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Statistical Mechanical Treatment of the Activated Complex in Chemical Reactions¹LOUIS S. KASSEL,² *U. S. Bureau of Mines*

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A possible error in Eyring's recent calculations of absolute reaction rates due to the short life and consequent unsharp quantization of the activated complex is noted. The existence of this error is made more probable by a consideration of the target area required by Eyring's equations at low temperatures. There is no doubt that his treatment becomes asymptotically correct at high temperatures.

THE purpose of this paper is to comment on some aspects of the recent interesting attempt by Eyring³ to compute absolute rates of chemical reaction from the geometry of the potential surface. Eyring considers that the activated complex has all the properties of a stable compound except for one degree of freedom which may be treated as a translation. He calculates the partition function and hence the equilibrium constant from the vibrational frequencies just as is done for stable molecules. It would seem that this procedure is open to question on the basis of the uncertainty principle, for with a velocity of 10^6 cm/sec. and a very generous reaction zone 5×10^{-9} cm deep, the complex exists for only 5×10^{-14} sec. and has an uncertainty in energy of 2×10^{13} sec.⁻¹ or 700 cm⁻¹. The vibrational quantization of the complex is thus very imperfect.

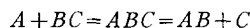
If the quantum-mechanical transmission coefficients could be calculated for a simplified potential surface the correctness of Eyring's procedure could be decided definitely. The simplest surface which retains the essential features of the problem is

$$E = 0 \quad \text{for } |x| > a,$$

$$E = E_0 + 2\pi^2\nu^2my^2 \quad \text{for } |x| \leq a.$$

Here the barrier is a parabolic cylinder. Unfortunately it has not been found possible to calculate the transmission of such a barrier. Some information can be gained, however, by studying the classical treatment of a similar

barrier. To make the problem correspond more closely to that solved by Eyring we suppose a reaction



with the potential energy surface

$$E = 2\pi^2\nu_0^2\mu d^2 \quad \text{for } x > a,$$

$$E = 2\pi^2\nu_0^2\mu d^2 + E_0 + 2\pi^2\nu^2mr^2 \quad \text{for } x \leq a.$$

Here d is the separation between B and C , μ the reduced mass of BC and ν_0 its vibration frequency; x is the distance between the center of gravity of BC and the projection of A on the BC axis; $r^2 = y^2 + z^2$, where y and z are perpendicular to the BC axis; m is the mass of A and ν the doubly degenerate bending frequency of the complex. For convenience we assume that μ is very much larger than m and that the moment of inertia of ABC equals that of BC . We are not concerned with the nature of the potential surface beyond the (degenerate) saddle point, since this will not affect the rate. For calculating the number of collisions the molecule BC may now be replaced by the plane $x = a$. The number of collisions per cm² on this plane when there is one atom of A per cc is $(kT/2\pi m)^{1/2}$. The number of collisions on the annulus r to $r + dr$ with a perpendicular component of velocity R to $R + dR$ is

$$\begin{aligned} dZ &= (2\pi m/kT)^{1/2} e^{-mR^2/2kT} R r dR dr \\ &= (2\pi/mkT)^{1/2} e^{-E_0/kT} e^{-u/kT} r du dr, \end{aligned}$$

where $u = mR^2/2 - E_0$. If every atom penetrates the potential barrier whose kinetic energy perpendicular to the barrier at least equals the height of the barrier where it strikes, the rate of reaction will be

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³ H. Eyring, J. Chem. Phys. **3**, 107 (1935).

$$\begin{aligned}
 k_1 &= \int_{u=0}^{\infty} \int_{r=0}^{(u/2\pi^2\nu^2m)^{\frac{1}{2}}} dZ \\
 &= \nu^{-2}(2\pi m)^{-\frac{1}{2}}(kT)^{-\frac{1}{2}}e^{-E_0/kT} \int_0^{\infty} ue^{-u/kT} du \\
 &= \nu^{-2}(kT/2\pi m)^{\frac{1}{2}}e^{-E_0/kT}.
 \end{aligned}$$

For this same potential energy surface Eyring's method gives

$$k_1 = (h/kT)^2(kT/2\pi m)^{\frac{1}{2}}e^{-E_0/kT}(1 - e^{-h\nu/kT})^{-2}$$

which reduces to the classically calculated value when $h\nu \ll kT$, but in general exceeds it by the factor $(h\nu/kT)^2(1 - e^{-h\nu/kT})^{-2}$. It is readily seen that if the classical reactivity of atoms with excess kinetic energy u is increased by a factor $f(u)$, the condition necessary to give Eyring's result is

$$\int_0^{\infty} uf(u)e^{-u/kT} du = (h\nu)^2(1 - e^{-h\nu/kT})^{-2}$$

for all T . It has not been found possible to solve this equation for $f(u)$, and it seems probable that no solution exists. Some light is cast upon this difficulty by a very simple calculation. We may certainly assume that no atom can react for which $u < 0$, since then the energy is insufficient to penetrate the barrier at its lowest point. The number of collisions per cm^2 with $u \geq 0$ is $(kT/2\pi m)^{\frac{1}{2}}e^{-E_0/kT}$. From Eyring's equation the number of successful collisions at very low temperatures is $(h/kT)^2(kT/2\pi m)^{\frac{1}{2}}e^{-E_0/kT}$. The ratio of these gives a target area of $h^2/2\pi mkT$, which is of the order of 10^{-16} cm^2 and replaces σ^2 of the usual theory, as Eyring has pointed out. Now for low temperatures the Maxwell distribution curve is very steep, and the atoms with $u \geq 0$ become a nearly homogeneous group with $u = 0$, thus permitting easy calculation of the low

temperature target area for any assumed $f(u)$. We need merely note that the target area from the generalized classical treatment is $(2\pi mkT\nu^2)^{-1} \int_0^{\infty} uf(u)e^{-u/kT} du$, and that for small values of T the integrand is appreciable only near $u = 0$. If $uf(u)$ vanishes with u and behaves near $u = 0$ as u^n , the target area for low temperatures will be proportional to T^n . If $uf(u)$ is finite at $u = 0$, the target area becomes constant as T approaches zero. If $uf(u)$ increases as u^{-m} when u goes to zero, the low temperature target area varies as T^{-m} ; the integral diverges, however unless $m < 1$ and hence can never quite represent the Eyring target area, which varies as T^{-1} . It seems less important to discuss this merely annoying inability to find an $f(u)$ exactly equivalent to Eyring's result than it is to note that his equation unquestionably requires an infinite target area for atoms with energy exactly E_0 . Such a requirement seems physically unsatisfactory.

It is recognized that arguments of this character are not absolutely decisive, but they do at least suggest that the quantization of the activated complex is not sharp enough to justify the statistical methods used by Eyring, except when $h\nu \ll kT$; in that case classical theory gives the correct partition function, and unsharp quantization cannot harm the result.

Note added in proof: Private correspondence and conversation with Dr. Eyring after this paper was written has revealed that he agrees with the preceding discussion. His statement that when more accurate values for any part of the partition function were known from a source other than the Eyring-Polanyi energy surfaces, they could of course be used, was intended to include refinements of the type discussed here. There may be some question as to the wisdom of stretching the term partition function so far, and some disagreement in estimating partition functions in particular cases, but there is no disagreement with regard to the general program outlined by Eyring.