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# PERSISTENCE OF VELOCITY AND THE THEORY OF SECOND ORDER GAS REACTIONS

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## Abstract

R. H. Fowler has stated that if, in second order gas reactions, it is supposed that reaction occurs whenever two reactant molecules collide with sufficient velocity, then the deviation from the Maxwell distribution law which would result is so great that this law cannot be used in calculating the rate of the reaction. It is shown that this view is sometimes in error, and that in a mixture of molecules of nearly equal mass reacting in this way the molecular velocities do not diverge appreciably from the predictions of the Maxwell law.

IT IS an experimental fact that the rates of all the known second order gas reactions can be represented, at least within a factor of 5 or 10, by the simple expression $Ze^{-E/RT}$, where $Z$ is the number of collisions between reactant molecules, calculated in accordance with the methods of kinetic theory, and $E$, the energy of activation, is an experimental constant for each reaction. There are a number of simple theories which are able to predict an equation of this form. In particular, if it is assumed that reaction occurs at every collision for which the relative velocity parallel to the line of centers at the instant of collision is at least $V_0$, it is found[1] that the rate is $Ze^{-E_0/RT}$, where $E_0 = MV_0^2/2$ and $M$ is the reduced molecular weight $M_1M_2/(M_1+M_2)$. If it is supposed that the reaction occurs whenever the relative velocity of the collision exceeds $V_0$, regardless of its direction with respect to the line of centers, it is found that the rate is given by $Ze^{-E_0/RT}(1+E_0/RT)$. Since in actual cases $E_0/RT$ is about 40, the form of this equation is not experimentally distinguishable from a simple exponential, though of course the predicted rate, for an experimentally determined temperature coefficient, is rather larger. This latter mechanism has been considered recently by Fowler[2] from the standpoint of persistence of velocity;[3] he has concluded that if reaction were to occur at every collision the number of high velocity molecules present in the gas would fall far below the Maxwell quota, so that the rate of reaction would be substantially less than that calculated; if the mechanism of any actual second order reaction were of this simple type, and if the theory were subject to the correction suggested by Fowler, then we should expect the rate to be very considerably increased by the addition of an inert gas, which would tend to maintain the Maxwell quota, and an effect of this kind has not been observed.

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[1] See, for example, Tolman, Statistical Mechanics, (1927) p. 272.

[2] R. H. Fowler, Statistical Mechanics, (1929), p. 461.

[3] Jeans, Dynamical Theory of Gases, (1925), pp. 260, 275, 312.

It seems, however, that when the molecular masses are nearly equal Fowler's correction is actually inappreciable; qualitatively this is so because in most of the collisions with relative velocity of $V_0$ or more, each of the colliding molecules has velocity of about $\frac{1}{2}V_0$; hence if reaction did not occur, each of them would leave the collision with velocity about $\frac{1}{2}V_0$, and, since this is very much greater than the mean velocity of all the molecules, in the vast majority of cases each of them would next collide with a slower molecule; at such a collision the relative velocity could not be greater than $V_0$, so that reaction could not occur. Fowler has written, "A certain proportion of collisions with relative energy more than $\xi$ will concern at least one molecule whose last collision was also one of the same class. This is the phenomenon *of the persistence of velocities.*" This, however, is not exactly what Jeans has meant by the term; he has taken as a measure of the persistence the ratio of the expected component of velocity after the collision in the direction of the original velocity to this original velocity, and found for this ratio a value of about 40 percent. Fowler is interested not in this, but in the value of the proportion mentioned in the preceding quotation, which is a very different thing.

Since an exact calculation would involve the quadrature of some rather cumbersome integrals, it will be considered sufficient to show that the effect in question is very small. First we notice that almost all of the collisions with relative velocity greater than $V_0$ have relative velocity less than $9V_0/8$; the ratio of the number which exceed this limit to the number which exceed $V_0$ is about $e^{-17E_0/64RT}$, which is of the order of $10^{-4}$.[4] We shall use the methods given by Jeans.[5] Instead of the three velocity components for each of the two molecules which are involved in the collision, we take three for the center of gravity, and three for the relative velocity. When we do this, we find that, both before the collision and afterwards, the relative velocity of each molecule is about $\frac{1}{2}V$. Jeans' treatment shows that the motions of the centers of gravity of the various collision complexes obey the Maxwell law for molecules of the appropriate mass, and that there is no correlation between the relative velocity of the collision and the velocity of the center of gravity of the colliding molecules. Since this is so, we can calculate the chance that the relative velocity of the center of gravity and the next molecule with which either of the original ones will collide shall exceed any specified value. We have seen that only in a negligible fraction of the collisions which concern us will the relative motion of the center of gravity of the colliding molecules and either of the molecules exceed $9V_0/16$. Now it is plainly necessary (though not sufficient), in order for the relative velocity of the next collision to exceed $V_0$, for the relative velocity of the colliding molecule and the center of gravity of the two original molecules to exceed $7V_0/16$. This chance is easily calculated as about $10^{-3}$. Hence we may state confidently that the proportion in which Fowler is interested is less than one in a thousand, and may be neglected. A similar treatment can be given for the case that the relative velocity along the line of

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[4] In all the following calculations, the value 40 will be used for $E_0/RT$.

[5] Jeans, reference 3, p. 35.

centers must exceed a critical value for reaction to occur. Hence the simple expressions $Ze^{-E_0/RT}$ and $Ze^{-E_0/RT}(1+E_0/RT)$ are the correct rate expressions for the mechanisms which have been described when the molecular masses are nearly equal.

When the masses of the two molecules are very different, the situation is entirely changed, and the correction discussed by Fowler becomes of importance. Thus in a collision between a molecule of hydrogen and a molecule of iodine, where the ratio of the masses is about 127, the hydrogen contributes practically all the velocity of the collision; in a large fraction of all the collisions with relative velocity greater than $V_0$, the hydrogen molecule itself has a velocity greater than this value, and can be expected to produce another collision of the same type if it survives the first one. The correction would be most important when the concentration of hydrogen was much less than that of iodine; then hydrogen molecules would have been expected to execute fairly long series of collisions with iodine, all with relative velocity greater than $V_0$, if the system did not react; the reaction mechanism which has been postulated would cut off these series at the first member, and the rate would therefore be much less than that given by the naive calculation. There is no experimental evidence for such behavior, which indicates either that this is not the mechanism of the reaction or that if it is, then reaction occurs only at a small fraction of the collisions for which the energy condition is satisfied.

With regard to the question of the actual mechanism of second order reactions, the writer does not believe that either of these simple mechanisms is correct. It seems likely to him as it does to Fowler also, that translational, vibration, and rotational energy must all be considered, and that in most cases the effective target area for reaction will be small compared to the kinetic theory cross-section.