On the Statistical Mechanical Treatment of the Absolute Rate of Chemical Reaction.

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By "chemical reaction" we understand simple rearrangements of chemical combinations among a group of atoms. It is the object of the present article to discuss in general the statistical method for treatment of the absolute reaction rate with a group of atoms having the following properties: (1) displacements of atoms take place adiabatically with regard to the electronic configuration; (2) classical mechanics holds for the motion of centres of gravity of atoms; (3) the group has more or less chance of interchanging energy with its surroundings at a definite temperature by interaction with radiation or with other material system; the interaction will be called "collision" in what follows; (4) the group can stably exist in the initial and the final state, which are distinctly different with each other in spacial relative configuration of atoms. Such a group of atoms will be called "chemical system" in what follows.

The rate constant of the reaction is now the probability with which the chemical system transits from the configuration of the initial state to that of final one per unit time. The transition and its probability will be treated with special reference to the configuration space, rather than with reference to the phase space, since we are interested in the spacial rearrangements of atomic nuclei rather than in those of momenta. The representative point of our chemical system will thus move in the configuration space along a trajectory belonging to a definite energy state until interrupted by a collision and switched over to another trajectory. Time interval and the portion of trajectory marked off by two successive collisions will be called in what follows, "life time" and "free path" respectively. Further aspects of the motion of the representative point are those imposed by (4), i.e. the point may move about within either of two separate regions in the configuration space corresponding to the initial and the final state for a long time without traversing the critical regions intermediate between them. With this manner of representation the probability is now that with which a representative point escapes the initial region towards the final one. One may of course consider, if one prefers although it is not absolutely necessary, an assemblage of such points contained in the initial region, and use the terminology of the gas kinetic theory: the fraction of points out of the total contained in the initial region, which escape the latter per unit time, is the probability in question. It will be meant by the statistical equilibrium of the assemblage that the number of points contained in any assigned volume in the configuration space is proportional to the phase integral over the volume.

The probability will be dealt with for three different types of flow of points arising from different magnitudes of the free path. If the free path is small compared to the extension of the critical region and still less compared to that of the initial and the final regions, the representative point would, when situated at the critical regions, move back and forth and hesitate to reach either of regions. Even if it has once transited any fixed point on the critical region toward the final region, it would with almost equal probability, go back home as arrive at the destination and it is only with very small probability that one may expect it at the final region some time after the transition.

The assemblage of points, if it is at the distribution departing from that of statistical equilibrium, would thus flow with mass velocity less than that of thermal motion. Since momenta of points contained within any elementary volume, whose extention is larger than the free path, accord with Boltzmann's distribution because of sufficient collisions, the flow of points may be treated like diffusion if such volume is small enough.

According to (4) further, we have a steady flow in the neighbourhood of the critical region. In this case we may set up lines of flow and surfaces orthogonal to latters along which no resultant flow of points takes place. The main line of flow may duly be termed the "reaction coordinate"(1)(2) but the number of points which pass through the surface from the side of the initial region to that of the final region is by no means equal to that of the mass flow, the latter giving the reaction rate in this case.

This effect diminishes the reaction constant the more, the broader is the critical region measured along lines of flow and the more frequent are the collisions. So far as the latter frequency does not appreciably depend upon the temperature, the resulting depression is mainly imposed upon the temperature independent factor or the "collision factor" Z of the reaction constant $\mathfrak{f}$ as expressed by $\mathfrak{f} = Ze^{-\frac{U^*}{kT}}$ where U^* is the activation energy. The frequent occurrence of collisions in the present sense thus diminishes "collision factor".

This effect may account for the so-called slow reaction in the solution raised by Moelwyn-Hughes and Hinshelwood(3) where frequent collisions are expected.

In the other extreme case when the free path is large compared with the extension of both the initial and the final regions, the representative point, moving on a trajectory of a single energy state, is able to fly through both the regions over and over again without being hit by a collision. The reaction is completed by a timely collision when the representative point is just flying through the final region. This case was thoroughly discussed by Wigner from a different angle with special reference to the association reaction stabilised by three body collisions.(4)

The intermediate case is now that in which the free path is longer than the extension of the critical region but shorter than that of the initial and the final region. The representative point, when it has entered either of the regions, thus collides once at least and assumes an energy state in the region with a probability proportional to the Boltzmann factor but it traverses the critical region with one flight.

As to the manner of flow of points the following can be inferred. Suppose a surface S were stretched between the initial and the final region so that a point in the initial region has once at least to pass through it and that a large number of points exist in the initial region while none in the final region. The points which pass through the surface are those moving along trajectories which lead to the final region with a single pass through the surface or after once or many times passed in and out the

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

(2) Evans and Polanyi, *Trans. Faraday Soc.*, **31** (1935), 875.

(3) Moelwyn-Hughes and Hinshelwood, *J. Chem. Soc.*, **1932**, 230.

(4) Wigner, *J. Chem. Phys.*, **5** (1937), 720.

surface, and those moving on trajectories which pass the surface in and out without leading to the final region. The former group of points is assured of passage into the final region since none of them are struck out of their route in the critical region, the number of their passages per unit time being the point in question. If, on the other hand, the assemblage were at statistical equilibrium over the whole configuration space, the number of points in the initial region being the same as before, the total number of passages through the surface is increased by the number of in-and-out passages of trajectories which are traced by points coming from the final region: points from the final region which arrive at the initial region with a single pass through the surface contribute nothing to the total number since they do not encounter collisions within the critical region. The total number is thus the upper limit of that in question and the minimum value obtained by varying the surface is the best approximation. The minimum will give the exact number in question if it is the case that trajectories are not entangled within the critical region, which might be satisfied if the potential energy is not very complicated there. Such type of flow of points may be called "effusion". The reaction rate can be calculated as given below by counting the number of points falling on the surface S, and by minimizing the latter. The number is given by

$$-\frac{dN}{dt} = N\frac{\int^{S}\!\cdots\int c_1 e^{-\frac{\mu_1 c_1^2}{2kT}-\frac{E^*}{kT}} dq_2 dq_3 \cdots\, dq_n dp_1 dp_2 \cdots\, dp_n}{\int^{V}\!\cdots\int e^{-\frac{E}{kT}} dq_1 dq_2 \cdots dq_n\, dp_1 dp_2 \cdots dp_n} \qquad (1),$$

where $$E^* = E_{\mathrm{K}}^* + U^*\,,$$

and $$E = \frac{1}{2}\mu_1 c_1^2 + E_{\mathrm{K}} + U\,.$$

$q_1, q_2, \ldots, q_n$ are orthogonal curvilinear coordinates, q_1 being normal to the surface, n three times the number of nuclei of the chemical system, and p's conjugated momenta, while μ_1 and c_1 are respectively the reduced mass and the velocity associated with q_1. E is the total energy, E_{K} the kinetic energy in the degree of freedom 2, 3,..., n and U the potential energy where asterisks denote those quantities on surface S. Integration S is to be taken over whole S surface, over positive value of p_1 and over whole momentum space of remaining momenta and N the total number of representative points distributed over the region. Integration V is the phase integral of the initial region bounded by S. Integration over c_1 being carried through, the above equation becomes

$$-\frac{dN}{dt} = NkT\,\frac{\int^{S}\cdots\int e^{-\frac{E^*}{kT}}\,dq_2dq_3\cdots\cdots dq_n\,dp_2dp_3\cdots\cdots dp_n}{\int^{V}\cdots\int e^{-\frac{E}{kT}}\,dq_1dq_2\cdots\cdots dq_n\,dp_1dp_2\cdots\cdots dp_n} \qquad (2).$$

The integral in the numerator is nothing but the phase integral of the motion restricted on the surface S. A surface S_0 which minimizes the rate (2) will be called "critical surface". S_0 satisfies the condition:

$$\delta\int^{S}\cdots\int e^{-\frac{E^*}{kT}}\,dq_2dq_3\cdots\cdots dq_n\,dp_2dp_3\cdots\cdots dp_n = 0\ ,$$

since $N\Big/\int^{V}\cdots\int e^{-\frac{E}{kT}}\,dq_1dq_2\cdots dq_n\,dp_1dp_2\cdots dp_n$ remains unchanged by shifting surface S, because of the statistical equilibrium of points over the configuration space. Integrating over p, the variation equation becomes

$$\int^{S}\cdots\int\prod^{i=2,3,\cdots,n}\sqrt{2\pi\mu_ikT}\,e^{-\frac{U^*}{kT}}\left(-\frac{1}{kT}\frac{\partial U^*}{\partial q_1}+\sum^{i=2,3,\cdots,n}\frac{1}{\rho_i}\right)(\delta q_1)^*dq_2dq_3\cdots dq_n=0,$$

or

$$\frac{1}{kT}\frac{\partial U^*}{\partial q_1}=\sum^{i=2,3,\cdots,n}\frac{1}{\rho_i} \qquad (3),$$

where μ_i's are reduced masses associated with i-th coordinates and ρ_i's principal radii of curvature.

The reaction rate can thus be calculated according to Eq. (2) by determining the critical surface by means of (3).

The present procedure will be discussed and exemplified in some special cases assuming the fulfilment of conditions for "effusion".

(i) Eq. (2) may be expressed in terms of partition functions by dividing both numerator and denominator throughout by h^n:

$$-\frac{dN}{dt} = N\frac{kT}{h}\frac{Q^*}{Q} \qquad (4),$$

where $$Q^* = \frac{1}{h^{n-1}}\int\cdots\cdots\int e^{-\frac{E^*}{kT}}\,dq_2dq_3\cdots\cdots dq_n\,dp_2dp_3\cdots\cdots dp_n\ ,$$

and $$Q = \frac{1}{h^{n}}\int\cdots\cdots\int e^{-\frac{E}{kT}}\,dq_1dq_2\cdots\cdots dq_n\,dp_1\,dp_2\cdots\cdots dp_n\,.$$

This is formally equivalent to the equations given by Eyring,(1) Wigner,(4) Evans and Polanyi(2) but different from those in the nature of the surface S for counting the passage of points; the method of the latter authors is equivalent to reckon the passage through a surface $\frac{\partial U}{\partial q_1} = 0$. In a special case when $\frac{\partial U}{\partial q_1} = 0$ happens to be a Cartesian plane Eq. (3) is satisfied and hence the difference in the two procedures vanishes.

In such a case Eq. (2) assumes the familiar form of the expression for effusion,

$$-\frac{dN}{dt} = N\sqrt{\frac{kT}{2\pi\mu_1}}\,\frac{\int^{S}\!\cdots\!\int e^{-\frac{U^*}{kT}}\,dq_2 dq_3 \cdots dq_n}{\int^{V}\!\cdots\!\int e^{-\frac{U}{kT}}\,dq_1 dq_2 \cdots dq_n} \tag{5}$$

integrating over associated momenta, $q_2, q_3, \ldots, q_n$ being now Cartesian coordinates. Integrals S and V give the area of the orifice and the volume of the containing vessel in the case of the effusion of real gas, where $U^* = U = \text{const.}$

(iia) The present procedure is applied to the association of two atoms, whose mutual potential energy $U(r)$ depending only on the distance r has no maximum. This is a case when the transition state method(1)(2)(4) can not be applied. Surface S is now $r_i > r > r_f$ in the six dimensional configuration space, where r_i and r_f are nuclear separations at the initial and at the final state respectively. Critical surface S_0 can be located by (3) that,

$$r = r_0,$$

where

$$\frac{1}{kT}\frac{\partial U^*}{\partial r_0} = \frac{2}{r_0} \tag{6}$$

r_0 is such a distance that if two nuclei are destined to approach each other within r_0 they probably react, but not otherwise. This might be interpreted as the sum of collision radii of the two nuclei or when two atoms are identical as the collision diameter. It may be noted that r_0 depends on the temperature or on the mean relative velocity of the two nuclei. If, for instance, $U^*(r)$ is that of Coulomb attraction, the collision diameter is inversely proportional to the temperature.

(iib) If $U^*(r)$ has a maximum, the transition state method would reckon the passage of representative points through the surface $\frac{\partial U^*}{\partial r} = 0$, while the present one that through the surface $\frac{\partial U^*}{\partial r} = \frac{2kT}{r}$. Assuming that $\frac{\partial U^*}{\partial r} = 0$ at $r = r_0' = 1\,\text{Å}$ and $-\frac{\partial^2 U^*}{\partial r^2} = 1 \sim 0.1\,\text{e.v./Å}^2$ in its neighbourhood, the ratio of the reaction rate v_T due to the transition state method to that due to the present procedure is calculated by Eq. (2) and Eq. (6)

$$\frac{v_T}{v} = \frac{r_0'^2}{r_0^2} e^{-\frac{U^*(r_0') - U^*(r_0)}{kT}} = 1.1 \sim 1.5 \qquad \text{at} \quad 25^\circ\text{C}.$$

The ratio is only trifling at room temperature but increases rapidly with increasing temperature.

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