

along with it. In other words, the hydrogen ion or proton is hydrated in the glass.

7. The results indicate that the glass electrode when made of the glass used in this research may not be used to measure the hydrogen ion activity of non-aqueous solutions.

8. By combining the equation for the glass electrode in acid solutions with the equation for the glass electrode in alkaline solutions given in the author's last paper, an equation for the glass electrode over an extensive P_H range is obtained.

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THE RELATION BETWEEN THE TWO CONSTANTS OF THE ARRHENIUS EQUATION

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Introduction.—The rate constants of both first order and second order reactions can be represented by the following empirical equations

$$K = Se^{-Q/RT}; \log K = B - Q/4.58T \quad (1)$$

The simple collision hypothesis of gaseous bimolecular reactions yields the following equation for the second order rate constant

$$K = Ze^{-Q'/RT}; \log K = \log Z - Q'/4.58T \quad (2)$$

Z is proportional to the square root of the absolute temperature and is equal to the number of collisions between the reacting molecules, in moles per liter per second, when the concentration of each of the two reactants is one mole per liter. Q' is the heat of activation and for reactions measured at or near room temperature it is smaller than Q by about 300 calories. Equation 2 is the mathematical equivalent of the statement that all collisions between two reactant molecules in which the energy of impact is equal to or larger than the heat of activation will result in chemical decomposition.¹

Several investigators tested the applicability of Equation 2 to second order rate constants in liquid solutions. In their calculations of the value of Z they assumed that the gas-kinetic formula may be relied upon to give the right order of magnitude for the number of collisions between the solute molecules. They found that the observed values of the tested rate constants were much smaller than those calculated by means of this formula.²

¹ Cf. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, Oxford, 1929, pp. 100, 105.

² (a) Christiansen, *Z. physik. Chem.*, **113**, 35 (1924). (b) Norrish and Smith, *J. Chem. Soc.*, 129 (1928). (c) Moelwyn-Hughes and Hinshelwood, *ibid.*, 230 (1932).

In a recent paper Moelwyn-Hughes³ listed a number of reactions in solution whose rate constants satisfy Equation 2. He also added several cases to the list of those reactions whose observed rate constants are much below the theoretical value. He was the first on record to make the observation that what he calls "normal" reactions are characterized by a heat of activation equal to about 21,000 calories, and that in other reactions the ratio between the calculated and the observed rates is the larger, the smaller the heat of activation. He tested several possible explanations of this parallelism and found them untenable, thus leaving the problem unsolved.

The object of the present contribution is to suggest an explanation of Moelwyn-Hughes' rule. It should be emphasized at this point that this explanation does not represent an attempt to reconcile the exceptions with the simple collision hypothesis. On the contrary, in the following discussion the point of view is taken that this hypothesis is too narrow to account for all known bimolecular reactions; attention is next called to the well-known fact that our restricted facilities for measuring rates in solution enable us to study only a fraction of all possible bimolecular reactions; finally, it is shown that all reactions suitable for investigation must satisfy the generalization announced by Moelwyn-Hughes.

The Present Status of the Simple Collision Hypothesis.—Hinshelwood¹ summarized in 1929 the then available data on gaseous bimolecular reactions. In six cases the observed rates agreed with those calculated by means of the simple collision hypothesis. In the seventh (the decomposition of ozone) the observed rate is higher than the calculated one. A few years ago it would have been difficult to explain a case in which the reaction takes place faster than the molecules can be activated by collisions. However, the modern theory of unimolecular reactions offers a simple explanation in the assumption that energy distributed among a large number of internal degrees of freedom can be converted into energy of activation.⁴ Finally, the reaction between nitrogen pentoxide and ozone is a bimolecular one, and the observed rate of reaction is about 90,000 times as great as that allowed by the simple collision hypothesis. According to Hinshelwood, this may indicate a chain mechanism, but it may also be connected with the many degrees of freedom possessed by the complex $N_2O_5 \cdot O_3$.

No gaseous bimolecular reaction is known in which the observed rate is much smaller than that calculated by means of Equation 2.^{4a} However, it was shown that the rates of reaction between triethylamine and ethyl iodide

³ (a) Moelwyn-Hughes, *Chem. Rev.*, **10**, 241 (1932); (b) *Nature*, **129**, 316 (1932).

⁴ Ref. 1, p. 152.

^{4a} Just before this paper was sent to print the author's attention was called to the case of polymerization of ethylene in the gaseous phase. This is a bimolecular reaction, and its observed rate is one two-thousandth of that calculated [Pease, *THIS JOURNAL*, **53**, 613 (1931)].

and between acetic anhydride and ethyl alcohol in the gas phase are not much higher than the rates in non-polar solvents.^{2c} The two reactions are bimolecular in solution, and it is very probable that they are of the same order in the gas phase. If their heats of activation are the same in the gas phase as in solution, then it follows from the available data that the rates calculated by means of Equation 2 are more than 100,000 times as large as the observed rates.

To summarize the evidence on the experimental side in the case of gaseous reactions, Equation 2 predicts correctly the rates of six known reactions; it gives too low values for two reactions and too high values for the last two reactions.

Equation 2 is derived on the assumption that all collisions in which the energy requirement is satisfied result in decomposition. Evidence from the field of unimolecular reactions throws some doubt on this assumption. The theory of unimolecular reactions is based on the fundamental assumption that the activated molecules are in thermal equilibrium with the unactivated ones. It follows that the average life of an activated molecule, with respect to decomposition, must be much larger than the average duration between two successive collisions. On the other hand, the time of contact between two colliding molecules is small in comparison with the duration between two successive collisions. It is not clear, then, why we must assume that in a bimolecular reaction all, or at least a large portion, of the activated collision complexes will undergo chemical decomposition during their relatively short life period. It seems more plausible that practically all complexes will separate into the original components and that only a small fraction will suffer decomposition.

On the Number of Collisions in Condensed Systems.—We can define with mathematical exactitude what we mean by a collision between two perfectly elastic and perfectly rigid spheres. With the use of statistical mechanics we can calculate the number of such collisions in a perfect hypothetical gas consisting of such ideal particles. If we pass to the case of a real gas, we lose some of the precision, but we are still in a position to calculate the number of collisions with an accuracy satisfactory enough for a kinetic interpretation of reaction rates. The introduction of an inert solvent gas in ordinary quantities does not call for a fundamental change in the collision formula. Unimportant corrections must be made to allow for the fact that the free space is reduced by the solvent particles and that intermolecular forces acquire an importance.

Let us suppose, however, that a sufficient quantity of the solvent gas is introduced to pack the space solidly with molecules. Under such conditions each of the solute molecules is in continuous contact with several solvent molecules. A definite portion of the solute molecules of the first kind are in continuous contact with molecules of the second kind. Evi-

dently, neither our usual definition of "collision" nor our usual formula for the number of collisions can be employed without making some fundamental changes in them. The mere application of the free-space correction factor is insufficient, since molecules having ordinary dimensions cannot move in such "free" space.

There is good evidence of the fact that molecules in the liquid phase are fairly closely packed. Thus, if we calculate the molecular diameters of molecules in the liquid phase on the assumption of close packing, we obtain values which are in fair agreement with those obtained by other methods.⁵ It follows from what has been said that the application of the gas-kinetic formula to the case of solutions may be incorrect not only in degree but also in kind.⁶

It was shown that on the empirical side the universal applicability of Equation 2 to gaseous bimolecular reactions is far from established; on the theoretical side there is no *a priori* reason why the rate of a reaction cannot be much smaller than that predicted by this equation; furthermore, this equation cannot even be relied upon to give the maximum limit for the rate of a bimolecular reaction at least in the case of molecules with a large number of internal degrees of freedom; finally, it was shown that the application of this equation in the case of liquid solutions is objection-

⁵ Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge, 1925, p. 332.

⁶ The question may be raised as to the nature of the process whereby molecules in a closely packed system change neighbors and position. The answer will probably be supplied by the statistical theory of fluctuations. As long as the molecules are not solidly packed, there is room for fluctuation in density. The fluctuation in a system consisting of a large number of molecules is very small. However, in a system consisting of from ten to fifty molecules the fluctuation may be violent enough to allow individual molecules a frequent change of neighbors and of position.

It should be pointed out that in a closely packed system bimolecular reactions call for second order rate equations, without the introduction of the idea of collisions. Thus, if we assume that in a dilute solution of substances A and B each molecule of solute A is in contact with eight other molecules most of the time, we arrive at the following formula for the concentration of the AB complex, in moles per liter

$$n_{AB} = 8s_2C_A C_B/n$$

where n is the number of moles of solution per liter (in a very dilute solution it is equal to the number of moles of solvent per liter); C_B/n is the molal fraction of B; s_2 is a statistical factor depending on the relative affinity between molecules A and the other molecules in solution; it is nearly equal to unity when the molecules of B and of the solvent are similar; it is much larger than unity if A and B are oppositely charged ions, and it is much smaller than unity if they are ions carrying charges of the same sign.

If k_2 is the probability that complex AB will undergo decomposition in the course of one second, then the rate of reaction is given by the equation

$$r_2 = 8k_2s_2C_A C_B/n$$

Similarly, the rate of a termolecular reaction is given by the following equation

$$r_3 = 56k_3s_3C_A C_B C_C/n^2$$

able because of the fact that "collisions" in solution are of a nature entirely different from that of collisions in the gas phase. One should not therefore be surprised to find a large number of cases which are not in agreement with Equation 2.

The *ad hoc* nature of the simple collision hypothesis was clearly recognized in the earlier discussions.⁷ However, in a series of recent papers there is shown a definite tendency to assume that conformity with Equation 2 is the normal rule, and elaborate *ad hoc* explanations are offered to reconcile the "exceptions" with the rule.^{2c,3,8} While one may criticize this tendency, there is no doubt that Moelwyn-Hughes' generalization regarding the parallelism between the heat of activation and the deviation from Equation 2 is well grounded. An explanation of this relation is offered in the following section.

The Relation between the Values of B and Q for Investigated Bimolecular Reactions in Liquid Solutions.—The study of reactions in solution is confined to a small range of temperatures. For this reason the value of $\log Z$ does not vary much from one reaction to another and is approximately equal to 11. Equation 2 can therefore be replaced by

$$\log K = 11 - Q'/4.58T \quad (3)$$

Moelwyn-Hughes' generalization is equivalent to the statement that the value of B in Equation 1 is much smaller than 11 for those reactions in which the value of Q is much smaller than 21,000 calories. It is also equivalent to an empirical generalization made by Holzschmidt,⁹ who found a linear relationship between B and Q .

If we search for the relation between the values of B and Q which is characteristic of all reactions having measurable speeds at ordinary temperatures, we shall find the solution in Equation 1. Thus, if a reaction is to have a value of $\log K$ which is not much different from some measurable value $\log K_1$, at a temperature T which is not far removed from some average temperature T_1 , then the two Arrhenius parameters of this reaction must satisfy approximately the equation

$$\log K_1 = B - Q/4.58T_1 \quad (4)$$

The B and Q values of all reactions investigated by ordinary methods must satisfy approximately such a linear equation. An inspection of Equation 4 will show that if the pair of values ($B = 11$, $Q = 21,000$) forms an approximate solution, then in other solutions $B \ll 11$ if $Q \ll 21,000$.

Figure 1 will be used to illustrate the relation developed in this section. It is a $\log K$ vs. $1/T$ plot for seven reactions measured by direct methods and

⁷ Ref. 1, p. 100.

⁸ For the extension of the simple collision hypothesis to the case of first order reactions in solution see Moelwyn-Hughes, *J. Chem. Soc.*, 95 (1932); Moelwyn-Hughes and Rolfe, *ibid.*, 241 (1932).

⁹ Holzschmidt, *Z. anorg. allgem. Chem.*, 200, 82 (1931).

three reactions investigated by indirect methods. The short segments within the small rectangle represent the temperature regions within which measurements were actually made. The light lines outside the rectangle are the graphical equivalent of the extrapolation by means of which the

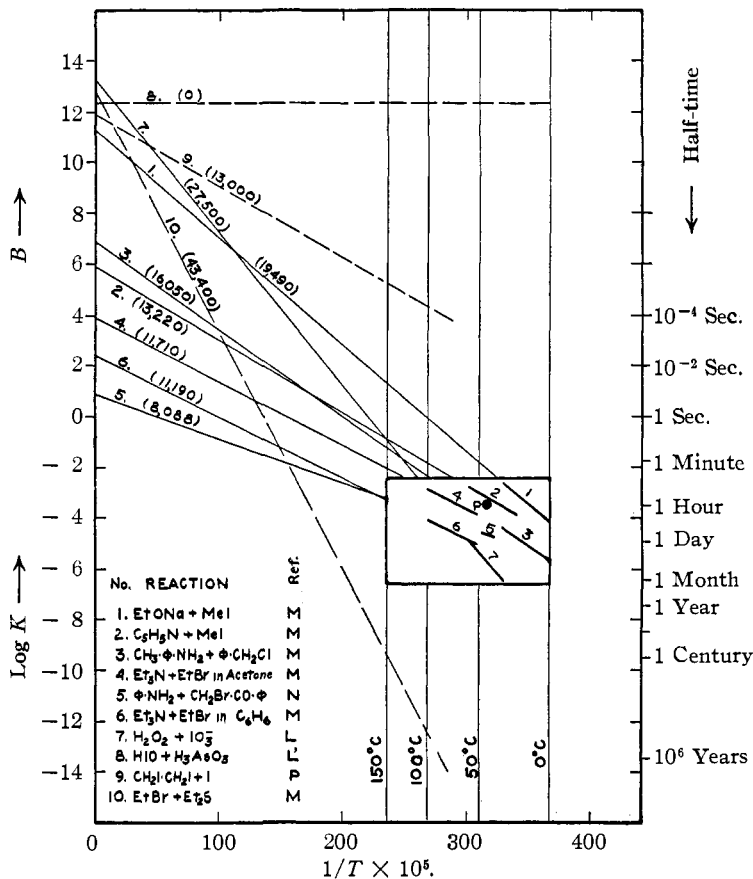


Fig. 1.—The relative size of the field within which the great majority of reactions in solution had been studied. Reactions with large values of B and small values of Q , or with small values of B and large values of Q , are ordinarily not to be found in the literature, since their Arrhenius lines do not cross the small rectangle.

References: M., Moelwyn-Hughes; N., Norrish and Smith; L., Lieb-hafsky, *THIS JOURNAL*, 53, 896 (1931); P., Polissar.

value of B is obtained. The slope of each line is equal to $Q/4.58$. The intercept on the $\log K$ axis is equal to B . The respective values of Q are marked along each line. The scale of ordinates on the right gives for each value of K the half-time of reactions in which the initial concentrations of the two reactants are one mole per liter. The small rectangle was

drawn in to show broadly the region within which the great majority of measurements of reaction rates in solution had been carried out.

It is evident that all reactions suitable for direct investigation have the common characteristic that their Arrhenius lines cross the small rectangle. An inspection of Fig. 1 will show that for such reactions small values of Q must be coupled with small values of B . Thus, reaction 9 cannot be studied by ordinary methods, since its rates at ordinary temperatures are too high.¹⁰

While it is true that reactions whose Arrhenius lines are far removed from the rectangle cannot be measured directly, it would be erroneous to assume that they cannot be measured at all. Thus, the data for the three broken lines in Fig. 1 were obtained by indirect methods. Line 10 (the reaction between ethyl bromide and diethyl sulfide) was obtained from a study of the reverse reaction and the reaction isochore.^{3a} The position of line 9 (the catalytic decomposition of ethylene iodide in the presence of atomic iodine) was estimated from the kinetics of the decomposition in the presence of iodine and the degree of dissociation of molecular iodine.¹¹ Finally, the data for line 8 (the reaction between hypiodous and arsenious acids) were obtained from measurements of the rate of reaction between iodine and arsenious acid, in the presence of hydriodic acid.¹² It is hardly necessary to add that the usefulness of the three reactions as examples of cases investigated by indirect methods is independent of the fact that the kinetic interpretations given by the three authors may be tentative.

Summary

A critical examination of the simple collision hypothesis leads to the conclusion that the latter is too narrow to account for all known bimolecular reactions.

Attention is called to the fact that the application of the gas-collision formula to the case of liquid solutions may be incorrect not only in degree but also in kind.

A simple explanation is offered of the linear relationship between the two Arrhenius constants of bimolecular reactions in solution.

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¹⁰ If all the lines were to pass through a point P inside the rectangle, their B - Q value would have to satisfy Equation 4, with K_1 and T_1 equal to the coördinates of point P . Since the lines pass near that point but not through it, the pairs of values satisfy only approximately a common linear equation. Point P was not selected arbitrarily; its coördinates were chosen in such a way as to give the equation of Holzschmidt's line when substituted in (4). Allowance had to be made for the fact that Holzschmidt used the minute, and not the second, as the unit of time.

¹¹ Polissar, *THIS JOURNAL*, **52**, 956 (1930).

¹² Liebhaftsky, *J. Phys. Chem.*, **35**, 1648 (1931).