mass spectrometer ion source under a constant electric field, and the ratio of secondary to primary ions is recorded as a function of time. Two assumptions lay behind the original treatment, namely that the energy spread of the primary ions at a given time was small, and that reactions taking place during the application of an ion-removal field were negligible. The present paper takes an idealized view of the ion source by ignoring possible effects of non-uniform electric fields and extraneous magnetic fields. Calculations are made which show that both ion-removal time and thermal energy are important. The initial thermal velocity and the electric field in the ion source interact to produce a large energy spread. For energy-independent reactions, a simple correction of experimental results should give true specific reaction rates.

I. Introduction

Recently, Ryan and others (Ryan and Futrell 1965*a*, 1965*b*; Ryan, Futrell, and Miller 1966) described a mass spectrometer experiment designed to investigate the dependence of ion–molecule specific reaction rates on the energy of the reactant ions. This experiment was based on the pulsed-source technique of Tal'roze and Frankevitch (1960), which may be described briefly as follows. An ionizing electron beam flows through the ion source for about 1 μsec and each ion–molecule reaction proceeds with both partners at thermal energies until, at some known time T later, an ion-extracting pulse removes both primary and secondary ions. Ryan and co-workers developed this experiment by adding a steady field E_1, always present. In principle, therefore, the energy of the primary ions at any time t could be calculated and the contribution to the secondary ion concentration at this instant could be ascribed to reactions with primary ions at this energy. In general,

$$dN_s = n_0 N_p k \, dt,$$ (1)

where n_0 is the molecular concentration, N_p the primary and N_s the secondary ion concentrations, and k the energy-dependent specific reaction rate. Thus, the slope of a plot of the corresponding ion current ratios against T should show the dependence of k on the drift time T.

To investigate the variation of k with ion energy E it is necessary to know E as a function of the time t since formation. The contribution of thermal energy to the ion energy was assumed by Ryan and co-workers to be insignificant, the only

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energy spread present being caused by the finite duration of the ionizing pulse. This pulse was of short duration (20 nsec) and the energy spread from this cause was therefore negligible. In the present investigation, we shall see that the effect of the electric field on the initial thermal velocity is to introduce a large energy spread.

A second assumption made was that the time taken for the ions to be swept out of the source, T_R, was small compared with the drift time T and that consequently reactions taking place during this time could be ignored. It is shown here that such reactions must be considered to avoid significant errors. It should be noted that the present calculations deal with an ideal physical situation. The ion source is regarded as a region where a uniform electric field exists. The effects of possible extraneous magnetic fields are neglected.

II. GLOSSARY OF TERMS

The following nomenclature is used:

$a_1 = E_1 e/m$	acceleration of ions under steady field E_1
$a_2 = E_2 e/m$	acceleration of ions under removal field E_2
E_1	steady electric field in ion source
E_2	ion-extraction pulse field in ion source
$E = \frac{1}{2}mv^2$	ion energy
$E_T = \frac{1}{2}mU^2$	initial ion thermal energy
$E_E = \frac{1}{2}m(a_1 t)^2$	ion energy in absence of initial velocity
$f(E_T)$	thermal energy distribution function
I_p	primary ion current
I_s	secondary ion current
k	true specific reaction rate
k'	apparent specific reaction rate
k_B	Boltzmann constant
L	distance between filament and exit slit of ion source
m	ion mass
N_p	primary ion concentration
N_s	secondary ion concentration
n_0	molecular concentration
t	time after ionizing pulse
T	drift time (time between ionizing and extraction pulses)
T_R	ion-removal time (time for extraction pulse to remove ions)
T'	temperature (°K)
U	ion thermal velocity
$\bar{U} = (8k_B T'/\pi m)^{\frac{1}{2}}$	mean ion thermal velocity
v	ion velocity
α	polarizability of molecule
μ_D	permanent dipole moment of molecule
μ	reduced mass of ion–molecule pair
σ	reaction cross section
$\sigma_D = \pi e \mu_D m/\mu$	dipole moment contribution factor
$\sigma_L = \pi e (2\alpha m/\mu)^{\frac{1}{2}}$	polarization contribution factor
θ	direction of thermal velocity vector

III. Thermal Energy Considerations

It is instructive to first consider the simplified case where all ions possess the same initial velocity $\bar{U} = (8k_B T'/\pi m)^{\frac{1}{2}}$, the mean thermal velocity, where T' is the temperature, m the ion mass, and k_B the Boltzmann constant. Their acceleration is a_1 under the steady field E_1. If N is the total number of ions leaving the formation point A (see Fig. 1), the number of ions leaving A in directions between θ and $\theta + \delta\theta$ is given by

$$\delta N = N(2\pi \sin\theta\, \delta\theta)/4\pi = \tfrac{1}{2}N \sin\theta\, \delta\theta\,,$$

or

$$\mathrm{d}N/\mathrm{d}\theta = \tfrac{1}{2}N \sin\theta\,. \tag{2}$$

The energy E of these ions at time t after formation is

$$E = \tfrac{1}{2}m(\bar{U}\cos\theta + a_1 t)^2 + \tfrac{1}{2}m(\bar{U}\sin\theta)^2$$

$$= \bar{E}_T + E_E + 2(\bar{E}_T E_E)^{\frac{1}{2}}\cos\theta\,, \tag{3}$$

where $\bar{E}_T$ is the initial mean energy, $\tfrac{1}{2}m\bar{U}^2$, and E_E is the energy the ions would possess in the absence of an initial velocity. Thus the maximum and minimum
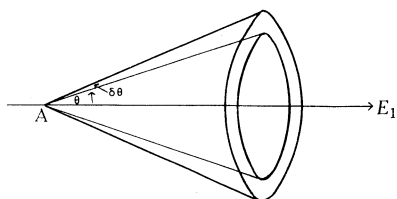

Fig. 1.—Geometry of ion motion. A is any point in the ion-formation area.

energies are separated by $4(\bar{E}_T E_E)^{\frac{1}{2}}$. However, it is important to know what proportion of the ions actually possess energies near these limits, i.e. to know the distribution function $\mathrm{d}N/\mathrm{d}E$ as a function of energy,

$$\frac{\mathrm{d}N}{\mathrm{d}E} = \frac{\mathrm{d}N/\mathrm{d}\theta}{\mathrm{d}E/\mathrm{d}\theta} = \frac{\tfrac{1}{2}N \sin\theta}{2(\bar{E}_T E_E)^{\frac{1}{2}}\sin\theta}$$

$$= \tfrac{1}{4}N(\bar{E}_T E_E)^{-\frac{1}{2}}\,. \tag{4}$$

Thus the distribution of energy is even between the limits $\bar{E}_T + E_E \pm 2(\bar{E}_T E_E)^{\frac{1}{2}}$. For $\bar{E}_T = 0\cdot05$ eV and $E_E = 1$ eV this spread is nearly $0\cdot9$ eV. Hence, even when the initial energy spread is assumed to be zero, the resulting energy spread is, in this example, almost as large as the mean energy.

We now consider the realistic case of an initial Maxwellian energy distribution; the number of ions with initial thermal energies in the range $\mathrm{d}(E_T)$ is then

$$\mathrm{d}N = N f(E_T)\, \mathrm{d}E_T$$

$$= 2N\pi^{-\frac{1}{2}}(k_B T')^{-3/2} E_T^{\frac{1}{2}} \exp(-E_T/k_B T')\, \mathrm{d}E_T\,. \tag{5}$$

After acceleration by the steady field E_1, an initial thermal energy E_T will be responsible for energies in the band $E = E_T + E_E \pm 2(E_T E_E)^{\frac{1}{2}}$. It can be simply

shown from this that initial thermal energies in the range $E+E_E-2(E_E E)^{\frac{1}{2}}$ to $E+E_E+2(E_E E)^{\frac{1}{2}}$ contribute to a final energy E. Thus the distribution becomes

$$\frac{\mathrm{d}N}{N} = \frac{1}{4} \int_{E_T=E+E_E-2(E_E E)^{\frac{1}{2}}}^{E+E_E+2(E_E E)^{\frac{1}{2}}} (E_E E_T)^{-\frac{1}{2}} f(E_T) \, \mathrm{d}E_T \tag{6}$$

$$= \frac{E_E^{-\frac{1}{2}}}{2\pi^{\frac{1}{2}} (k_B T')^{3/2}} \int_{E_T} \exp(-E_T/k_B T') \, \mathrm{d}E_T \tag{7}$$

$$= (\pi E_E k_B T')^{-\frac{1}{2}} \exp\{-(E+E_E)/k_B T'\} \sinh\{2(E_E E)^{\frac{1}{2}}/k_B T'\}. \tag{8}$$

Figure 2 shows, for a number of examples:

(1) the energy E_E that the ions would obtain in the absence of a thermal velocity, and the spread in E_E caused by the finite duration of the ionizing pulse alone;

(2) the ion energy distribution for the simplified case of uniform thermal velocity (equation (4));

(3) the ion energy distribution for an initial Maxwellian distribution (equation (8)).

These examples show that the energy spread caused by thermal energies is very much greater than the spread caused by the duration of the ionizing pulse. In the lowest energy example (Fig. 2(a), $E_E = 0 \cdot 013$ eV), not only the energy spread but also the mean energy is greatly altered. Consideration of the actual Maxwellian distribution is most important in this example. The effects of these distributions on experimental results are discussed in Section V(b).

IV. Ion-removal Time

The second assumption made by Ryan and co-workers was that reactions taking place while the ions were being swept out by the extraction pulse were negligible. This ion-removal time can be shown to be

$$T_R = a_2^{-1}[-a_1 T + \{(a_1 T)^2 + 2a_2(L - \tfrac{1}{2}a_1 T^2)\}^{\frac{1}{2}}], \tag{9}$$

where L is the length of the ion path, T is the time between ionizing and extraction pulses, $a_1 = E_1 e/m$, and $a_2 = E_2 e/m$.

Figure 3 shows the variation of ion-removal time T_R with drift time T for three ion masses and two values of steady field E_1. (An extracting pulse E_2 of 80 V/cm and an ion path length L of $0 \cdot 125$ cm were used in the calculations.) The figure shows also the instantaneous kinetic energy at points along the ion path; the ratio T_R/T at a given energy is seen to be independent of ion mass and dependent only on the field strengths E_1 and E_2. We can see that under many conditions the ion-removal time T_R is an appreciable fraction of the total time in the ion source (T_R+T).
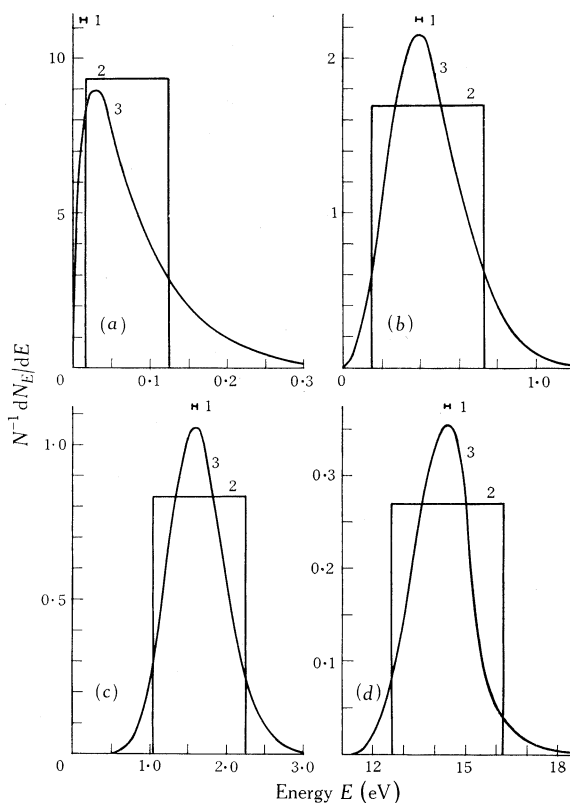
Fig. 2.—Curves for ions of mass 30 (under a 10 V/cm steady field and at a temperature of 520°K) showing (1) spread of energy E_E for ions in the absence of thermal velocity, (2) ion energy distribution for uniform thermal velocity, and (3) ion energy distribution for an initial Maxwellian distribution: (a) $E_E = 0 \cdot 013 \pm 0 \cdot 003$ eV, $T = 0 \cdot 1$ μsec; (b) $E_E = 0 \cdot 386 \pm 0 \cdot 016$ eV, $T = 0 \cdot 5$ μsec; (c) $E_E = 1 \cdot 58 \pm 0 \cdot 03$ eV, $T = 1 \cdot 0$ μsec; (d) $E_E = 14 \cdot 37 \pm 0 \cdot 09$ eV, $T = 3 \cdot 0$ μsec.
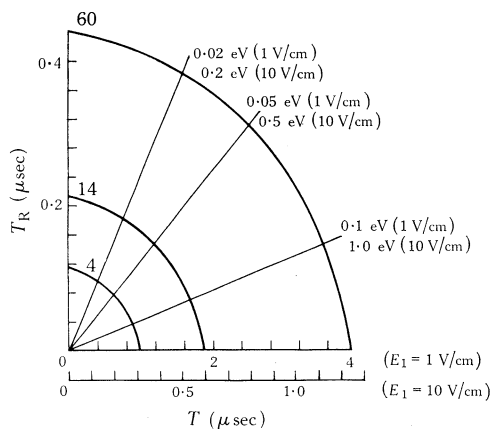

Fig. 3.—Curves showing the variation of ion-removal time T_R with drift time T for ions of mass 4, 14, and 60. Time scales appropriate to $E_1 = 1$ and 10 V/cm are shown. The intersections of the radial lines with the curves give the times at which the given energies are obtained.

V. APPLICATION

We now illustrate the effect of ion-removal time and thermal energy on the measurement of specific reaction rates by considering two idealized reactions. We consider the effect of ion-removal time by assuming a reaction whose specific rate is independent of energy, and the effect of energy spread by assuming a reaction to possess a specific rate simply dependent on energy.

(a) Ion-removal Time

Ryan and co-workers found that for some of the ion–molecule reactions studied the curve of I_s/I_p against drift time had a linear slope that was dependent upon the steady electric field. Hyatt, Dodman, and Henchman (1966) have since pointed out that unpublished calculations by Harrison show that when ion-removal time is taken
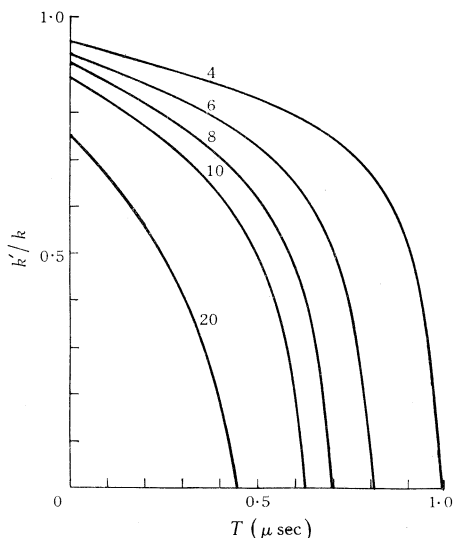

Fig. 4.—Variation of the ratio of apparent to true specific reaction rates, k'/k, with drift time T for ions of mass 15, $E_2 = 80$ V/cm, and steady fields E_1 of 4, 6, 8, 10, and 20 V/cm.

into account one obtains the same specific reaction rates for different values of the steady field. If we take a simplified form of an equation deduced by Tal'roze and Frankevitch (1960), for an energy-independent reaction,

$$I_s/I_p = n_0 kT + n_0 kT_R, \tag{10}$$

then

$$\frac{d}{dT}\left(\frac{I_s}{I_p}\right) = n_0 k\left\{1 + \frac{d}{dT}\left(T_R\right)\right\}. \tag{11}$$

The apparent specific rate k' is thus given by $k\{1 + d(T_R)/dT\}$, and the I_s/I_p versus T plot will be curved. Figure 4 shows the expected variation of k'/k with drift time T for five values of steady field E_1 and for a primary ion of mass 15. It is clear that k'/k varies with T and so with ion energy E, although, if T is not allowed to approach its maximum possible value too closely, this variation may be masked by experimental

error. The apparent specific reaction rate k', as $T \to 0$, is related to the true value k by

$$(k'/k)_{T \to 0} = \lim_{T \to 0}\{1 + \mathrm{d}(T_\mathrm{R})/\mathrm{d}T\} = 1 - E_1/E_2. \tag{12}$$

Ryan and Futrell (1965b) have published values of k'/k_p for five reactions, k_p being the specific reaction rate measured by the conventional pressure method using the same instruments. For four of these reactions the values are in close agreement and have a mean value of $0 \cdot 88$. However, substituting the fields used in Ryan and Futrell's experiment, namely $E_1 = 10$ and $E_2 = 90$ V/cm, in the present equations gives a value of k'/k of $0 \cdot 89$, and we may conclude that ion-removal time explains the discrepancy. Thus, if we can assume energy independence, equation (12) can be used to correct apparent specific reaction rates for ion-removal time.

(b) Thermal Energy and Ion-removal Time

We illustrate the effect of thermal energy with the reaction

$$HCl^+ + HCl \to H_2Cl^+ + Cl. \tag{13}$$

The HCl molecule possesses a permanent dipole moment μ_D, and, for the purpose of this illustration, we assume that the reaction is not complicated by any parallel or secondary reactions, that the reaction cross section σ is equal to the collision cross section, and that the collision cross section in the low energy region follows the theory of Moran and Hamill (1963), i.e.

$$\sigma = \sigma_\mathrm{D} E^{-1} + \sigma_\mathrm{L} E^{-\frac{1}{2}}, \tag{14}$$

where $\sigma_\mathrm{D} = \pi e \mu_\mathrm{D} m/\mu$, is the dipole moment contribution factor, $\sigma_\mathrm{L} = \pi e(2\alpha m/\mu)^{\frac{1}{2}}$ is the polarization contribution factor, μ is the reduced mass of the pair, and α is the polarizability.

As the mean vector velocity of the molecular partner in the reaction is zero, we assume here that the relative velocity of the pair is equal to the ion speed v, in which case

$$k = \sigma v = \sigma_\mathrm{D}(2/mE)^{\frac{1}{2}} + \sigma_\mathrm{L}(2/m)^{\frac{1}{2}}. \tag{15}$$

We find below (Fig. 5, curves 1) that the first term of this expression, which determines the change of k with E, is small for energies above $0 \cdot 1$ eV. During ion removal, energies will almost always exceed this value, and hence the term may be neglected during this time.

The expression for $I_\mathrm{s}/I_\mathrm{p}$ for a drift time T is

$$I_\mathrm{s}/I_\mathrm{p} = n_0 \int_0^{T+T_\mathrm{R}} k \, \mathrm{d}t$$

$$= n_0 \int_0^T \{2\sigma_\mathrm{D}/mv + (2/m)^{\frac{1}{2}}\sigma_\mathrm{L}\} \, \mathrm{d}t + n_0 \int_T^{T+T_\mathrm{R}} (2/m)^{\frac{1}{2}}\sigma_\mathrm{L} \, \mathrm{d}t \tag{16}$$

$$= n_0\left(\int_0^T 2\sigma_\mathrm{D}/mv \, \mathrm{d}t + (2/m)^{\frac{1}{2}}\sigma_\mathrm{L}(T + T_\mathrm{R}) \right), \tag{17}$$

and

$$\frac{d}{dT}\left(\frac{I_s}{I_p}\right) = n_0\left[\frac{2\sigma_D}{mv}+\left(\frac{2}{m}\right)^{\frac{1}{2}}\sigma_L\left\{1+\frac{d}{dT}\left(T_R\right)\right\}\right].$$ (18)

We can divide equation (18) into two parts:

$$A = n_0\left\{\frac{2\sigma_D}{mv}+\left(\frac{2}{m}\right)^{\frac{1}{2}}\sigma_L\right\}$$ (19)

and

$$B = n_0\left(\frac{2}{m}\right)^{\frac{1}{2}}\sigma_L\frac{d}{dT}\left(T_R\right),$$ (20)

part B being the correction for reactions that occur during the ion-removal time.

If we now consider the initial thermal velocity (U, θ) of the ions

$$A = n_0\int_{E_T}\int_\theta f(E_T)\tfrac{1}{2}\sin\theta\,(2\sigma_D/m)\{(U\cos\theta+a_1T)^2+U^2\sin^2\theta\}^{-\frac{1}{2}}\,d\theta\,dE_T+(2/m)^{\frac{1}{2}}\sigma_L$$ (21)

and

$$B = n_0(2/m)^{\frac{1}{2}}\sigma_L\int_{E_T}\int_\theta f(E_T)\tfrac{1}{2}\sin\theta\,d(T_R)/dT\,d\theta\,dE_T,$$ (22)

where

$$U = 2(E_T/m)^{\frac{1}{2}}.$$

T_R is dependent on the initial thermal velocity U as

$$T_R = a_2^{-1}[-(U\cos\theta+a_1T)+\{(U\cos\theta+a_1T)^2+2a_2(L-UT\cos\theta-\tfrac{1}{2}a_1T^2)\}^{\frac{1}{2}}]$$ (23)

and

$$d(T_R)/dT = (U\cos\theta+a_1T)(a_1-a_2)\{(U\cos\theta+a_1T)^2$$
$$+2a_2(L-UT\cos\theta-\tfrac{1}{2}a_1T^2)\}^{\frac{1}{2}}-a_1/a_2.$$ (24)

In Figure 5 curves of $n_0^{-1}d(I_s/I_p)/dT$ for reaction (13) are presented for the following cases:

(1) No corrections $(U = 0)$. This is the ideal case where $n_0^{-1}d(I_s/I_p)/dT = k$.

(2) Thermal energy effect included (equation (21)).

(3) Both thermal energy and ion-removal time effects included (equations (21) and (22)).

The points marked X on curves 1 of Figure 5 are at an energy of $0\cdot1$ eV. This corresponds to the mean energy of molecules at nearly 1000°K, so reactions taking place at energies below this value are of great interest. Here the curves 1 and 2 diverge rapidly and the thermal energy effect is serious.

The thermal energy effect at low energies may be a little greater than that suggested by Figure 5. The expressions for σ_D and σ_L (equation (14)) assume that only the ion velocity contributes to the centre-of-mass energy of the collision system. However, the molecular partners in the reaction also possess thermal velocities and, although (unlike the ion case) the effect of this will not be "amplified" by the electric field, it will still contribute to the total energy spread, particularly at lower energies, and so will increase slightly the deviation of curves 1 and 2.
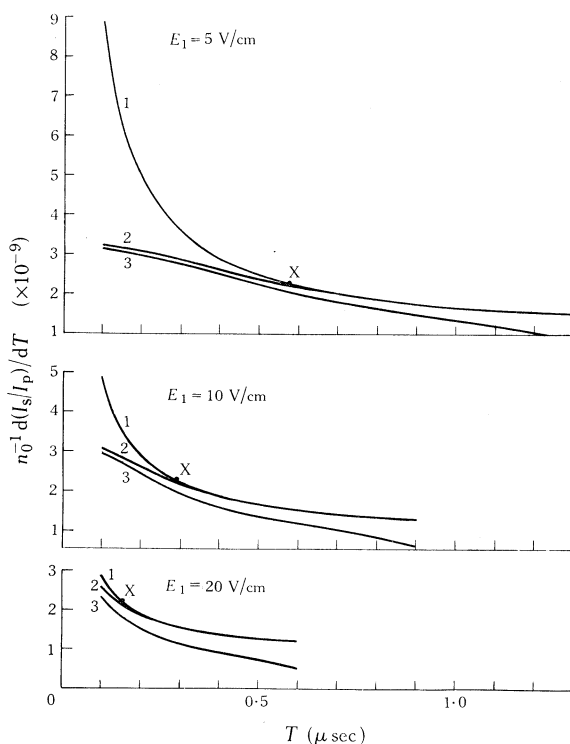

Fig. 5.—Effect of thermal energy and ion-removal time on the secondary to primary ion current ratio, I_s/I_p, for an energy-dependent reaction: curves 1, no corrections; 2, thermal energy effect included; 3, both thermal energy and ion-removal effects included. The points marked X correspond to ion energies of $0 \cdot 1$ eV.

Also, the energy distribution in a practical ion source may differ somewhat from the present idealized solution. For example, ions initially moving in the line joining the source to the exit slit contribute to the tails of the distribution. If therefore, as seems likely, these ions have a greater chance of being collected, the tails of the distribution will be emphasized.

Because of the complexity of equations (21) and (22), it is unlikely that a simple correction for thermal energy can be found. The most hopeful way of investigating these low energies is probably to assume a model depicting the variation of specific reaction rate k with energy E and to predict the shape of experimental curves for this model. The degree of fit between predicted and experimental curves should then be an indication of the correctness of the model.

VI. ADDENDUM

After this paper was written, Professor R. L. F. Boyd and the referee drew the authors' attention to the solutions of problems analogous to the present thermal energy problem. Massey (1964) calculated energies of atmospheric molecules relative to a moving space craft, and Chantry and Schultz (1964) studied an experiment on dissociative attachment or ionization of molecules.

VII. ACKNOWLEDGMENT

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