

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.]

## NOTE ON THE THEORY OF MONOMOLECULAR REACTIONS.

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It has long been known that for reactions in dilute homogeneous systems, the dependence of specific reaction rate on temperature can be somewhat successfully represented by the empirical equation,

$$k = se^{-Q/RT}$$

where  $k$  is the specific reaction rate,  $s$  is a quantity which has the dimensions of frequency and is experimentally found to be nearly constant,  $Q$  is a quantity which has the dimensions of energy and is also experimentally found to be nearly constant, and  $R$  and  $T$  have their customary significance.

Attempts to develop satisfactory theoretical interpretations of Equation 1 have been made by Arrhenius,<sup>1</sup> Trautz,<sup>2</sup> Marcelin,<sup>3</sup> Rice,<sup>4</sup> W. C. M. Lewis,<sup>5</sup> Perrin,<sup>6</sup> Dushman,<sup>7</sup> Tolman<sup>8</sup> and others. These investigators have come to somewhat different conclusions as to the significance of the quantities  $Q$  and  $s$  occurring in Equation 1.

The quantity  $Q$  has been variously called the "heat of activation," the "energy of activation" and the "critical increment." Arrhenius, basing his considerations on the assumption that reacting substances exist in 2 tautomeric forms and that only the "active" form can react, takes  $Q$  as the heat of reaction when the "passive" forms of the reacting substances change into the "active" forms. Trautz has developed various more or less empirical rules for calculating this "heat of activation" from a consideration of the "heats of activation" of the individual atoms in the molecule. Marcelin and Rice on the basis of certain statistical mechanical considerations find  $Q$  to be the energy of the molecules in the "active" state minus their mean energy. W. C. M. Lewis and Perrin take  $Q$  as the radiant energy,  $Nh\nu$ , of activating frequency  $\nu$ , which must be absorbed in order to put the molecules into a reactive condition, and Dushman puts  $Q = Nh\nu$  without specifying any mechanism of activation. The present writer,<sup>9</sup> on a statistical mechanical basis, finds  $Q$  to be the difference between the mean energy of the molecules and modes of electromagnetic vibration when they take part in the reaction and their mean energy whether or not they are in a reactive condition.

<sup>1</sup> Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

<sup>2</sup> Trautz. See his summary, *Z. anorg. Chem.*, **102**, 81 (1918).

<sup>3</sup> Marcelin, *Ann. phys.*, **3**, 120 (1915).

<sup>4</sup> Rice, *Rep. Brit. Assn.*, **1915**, p. 397.

<sup>5</sup> W. C. M. Lewis, *Trans. Chem. Soc.*, **113**, 471 (1918); *Phil. Mag.*, **39**, 26 (1920).

<sup>6</sup> Perrin, *Ann. phys.*, **11**, 5 (1919).

<sup>7</sup> Dushman, *J. Franklin Inst.*, **189**, 515 (1920).

<sup>8</sup> Tolman, *THIS JOURNAL*, **42**, 2506 (1920).

<sup>9</sup> *Loc. cit.*

As to the significance of the quantity  $s$  in Equation 1, there has also been considerable speculation. In the case of bimolecular reactions, Trautz, W. C. M. Lewis and Dushman place  $s$  proportional to the number of collisions which would occur at the temperature in question and at unit concentration between molecules of the substances involved, in the right proportions to react. To do this they make use of familiar kinetic considerations and use values for the molecular diameters that are commonly used in other applications of the kinetic theory. They have in this way achieved a considerable measure of success in the prediction of bimolecular reaction rates.

In the case of monomolecular reactions, there is much greater divergence in opinion as to the significance of the quantity  $s$ .

Trautz endeavors to develop a theory in which  $s$  depends on the number of collisions between the constituent parts within the molecule. The final equation<sup>1</sup> which he applies to his own measurements of the monomolecular rate of decomposition of phosphine may be written, using C. G. S. units in the form,

$$k = \frac{8.72 \times 10^4}{\sigma} \sqrt{\frac{A+B}{AB}} T^2 \epsilon^{-\frac{Q}{RT}} \quad (2)$$

where  $\sigma$  is the diameter of the decomposing molecule and  $A$  and  $B$  are the molecular weights of the 2 parts into which the molecule decomposes.

W. C. M. Lewis has tried 3 methods of predicting  $s$  for monomolecular reactions. In one method he makes the assumption that the molecule receives its energy of activation at the rate predicted by Planck for the continuous absorption of radiant energy by an oscillator. In another method he calculates the value of  $s$  on the assumption that activation occurs during the collision of the molecule with a discrete quantum of radiant energy such as has been postulated by Einstein and others, assuming that these quanta have dimensions comparable to those of the electron. Since neither of the above methods leads to results which are anywhere nearly of the same order of magnitude as those actually found by Trautz and Bhandarkar<sup>2</sup> for the monomolecular decomposition of phosphine, Lewis reverts to an empirical formula<sup>3</sup> which may be written, using C. G. S. units in the form,

$$k = \frac{102.3 \times 10^{50}}{Q^3} \epsilon^{-\frac{Q}{RT}} \quad (3)$$

<sup>1</sup> See Trautz and Bhandarkar, *Z. anorg. allgem. Chem.*, **106**, 121, 122 (1919). This final form of Trautz's equation is apparently an approximation of his earlier form given in the summary of his work already referred to. Our conclusion that the Trautz equation is incorrect would be the same whichever form is used.

<sup>2</sup> Trautz and Bhandarkar, *Z. anorg. allgem. Chem.*, **106**, 95 (1919).

<sup>3</sup> This equation is obtained from Lewis' equation. *Phil. Mag.*, **39**, 31 (1920), by putting  $\nu = \frac{Q}{Nh}$ .

Dushman,<sup>1</sup> on the basis of certain quantum theory speculations, proposes for monomolecular specific reaction rates the formula,

$$k = \frac{Q}{4.00 \times 10^{-3}} \epsilon^{-\frac{Q}{RT}} \quad (4)$$

where the quantities involved are again expressed in C. G. S. units.

The possibility of testing these various equations for monomolecular specific reaction rate has recently been greatly increased through measurements carried out in this laboratory by Daniels and Johnston,<sup>2</sup> on the decomposition of nitrogen-pentoxide. This is found to follow a monomolecular reaction. Expressing time in seconds, they find the values of  $k$  to be  $4.87 \times 10^{-3}$  and  $3.38 \times 10^{-5}$  at the absolute temperatures  $338^\circ$  and  $298^\circ$ , respectively.

Substituting the 2 pairs of values for  $T$  and  $k$  into Trautz's equation (2), and dividing, we obtain,

$$\frac{4.87 \times 10^{-3}}{3.38 \times 10^{-5}} = \left(\frac{338}{298}\right)^2 \frac{\epsilon^{-\frac{Q}{8.32 \times 10^7 \times 338}}}{\epsilon^{-\frac{Q}{8.32 \times 10^7 \times 298}}}$$

which can be solved for  $Q$ , giving us,  $Q = 0.994 \times 10^{12}$  ergs. This value of  $Q$  may now be used to test the absolute magnitude of the reaction rate as predicted by Equation 2. For this purpose let us assume  $\sigma = 4 \times 10^{-8}$  cm. and assume that the reaction proceeds according to the equation,  $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \text{O}$ , so that  $A$  is the molecular weight of nitrogen tetra-oxide and  $B$  the atomic weight of oxygen. We obtain at  $338^\circ$  absolute,

$$k = \frac{8.72 \times 10^4}{4 \times 10^{-8}} \sqrt{\frac{108}{92 \times 16}} (338)^2 \epsilon^{-\frac{0.994 \times 10^{12}}{8.32 \times 10^7 \times 338}} = 32$$

as against the experimental value  $4.87 \times 10^{-3}$ . The divergence is so great, that it is obvious that no mere change in the values assumed for  $\sigma$ ,  $A$  and  $B$  could bring an agreement between Trautz's theory and the experimental value.

Turning now to Lewis' Equation 3, and substituting into it the 2 pairs of experimental values for  $T$  and  $k$  we obtain,

$$\frac{4.87 \times 10^{-3}}{3.38 \times 10^{-5}} = \frac{\epsilon^{-\frac{Q}{8.32 \times 10^7 \times 338}}}{\epsilon^{-\frac{Q}{8.32 \times 10^7 \times 298}}}$$

which can be solved for  $Q$  giving us,

$$Q = 1.047 \times 10^{12} \text{ ergs.}$$

This value of  $Q$  may now be used to test the absolute magnitude of the reaction rate as predicted by Equation 3. We obtain at  $338^\circ$  absolute,

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Daniels and Johnston, *THIS JOURNAL*, 43, 53 (1921).

$$k = \frac{102.3 \times 10^{50}}{(1.047 \times 10^{12})^3} \epsilon^{-\frac{1.047 \times 10^{12}}{8.32 \times 10^7 \times 338}} = 0.66$$

as against the experimental value  $4.87 \times 10^{-3}$ . The experimental value and the value predicted by Lewis' equation differ by a factor of more than 100.

Finally taking Dushman's Equation 4, we obtain for  $Q$  the same value  $1.047 \times 10^{12}$  ergs as with Lewis' equation. Substituting into Equation 4 we obtain at  $338^\circ$  absolute,

$$k = \frac{1.047 \times 10^{12}}{4.00 \times 10^{-3}} \epsilon^{-\frac{1.047 \times 10^{12}}{8.32 \times 10^7 \times 338}} = 19 \times 10^{-3}$$

as against the experimental value  $4.87 \times 10^{-3}$ .

It is to be noted that Dushman's equation is the only one which anywhere nearly fits the experimental results for the rate of decomposition of nitrogen pentoxide, and it should be further noted that Dushman has shown<sup>1</sup> that his equation agrees with Trautz and Bhandarkar's measurements for the rate of decomposition of phosphine. The partial success thus achieved by Dushman's equation makes it possible that he is working on the right track.

Referring again to the original equation for specific reaction rate (1),

$$k = s \epsilon^{-\frac{Q}{RT}}$$

let us examine the steps by which Dushman arrives at his Equation 4. Dushman, in accordance with the quantum theory and in agreement with W. C. M. Lewis and Perrin, although without making any assumptions as to the interaction of radiant energy, writes,

$$Q = N h \nu \quad (5)$$

where  $N$  is the number of molecules in a mol and  $h\nu$  is the energy in a single quantum. Substituting in Equation 1 we obtain,

$$k = s \epsilon^{-\frac{N h \nu}{RT}} \quad (6)$$

It should now be noted that the unknown quantity  $s$  has the dimensions of frequency which leads Dushman to the hypothesis that  $s$  is the same frequency  $\nu$  already introduced. Substituting in (6) we obtain,

$$k = \nu \epsilon^{-\frac{N h \nu}{RT}} = \frac{Q}{N h} \epsilon^{-\frac{Q}{RT}}$$

or in C. G. S. units Dushman's final Equation 4,

$$k = \frac{Q}{4.00 \times 10^{-3}} \epsilon^{-\frac{Q}{RT}}$$

To recommend Dushman's procedure in postulating the identity of  $s$  and  $\nu$ , we have (1) the extraordinary ingenuity of the idea, (2) the dimensional correctness of the expression thus obtained, and (3) the approx-

<sup>1</sup> *Loc. cit.*

imate although not exact agreement of the equation thus obtained with experimental results. Furthermore, it might not be entirely unreasonable to expect that the chance which a molecule has of picking up radiant energy should be proportional to  $\nu$ , that is, to the number of times per second that the electromagnetic mode of vibration, from which the molecule obtains its energy of activation, passes through a given and perhaps critical configuration. It is also interesting that the same suggestion as to the possible identity of  $s$  and  $\nu$  was made independently about the same time by Dr. Eric K. Rideal,<sup>1</sup> at least in conversation with the writer.

Against Dushman's method of procedure, we have, in addition to the only approximate agreement of his equation with the experimental results, the theoretical improbability that the energy of activation  $Q$  can always or even usually be regarded as a constant quantity corresponding to a single frequency of radiant energy. It is well known that photochemical reactions are often brought about by radiant energy having a wide range of frequencies and it is also probable that molecules having themselves different internal states may require different quantities of energy for activation. The present writer<sup>2</sup> has tried to develop a theory of chemical reactivity which will allow for this possibility and finds that  $Q$  must be taken as the difference between the mean energy of the molecules and modes of vibration which actually enter into the reaction and the mean energy of molecules and modes of vibration of this kind whether or not they are in a reactive condition. On this basis  $Q$  is in general not a constant nor does it correspond to a single frequency. Proceeding along these lines the writer has obtained an equation<sup>3</sup> which by changing to the present notation and putting into the integrated form may be written,

$$k = \epsilon \int \frac{Q}{RT^2} dT$$

If  $Q$  is a constant this equation reduces at once to,

$$k = \text{constant} \times \epsilon^{-\frac{Q}{RT}} = s \epsilon^{-\frac{Q}{RT}}$$

where  $s$  is a constant as assumed by Dushman. In general, however, the equation can be changed into,

$$k = \epsilon \int \frac{dQ}{RT} \epsilon^{-\frac{Q}{RT}} = s \epsilon^{-\frac{Q}{RT}}$$

where the quantity,  $s = \epsilon \int \frac{dQ}{RT}$ , is a variable, and hence cannot be put equal to a single frequency as is done by Dushman.

It has seemed to the present writer worth while to point out these

<sup>1</sup> See *Phil. Mag.*, **40**, 461 (1920).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Loc. cit.* Equation 39.

considerations since Dushman's theory certainly has some promise. A more complete theory of monomolecular reaction rate which would allow for the fact that the molecules which react are activated by radiant energy of a whole range of frequencies, and would at the same time introduce something equivalent to the fundamental Dushman hypothesis  $s = \nu$  would be an interesting development.

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### FURTHER STUDIES CONCERNING GALLIUM.

#### Its Electrolytic Behavior, Purification, Melting Point, Density, Coefficient of Expansion, Compressibility, Surface Tension, and Latent Heat of Fusion.

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#### I. Electrolytic Behavior.

**Introduction.**—The study of the electrolytic behavior of gallium naturally had precedence in this investigation, because this behavior had an important bearing on the preparation of the material needed for the rest of the work. The earlier experimenters upon gallium commonly used electrolysis rather as a means of precipitating the metal from purified salts than as a means of purification. In a recent paper, Dennis and Bridgman<sup>1</sup> have pointed out the value of electrolysis for the latter purpose. Independently, we also had simultaneously thus used electrolysis.<sup>2</sup> Whereas the earlier experimenters commonly used alkaline solutions, Dennis and Bridgman, as well as ourselves, worked with more or less acid ones, free from alkali salts, thus eliminating the danger of contamination with alkali metals.

Although in the main the verdicts of the recent researches agree, several obscure points need elucidation before the matter is entirely consistent and comprehensible. The points especially to be investigated were the following: first, the single electrode potential of gallium, and secondly, the order of precipitation of indium, zinc and gallium, with several different current densities from solutions of several different acidities.

**The Single Electrode Potential of Gallium.**—No adequate measurements of this potential appear in the literature, but the element is usually considered as coming between zinc (0.52) and aluminum (1.0), being

<sup>1</sup> Dennis and Bridgman, THIS JOURNAL, 40, 1540 (1918). On p. 1537 references to earlier work are given.

<sup>2</sup> Richards and Boyer, *ibid.*, 41, 133 (1919).