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Some properties of microcanonical rate constants

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An isolated body is characterized by conserved properties such as its energy and angular momentum. The rates of processes occurring in that body can thus be investigated as a function of these properties. On the other hand the rates may be better known, both conceptually and experimentally, as a function of temperature. This paper surveys relations between rate descriptions in the two domains, as deduced using steepest descent techniques. The rudiments of these techniques are given in an appendix.

1. Introduction

In 1937 Weisskopf [1] set out a discussion of the evaporation of neutrons from an atomic nucleus. He developed an expression for the distribution of the kinetic energies that they carry off. By way of delineating the subject under review here, it will be useful to look at a simplified version of his argument. Consider a molecule which has an energy E , greater than the amount E_0 needed for its dissociation. That extra amount $E - E_0$ might be distributed among the various internal degrees of freedom of the products, or perhaps as ε , the relative kinetic energy as they separate. A plausible formula for the distribution of these kinetic energies is

$$p(\varepsilon) \sim \rho_1(E - E_0 - \varepsilon) \quad (1)$$

where ρ_1 is the density-of-states of the internal degrees of freedom. Figure 1 sketches schematically this distribution. It is a roughly exponentially decreasing function, suggestive of a two-dimensional Maxwellian distribution. A temperature is then called for, and in this case there is no shortage of candidates. One can use a steepest descent argument [2] to show that the initial slope of the distribution is given by

$$\frac{d \ln p_1(\varepsilon)}{d \varepsilon} = -(k_B T)^{-1} \quad (2)$$

with the temperature defined by

$$E - E_0 = \overline{E}_1(T) - k_B T \quad (3)$$

where $\overline{E}_1(T)$ is the canonical energy that the internal degrees of freedom would have in a real heat bath. Alternatively, the average slope of the distribution is given by

$$\overline{d \ln p_1(\varepsilon) / d \varepsilon} = -(k_B T)^{-1} \quad (4)$$

where the temperature is now given by

$$E - E_0 = \overline{E}_1(T). \quad (5)$$

Finally the average kinetic energy is given by $\bar{\varepsilon} = k_B T$, with

$$E - E_0 = \overline{E}_1(T) + k_B T. \quad (6)$$

The model which this figure describes is now known technically as the low angular momentum phase-space limit. Although never observed in nature, it is sometimes

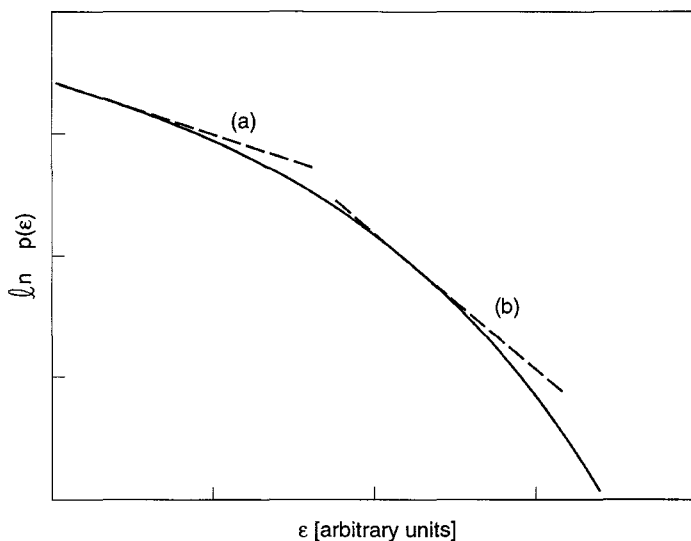


Figure 1. Schematic kinetic energy distribution in the low angular momentum phase-space limit. Formulas for (a) the initial slope, (b) the average slope, and the average energy are given in the text.

closely approached, and serves as a useful starting point for more sophisticated models. Weiskopf, for example, went on to develop what is now known as the low angular momentum thermodynamic limit of the infinite-well potential. In any case we observe that the three temperatures defined above will agree only in the limit of a very large molecule. Short of that point they are only metaphors.

By contrast the present paper is concerned with relations involving certifiable temperatures and small molecules. They are precise and universally applicable, unlike the highly idealized situation described above. Nevertheless they stem from the same idea of a molecule being in part a heat bath. They constitute what has been called ‘finite heat bath theory’.

2. Energy and temperature

The seminal result in this subject is due to Forst [3]. He used Laplace transform theory to show that, if a canonical rate constant can be expressed exactly in the Arrhenius form, i.e. as

$$k(T) = A \exp\left[-\frac{E_0}{k_B T}\right], \quad (7)$$

where A and E_0 are strictly independent of temperature, then the corresponding microcanonical rate constant is given by

$$k(E) = \frac{A\rho(E - E_0)}{\rho(E)} \quad (8)$$

where the two densities-of-states are those of the parent molecule. With a knowledge of the Arrhenius parameters one can thus quickly generate microcanonical rate constants; conversely, from the latter the Arrhenius parameters can (see also below) be derived.

Arrhenius parameters are essentially never independent of temperature, however,

and so the reliability of Forst's relation needs to be examined. This has been done using the more powerful technique of steepest descents. Let us define a temperature by the relation

$$E = \Delta E_a(T^\ddagger) + \overline{E}_p(T^\ddagger) - k_B T^\ddagger \quad (9)$$

where $\overline{E}_p(T^\ddagger)$ is the canonical energy of the parent and where $\Delta E_a(T^\ddagger)$ is the activation energy. It may then be shown [4] that a rate constant is given by

$$k(E) = A(T^\ddagger) \left[\frac{\rho(E - \Delta E_a(T^\ddagger))}{\rho(E)} \right] \left[1 + \frac{(d\Delta E_a/dk_B T)}{C} \right]^{-\frac{1}{2}} \quad (10)$$

where the Arrhenius parameters are evaluated at the temperature T^\ddagger , and where C is one less than the heat capacity of the parent molecule in units of k_B . The modifications required by the Forst relation are thus minimal and may often be ignored. Let us nevertheless look at a simple model to see that in principle they should be there.

For a chemical reaction occurring on a well-defined potential surface, the thermal rate constant can be written as [5]

$$k(T) = \left(\frac{k_B T}{h} \right) \frac{Q^\ddagger}{Q} \exp(-E_0/k_B T) \quad (11)$$

where Q^\ddagger and Q are the partition functions of the transition state and the parent molecule, respectively. We assume that the third law of thermodynamics applies to each, and thus that at low temperatures their ratio will go to unity. The activation energy will then be $E_0 + k_B T$, and the Arrhenius pre-exponential factor becomes $k_B T e/h$. We may use steepest descent theory to write

$$\rho(E - \Delta E_a) = \rho(E) ((C + 1)/C)^{\frac{1}{2}} / e \quad (12)$$

and then

$$\rho(E - E_0) = \frac{\omega(E - E_0)}{k_B T^\ddagger}, \quad (13)$$

where ω is the sum-over-states of the parent molecule, to obtain from (10) the relation

$$k(E) = \frac{\omega(E - E_0)}{h\rho(E)}. \quad (14)$$

Rate constants near threshold might thus be obtained solely from a knowledge of E_0 and the properties of the parent molecule.

This improbable result is not apt to find much use in practice other than as an extreme limiting case. It nevertheless serves our present purpose quite well. We note that it could have been obtained directly from the microcanonical equivalent [6] of equation (11),

$$k(E) = \frac{\omega^\ddagger(E - E_0)}{h\rho(E)}. \quad (15)$$

If by assumption the ratio of partition functions in (11) is unity, then so must be the ratio of the corresponding sums-over-states. The result obtained from the modified Forst relation is thus confirmed. Our ability to pass from either the energy or the temperature domain to the other hence appears to be quite general.

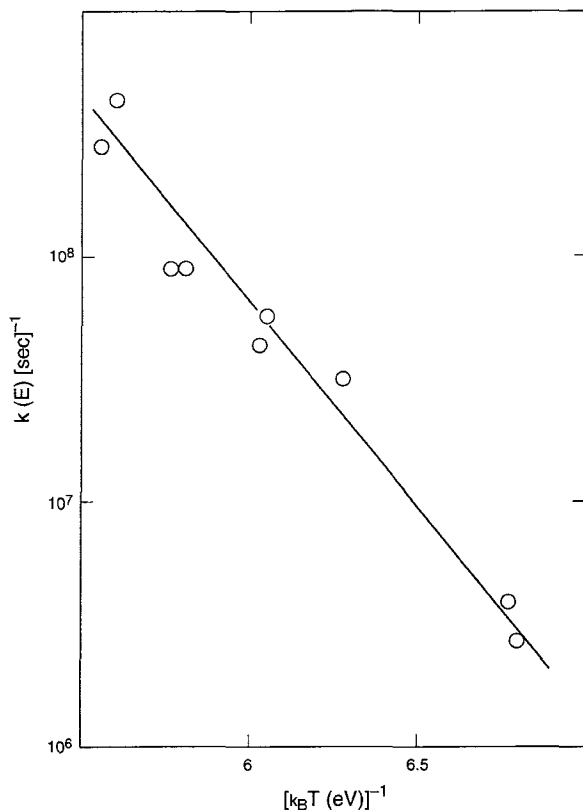


Figure 2. Generalized Arrhenius plot of rate constants for reaction (18), reported in reference [7].

A differential form of these results can be useful for effecting such passages. We define a temperature of a molecule via the relation

$$E = \bar{E}_p(T) - k_B T, \quad (16)$$

and then, using a steepest descent theorem, differentiate (10) to obtain

$$\frac{d \ln k(E)}{dE} = (k_B T^\ddagger)^{-1} - (k_B T)^{-1}. \quad (17)$$

The energy dependence of a rate constant is thus linked, via the definition in (9), to an activation energy. The transfer of information between the energy and temperature domains is accordingly facilitated.

Let us pause to entertain an example. We consider some data of Reddy and Berry [7] for the reaction



measured originally as a function of energy. The data were said at one time to be incompatible with the quasiequilibrium hypothesis. We present them in figure 2 in a generalized Arrhenius plot. Their logarithms are plotted versus the reciprocal of their associated temperatures, as defined in (16). From the slope, and using (9) and (17), an Arrhenius activation energy equal to 1.56 eV is obtained. Upon inserting it into (10)

and calculating a pair of densities-of-states, An Arrhenius pre-exponential factor equal to $2.3 \times 10^{13} \text{ sec}^{-1}$ then ensues. The results of Reddy and Berry have thus been nicely compressed to two parameters.

In this form they can conveniently be compared with theory or with data gathered in an infinite heat bath. With one proviso, they should agree. The data used above were obtained from molecules which had been photo-excited to a substantial level, but which were still rotationally cool. Strictly speaking, they are therefore comparable only to data from a heat bath consisting solely of rotationally cool molecules. The pre-exponential factor which one might only think about measuring in such a bath will be less than it would be in a more realizable but unconstrained heat bath, as first discussed by Rynbrandt and Rabinovitch [8]. Only for 'loose' transition states will these factors differ significantly, however [9]. The value reported above makes it clear that reaction (18) does not fall into this category. It thus offers a reliable measure of what to expect in a heat bath.

We now consider one additional facet to the relation between a microcanonical and a canonical rate constant. It is often convenient to have an explicit relation between an energy and the temperature linked by the isokinetic condition

$$k(E) \equiv k(T_b). \quad (19)$$

This relation can be obtained as follows. The derivative of the left-hand side of this stipulation has already been given in (17), and may be rewritten as

$$\frac{\partial \ln k(E)}{\partial E} = \frac{\Delta E_a(T^\ddagger)}{\bar{C}(k_B T^\ddagger T)} \quad (20)$$

where \bar{C} is again one less than the heat capacity of the parent molecule (in units of k_B), now evaluated at a mean value between T and T^\ddagger . The derivative of the right-hand side of (19) meanwhile yields

$$\frac{\partial \ln k(T_b)}{\partial E} = \left[\frac{\Delta E_a}{(k_B T_b)^2} \right] \left(d \frac{k_B T_b}{dE} \right). \quad (21)$$

In the limit of a very large molecule we expect that the temperature defined by (16) will satisfy the isokinetic condition. The final factor on the right-hand side of (21) could then be identified with \bar{C} , and the isokinetic temperature would then equal the geometric mean value of T and T^\ddagger . Using this as a first approximation then permits higher order terms to be generated. They may be collected in order of increasing reciprocal powers of the heat capacity, and yield

$$E = \bar{E}(T_b) - k_B T_b + \frac{\Delta E_a}{2} + \Delta E_a \left(\frac{\Delta E_a}{12 C k_B T_b} \right) + \dots \quad (22)$$

for the first few terms. It is understood that the activation energy, the heat capacity, and its derivative are all to be evaluated at the temperature T_b .

Beyond this point the expansion becomes quite complicated. Nevertheless these first terms are adequate for all but the smallest molecules. In particular, they suffice for deducing the pre-exponential factor from data such as those in figure 2, but without having to calculate any densities-of-states. It has also been shown how this relation illuminates the origin of kinetic isotope effects in isolated molecules [4]. Let us address some additional examples.

2.1. Kinetic shifts

In 1959 Chupka [10] distinguished between the threshold energy of a reaction and that energy at which its rate is large enough to be discernible. The latter energy is often called the 'appearance potential', and its displacement from the former is the 'kinetic shift'. If we have some idea of the temperature in a heat bath at which a given rate is sustained, then (22) will give us directly the isokinetic energy. The necessary information may have been originally garnered in a heat bath or it may come from a calculation carried out perhaps more simply as a function of temperature.

The thermionic emission of electrons from molecules poses a recent example of how working in the temperature regime can be useful. While lingering there, the theoretical expressions [11, 12] could be checked for their compatibility with the Richardson equation for emission from metallic surfaces. Having survived that test, they could then be transferred to the energy regime. As an explicit example, let us consider the reaction



A pre-exponential Arrhenius factor equal to $2 \times 10^{16} \text{ sec}^{-1}$ and an activation energy equal to the ionization potential plus $k_B T$ may be estimated for it. To sustain a rate constant equal to, say, 10^5 sec^{-1} , a value of $\Delta E_a/k_B T_b$ equal to 26.0 is thus indicated. Equation (22) then implies an appearance potential of 44 eV, consistent with a recent measurement [13].

Similarly one may speak of the 'disappearance potential' of an ion such as C_{60}^- . It is the energy at which the ion, having been formed by electron attachment, disappears as a result of re-emission of the electron. It has been understood [14] for a long time that the lifetime of an ion can be limited by this process, and an early theorem [15] in fact states that the lifetime will be less than or equal to the microcanonical result. Nevertheless the very large kinetic shifts now being observed [16] permit, perhaps for the first time, a meaningful comparison between experiment and theory. Good agreement exists in the case of C_{60}^- [17].

These large kinetic shifts are of course a reflection of the 'degrees of freedom' effect. Let us consider this effect more generally. It may be formulated as the quantity $(\partial E/\partial n)_k$, where n is the number of degrees of freedom, and may be written as

$$\left(\frac{\partial E}{\partial n}\right)_k = \left(\frac{\partial E}{\partial n}\right)_{T_b} - \frac{(\partial \ln k/\partial n)_{T_b}}{(\partial \ln k/\partial E)_n}. \quad (24)$$

Consider then a molecule containing a reaction centre to which additional degrees of freedom are added. Let us assume that they function only as spectator modes, i.e. that they have no effect on a rate constant in the infinite heat bath. The second term on the right-hand side of (24) will then be zero. The first term can meanwhile be obtained by differentiating (22). The major contribution comes from the first term of this relation. It equals the thermal energy of the new degree of freedom, and is necessarily positive. Differentiation of the final (and of still higher order) terms will introduce negative contributions.

We may estimate the point where they are of comparable importance as follows. Suppose we are considering a reaction which in a heat bath has a pre-exponential Arrhenius factor of 10^{14} sec^{-1} , again being studied in an apparatus sensitive to rate constants greater than 10^5 sec^{-1} . At this threshold, the isokinetic rate constant will be characterized by a value $(\Delta E_a/k_B T_b)$ equal to 20.7. Figure 3 illustrates equation (22) as applied to this hypothetical situation. It will be seen that molecules with a heat

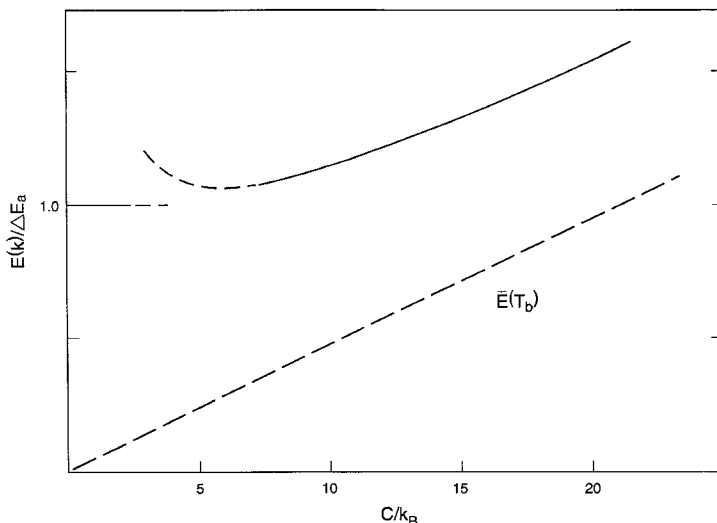


Figure 3. The solid curve traces the energy needed to sustain a typical threshold rate constant, in units of the activation energy, as a function of molecular size, as given by (22).

capacity (at T_b) less than about six will exhibit a negligible kinetic shift. Above that point, however, the shift will increase inexorably with molecular size.

2.2 Other variables

The relations developed above all have a generalization of Forst's result at their core. We now turn to a quite different theorem. Rate constants are determined by many parameters beside the energy. Angular momentum is an obvious example, but the masses of the constituent atoms and the forces between them are also of interest. For any such parameter, say α , it has been shown [4] that one can write

$$\frac{\partial \ln k(E, \alpha)}{\partial \alpha} = \frac{\partial \ln k(T^\ddagger, \alpha)}{\partial \alpha} + \frac{\partial \ln [Q(T^\ddagger)/Q(T)]}{\partial \alpha} \quad (25)$$

where T^\ddagger is just the temperature already defined in (9) and Q is the partition function of the parent molecule.

These parameters can be divided into two groups. Some, such as the mass of an atom subject to isotopic substitution, affect the properties of the parent molecule and hence of its partition function. Others, such as the magnitude of a potential barrier, do not. The impact of an alteration in their magnitude will hence be confined to the first term on the right-hand side of (25). It will equal the effect of that same alteration in an infinite heat bath set, not to the isokinetic temperature but to a lower one.

A parameter which requires consideration of both terms is angular momentum. Consider a heat bath composed of molecules all of which have the same angular momentum, J . The rotational partition function may be written as

$$Q = (2J+1)^2 \exp\left(-\frac{BJ^2}{k_B T}\right) \quad (26)$$

where B is the average rotational constant. The final term in (25) is thus readily evaluated. To obtain the term $\partial \ln k(T^\ddagger)/\partial J^2$ in that equation, however, we will need to adopt a model. It will be assumed, following Rice and Gershinowitz [18], that angular

momentum affects a thermal rate constant by increasing the activation energy by the amount $(B^\ddagger - B)J^2$. In the case of chemistry occurring on a Born–Oppenheimer surface, B^\ddagger can be thought of as the (average) rotational constant of the transition state. We assume in any case that this term occurs in a rate constant solely via a Boltzman factor. If so we shall then have

$$\frac{\partial \ln k(T^\ddagger)}{\partial J^2} = \frac{-(B^\ddagger - B)}{k_B T^\ddagger} \quad (27)$$

and hence

$$\frac{\partial \ln k(E)}{\partial J^2} = \frac{B}{k_B T} - \frac{B^\ddagger}{k_B T^\ddagger} \quad (28)$$

Applications of this result in several contexts have been given [19, 20]. It must be emphasized however that, despite a superficial similarity to (17), this relation is on a more tenuous footing. It rests upon the Rice–Gershinowitz supposition and thus it can fail. One instance, the phase-space limit, has recently been identified [21]. Nevertheless for qualitative purposes the relation in (28) has been quite useful.

Let us consider then a more clear-cut application—to an elementary barrier, say E_0 , which must be surmounted for a reaction to proceed. It will certainly appear in a canonical rate constant expression via a simple Boltzman factor. Equation (25) then reduces to

$$\frac{\partial \ln k(E, E_0)}{\partial E_0} = -(k_B T^\ddagger)^{-1} \quad (29)$$

This relation, useful as it is, is even more interesting when combined with (17) to yield

$$\left(\frac{\partial E}{\partial E_0} \right)_k = \frac{T}{(T - T^\ddagger)} \quad (30)$$

Suppose for example that the size of the barrier is increased by ∂E_0 . The work which must be expended to overcome it increases accordingly. One can compensate for the attendant decrease in the rate constant by increasing the heat content of the molecule. According to (3), that increment is given by the inverse efficiency of a steam engine operating between the temperatures defined in (9) and (16). The right-hand side of (30) is thus known as a Carnot–Kelvin factor.

It is, of course, a number greater than unity. Thus small variations in a barrier size can be magnified into much larger displacements of the energy needed to maintain a given rate constant. An ‘appearance potential’ is an example of just such an energy. Let us look at how its magnitude can be illuminated by (30).

Wörgötter *et al.* [22] have reported the appearance potentials of a number of ions formed by successive evaporations of C_2 , beginning with the C_{60}^+ ion. The measured values are listed in table 1. They have been corrected for the thermal energy of the C_{60} progenitor and its ionization potential, and for the calculated (see below) activation energies of any preceding dissociations. These numbers thus constitute the energy needed to make the ion ‘appear’, interpreted in their apparatus to mean that energy needed to sustain a threshold rate constant equal to $3 \times 10^4 \text{ sec}^{-1}$.

For the dissociation



an activation energy equal to 7.1 eV may be adopted from earlier work [23]. It can be obtained by assuming that the pre-exponential Arrhenius factor for the reaction

Table 1. Corrected appearance potentials and inferred activation energies for $C_{n+2}^+ \rightarrow C_n^+ + C_2$.

Ion (n)	Corrected AP (eV)	ΔE_a (eV)
C_{58}^+	41.8	7.06
C_{56}^+	39.8	6.77
C_{54}^+	38.5	6.59
C_{52}^+	37.5	6.45
C_{50}^+	36.1	6.25
C_{48}^+	38.2	6.55
C_{46}^+	36.9	6.36
C_{44}^+	36.9	6.36

equals $4 \times 10^{15} \text{ sec}^{-1}$. This value identifies the ratio $\Delta E_a/k_B T_b$ as equal to 25.6 for a rate constant isokinetic with the threshold rate. The observed magnitude of the threshold together with (22) then gives a value for ΔE_a itself.

The subsequent dissociations seem to require smaller amounts of energy to sustain the threshold rate. Let us assume that this arises from smaller barriers, i.e. that they all have the same pre-exponential Arrhenius parameter. One might follow Wörgötter *et al.* [23] and extract in turn from (22) a value of ΔE_a for each dissociation. It is much easier however to take the difference between each observed threshold energy and 41.2 eV, and to then divide this by the appropriate Carnot–Kelvin factor to obtain directly the shift in the barrier size.

This is readily done. The Carnot–Kelvin factor can be written as

$$\frac{T}{(T-T^\ddagger)} \approx \left(\frac{Ck_B T_b}{\Delta E_a} \right) \left(1 + \left(\frac{\Delta E_a}{2Ck_B T_b} \right) + \dots \right) \quad (32)$$

and estimated here to equal 7.15. The barrier sizes which then ensue are listed in table 1. They are identical with those found by Wörgötter *et al.* [22].

Apart from simplicity, the above procedure shows directly how large shifts in appearance energies originate from subtle differences in barrier height. A convincing picture emerges of a gentle decline in the dissociation energies, beginning at C_{60}^+ . Clearly this ion is not an isolated outcropping of magic.

Let us consider one more example of a change in barrier size, and the subsequent change in an appearance potential that can ensue. The ionization potential of an atom can be lowered by the application of an external electric field. Classically, and to a good approximation experimentally, that decrease is given by

$$A = -2F^{1/2} \quad (33)$$

where A is the shift, and F is the electric field strength, each expressed in atomic units. To extend this treatment to larger species, one may assume that the electron moves in a potential given by

$$V = -\frac{e^2}{R} - \frac{C_4}{R^2(R^2 - R_0^2)} \quad (34)$$

where C_4 is the charge-induced dipole coefficient and R_0 is the radius of the central ion. For very large molecules this term will be dominant, and field ionization is then given by [17]

$$A = -F^{1/2} \quad (35)$$

This relation is equivalent to Schottky's result, obtained by him in connection with the

effect of an electric field on the rate of thermionic emission of electrons from a metal surface [24]. Note that the magnitude of the electric field effect has hardly changed in going from an atom to matter of macroscopic dimensions, and so can be estimated with little ambiguity for small molecules.

Thermionic emission from small molecules such as C_{60} can also occur. We saw earlier that its appearance potential should be much higher than the ionization potential, in accord with (22). Gallogly *et al.* have in fact reported an appearance potential in good agreement with expectations [13]. They noticed a marked sensitivity of their result to electric fields, however, and so supposed that they were observing the classic field ionization of a Rydberg electron. They were surely observing instead the much larger shift in the kinetic shift arising from a magnification of the electric field effect by a substantial Carnot–Kelvin factor. As before, we can easily estimate its size. Experiments to test this mechanism are in progress.

Another example of an intramolecular parameter, i.e. of one which does not affect the properties of a parent molecule, is a label specifying the final state of a product of a reaction. Recall the discussion with which we began this paper. It was noted how certain model situations invited the use of the word temperature. Equation (25) goes much further. It tells us that the product state distributions and branching ratios which emanate from *any* isolated molecule characterized by any potential and with any angular momentum are related to those which one might measure in a certified heat bath. Temperature in that context is no longer only a useful metaphor.

Alternatively the distribution might be obtained from a model, calculations for which are invariably more easily effected using the canonical ensemble. Several applications of this possibility have been discussed elsewhere [20, 21]. We can illustrate them by considering again the low angular momentum limit of the phase-space model of figure 1. Equation (25) tells us that the *slope* of a distribution is to be obtained from the slope of a canonical distribution, calculated at the temperature satisfying (9) in which the kinetic energy-dependent activation energy has been entered. Suppose that as a first approximation we use only the activation energy associated with the entire distribution. It is easy to show that, for the elementary phase-space model, this procedure will generate the temperature defined by (4), and thus curve (b) in figure 1. This result is clearly a useful starting point, to which the higher-order refinements discussed elsewhere [20, 21] may be brought.

Let us close here by shedding new light on another old subject. Figure 4 shows measurements [25] of the kinetic energy distribution for the products of the reaction



The open circles were obtained when photoionization led to an ion in its ground electronic state; the filled symbols reflect photoionization into various vibrational levels of the first electronically excited state. In each case the observed distribution has been scaled by the average kinetic energy. This coalescing of data obtained at different vibrational levels reveals clearly two very different distributions, reflecting two different potential energy surfaces. Evidently dissociation from the first excited state occurs prior to internal conversion.

This scaling procedure did not require that Miller and Baer know anything about the two surfaces, nor about the activation energies associated with each. When it was first introduced [26], the reason why the procedure worked was understood only nominally. We can now frame that reason more succinctly. If a kinetic energy distribution can be evaluated at a temperature, then its average energy, say $\bar{\epsilon}$, can also

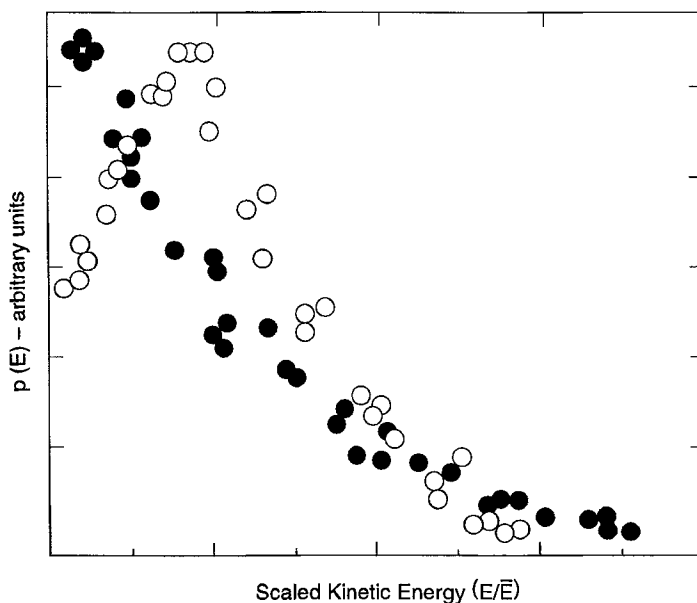


Figure 4. Scaled kinetic energy release distributions for reaction (36), from reference [26].

be investigated as a function of the temperature. For radially symmetric potentials, and for low values of the angular momentum, it is found [9] that their ratio is circumscribed by the relation

$$1 \leq \frac{\bar{\epsilon}}{k_B T^\ddagger} \leq 2. \quad (37)$$

We may see this explicitly with the infinite well potential

$$V = 0, R > R_0 \quad (38a)$$

$$V = -\infty, R < R_0 \quad (38b)$$

which yields

$$\bar{\epsilon} = k_B T^\ddagger \frac{[2(I_1 + I_2) + \mu R_0^2]}{[I_1 + I_2 + \mu R_0^2]} \quad (39)$$

where μ is the reduced mass and I_1 and I_2 are the moments of inertia of the two products. The phase-space and the thermodynamic limits are readily apparent. Note also that the ratio $\bar{\epsilon}/k_B T^\ddagger$ is independent of the total energy. For more complicated potentials this ratio need not be constant, but is found in practice to be very nearly so. The scaling property, so beautifully exploited by Miller and Baer, then follows.

3. Summary

The relations presented in this paper all flow from the steepest descent approximation as applied to microcanonical rate constants. We have seen several examples of how they can be used to obtain numbers. Many others could have been given. Perhaps more important are the insights which these relations can provide. Why are isotope effects enhanced upon isolation? When might a rate constant go through a maximum as a function of energy? Why does a small amount of magic make a particular structure jump out of a mass spectrum? It has been shown above, in the cited literature and elsewhere, how questions such as these can be answered.

Acknowledgements

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Appendix

Repeated references to steepest descent theory will be found in the above, and its origin in the paper of Hoare and Ruijgrok has been cited. They had observed that a density-of-states of a system with energy E (as measured from its zero-point) could be calculated as

$$\rho(E) = \frac{Q(T) \exp(E/k_B T)}{k_B T (2\pi C)^{1/2}} \quad (\text{A } 1)$$

where the partition function Q and the heat capacity C (in units of k_B) are evaluated at the temperature defined by

$$E = \bar{E}(T). \quad (\text{A } 2)$$

They also noted that a sum-over-states $\omega(E)$ could be estimated as

$$\omega(E) = \rho(E) k_B T \quad (\text{A } 3)$$

i.e. that

$$\frac{d \ln \omega(E)}{dE} = (k_B T)^{-1}. \quad (\text{A } 4)$$

These relations are indeed useful, but fail badly as the energy approaches zero. Yet equations (10) and (15) make it clear that this limit is often called for. This need can be accommodated by noting that a density-of-states can also be thought of as the sum-over-states of a system whose partition function equals $Q(T)/k_B T$. One can then write

$$\rho(E) = \frac{Q(T) \exp(E/k_B T)}{k_B T (2\pi(C-1))^{1/2}} \quad (\text{A } 5)$$

where the temperature is now given by

$$E = \bar{E}(T) - k_B T. \quad (\text{A } 6)$$

Similarly a sum-over-states can be thought of as a density-of-states of a system whose partition function equals $Q(T)k_B T$. One then has

$$\omega(E) = \frac{Q(T) \exp(E/k_B T)}{(2\pi(C+1))^{1/2}} \quad (\text{A } 7)$$

where now

$$E = \bar{E}(T) + k_B T. \quad (\text{A } 8)$$

These relations, which are well-behaved as the energy vanishes, constitute the essential underpinnings of finite heat bath theory.

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