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# On Intramolecular Diffusion, Quantum Theory, and the Calculation of Unimolecular Velocity-Constants\*

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The internal rearrangement of molecules can be considered as the diffusion from one part of a potential energy surface to another. It is suggested that the ordinary diffusion equations might be applied to these cases. The viewpoint is alternative to the method of the activated state. An attempt is made to place this approach on a quantitative basis and to treat it with the help of quantum theory.

## PART I

### On the connection between quantum theory and the theory of intramolecular diffusion

FROM earlier considerations it is known that it seems natural to describe a chemical process as an intramolecular diffusion.<sup>1</sup> But if this were true, it would seem a very natural conclusion, that all intramolecular motions should be described as diffusion processes.

To investigate this question we start to consider the diffusion of a particle in the absence of forces, and to simplify the mathematics, we shall consider only the unidimensional case. The intensity of flow will be then

$$s = -Dc'$$

( $c' = dc/dx$ ), where  $x$  is the space coordinate and  $c$  the density of points or the density of probability at place  $x$ . The velocity at the place  $x$  will be  $v = s/c$ . We are thus able to calculate the kinetic energy  $L$ . To do this, we replace  $c$  by  $\psi^2$  and get

$$L = 2mD^2(\psi')^2/\psi^2.$$

The energy thus becomes

$$E = 2mD^2(\psi')^2/\psi^2 + U$$

( $U$  = the potential energy)

and the average energy of the whole molecule is defined as

$$\bar{E} \int \psi^2 dx = 2mD^2 \int (\psi')^2 dx + \int U \psi^2 dx.$$

\* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 633. This article replaces the one originally published as a preprint for the symposium.

<sup>1</sup> Zeits. f. physik. Chemie B33, 145 (1936).

We now apply a reasoning used by Hellmann. It is a matter of course that  $E$  is completely undefined as long as  $\psi$  is an unknown function of  $x$ . But we know that atoms and molecules have a tendency to give up energy to the surroundings until they reach a state with minimum energy. This assumption is equivalent to Bohr's postulate of the existence of stationary states. We therefore define  $\psi$  so that any variation in its course will, in the first approximation, leave the average energy of the molecule  $\bar{E}$  unaltered. If we perform the variation we thus get

$$2\bar{E} \int \psi \delta\psi dx = 4mD^2 \int \psi' \delta(\psi') dx + 2 \int U \psi \delta\psi dx.$$

Now the variation and the differentiation in the second integral may be interchanged, and we thus get by partial integration of this integral

$$I_2 = - \int \psi'' \delta\psi dx + [\psi' \delta\psi].$$

But if the integral  $\int \psi^2 dx$  which represents the total number of particles or the total probability is to have a definite meaning, the integrand must disappear at the limits, and this must be true also in the varied state. Therefore  $\delta\psi$  must disappear at both limits and we get

$$\int [2mD^2\psi'' + (E - U)\psi] \delta\psi dx = 0.$$

But as  $\delta\psi$  is to be a completely arbitrary function of  $x$  this equation can only be true if

$$2mD^2\psi'' + (E - U)\psi = 0$$

<sup>2</sup> H. Hellmann, *Einführung in die Quantenchemie* (Leipzig, Deuticke, 1937), p. 49.

is true everywhere. This however is simply Schrödinger's equation if  $D = h/4\pi m$ , and as this equation has been amply verified by experiment, it must be permissible to describe the intramolecular motions as a diffusion process.

In the case, where we have to do with a diffusion in a field of force, the expression for the intensity of flow becomes a bit more complicated. The expression given originally by A. Einstein becomes with the transformation  $U'/RT = V'$ , and  $\ln \varphi = V$

$$s = -D\varphi^{-1}(c\varphi)'$$

and consequently  $v = -D(c\varphi)^{-1}(c\varphi)'$ .

Thus our equation for the energy has exactly the same form as before and therefore leads to an equation for  $\psi$  of the same form as before if and only if we place  $\psi^2 = c\varphi$ . As  $s = 0$  when  $c\varphi = a$  constant  $\varphi$  obviously plays the role of an activity coefficient. Thus  $c\varphi = \psi^2$  may be called the activity at a definite place, and the integral  $\int \psi^2 dx$  the total activity of the molecule. But this quantity must be the same for all molecules in thermal equilibrium with each other independently of their state. Therefore we must always, in cases where thermal equilibrium must be assumed, normalize  $\psi$  so that  $\int \psi^2 dx = 1$  for all molecules, even if their  $\psi$ 's are different.

(It is well known that equations of the Schrödinger type usually have solutions for which this normalization is possible only for discrete values of  $E$ , and that the corresponding functions  $\psi$  are all different.)

If now the Schrödinger equation has been solved, we get for the flow  $s$

$$s\varphi = -D(\psi^2)'.$$

But this becomes zero at the limits as we have assumed  $\psi = 0$  at these limits and the assumption  $c\varphi = \psi^2$  therefore cannot be used, when we want to describe a molecule capable of chemical reaction, that is a molecule where the particles really may pass the limits which define the molecule chemically.

Instead of  $\psi^2$  we therefore write  $y_1 y_2$  where  $y_1$  and  $y_2$  are two different solutions of the same equation as before:

$$2mD^2\psi'' + (E - U)\psi = 0.$$

But the integral  $\int y_1 y_2 dx$  must still have a definite value. Now, if  $\psi_1$  is the solution, for

which the integral  $\int \psi_1^2 dx$  has a definite value, the corresponding solution  $\psi_2$  defined by

$$\psi_2 = \psi_1 \int_0^x \frac{K}{\psi_1^2} dx,$$

where  $K$  is the constant differential determinant,  $\psi_1 \psi_2' - \psi_1' \psi_2$ , will be infinite at large positive and negative values of  $x$ . Therefore the product  $y_1 y_2$  cannot contain  $\psi_2^2$  but it may be of the form  $\psi_1(\psi_1 - \alpha\psi_2)$  where  $\alpha$  is a constant. We get in this case

$$\int_{-\infty}^{+\infty} y_1 y_2 dx = \int_{-\infty}^{+\infty} \psi_1^2 dx - \alpha \int_{-\infty}^{+\infty} \psi_1 \psi_2 dx.$$

Now  $\psi_2$  obviously is an even function, when  $\varphi_1$  is uneven and vice versa. Furthermore, for the important case where  $2U = px^2$ ,  $\psi_1 \psi_2$  disappears as  $1/x$  at  $x \rightarrow \infty$ . Therefore the second integral disappears in this case. (It will probably be so in all important cases, but to prove this a more general mathematical investigation is necessary.) If the limits are not both infinite, the integral is not exactly zero, but if only  $\alpha$  is very small, we shall not commit any appreciable error by placing  $\alpha \int \psi_1 \psi_2 dx = 0$  as it will then in any case be very small as compared to  $\int \psi_1^2 dx$ .

We have thus shown that it is permissible to replace  $\psi^2$  by  $y_1 y_2 = \psi_1(\psi_1 - \alpha\psi_2)$  and we get with sufficient accuracy

$$\int y_1 y_2 dx = \int \psi_1^2 dx.$$

## PART II

### Calculation of reaction velocity

The intensity of flow at any point was given by the equation

$$s = -D\varphi^{-1}(\psi^2)'.$$

This is equal to the unimolecular velocity constant if  $\varphi$  and  $\psi^2$  are correctly normalized, and if we know where the flow is to be measured.

$\ln \varphi = V$  is defined by the differential equation

$$V' = U'/RT.$$

We may therefore put  $V = (U - A)/RT$ , where  $A$  is a constant. We now normalize  $\varphi$  by putting

$$1 = a = \int \psi^2 dx = e^{A/RT} \int e^{-U/RT} \psi^2 dx.$$

This means that we multiply the integral  $N_n = \int c_n dx$  with an average activity coefficient  $e^{A/RT} = \bar{\varphi}$  so defined, that  $N\bar{\varphi} = a = 1$ . When  $\psi$  is a known function it is possible to perform the integration and thus  $A$  may be determined. It is seen that these average activity coefficients are different for different functions  $\psi$ , that is, for different states of the molecules, and thus the relative numbers of molecules in different states are different.

The place where we want to know the intensity of flow must be the point which separates two forms of the molecule. The question is how are we to characterize this point. Now if a reaction is going on, the activity in parts of space belonging to one form must always increase with time and in parts belonging to the other form must always decrease with time or vice versa. But this is the same as to say that at the point of separation  $\varphi(\partial c/\partial t) = 0$ . At the same time it will be natural to assume that at the point of separation  $U' = 0$ . But generally  $-s' = dc/dt$  so that to assume that at the point of separation  $c$  or  $c\varphi$  is constant in time is the same as to say that  $s'$  is zero.

Consequently we must have at the point of separation

$$0 = \frac{d}{dx}(y_1 y_2)' = y_1 y_2'' + y_1'' y_2 + 2y_1' y_2'$$

or

$$0 = -(E - U)y_1 y_2 + 2mD^2 y_1' y_2'.$$

But  $x$  is not infinite at the point of separation and consequently  $y_1$  and  $y_1'$  cannot be zero. But we may place  $y_2' = \psi_1' - \alpha\psi_2' = 0$  at the point of separation, so that  $\alpha$  is defined. If thus we put  $E = U$  and  $y_2' = 0$  at  $x = l$ , we get when  $x = l$

$$(\psi^2)' = (y_1 y_2)' = y_1' y_2 + y_1 y_2' = \frac{\psi_1'(l)}{\psi_2'(l)} K = \alpha K;$$

$$s = -De^{(A-E)/RT} \alpha K.$$

At the other limit,  $x = -\infty$ , we get

$$(y_1 y_2)' = 2\psi_1' \psi_1 - \alpha \frac{d}{dx} \psi_1 \psi_2.$$

Here  $\psi_1' \psi_1$  is certainly zero and the flow at this point will be

$$s = De^{(A-U)/RT} \alpha \frac{d}{dx} \psi_1 \psi_2,$$

which is certainly zero as  $e^{-U/RT}$  decreases exponentially with increasing values of  $U$  and  $(d/dx)\psi_1 \psi_2$  at least does not increase exponentially. Therefore the loss of activity, which is equal to the relative number of particles lost by chemical reaction, becomes  $s(l)$ . We thus get for the velocity constant

$$k = -De^{(A-E)/RT} \alpha K,$$

where

$$\alpha K = K \cdot \frac{\psi_1'(l)}{\psi_2'(l)} = K \frac{\psi_1 \psi_1'}{\psi_1' \psi_2 + K}; \quad \int \psi_1^2 dx = 1.$$

In most cases  $\psi_1' \psi_2$  will be small as compared to  $K$  and in these cases we get simply

$$k = -De^{(A-E)/RT} \psi_1 \psi_1'.$$

When the Schrödinger equation has been solved, all the quantities in these equations are known, and the problem is thus solved. The actual calculation for a special case  $2U = px^2$  will be postponed to a later paper. In this one only two general remarks may be made.

One is, that  $E$  is quantized. This appears directly from the derivation.

The second one refers to the quantity  $A$ .

We want to determine the heat of activation  $Q$  by means of the well-known relation

$$RT^2 \frac{d \ln k}{dT} = Q.$$

Now by definition:

$$\frac{A}{RT} = -\ln \int e^{-U/RT} \psi^2 dx$$

from which

$$T^2 \frac{d}{dT} \left( \frac{A}{T} \right) = - \int U e^{-U/RT} \psi^2 dx / \int e^{-U/RT} \psi^2 dx$$

$$= -\bar{U},$$

where  $\bar{U}$  means the average value of  $U$ . This average value must depend on  $T$  and on the quantum number, that is on the function  $\psi$ . We thus get

$$RT^2 \frac{d \ln k}{dT} = E - \bar{U} = Q,$$

that is  $Q$  depends on temperature. But  $\bar{U}$  is not the average potential energy of all the molecules,

but only this average for molecules with a given quantum number, corresponding to the value of  $E$ .

#### DISCUSSION

**J. O. Hirschfelder, *University of Wisconsin*:** This diffusion approach to the theory of reaction rates is similar to that of the activated state method. The concentration of systems on the potential energy surface is given by the ratio of the partition function per unit length along the reaction path,  $F_t$ , to the partition function in the initial state,  $F_i$ .  $c = F_t/F_i$ . This formula assumes statistical equilibrium (sufficiently high pressures for the reacting system). In both the diffusion method of Christiansen and the activated state method, this concentration must be calculated. The difference between the two methods appears in the value which they take for the rate of flow,  $s$ .

According to the activated state method:

$$s = c\bar{v} = c(kT/2\pi m)^{1/2},$$

where  $\bar{v}$  is the average Maxwell-Boltzmann velocity. Professor Christiansen has to evaluate the diffusion constant,  $D$ . This difficulty does not appear in the activated state calculations. Instead of starting out from the principles of statistical mechanics (which lead directly to the activated state method) Professor Christiansen proceeds from the ordinary diffusion equations which were derived for an entirely different type of application. It becomes necessary to evaluate the diffusion constant in order to complete the analogy. It is difficult to see how the frequency factor of  $10^{13}$  for a unimolecular reaction can be readily obtained from this presentation. In the activated state method, it arises from the factor  $kT/h$  and it is clear that the other factors are of the same order of unity. Then, formally the two theories must give the same results when they are both properly treated since they have arisen from the same set of physical assumptions.

**J. A. Christiansen, *Royal Polytechnic Institute, Copenhagen*:** From the diffusion equation one actually gets frequency factors of the order of magnitude of  $10^{13}$  and in addition some connection between the activation energy and the frequency factor. But it is true that the fre-

quency factor becomes different in different cases and not exactly like  $kT/h$ . I am not quite sure that this is a disadvantage.

**K. F. Herzfeld, *The Catholic University of America*:** The transition state method gives only the high pressure rate and the use of the diffusion method might permit a calculation of rates in the low pressure region.

**J. A. Christiansen, *Royal Polytechnic Institute, Copenhagen*:** I consider this one of the advantages of the diffusion method. It assumes a stationary state but not necessarily an equilibrium state.

**Henry Eyring, *Princeton University*:** The general theory of the activated complex (transition state) method is, I think, well understood. One can treat each system approaching the activated state as a wave packet crossing a potential energy barrier. The various wave packets can then be averaged over energy and phase and the proper rate for each temperature found. The fact that the detailed calculation is laborious and difficult leads one to define an average transmission coefficient  $\kappa$  in the expression for the specific reaction rate  $k' = \kappa(kT/h)(F^*/F_n)$ . This  $\kappa$  certainly, in general, has a small dependence on temperature and on pressure and is not exactly unity for activated complexes corresponding to a single potential barrier, or exactly one-half when there are two successive barriers of equal height. However, experimental evidence of divergence from such well understood values would be extremely interesting and unfortunately extremely difficult to demonstrate. There is, however, no difficulty in principle in treating such a  $\kappa$  when and if it arises or in anticipating where such divergence is most likely to occur. If one accepts this as a complete theory then any advantage of the interesting proposals of Professor Christiansen must lie in providing a more expeditious method of treating the transmission coefficient which I am convinced is already known within narrow limits.