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⁶ Eastman and Rodebush, *J. Amer. Chem. Soc.*, **40**, 489 (1918).
⁷ Haber and Zisch, *Zeit. Physik*, **9**, 325 (1922).
⁸ Rodebush and Dixon, *Physic. Rev.*, **26**, 851 (1925); Fogler and Rodebush, *J. Amer. Chem. Soc.*, **40**, 2080 (1923).
⁹ Simon, *Ann. Physik*, **68**, 241 (1922).
¹⁰ Schottky, *Physik. Zeit.*, **22**, 1 (1921).
¹¹ Fowler, *Phil. Mag.*, **45**, 32 (1923).
¹² Taylor, *Physic. Rev.*, **28**, 576 (1926).
¹³ Pauling and Tolman, *J. Amer. Chem. Soc.*, **47**, 2148 (1925).
¹⁴ Ehrenfest and Trkal, *Proc. Amsterdam Akad.*, **23**, 162 (1920).
¹⁵ Fowler, *Phil. Mag.*, **44**, 823 (1922).

ON CHEMICAL ACTIVATION BY COLLISIONS

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1. *Introduction.*—In the case of first order unimolecular gas reactions, such as the decomposition of nitrogen pentoxide, there is a well-known, theoretical difficulty¹ in discovering any process of activation rapid enough to maintain the full Maxwell-Boltzmann quota of activated molecules and thus to assure a first order course to the reaction. This problem has recently been treated anew by Fowler and Rideal,² who consider, in a somewhat new light, the possibility of activation by molecular collisions. By assuming that activation occurs as the result of practically every collision in which the sum of the internal energies ϵ_1 and ϵ_2 carried by the two molecules and their relative kinetic energy η is greater than the energy necessary for activation ϵ , Fowler and Rideal find it possible, even using kinetic theory diameters, to obtain rates of activation considerably greater than known rates of reaction. The purpose of the present note is to emphasize, rather more strongly than has been done by Fowler and Rideal, the difficulties involved in making the assumption that activation occurs at every collision where the energy available is sufficient for the purpose.

2. *General Plausibility of the Assumption.*—The first difficulty concerns itself with the general plausibility of the assumption. Since the expression for the fraction of all collisions, in which the total energy available is greater than any value ϵ , is mainly determined by an exponential factor of the form $e^{-\epsilon/kT}$ it is evident, with the large values of the energy of activation actually encountered, that in the great majority of activating collisions the total energy available would only be slightly greater than that necessary for activation, and hence practically all the energy would have to flow into one of the two molecules.

This seems, however, a somewhat surprising conclusion, since, on the rather uncertain grounds of ordinary physical intuition, we should expect in the case of collisions between two similar structures with equal capacities for holding energy, that there would be a strong tendency towards equalization in the energy contents of the two structures rather than an absolute necessity for practically all the energy to accumulate in one of the structures.

It is, of course, doubtful how far we should trust old-fashioned physical intuition in the case of quantum phenomena. Nevertheless, there is one case in which we can feel sure that the energy would not all accumulate in one of two colliding molecules, namely, when we have a symmetrical collision between molecules in the same quantum state, since in such a collision neither molecule could be regarded as having a greater power than the other of drawing energy from their common total supply. Such symmetrical collisions would perhaps form only an infinitesimal fraction of all collisions, nevertheless the consideration helps to illustrate the point.

3. *Calculation of Deactivational Diameters.*—The other difficulties which we wish to consider have to do with the large deactivational diameters necessitated by their assumption. For this purpose it will be desirable to obtain what may be regarded as an average value for the deactivational diameter in the following manner. Consider a gas containing N molecules per cubic centimeter, each molecule having s variables (coördinates or momenta) which contribute classical quadratic terms to the internal energy of the molecule. Then, as shown by Fowler and Rideal, the number of molecules at equilibrium having energy greater than that necessary for activation, ϵ_0 , would be

$$N_{\text{act.}} = N \frac{1}{\Gamma(1/2 s)} \left(\frac{\epsilon_0}{kT} \right)^{1/2s-1} e^{-\frac{\epsilon_0}{kT}} \quad (1)$$

If we assume now that the process of activation is collisional, then in accordance with the principle of microscopic reversibility this quota of activated molecules would be maintained constant under equilibrium conditions by an equality in the number of activational and deactivational collisions. The maximum possible rate of deactivation by collisions with unactivated molecules of reactant can be taken, however, equal to the *total* number of collisions made per second as predicted by the ordinary kinetic theory formula, giving us,

$$Z_{\text{deact.}} = 4N N_{\text{act.}} \sigma^{*2} \sqrt{\pi kT/m} \quad (2)$$

where N may be taken without appreciable error as the total number of molecules of reactant per cubic centimeter and σ^* is, on the average, the mean diameter for a deactivational collision. Substituting (1) in (2) and making use of the equality between rates of activation and deactiva-

tion, we then obtain for the maximum possible rate of activation by collisions with unactivated molecules of reactant,

$$Z_{\text{act.}} = 4N^2\sigma^{*2}\sqrt{\pi kT/m} \frac{1}{\Gamma(1/2s)} \left(\frac{\epsilon_0}{kT}\right)^{1/s-1} e^{-\frac{\epsilon_0}{kT}}. \quad (3)$$

This expression has been derived, of course, for the case of equilibrium, but since we should not expect important variations in the specific rate of activation during the course of the reaction, we may assume it to hold under the actual conditions of the rate measurements, and use it to obtain information as to σ^* . The mode of treatment has advantages for our present purposes over that of Fowler and Rideal, since it will give us actual numerical values for what may be regarded as an average value of σ^* for all deactivational collisions, rather than merely a functional relation connecting the deactivational and activational diameters for each particular kind of collision.

4. *Comparison with Data on the Decomposition of N_2O_5 .*—We may now compare the results of equation (3) with the rate of decomposition of N_2O_5 using the same assumptions as Fowler and Rideal. For s we shall take their value

$$s = 14 \quad (4)$$

which seems reasonable since it would give nitrogen pentoxide a heat capacity per mol of about 17 cal. per degree. And for ϵ_0 we shall use *their* relation (24)

$$\epsilon_0 = q + (1/2s-1)kT \quad (5)$$

connecting it with the quantity q in the Arrhenius expression for temperature coefficient of specific reaction rate

$$\frac{d \log k_1}{dT} = \frac{q}{kT^2} \quad (6)$$

and derived by Fowler and Rideal on the assumption that all molecules of internal energy greater than ϵ_0 have the same chance of decomposition.

Substituting (4) and (5) in (3), we obtain

$$Z_{\text{act.}} = 6.52 \times 10^5 \sigma^{*2} N^2 e^{-\frac{q}{kT}} \quad (7)$$

which is to be compared with the experimental rate of decomposition

$$Z_{\text{react.}} = 2.53 \times 10^{14} N e^{-\frac{q}{kT}} \quad (8)$$

which is taken by Fowler and Rideal as representing the results of Hirst and Rideal³ at pressures of N_2O_5 as low as of 0.05 mm. of Hg.

Taking now the number of molecules per cc. at 0.05 mm. of Hg as being⁴ 1.775×10^{15} , and using, as did Fowler and Rideal, a rate of activation one

hundred times greater than the rate of decomposition, we obtain for σ^* the very large value

$$\sigma^* = 4.7 \times 10^{-3} \text{ cm.}$$

and even assuming the case, which is impossible for a first order reaction, of equality of the two rates we obtain the large value,

$$\sigma^* = 4.7 \times 10^{-4} \text{ cm.}$$

5. *Difficulties with Large Diameters.*—There are perhaps no certain theoretical obstacles to such large diameters for activated molecules, and molecular diameters for activated molecules somewhat larger than the ordinary kinetic theory values have certainly been found by Stuart⁵ from experiments on the deactivation of excited mercury atoms. Nevertheless, three remarks concerning the extremely large diameters occurring in the theory of Fowler and Rideal must be made.

In the first place, if we have to invent a mechanism involving the transfer of large quantities of energy which is brought about by the approach of the centers of gravity of two molecules to a distance of 4.7×10^{-3} cm. it might be better perhaps to resort to a radiational than a collisional process, since certainly the major portion of the mass of the two molecules is concentrated within distances of the order of 10^{-7} cm. of their centers of gravity.

In the second place, with a total concentration of 1.775×10^{15} molecules per cc. an activated molecule having a diameter of the order of 4.7×10^{-3} cm. would occupy a volume large enough to contain in the neighborhood of 10^8 ordinary molecules. This surprising conclusion is very bothersome. If we assume that other molecules have to stay outside this volume, then we become fearful of the underlying assumptions of the Fowler and Rideal calculations, since as is well known we could not then use the Maxwell-Boltzmann distribution law in its *simple form* to calculate the number of molecules in the activated states. On the other hand, if we assume that other molecules are permitted within this volume, we are surprised that they do not produce the same deactivation that will result from molecules which only reach the boundary of this volume.

Finally there is a difficulty in connection with the use of different diameters σ and σ^* for activational and deactivational collisions. In accordance with the principle of dynamical reversibility, there corresponds to each type of deactivational collision an activational collision which can be obtained from the former solely by a time reversal. The deactivational collision is initiated, however, by the approach of two molecules to the distance σ^* and the activational collisions by their approach to the very much smaller distance σ . Hence we must conclude from the reversibility of the two processes, that in the deactivational collisions molecules that come within

the very large distance σ^* will be mysteriously drawn together to the very much smaller distance σ and will then fly apart in deactivated states.

We have called attention to the foregoing difficulties, recognizing that Fowler and Rideal have themselves been cognizant of difficulties, and not in any way to disparage the useful and beautiful theoretical work which they have done.

¹ See, for example, Tolman, *J. Amer. Chem. Soc.*, **47**, 1524 (1925), where references to other work will be found.

² Fowler and Rideal, *Proc. Roy. Soc.*, **A**, **113**, 570 (1927).

³ Hirst and Rideal, *Ibid.*, **A**, **109**, 526 (1925).

⁴ This figure is used in order to agree with the calculations of Fowler and Rideal. It is, however, apparently the number of molecules at 273°K. rather than that at 300°K. which was approximately the actual temperature of the experiments of Hirst and Rideal.

⁵ Stuart, *Zts. Phys.*, **32**, 262 (1925).

A CASE OF NEGATIVE CATALYSIS IN A HOMOGENEOUS SYSTEM

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Introduction.—The purpose of a series of studies² made recently has been to elucidate the mechanism of the so-called promoter action on reactions taking place in homogeneous systems. The reactions chosen for this purpose were the catalytic decompositions of hydrogen peroxide as effected by various salts. Hydrogen peroxide was selected because its decomposition products, oxygen and water, have no effect upon the reaction, and because the mechanism of some of its catalytic decompositions are well enough known to admit of the study of the anomalous effects observed when two or more catalysts are present at once. Sometimes the effect of mixed catalysts is the sum of their separate effects, as when hydrogen peroxide is decomposed by sols of platinum and gold.³ However, in many cases, the total effect is much greater than the sum of the individual effects; one of the catalysts being then said to exert a promoter action. In other cases, the resultant effect is less than the sum of the individual effects, and one of the substances is then said to produce negative catalysis.

These effects are well illustrated by the reactions involving hydrogen peroxide. The catalytic decomposition of this substance usually involves two interdependent simultaneous reactions, by one of which an intermediate compound is formed, and by the other of which it is decomposed.