

# The Reaction Coordinate and Its Limitations: An Experimental Perspective

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## Introduction

A framework for a great deal of our modern understanding was laid out in 1927 when Born and Oppenheimer<sup>1</sup> legitimized the concept of the potential energy surface. They noted that, because of the disparity in the masses of the electrons and the nuclei which compose a molecule, the former will adjust very nearly instantly to small displacements of the latter. The nuclei will thus "see" a more or less well-defined set of forces, independent of their own velocity. These forces could then be used to define a potential surface and so to visualize those kinds of changes we call chemistry.

Five years later Pelzer and Wigner<sup>2</sup> provided an essential elaboration when they suggested that chemical reactions are mediated by the need to traverse a saddle point on such a Born-Oppenheimer surface. It remained nevertheless for Henry Eyring<sup>3,4</sup> to make something concrete of this proposal. He postulated that the only important motion in the saddle point was confined to a single coordinate. It could be identified with the direction of steepest descent in the potential energy. He called this the reaction coordinate and supposed its allowable energy levels to be those of a one-dimensional box. He was then able to calculate rate constants. It was that simple—daring in 1935 and astonishing to this day.

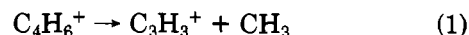
In linking the topology of potential surfaces with macroscopic change, Eyring's construct has become one of the cornerstones of modern chemistry. Direct experimental manifestations of the reaction coordinate would thus be pedagogically useful but are not easily cited. We shall argue below that Eyring's formulation can find palpable expression in the kinetic energy distribution of the fragments from a unimolecular reaction. In making this argument, we will cite evidence from the literature, some of which is now over 15 years old. Since then there has been a great deal of interest in spectroscopic probes of the transition state. If a kinetic energy distribution can offer just such a glimpse of the reaction coordinate, then this perspective merits emphasis. But we are also concerned here with an application of these distributions which has only recently come to light—that they can be used to assign a temperature to the transition state. We therefore go to some length to establish the linkage from kinetic energy distributions to both the reaction coordinate and thermometry.

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## Unimolecular Reaction Theory

The central point is elementary. Standard unimolecular theory<sup>5,6</sup> assumes that a collection of reacting systems, each of some well-defined energy  $E$ , may be represented by an equilibrium ensemble. This should pertain also to any separable part of a system, and thus to a reaction coordinate. If the degrees of freedom orthogonal to this coordinate are numerous enough (and the total energy sufficiently large) as to constitute a heat bath, then an equilibrium distribution among its energy levels will be that of a one-dimensional Maxwell-Boltzmann gas. The rate at which systems pass through the saddle point will be weighted, however, by their velocity; the distribution in the flux emerging from the transition state will then be that of a two-dimensional gas—and hence an exponentially decreasing distribution in energy.<sup>7</sup>

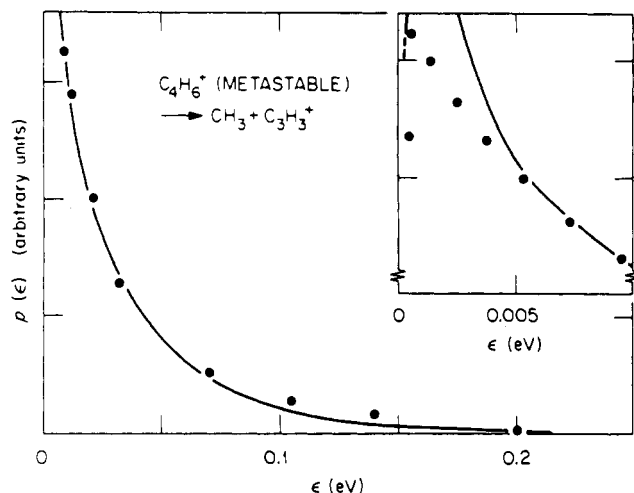
Figure 1 illustrates<sup>8</sup> the kinetic energy distribution<sup>9</sup> of the fragments from the reaction



The energy of the parent ion was in this case known and well-defined. The distribution is seen, without too close an inspection, to be a monotonically and very nearly an exponentially decreasing function of the energy.

Other examples of such distributions exist. Careful scrutiny will nevertheless be needed before these can be accepted as reflections of a reaction coordinate. We pass over, for example, several reports<sup>10-14</sup> of kinetic energy distributions of the fragments produced by the photoexcitation of van der Waals molecules. These are often said to be of the form of Figure 1 and hence would seem consistent with Eyring's treatment. The energies in these experiments were, however, much too small to support any sort of "infinite" heat bath. The reported kinetic energy distributions are in fact quite unintelligible in terms of the ideas which concern us here.

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**Figure 1.** Comparison of the observed kinetic energy release distribution from metastable  $C_4H_6^+$  (points), from ref 9, with predictions of unimolecular reaction theory. From ref 8.

The construction of the solid line in Figure 1 made use (in a way we shall describe shortly) of actual phase-space calculations and hence is legitimate on the above account. Close inspection of it, and of the underlying data, will nevertheless show that each goes through a maximum at low energies. We therefore focus on this feature.

Experimental measurements are made after the fragments have separated to infinity, whereas saddle points surely occur at smaller separations. A true saddle point will indeed be followed by a drop in the potential energy. What will happen to the relative kinetic energy of the fragments in negotiating this drop?

One attractive supposition is that the decrease will simply get added on to the kinetic energy already present in the reaction coordinate. If so, we would still expect to see at infinite separation an exponentially decreasing distribution, but one whose origin is displaced outward from the zero of energy.

In suggesting the plausibility of this model, Taubert<sup>15,16</sup> recognized that it was little more than a guess. His cautionary note has not always been heeded—sometimes with unfortunate consequences. Nevertheless, the model is not without foundation. Let us suppose that the potential energy between two fragments is of the form

$$V = V_e(r) + L(L + 1)\hbar^2/2\mu r^2 \quad (2)$$

The first term on the right-hand side represents some sort of (ultimately attractive) Born–Oppenheimer potential, a function only of the radial separation. It is often taken as proportional to an inverse power of the separation, but this is by no means necessary for what follows. The second term describes a centrifugal repulsion. It contains  $L$ , the orbiting angular momentum quantum number, and  $\mu$ , the reduced mass of the two fragments. When the attractive term in eq 2 is of sufficiently short range, the potential will have a maximum as a function of the radial separation. This criterion can then be used to locate the transition state.<sup>17,18</sup>  $V^\ddagger(r^\ddagger, L)$ , the potential energy at the maxi-

mum, will give the height of the saddle point above the potential at infinite separation. It is also the energy which must be added to the kinetic energy at the saddle point to give that which will be observed.

One can thus envisage circumstances in which Taubert's conjecture will be valid. Let us consider then a molecule with some initial angular momentum, indicated by the quantum number  $J_0$ , and an energy,  $E$ , sufficient to permit dissociation to some pair of products. These two quantities must of course be conserved during the reaction. We then use unimolecular reaction theory<sup>19,20</sup> to calculate the rate of dissociation to the array of possible final states of the product consistent with the conservation laws. In doing so we ignore at first any restrictions which might be interposed by a putative activation energy. This might be called a phase-space calculation.<sup>21</sup> It makes use of nothing other than thermodynamics and microscopic reversibility. In particular, it does not presuppose the Eyring model.

Of these final states we then focus on a subset comprising those which are reached by some particular value of the orbiting quantum number,  $L$ . It is found that the kinetic energy distribution among the final states within this subset is predicted to be roughly of the form

$$p(\epsilon) \sim \exp(-\beta\epsilon) \quad (3)$$

where the parameter  $\beta$  may be a function only of  $L$ ,  $J_0$ , and  $E$ , the parameters which define the subset. In practice, it is an important function only of the energy. Taking an appropriate average over all values of  $L$  (compatible with the given  $J_0$  and  $E$ ), in order to get something which might be measurable, thus yields<sup>7</sup> a result also of the form of eq 3.

We retreat from this step, however, in order to consider the role of the activation energies defined earlier. They will block<sup>22</sup> all of the bimolecular association channels for which the initial kinetic energy is less than the  $V^\ddagger(L)$ . Accordingly, all of the unimolecular dissociation channels for which the final kinetic energy is less than this  $V^\ddagger(L)$  will also be blocked. The distribution of the survivors will be truncated, given by

$$p(\epsilon) \sim \exp\{-\beta[\epsilon - V^\ddagger(L)]\} \quad (4)$$

and thus will still be an exponential in the kinetic energy at the transition state. Experiments which are compatible with such a model might then be said to evince the Eyring picture.

The solid line in Figure 1 was calculated in just this way. Its shape, in particular its characteristic depletion at low energies, arises from a superposition of a large number of quasi-exponential functions, all truncated to one degree or another.

Each truncation, and the net depletion, will be lesser or greater as the term in the potential energy representing attraction is large or small. The calculation in Figure 1 presupposed a relatively strong ion induced-dipole source of attraction. The depletion is scarcely

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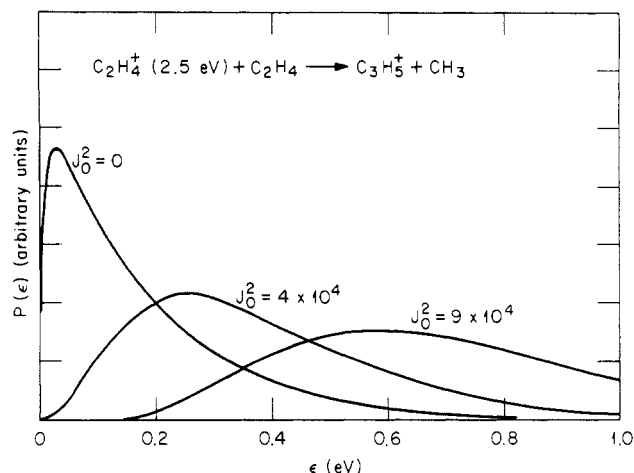
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**Figure 2.** Predicted kinetic energy spectra for reaction 6 at constant energy but varying angular momentum. From ref 31.

evident. By contrast, one predicts<sup>23</sup> for symmetric fissioning via a flat "hard-sphere" potential a kinetic energy distribution of the form

$$p(\epsilon) \sim \exp(-\beta\epsilon) - \exp(-6\beta\epsilon) \quad (5a)$$

and for a highly asymmetric fissioning

$$p(\epsilon) \sim \epsilon \exp(-\beta\epsilon) \quad (5b)$$

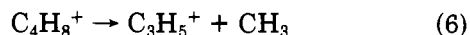
Experiments which measure the kinetic energy release, during evaporation following photoexcitation of a cold droplet, could be used to test these forms. The depletions should be readily discernible.

### The Role of Angular Momentum

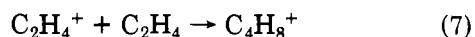
The first term on the right-hand side of eq 5a is the phase-space result. The second term then corrects it for the Langevin potential barriers. This separation into just two terms occurs only when it is assumed that  $J_0 = 0$ , i.e., that the parent molecule is not rotating.

The calculation of the solid line in Figure 1 also assumed a rotationless progenitor. This will often be a good approximation. Photoexcitation and electron-impact excitation are accompanied by strong selection rules. A molecule which is initially cold will not rotate much following excitation.

In other contexts this will be a very bad approximation. Many workers<sup>24-30</sup> have discussed, for example, the kinetic energy release in reactions such as



where the parent molecule itself had been prepared by chemical activation, in this case



Here the  $\text{C}_4\text{H}_8^+$  population will contain components with large amounts of angular momentum. Further, its presence can have profound effects on the kinetic energy release.

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Figure 2 contains the results of a systematic study<sup>31</sup> of this effect. Increasing angular momentum enormously increases the depletion at low energies. This is easily understood. The initial momentum, indicated by  $J_0$ , must be disposed of either as rotational excitation of the products or via orbiting angular momentum. A large fraction of the available exit channels implicates the latter, which in turn carries with it an activation energy and hence depletion.

A simple example of this can be given. When all of the degrees of freedom of a molecule are at the same well-defined temperature, and a dissociation occurs via a hard-sphere potential, then elementary considerations lead to a kinetic energy release distribution of the form

$$p(\epsilon) \sim \epsilon \exp(-\epsilon/kT) \quad (8)$$

regardless of the product geometries. The depletion will then be even more evident than that described by eq 5a.

We emphasize that these large depletions do not signal any departure from Eyring's treatment of the reaction coordinate. They obscure the connection, however, and render such measurements less convincing in support of it.

### Transmission Coefficients

The assumption was made earlier that all of the exit channels blocked by a potential barrier will not occur, while those classically permitted will proceed unimpeded. This is surely too drastic: nature abhors discontinuities. We must examine more carefully this all-or-nothing dichotomy.

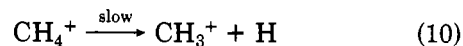
In order to do so, it will be useful to consider the bimolecular association reaction which is the reverse of the unimolecular process of interest. We focus on a pair of collision partners in states  $i$  and  $j$  and write their collision cross section to yield a bound entity as

$$(\sigma/\pi\lambda^2)_{ij,L} = (2L + 1)T_{ij}(L,\epsilon) \quad (9)$$

where  $\lambda$  is the de Broglie wavelength associated with their relative motion and  $L$  is, as before, the orbiting angular momentum. The factor  $T_{ij}$  is the transmission coefficient for the reaction. It will be a function of  $L$  and of  $\epsilon$ , the relative kinetic energy at infinite separation.

The cross section in eq 9 is understood to comprise all of the final angular momentum states compatible with the initial angular momentum and with  $L$ . The phase-space limit, which led to eq 3 and to the first term on the right-hand side of eq 5a, is then obtained by setting  $T_{ij}$  equal to unity for all energy-conserving collisions. The Langevin model amends this by setting those  $T_{ij}$  equal to zero for which the initial kinetic energy is less than  $V^2$ . It is this sharp demarcation in transmission coefficients which we must address.

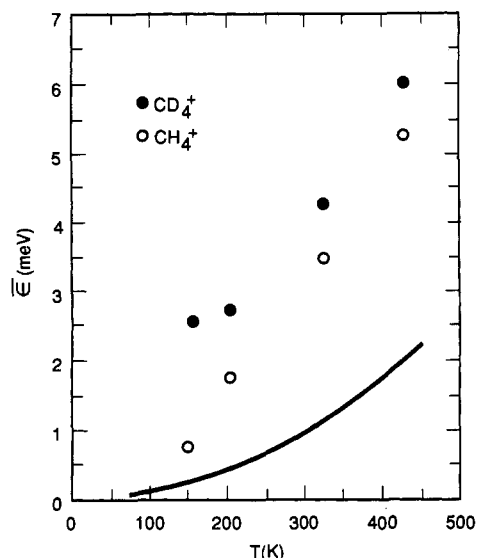
Tunneling through centrifugal barriers is well-known. An instructive example is the metastable fragmentation of the methane ion:



Measurements<sup>32</sup> of the kinetic energy released during

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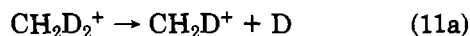


**Figure 3.** Comparison of average kinetic energy release in the metastable fragmentation of methane ions (points), from ref 32, with the average centrifugal barriers as a function of temperature, from ref 33.

this process are illustrated in Figure 3. The solid line represents the average potential barrier height<sup>33</sup> for those ions which can dissociate only via a tunneling mechanism. A decomposition fragment, in penetrating and emerging from such a barrier, will have an energy less than and, in the absence of additional knowledge, equal perhaps to one-half of it. The observed average energy releases clearly exceed these expectations. This arises, at least in part,<sup>32</sup> because experiment samples only those ions which dissociate in a narrow metastable window. The energy release during this period may then differ considerably from the time-integrated average.

The strong dependence on temperature of the time-integrated average is nevertheless reflected by both experiment and more detailed calculations.<sup>32</sup> This is then a useful signature for the tunneling mechanism and confirms its presence here. But one must then wonder if a tunneling mechanism made a contribution to, for example, the spectrum in Figure 1.

The answer is almost certainly no! The  $\text{CH}_2\text{D}_2^+$  ion can fragment in two ways:



Only the second route is observed to occur via the nonclassical mechanism. This however, is not due to the usual mass dependence of tunneling. Observe in Figure 3, for example, the evidence for a facile dissociation of  $\text{CD}_4^+$ . Its absolute abundance is every bit as large as that of  $\text{CH}_4^+$ . The reason is instead<sup>34</sup> that when a parent  $\text{CH}_2\text{D}_2^+$  ion has just enough energy to dissociate via tunneling along the first route, then because of zero-point energy differences it has more than enough energy to proceed via an open channel along the second. When classically allowed channels are open, they will overwhelm the tunneling mechanism.

The complement of tunneling beneath a saddle point is the reflection of a classically allowed trajectory upon

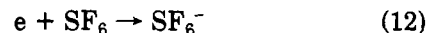
passage above the potential surface. In discussing this it is necessary to distinguish two distinct phenomena. One is classical and the other of an intrinsically wave-mechanical origin.

Eyring recognized in his landmark paper the possibility that a system, having passed through the transition state, might subsequently be deflected back toward its origin by some feature of the potential surface. If this occurred, and with a probability dependent on the kinetic energy, then the ensuing distribution would be distorted.

The high-speed computer has made feasible the trajectory calculations which can test this. These show<sup>35,36</sup> that, at low total energies, transmission is complete; at high energies, and thus perhaps at high kinetic energy in the reaction coordinate, reflection becomes discernible.

There are instances where the kinetic energy release is actually less than that calculated by the means outlined earlier. A depletion of the high-energy tail by reflection back across the saddle point could account for this. It seems unlikely though that any reaction encumbered by this sort of reflection would have a potential surface simple enough to conform to Taubert's conjecture. These instances thus cannot be simply rationalized and so underscore an earlier remark: an observed quasi-two-dimensional Maxwellian distribution in the kinetic energy release is not necessarily a manifestation of the reaction coordinate. Corroboration by way of consistency with some plausible model is surely also needed.

A second category of reflection, and one which is coextensive to the phenomenon of tunneling, can also play a role in unimolecular reactions. A number of molecules, exemplified by  $\text{SF}_6$ , are almost-perfect sinks for s-wave electrons; thus the reaction



seems to occur with a near-unit transmission coefficient when  $L$ , the orbiting angular momentum quantum number, is zero. At very low kinetic energy, however, the rate is less. A simple expression<sup>37</sup> has been proposed to describe this drop-off in the transmission coefficient.

Its underlying model is closely related to that used earlier<sup>34</sup> to estimate tunneling through centrifugal barriers. Attempts to identify its role in the unimolecular reaction channel—the reverse of eq 12—have been made but remain unconvincing. Careful measurements<sup>38</sup> of the attachment reaction nevertheless seem to be in excellent agreement with its predictions. A nearly ubiquitous role for nonintegral transmission coefficients is accordingly indicated.

They are expected, in particular, to attend those short-range potentials which can yield a maximum in eq 2. The leading edge of a truncated kinetic energy distribution will then be blurred, by reflection as well as by tunneling. The distribution itself will go smoothly to zero.

Nevertheless, this source of reflection could also be neglected in the construction of Figure 1. The circum-

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stances of reaction 12 are exceptional in having permitted a nonintegral transmission coefficient to be distinguished. When  $L$  is greater than zero, this blurring will always be less than the truncation due to the barrier itself. And when the reduced mass in the reaction coordinate is much greater than that of an electron, the blurring will be indiscernibly slight. This criterion for the reduced mass is, of course, a prerequisite of the potential surface itself.

### The Reaction Coordinate as a Molecular Thermometer

We spoke before of the reaction coordinate being coupled to the other degrees of freedom which then serve as a sort of heat bath. Yet the molecules we have been discussing are quite finite in both size and energy. They can thus constitute at best only a tenuous heat bath, and any ensuing kinetic energy distribution cannot strictly be that of a two-dimensional Maxwellian. Formulas such as in eq 3-5 are then to be understood as having no more than a schematic validity.

For systems which are circumscribed in energy and angular momentum it is nevertheless still possible to define a parameter which has many of the properties of a temperature. Thus, in calculating rate constants and kinetic energy distributions, one makes use of a quantity  $\omega(E)$ , the number of quantum states of a system with energy less than or equal to  $E$ . The phase-space term on the right-hand side of eq 5, for example, derives from just such an enumeration of the final states compatible with the conservation laws. Properly, it should be evaluated from<sup>27</sup>

$$p^\circ(\epsilon) \sim d\omega(E-\epsilon)/dE \quad (13)$$

An average  $\beta$ , defined by

$$\bar{\beta} = -d \ln p^\circ(\epsilon)/d\epsilon \quad (14)$$

is then given by

$$\bar{\beta} = d \ln \omega(E)/dE \quad (15)$$

With the plausible definition of an entropy

$$S = k_B \ln \omega(E) \quad (16)$$

the identification of  $\bar{\beta}$  as a reciprocal temperature is then seen to be quite tenable.

There is a second understanding which permits an even more direct identification. The average kinetic energy, defined by the phase-space limit, eq 13, and hence given by

$$\bar{\epsilon} = \overline{\epsilon p^\circ(\epsilon)} \quad (17a)$$

$$= \int_0^E \omega(x) dx / \omega(E) \quad (17b)$$

might plausibly be used to define a  $k_B T$ . It is in fact equal<sup>7</sup> to that temperature at which a canonical ensemble of transition states would have an average energy equal to the particular and well-defined total energy  $E$ .

The temperatures defined by these two prescriptions will be very nearly equal, even for a molecule comprising only a small number of degrees of freedom. Provided that it conforms sufficiently to that of a two-dimensional Maxwellian gas, a kinetic energy distribution can then be used as an unambiguous thermometer. If it can be corroborated by a plausible model, its reading may

also be meaningful. Even more satisfying would be an agreement with another well-calibrated thermometer. Just this possibility has recently become available.

An investigation of evaporation from isolated molecular aggregates<sup>39,40</sup> led to a simple rule; on a typical laboratory time scale of 10  $\mu$ s, the temperature of an isolated and evaporating cluster (to the extent that one can be defined) will be given by

$$k_B T = \Delta E_{\text{evap}}/25 \quad (18)$$

This relation will be reminiscent of Trouton's rule, and that is in fact how it can be rationalized.

Now, for very large clusters temperatures can be measured by macroscopic means. The results are in good agreement<sup>40</sup> with eq 18. For smaller clusters these methods are not possible. But measurements of the average kinetic energy of evaporation, when interpreted by way of eq 8, are again consistent<sup>40</sup> with the rule. The two thermometers agree.

### Conclusion

We see from this study that kinetic energy distributions can provide a legitimate portrait of the reaction coordinate and a measure of a temperature. The optimal conditions for a convincing likeness are that the dissociation occur along an attractive and well-defined potential surface, the initial angular momentum be small, and the initial energy be well above the dissociation asymptote. It is especially satisfying that studies of unimolecular reactions have aided in the delineation of these conditions.

The dissociation of the  $C_4H_6^+$  ion has served here as a useful example. One might equally well have cited measurements on  $C_2H_3Br^+$ ,<sup>41</sup>  $NF_3^+$ ,<sup>42</sup>  $C_2H_5I^+$ ,<sup>43</sup>  $C_6H_5CN^+$ ,<sup>27,44</sup>  $CH_4^+$ ,<sup>45</sup> and  $C_3H_7I^+$ .<sup>46</sup> The list is incomplete.<sup>47</sup> Nor does it contain reference to the kinetic energy distributions which have been measured following the breakup of a chemically prepared collision complex. As noted earlier, the connection with the reaction coordinate tends to be obscured by the initial angular momentum which is invariably present. Nevertheless, the good agreement often found<sup>27-30</sup> between theory and experiment cannot be entirely fortuitous.

The ability to assign a temperature to a transition state is of interest for two reasons. It may be used to characterize evaporating bodies even when they cannot be described by a canonical ensemble.<sup>39,40</sup> It may also be related to the variation of unimolecular rate constants with respect to small changes in the activation energy.<sup>48</sup>

Pedagogical value and thermometric applications aside, have we learned anything from these studies? It is interesting of course that reactions exist where the transition state is "loose"—i.e., where the relevant po-

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(48) Klots, C. E. *J. Phys. Chem.* 1986, 90, 6063.

tential surface is indeed of the form of eq 2. But then the kinetic energy distributions which ensue can also be rationalized with a simple collision theory. The more discernible the reaction coordinate is, the less unique a construct it would seem to be.

In fact, we have learned something useful. This is because, despite these real successes, a serious caveat must be attached to all of the above. Unimolecular reaction theory can calculate absolute rate constants as well as probability distributions among the final channels. In particular, this can be done<sup>38,49</sup> using the same centrifugal barriers described earlier to define the transition state. If one assumes that all exit channels are open, one obtains a phase-space rate constant. It constitutes a natural upper limit<sup>49</sup> to unimolecular rates. Consideration of those channels which are blocked by the centrifugal barriers will then lower the calculated rates. Nevertheless, they invariably remain much higher than those given by experiment.

Chesnavich and Bowers<sup>50</sup> have proposed a reconciliation: many and perhaps most unimolecular reactions must traverse two transition states. One is at a true saddle point in the energy, just as Eyring had envisaged.

(49) Klots, C. E. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* 1972, 27A, 553.

(50) Chesnavich, W. J.; Bass, L.; Su, T.; Bowers, M. T. *J. Chem. Phys.* 1981, 74, 2228.

If it lies at sufficiently large a radial separation, the emerging kinetic energy distribution will reflect this geometry. But then at smaller separations a second bottleneck in phase-space determines the rate constants. The implication is that incoming trajectories can traverse the saddle point only to be subsequently reflected. Equivalently, the rapid intramolecular vibrational relaxation which underlies unimolecular reaction theory would seem not to extend out to the saddle point.

This resolution is plausible but not without irony. Eyring's original intention was to calculate rate constants. This was to be done using the saddle point and its local properties. Perturbations such as tunneling, important or otherwise, were to be similarly comprehended.

If, as it appears, this does not suffice, further-ranging constructs such as variational transition-state theory may still prove adequate. Something of great simplicity will nevertheless have been lost. Thus, the study of unimolecular reactions, in rendering a unique prospect of the saddle point, will be seen also to have prompted a challenge to its relevance.

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