

Quasi-Equilibrium Theory of Ionic Fragmentation: Further Considerations *

CORNELIUS E. KLOTS

Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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A recent reformulation of quasi-equilibrium theory is extended to several additional classes of ionic decompositions. Formulae for calculating average translational and rotational energies of the fragments are presented, and kinematic corrections to the formulas are introduced. Illustrative calculations are compared with experiment, and the interesting possibility of maxima in rate constants is noted.

Introduction

In a recent reformulation of the quasi-equilibrium theory of unimolecular decompositions¹ it was shown how a first-order rate constant could be obtained from microscopic reversibility and cross sections for the bimolecular association step. The emphasis there, and below as well, was placed on the decomposition of a singly charged species to a charged and a neutral species, since it was argued that the appropriate cross sections could be plausibly obtained from the long-range forces. The reactions considered earlier were 1) a spherical top going to a spherical top and an atomic species, 2) to two linear fragments, and 3) to a linear and a monatomic fragment. We wish now to derive similar formulae for the cases of the spherical top producing 4) two spherical tops, and 5) a spherical top and a linear fragment. We will discuss also formulae for the average kinetic and rotational energies shared by the separating fragments, and finally a rather novel consequence of the present formalism.

Rate Constant Expressions

The rate constant for the decomposition of a species of total energy $(E + E_0)$, with E_0 the 0°K endothermicity of the reaction, is given by quasi-equilibrium theory¹ as:

$$k_i = \sum_{x=0}^E g_i(x, \alpha_i) \cdot \frac{\sigma(f, i)}{\pi \lambda^2} / h \varrho(E + E_0, \alpha_i) \quad (1)$$

where $g_i(x, \alpha_i)$ is the degeneracy factor for the separated fragments of internal energy x , $\sigma(f, i)$ is

the cross section for their association to form the activated species, and $\varrho(E + E_0, \alpha_i)$ the density of states of this activated species. These degeneracy factors are evaluated subject to whatever additional constraints α_i may be pertinent, as, for example, conservation of angular momentum.

We will be discussing here dissociating spherical tops, for which the rotational energy is given by $\varepsilon_r = B_0 J_0(J_0 + 1)$, where J_0 is the rotational quantum number. In Eqs. (8—10) of Ref. 1, expressions were presented for rate constants for the first three cases mentioned above. These were of the form

$$k(E + E_0, J_0) \cong \int_0^E \varrho_v(x) (E - x)^s dx / \beta h \varrho_v(E_v) \quad (2)$$

where $\varrho_v(x)$ is the density of vibrational states of the products and $\varrho_v(E_v)$ that of the activated complex. The parameter β is a function of the rotational constants of the products; it and the exponents S are reproduced in Table 1 for these three reactions. Although not shown in Eq. (2), a statistical reaction-path factor must be included, as discussed earlier¹, when rate constants are evaluated.

Let us now consider the further case of a sphere dissociating to two spheres, having rotational constants B_1, B_2 . In what follows, E is the total energy available to the products, x is that appearing as vibrational energy, and y is that appearing either as translational energy of the fragments or as rotational energy of the first sphere, so that $E = x + y + B_2 J_2(J_2 + 1)$. We will now assume that the cross-sections for complex formation are given by the Langevin method for ion-molecule collisions. With this model, the cross-section, in terms of the de Broglie wavelength λ associated with the relative motion, is $\sigma = (2L + 1) \pi \lambda^2$. The orbital angular momentum L may range from zero

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up to an L_{\max} given by

$$(L_{\max} + 1)^2 = \gamma[y - B_1 J_1(J_1 + 1)]^{1/2}. \quad (3)$$

The parameter γ is defined by

$$\gamma = (2\mu/m)(\alpha/Ra_0^3)^{1/2}$$

where μ is the reduced mass of the separating fragments, m that of an electron, α_0 the polarizability of the neutral fragment, a_0 the Bohr radius, and R the Rydberg energy. Thus one obtains the usual Langevin collision formula upon summing over $0 \leq L \leq L_{\max}$. In the present context, however, one must first consider the probability that L couples with the J_1 of the first sphere to yield some J_0' . From the correspondence principle this is just $(2J_0' + 1)/(2J_1 + 1)(2L + 1)$, provided that $J_1 + L \geq J_0' \geq |J_1 - L|$. Thus one obtains

$$(\sigma/\pi\lambda^2)(L, J_1 \rightarrow J_0') = (2J_0' + 1)/(2J_1 + 1). \quad (4)$$

We now sum Eq. (4) over all available L and then over all available J_1 . L is restricted to the range $|J_0' - J_1| \dots J_0' + J_1$, and J_1 is restricted by energy conservation to the range from zero to $(y/B_1)^{1/2}$. If we further make the approximation

$$y \ll \gamma^2 B_1^2 \quad (5)$$

then the additional restriction imposed by the Langevin model, represented by Eq. (3), becomes unimportant. This is illustrated by curve (b) in

Fig. 1 of Ref. 1. The physical meaning of this approximation, and necessary corrections arising from it, will be discussed below.

One must now multiply Eq. (4) by the rotational degeneracy of the first sphere, $(2J_1 + 1)^2$. Then on evaluating the summation, one obtains

$$\begin{aligned} (\sigma/\pi\lambda^2)(y \rightarrow J_0') &= (2J_0' + 1) \\ &\times [4/3 J_0'^3 + (2J_0' + 1)(y/B_1 - J_0'^2)], \quad y \geq B_1 J_0'^2 \\ &= (2J_0' + 1)[4(y/B_1)^{3/2}/3], \quad y \leq B_1 J_0'^2. \end{aligned} \quad (6)$$

We require now that J_0' couple with J_2 to yield J_0 , the probability for which is

$$(2J_0 + 1)/(2J_0' + 1)(2J_2 + 1),$$

subject to the limitation $J_0' = J_0 + J_2 \dots |J_0 - J_2|$. If the parent ion is scarcely rotating, so that $J_2 > J_0$, then there are $(2J_0 + 1)$ available values for J_0' , and the average value of these J_0' will be J_2 . Making this substitution in Eq. (6) and including the rotational degeneracy of the second sphere, one has

$$\begin{aligned} (\sigma/\pi\lambda^2)[(E - x) \rightarrow J_0] &= (2J_0 + 1)^2 \left\{ \int_0^a (2J_2 + 1) dJ_2 \right. \\ &\times \left[\frac{4}{3} J_2^3 + (2J_2 + 1) \left(\frac{(E - x) - B_2 J_2^2}{B_1} - J_2^2 \right) \right] \\ &\left. + \int_a^\xi (2J_2 + 1) dJ_2 \frac{4}{3} \left[\frac{(E - x) - B_2 J_2^2}{B_1} \right]^{3/2} \right\} \quad (7) \end{aligned}$$

with the limits of integration given by

$$a^2 = (E - x)/(B_1 + B_2), \quad \xi^2 = (E - x)/B_2.$$

Table 1. Parameters Appropriate to Rate Constants Given by Equation (11).

Reaction Products	S	β	β'	β''
Sphere and Atom	1	B_s	$\gamma^2 B^2$	$(\gamma^2 B^2)^{2/2}$
Two Linear	3/2	$\frac{3}{2} \left[\frac{B_1 B_2}{B_1^{1/2} + B_2^{1/2} - (B_1 + B_2)^{1/2}} \right]$	$\frac{75}{8} \gamma^2 (B_1 B_2)^3 \div$ $\beta \left[B_1^{3/2} + B_2^{5/2} + \frac{5}{2} B_1 B_2 (B_1^{1/2} + B_2^{1/2}) \right.$ $\left. + \frac{15}{8} (B_1 B_2)^{1/2} (B_1^{3/2} + B_2^{3/2}) - (B_1 + B_2)^{2/2} \right]$	—
Linear and Atom	1/2	$B_l^{1/2}$	$2 \gamma^2 B_l^2$	$8 (\gamma^2 B^2)^{2/7}$
Two Spheres	5/2	$\frac{15}{8} B_1 B_2 (B_1 + B_2)^{1/2}$	$7 (\gamma B_1 B_2)^2 / 4 (B_1 + B_2)^2$	—
Sphere and Linear	2	$(B_s + B_l)^2 \div$ $\left[\frac{1 - 2\epsilon}{2\epsilon} \right.$ $\left. + \frac{2}{\epsilon^{3/2} (1 - \epsilon)^{1/2}} \int_0^\epsilon dz z^{1/2} (1 - z)^{1/2} \right]$	$3 \gamma^2 B_s^3 B_l \div$ $\beta \left[(1 + \epsilon) \right.$ $\left. + \frac{3}{\epsilon^{1/2} (1 - \epsilon)^{3/2}} \int_0^\epsilon dz z^{3/2} (1 - z)^{1/2} \right]$	—
$\epsilon \equiv B_s / (B_s + B_l)$				

The integration is readily performed, and upon insertion of the result in Eq. (1), the rate constant expression obtained

$$k(E + E_0, J_0) \cong \frac{8}{15} \int_0^E \frac{\rho_v(x) (E - x)^{5/2} dx}{(B_1 + B_2)^{1/2} B_1 B_2} / h \rho_v(E_v) \quad (8)$$

which is seen also to be of the form of Eq. (2).

The case of the sphere dissociating to a sphere and a diatomic molecule follows through in a parallel manner. One considers the coupling of the orbital angular momentum with that of one of the fragments (either one) and then the coupling with the second fragment to yield the final J_0 . The resultant expression is also of the form of Eq. (2). The parameters S and β for reactions (4) and (5) are included in the table. Note that $2S$ is always equal to one less than the number of rotational degrees of freedom in the products.

Kinetic Energies of Fragmentations

Several years ago TAUBERT² began measuring the kinetic energies of the fragments of ionic dissociations, and then discussed some of their implications. These results were scrutinized³ in terms of quasi-equilibrium theory and found to be generally compatible with it. Since then measurements of kinetic energy have become a useful diagnostic technique⁴⁻¹¹. In view of the present reformulation of quasi-equilibrium theory, a reexamination of its predictions would seem to be in order, especially since it has been recently claimed¹² that some of the kinetic energy measurements are in flagrant

disagreement with theory. We shall indicate here how this can be done, leaving a detailed examination until a later publication. The average kinetic energy of fragmentation is to be evaluated from

$$\bar{\varepsilon}_t = \int_0^E P(E, \varepsilon_t) \cdot \varepsilon_t d\varepsilon_t$$

where $P(E, \varepsilon_t)$ is just the probability that an ion with available energy E dissociates via a channel yielding ε_t . In the formalism of Eq. (2), however, ε_t does not appear explicitly, since the term $(E - x)$ is the sum of the translational and rotational energies — which we shall call the “external energy”. Nevertheless $\bar{\varepsilon}_t$ may be obtained from an average $(\bar{E} - x)$, multiplied by the fraction of this external energy appearing as ε_t . Thus

$$\bar{\varepsilon}_t = \frac{\int_0^E \rho_v(x) \cdot (E - x)^{s+1} dx}{\int_0^E \rho_v(x) (E - x)^s dx} \cdot F_t \quad (9)$$

where F_t is this fraction. This parameter may be obtained by examining the derivation of the several rate constant expressions at, for example, the stage of Equation (7). The results are quite simple, and the F_t factors are given in Table 2 for the several reaction types. It is also possible to give a simple-minded justification of their magnitude. Any dissociation occurs in a plane of some suitable orientation, and in which there are two kinetic degrees of freedom. The number of effective degrees of rotational freedom is one less than the physical number, because of the constraint of angular momentum conservation. F_t should then be the fraction of the

Table 2. Parameters Describing Kinetic and Rotational Energy Production.

Reaction Products	F_t	$F(R_1)$	Range $F(R_1)$
Sphere and Atom	1/2	1/2	1/2
Two Linear	2/5	$\frac{2\beta}{15 B_1 B_2} \left[2 B_2^{1/2} + B_1^{1/2} - \frac{(B_1 + 2 B_2)}{(B_1 + B_2)^{1/2}} \right]$	1/5—2/5
Linear and Atom	2/3	1/3	1/3
Two Spheres	2/7	$\frac{3 B_1 + 2 B_2}{7 (B_1 + B_2)}$	2/7—3/7
Sphere (1) and Linear (2)	1/3	$\beta (B_s + B_l)^2 x$ $\left[\frac{1 + \varepsilon - 4 \varepsilon^2}{6 \varepsilon} + \frac{2}{\varepsilon^{3/2} (1 - \varepsilon)^{1/2}} \int_0^\varepsilon dz (1 - z)^{1/2} z^{3/2} \right]$	1/3—1/2
$\varepsilon = B_s / (B_s + B_l)$			

total effective number of degrees of freedom which are translational. Note thus that $F_t = (S + 1)^{-1}$.

Table 3 contains the kinetic energies of fragmentation so calculated for the reaction $\text{CH}_4^+ \rightarrow \text{CH}_3^+ + \text{H}$. The vibrational and rotational constants employed in the calculation were the same as used earlier¹. We shall make use of these results, below.

Table 3. Kinetic Energy Production in Reaction $\text{CH}_4^+/\text{CH}_3^+ + \text{H}$.

Excess Energy [eV]	Average Kinetic Energy
0.5	0.13
1.0	0.21
2.0	0.35
3.0	0.475
4.0	0.60
5.0	0.72

Rotational Energies of Fragmentation

The remaining fraction of $(\overline{E} - x)$ appears as rotational energy. The manner in which it is apportioned among the two fragments can also be investigated, again at the level of Equation (7). The resultant expressions for $F(R)$, the fraction of this "external energy" appearing in a given fragment, are functions of the rotational constants, and are given in Table 2. Included in the final column is the range over which, say, $F(R_1)$ can vary as B_1 ranges from $\ll B_2$ up to $\gg B_2$. It will be seen that this never vanishes, and thus that neither fragment is formed at a very low "rotational temperature", irrespective of its rotational properties. On the other hand it is also seen that the rotational temperatures of the two fragments need not be equal, except in the special case of identical fragments, nor need these temperatures equal the kinetic temperature.

This result would seem to be at odds with the results from reactive scattering experiments¹³, using Cs and SF_6 , where the products showed large and nearly equal rotational and translational temperatures. Actually there is no discrepancy. The results of the beam experiments are in accord with unimolecular decomposition theory as applied to crossed thermal beams¹⁴. The collision complexes are characteristically formed with large angular momentum arising from the orbital angular momentum about the centroid of the incoming reactants. Just the opposite has been assumed here.

This immediately points up a restriction on the present results. They are most pertinent where the

parent ion has a low rotational temperature as under photon or electron impact or low energy electron attachment. For interpretations of the dissociation of ion-molecule collision complexes, a more exacting analysis would be necessary. This can be accomplished by returning to the level of approximation represented by, for example, Eq. (7) of ¹ or Eq. (6) of this paper. Indeed, in the immediate vicinity of threshold, and especially when tunneling effects are being considered¹⁵, such a recourse is *de rigueur*.

Kinematic Corrections

It is to be noted that Eqs. (2) and (9) contain no reference to the parameter γ which appears in Eq. (3) and which contains the dynamic parameters of the Langevin model. This insensitivity to these kinematic parameters would seem welcome.

It is also disconcerting. A quasi-equilibrium rate constant, averaged over a thermal Boltzmann distribution, is related via an equilibrium constant to the bimolecular association rate constant, in which γ appears prominently. Hence such kinematic factors must enter into a carefully formulated quasi-equilibrium theory. Their absence here arises from the approximation adopted in Eq. (5), which permits, in effect, all dissociation channels to occur, subject to energy and angular momentum conservation, but without regard to a possible centrifugal barrier.

A first order correction procedure to amend this situation is readily illustrated. Consider a spherical top of angular momentum (J_0) dissociating to a sphere and an atom. One has

$$(\sigma/\pi\lambda^2)(L, J \rightarrow J_0) = (2J_0 + 1)(2J + 1),$$

to be summed over all possible J , from zero up to some J_{max} . For $J_0 \approx 0$, J_{max} is given by the intersection of $L = J$ and the curve defined by Eq. (3). Upon expansion, this is given by

$$J_{\text{max}}^2 = y/B[1 - y/\gamma^2 B^2 + \dots]. \quad (10)$$

Use of just the first term leads eventually to the earlier result of the form of Eq. (2), and which we label k_0 . Inclusion of the second term yields $k = k_0[1 - 2\bar{\epsilon}_t/\gamma^2 B^2 + \dots]$ with $\bar{\epsilon}_t$ to be calculated from Equation (9).

For the reaction $\text{CH}_4^+ \rightarrow \text{CH}_3^+ + \text{H}$, one finds $\gamma^2 B^2 \cong 4.72$ eV. Inspection of the $\bar{\epsilon}_t$ results given in Table 3 shows then that kinematic corrections

become important at energies several eV above threshold. Thus results of the form of Eq. (2) are seen to occupy a sort of middle ground. At threshold, rotations must be treated more cautiously, while at very high energies kinematic corrections will need to be effected.

The kinematic corrections for the other reaction types may be investigated similarly. We find in each case that these corrections are of similar form and expressible in terms of a generalization of Equation (2):

$$k(E + E_0, J_0) = [h q_v(E_v)]^{-1} \int_0^E \frac{q_v(x)(E-x)^s dx}{\beta} \cdot \left[1 - \frac{(E-x)}{\beta'} + \frac{(E-x)^2}{\beta''} \dots \right]. \quad (11)$$

The several coefficients (β , β' , β'') are included in Table 1. These were obtained in each case via an expansion analogous to Equation (10). Although these expansions are not universally convergent, they are often so in the energy regime of practical interest, where the contents of Table 1 should then suffice quite well.

Occasions nevertheless arise when the above procedure will be quite inappropriate. An example is offered by the decomposition

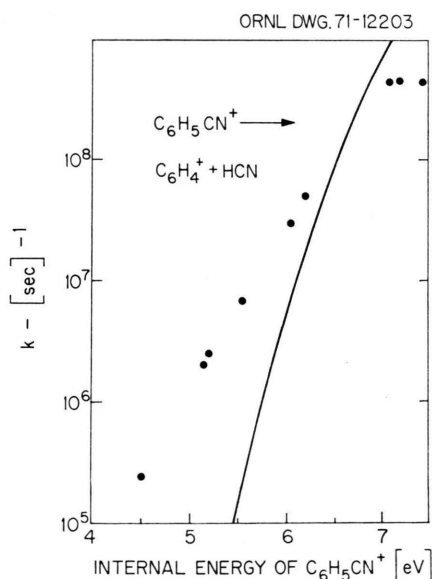
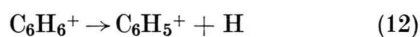


Fig. 1. Comparison of calculated and experimental rate constants for $\text{C}_6\text{H}_5\text{CN}^+ \rightarrow \text{C}_6\text{H}_4^+ + \text{HCN}$.

a reaction currently of great interest¹⁶. Its characteristic parameter $\gamma^2 B^2$ occurring in Eq. (10) is estimated to be $\cong 1.54 \times 10^{-3}$ eV, so that the expansion implied there would be quite useless and, indeed, nonconvergent. This is apt to occur whenever the products of the decomposition comprise a low molecular weight species and one with a large moment of inertia. The kinematics of the situation are now represented more nearly by curve (a) in Fig. 1 of ¹, and it is useful to proceed now from that rather different starting point.

In a manner analogous to the derivation of Eq. (10), one may expand Eq. (3) to obtain

$$L_{\max}^2 = \gamma y^{1/2} \left[1 - \frac{\gamma B}{2 y^{1/2}} + \frac{\gamma^2 B^2}{8 y} \dots \right] \quad (13)$$

which is clearly more suitable in the present circumstances. Proceeding, further, to count phase space by methods entirely analogous to what were used before, one finds that rate constant expressions ensue of the form

$$k(E + E_0, J_0) = [h q_v(E_v)]^{-1} \int_0^E dx q_v(x) \times \frac{(E-x)^l}{\lambda} [1 - \lambda'(E-x)^{-1/2} + \lambda''(E-x)^{-1} \dots] \quad (14)$$

analogous to Equation (11). The parameters pertinent to the several classes of reaction products are given in Table 4, to the extent that we have been able to find them. It might be noted that a rate

Table 4. Parameters Appropriate to the Rate Constants Given by Equation (14).

Reaction Products	l	λ	λ'	λ''
Sphere plus Atom	1/2	γ^{-1}	$\gamma B/2$	$(\gamma B)^2/8$
Two Linear	1	$4(B_1 + B_2)^{1/2}/\pi\gamma$	—	—
Linear plus Atom	1/4	$\gamma^{-1/2}$	$\gamma B/4$	$(\gamma B)^2/32$
Two Spheres	2	$4(B_1 + B_2)^{3/2}/\pi\gamma$	—	—
Sphere plus	3/2	$3(B_1 + B_2)/2\gamma$	—	—

constant expression derived some time ago by the present author³ is seen to be justified only as the first-order term for reactions producing a sphere and an atom. It is thus quite satisfactory for reaction (12), above, for example, but not at all in the general sense assumed at that time.

Thus two limiting kinematic situations occur wherein it is possible to obtain rather simple expressions for rate constants. Intermediate cases will of course arise, where the analysis will be rather

more difficult. It is surprising nevertheless how often the limiting cases do obtain, and we shall illustrate some such instances below. Before doing so, however, some general comments concerning the physical content of these extremes are in order.

The limiting case embodied in Eq. (2) contains no reference to kinematic parameters or to features of the potential energy surface. As noted before, all final states consistent with energy and momentum conservation are allowed — any centrifugal barrier to decomposition being so small to block a significant number of exit channels. Now the centrifugal barrier is viewed in the Langevin model as arising from a superposition of a repulsive centrifugal energy and a van der Waals attractive potential, varying with the inverse-fourth power of the radial separation of the fragments. If the real attractive potential is everywhere at least as strong as this polarization potential, then the net centrifugal barrier cannot exceed the Langevin barrier. Those deviations from the inverse-fourth dependence which do occur will then merely justify further any neglect of the barrier. Indeed, one is led to a useful theorem: a rate constant evaluated by means of Eq. (2) constitutes an upper limit to quasi-equilibrium theory. An observed rate constant which exceeds this value constitutes *prima facie* evidence for the breakdown of the quasi-equilibrium hypothesis. Equation (2) corresponds in effect to the loosest of all possible transition states.

This freedom from ambiguities in the collision forces can be useful in still another respect, exemplified by the previously discussed¹ reaction: $\text{CH}_4^+ \rightarrow \text{CH}_2^+ + \text{H}_2$. At that time CH_2^+ was assumed to be linear, and the calculated rate constant led to a

fairly good agreement between the calculated and experimental break-down curves for CH_4^+ . It now appears that CH_2 is substantially bent in its ground state¹⁷. Absorption spectra connecting this species to its Rydberg states show very little vibrational structure¹⁸, implying that they, and by inference the CH_2^+ ion, are also non-linear. The rate constant calculation has been repeated then, assuming CH_2^+ to be a three-dimensional rotor. The agreement with the experimental break-down curve is greatly improved, suggesting that quasi-equilibrium theory may in favorable instances be of some use as a probe of molecular structure.

The second extreme case, embodied by Eq. (13), is quite different. The features of the potential surface are of paramount importance and an observed rate constant may deviate from a calculated value insofar as the potential is not dictated by the long range forces. In this sense quasi-equilibrium theory can constitute a useful adjunct to the investigation of potential surfaces. It can be shown also that in this extreme, rotational excitation of the fragments scarcely occurs, the non-vibrational energy appearing mainly in the translational mode. This is implied in Eq. (13), where $BJ(J+1)$ must be $\ll y$, even for J^2 as large as $\gamma y^{1/2}$.

Discussion

The evaluation of expressions of the form of Eqs. (2) or (9) need not pose any difficulty. Thus an integral such as $\int_0^E dx \rho_v(x) (E-x)^s / \beta$ can be viewed as the density-of-states of a fictitious system containing the several vibrational degrees of freedom

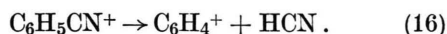
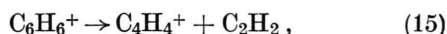
Table 5. Vibrational Energies (with degeneracy factors) and Rotational Parameters (in units of eV), and Reaction Parameters.

C_6H_6^+	C_6H_5^+	C_6H_4^+	C_4H_4^+	$\text{C}_6\text{H}_5\text{CN}^+$	C_2H_2	HCN
0.382 (6)	0.382 (5)	0.382 (4)	0.382 (4)	0.382 (5)	0.424 (1)	0.248 (1)
0.198 (6)	0.198 (6)	0.198 (5)	0.198 (4)	0.198 (6)	0.408 (1)	0.094 (2)
0.135 (10)	0.135 (9)	0.135 (7)	0.135 (6)	0.135 (9)	0.246 (1)	0.428 (1)
0.105 (3)	0.105 (2)	0.105 (3)	0.105 (2)	0.105 (2)	0.090 (2)	—
0.063 (5)	0.063 (5)	0.063 (5)	0.063 (2)	0.063 (5)	0.075 (2)	—
—	—	—	—	0.050 (2)	—	—
—	—	—	—	0.185 (1)	—	—
—	—	—	—	0.060 (2)	—	—
—	—	—	—	0.400 (1)	—	—
—	0.188 ^a	0.432 ^a	0.632 ^a	—	1.84 ^a	1.81 ^a

$\text{C}_6\text{H}_6^+/\text{C}_6\text{H}_5^+ + \text{H}$: $E^0 = 4.55$ eV, $g = 6$, $(\alpha/a_0^3) = 4.5$; $\text{C}_6\text{H}_6^+/\text{C}_4\text{H}_4^+ + \text{C}_2\text{H}_2$: $E^0 = 4.75$, $g = 3/4$, $(\alpha/a_0^3) = 21.5$;
 $\text{C}_6\text{H}_5\text{CN}^+/\text{C}_6\text{H}_4^+ + \text{HCN}$: $E^0 = 4.65$, $g = 1$, $(\alpha/a_0^3) = 16.8$.

^a $B \times 10^4$.

and a $2(S + 1)$ -dimensional rotor, whose partition function is $Q = F(S + 1) (kT)^{S+1}/\beta$. The formalism of HOARE¹⁹ is quite suitable for calculating the densities-of-states of such compound systems. We have used this formalism to calculate rate constants for reaction (12) as well as for



The assumed vibrational and rotational parameters for the several products are given in Table 5, along with the threshold energies (E_0), the reaction-path degeneracy factors (g), and the relevant polarizability (α/a_0^3) for each reaction. The vibration energies, when unknown, were estimated from group frequencies of analogous compounds; similarly, the moments of inertia were crudely estimated for each of the product species for which they are not known. For the species C_4H_4^+ , C_6H_4^+ and C_6H_5^+ which were treated as spherical tops, a geometric mean of the principle moments of inertia was then used. The polarizabilities of the neutral species H, C_2H_2 and HCN are well-known in the literature. Reaction (12) constitutes a case where the centrifugal barrier is dominant, whereas reactions (15)–(16) correspond to the negligible-barrier extreme. A detailed evaluation of the relevant higher-order terms in Eqs. (11) and (14) shows them indeed to be negligible.

Figures 1 and 2 illustrate the calculated rate constants, as functions of internal energy of the parent ion, and a comparison with the unique measurements of ANDLAUER and OTTINGER¹⁶. Focussing on Reactions (15) and (16), we see that the observed rate constants exceed the theoretical values throughout most of the energy range considered. As discussed earlier, this would seem then to constitute clearcut evidence against the quasi-equilibrium hypothesis. While this might be alleviated to some extent through a loosening of the product species, such a recourse will clearly be inadequate in the threshold region. Yet it is just this threshold region which raises doubts concerning the efficacy of Andlauer and Ottinger's charge-transfer technique. It seemingly leads to sizeable rate constants for reaction (16), for example, at energies barely above and indeed somewhat less than the thermochemical threshold of 4.65 eV.

This result would seem sufficiently interesting to warrant closer examination. In plotting the data of

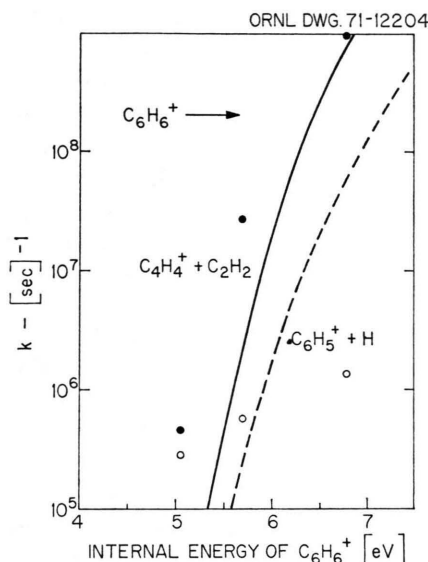


Fig. 2. Comparison of calculated and experimental rate constants for the fragmentation of C_6H_6^+ to $\text{C}_4\text{H}_4^+ + \text{C}_2\text{H}_2$ (closed circles) and $\text{C}_6\text{H}_5^+ + \text{H}$ (open circles).

Andlauer and Ottinger, we have assumed that the parent ions are excited by the difference in recombination energies in the charge-exchange process, plus ~ 0.25 eV. This last quantity is an estimate of the average thermal energy in the vibrational motions of the molecules, together with a small contribution arising from momentum transfer in the charge-exchange reaction¹⁶. It is true that we cautioned earlier about using the present theory "in the immediate neighborhood of threshold". But this caution is largely unnecessary — it is equivalent to saying that only a part of the thermal rotational energy is available for the decomposition.

Only two possibilities seem to exist then for reconciling the data with the theory. One is that Andlauer and Ottinger have greatly underestimated the momentum transfer or the rotational excitation which might occur in the charge transfer process. This is unlikely for two reasons. Their rate constants are smooth, monotonic functions of energy, and at a given energy the apparent rate constant seems indeed to be a single-valued constant.

The second possibility is more likely. It is probable that the published heats of formation for C_6H_4^+ and C_4H_4^+ should be considerably reduced. They are based on "appearance potentials" in experiments, of which the charge-transfer technique itself is a good example. But this procedure takes no

account of the "kinetic shift" — that is, that a decomposition should not be observable until there is at least enough energy available to make it so. In molecules of the size we are considering here this will be considerably more than the thermodynamic requirement — as the theoretical curves illustrate.

This explanation will probably not suffice to explain the fact that reaction (12) also occurs faster than expected near threshold. The heat of formation of $C_6H_5^+$ has been established by methods other than "appearance potentials" and so is more reliable. Note also that this reaction, the barrier dominated example, reveals in addition a quite different failing — calculated rate constants are greater than the experimental results at the higher energies. Now, ANDLAUER and OTTINGER¹⁶ note that reactions (12) and (15) do not compete with each other. One might then postulate two sets of "isolated states" of the parent ion and hope that a quasi-equilibrium model would apply to each set individually. But this can only lead to a shortening of the calculated lifetime of the parent ion, compared with that based on its complete thermodynamic complement of states. One is thus led inexorably to the conclusion that the reverse of reaction (12) is very much slower than predicted by the Langevin model.

This is surprising in view of its simplicity — even more so in the light that reactions (15) and (16), while symmetry forbidden as concerted processes, apparently suffer from no comparable restriction. Again, there is room here for further inquiry. More immediately, these results, while containing little of comfort to the quasi-equilibrium enthusiast, serve at least to illustrate rather nicely the place of unimolecular decompositions within the mainstream of chemical kinetics.

A novel consequence of the present theory can be seen by using in Eq. (2) the so-called classical expressions for densities-of-vibrational states, viz.

$$\rho_v(x) = (x)^{N-1} \Gamma(N) \prod_i^N h \nu_i$$

where N is the number of harmonic oscillators. One finds that at high energies, the rate constant is predicted to go through a maximum. Thus, a point is reached where, the hotter an ion is, the more slowly it should dissociate. This runs contrary to one's intuition, shaped as it is by the early work of KASSEL²⁰. It arises from the following considerations. The number of initial oscillators (N), final

oscillators (F) and rotations (R) are related by $N = F + R$. But classical rotations have only half the heat capacity of classical vibrations, so a point can be reached where this entropy effect overcomes the initial prejudice of the endothermicity factor.

These maxima are not apt to be observable. They are predicted to occur at quite high energies, where considerations of anharmonicities, excluded states²¹ and, indeed, the fundamental validity of the theory obscure the issue. It might be noted, nevertheless, that KNEWSTUBB²² has predicted similar behavior, arising from an energy-dependent correction factor to quasi-equilibrium theory. We see here that such behavior can occur within the framework of the theory itself.

Although the parameters presented in Tables 1 and 4 have been derived for spherical tops, they can be readily extended to linear parent ions, merely by multiplying the appropriate rate constant expression in Eq. (2) by $(2J_0 + 1)$ where J_0 is the rotational quantum number. This arises simply because the parent-ion density-of-states in the denominator of Eq. (1) will contain one less such factor than in the case of the spherical top.

Real molecules, of course, do not so conveniently divide themselves into these two categories. The procedure we have employed has been to use a geometric mean of the principal moments of inertia. One may presume that the dimensionality of the final expression for rate constants will not be seriously modified in a more detailed treatment. Nevertheless, some of the complications which can arise in such a treatment have been discussed by NIKITIN²³. Until these have been more carefully examined, a degree of ambiguity will necessarily accompany any application of the theory. If the quasi-equilibrium concept has evolved considerably since its inception^{24, 25}, further progress does not promise to be simple.

Appendix

We would like to point out a very simple "step-up" relation between integrals such as

$$\int_0^E dx \rho_v(x) (E - x)^s \quad \text{and} \quad \int_0^E dx \rho_v(x) (E - x)^{s+1}.$$

A facile technique for evaluating the ratio of two such integrals would be useful both in determining the relative importance of the "kinematic cor-

rections", as in Eq. (11), and also for calculating kinetic energies as in Equation (9).

First one notes that, through integration-by-parts, one can write

$$\int_0^E dx \varrho_v(x) (E-x)^{s+1} = (s+1) \int_0^E dz \int_0^z \varrho_v(x) (z-x)^s dx. \quad (17)$$

The right-hand side of this equation, except for the $(s+1)$ factor, may be viewed as the totality of states of the several vibrations and a $2(s+1)$ -dimensional rotor with total energy $\leq E$. Denoting this totality of states by $W(E)$, one then has in the steepest descent approximation¹⁹:

$$W(E) \cong g(E)/\beta$$

where $g(E)$ is the density of states for such a system, given by

$$g(E) = \int_0^E \varrho_v(x) (E-x)^s dx.$$

The parameter β is defined by

$$E = (s+1)/\beta + \sum_v \varepsilon_v (\exp(\varepsilon_v \beta) - 1)^{-1}$$

if the vibrations are treated as harmonic oscillators with $\varepsilon_v = \hbar \omega_v$. We thus finally obtain

$$\int_0^E \varrho_v(x) (E-x)^{s+1} dx / \int_0^E \varrho_v(x) (E-x)^s dx = (s+1)/\beta \quad (18)$$

which thus offers a facile expression for the ratio of the two integrals.

The parameter β clearly defines a temperature via the relation $\beta = (kT)^{-1}$. One sees then that it was with some justification that we spoke earlier of kinetic and rotational "temperatures".

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