

## THE RATES OF SECOND-ORDER GAS REACTIONS

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*Introduction.*—It has been customary for some time to express the rate of second-order gas reactions by the formula<sup>1</sup>

$$-dN/dt = Ze^{-E/RT} \quad (1)$$

where  $Z$  represents the number of collisions between reactant molecules and  $E$  is an empirically determined energy of activation. It is possible to derive a theoretical formula of this type by assuming that every collision for which a specified energy condition is fulfilled results in reaction; the nature of this energy condition varies somewhat, but it always reduces to the requirement that the energy in two specified squared terms shall exceed  $E$ .

There are, however, several reasons why (1) should not be expected to give an entirely satisfactory representation of experiment. In most bimolecular reactions there will be more than two squared terms which might be expected to contribute to the process of activation and there is no reason evident why only two of them should be effective. Furthermore, it might well be anticipated that the chance of reaction at a collision considered as a function of the energy of the molecules can have other values than 0 and 1; in this connection it may be recalled that the theory of unimolecular reactions which assigns a zero chance of reaction to molecules with total energy below some critical limit, and an equal chance to all molecules whose energy exceeds this limit is not satisfactory; it is necessary to make the chance of reaction increase as the energy increases in order to obtain a valid description of the experimental results.<sup>2</sup> For bimolecular reactions also we might expect that it would be necessary to introduce a reaction probability which would increase with the total energy available in the collision. There is one case, at any rate, in which it is definitely known that (1) cannot be correct; this arises when we are dealing with a bimolecular reaction whose reverse is also bimolecular; in that case the equilibrium constant will be given by the ratio of the two reaction rate constants and would thus be required by (1) to have a simple exponential temperature dependence; equilibrium constants do not depend thus simply on the temperature, and the universal application of (1) is thus thermodynamically impossible; this has, of course, long been known, but it has frequently been lost sight of.

*Empirical Results.*—From the experimental standpoint also (1) is not acceptable. There are only three second-order gas reactions known

which have been shown to be simple in nature and have been studied over a wide range of temperature. These are the formation and decomposition of hydrogen iodide<sup>3</sup> and the decomposition of nitrous oxide.<sup>4</sup> In his original papers on the hydrogen iodide reactions, Bodenstein used two different empirical formulæ to express his results:

$$\log k = A/T + B \log T + C \quad (2)$$

$$\log k = A/T + B \log T + CT + D. \quad (3)$$

He considered that only the second of these was really satisfactory since a formula of that type was needed to fit the equilibrium measurements. Within the accuracy of the reaction rate experiments, however, (2) gives a satisfactory representation, while (1) definitely does not. For the decomposition of nitrous oxide also (2) is superior to (1). The extent of this superiority is shown by Tables I-III.

TABLE 1

## DECOMPOSITION OF HYDROGEN IODIDE

<i>T</i>	LOG <i>k</i> <sub>obs.</sub>	LOG <i>k</i> <sub>calc. I</sub>	Δ	LOG <i>k</i> <sub>calc. II</sub>	Δ
781°	1.597	1.523	-0.074	1.596	-0.001
716	0.398	0.393	-0.005	0.391	-0.007
700	0.063	0.084	+0.021	0.068	+0.005
683	-0.291	-0.262	+0.029	-0.287	+0.004
666	-0.659	-0.624	+0.035	-0.656	+0.003
647	-1.066	-1.052	+0.014	-1.087	-0.021
629	-1.520	-1.481	+0.039	-1.511	+0.009
575	-2.915	-2.926	-0.011	-2.911	+0.004
556	-3.454	-3.501	-0.047	-3.453	+0.001

$$\log k_{calc. I} = -9555/T + 0.5 \log T + 12.311$$

$$\log k_{calc. II} = -5196/T + 16 \log T - 38.032$$

TABLE 2

## FORMATION OF HYDROGEN IODIDE

<i>T</i>	LOG <i>k</i> <sub>obs.</sub>	LOG <i>k</i> <sub>calc. I</sub>	Δ	LOG <i>k</i> <sub>calc. II</sub>	Δ
781°	3.126	3.082	-0.044	3.130	+0.004
716	2.146	2.075	-0.071	2.075	-0.071
700	1.808	1.799	-0.009	1.789	-0.019
683	1.391	1.491	+0.100	1.476	+0.085
666	1.151	1.169	+0.018	1.149	-0.002
647	0.718	0.787	+0.069	0.765	+0.047
629	0.402	0.404	+0.002	0.386	-0.016
599	-0.264	-0.282	-0.018	-0.288	-0.024
575	-0.880	-0.883	-0.003	-0.871	+0.009
556	-1.352	-1.396	-0.042	-1.362	-0.010

$$\log k_{calc. I} = -8499/T + 0.5 \log T + 12.518$$

$$\log k_{calc. II} = -5678.5/T + 10.5 \log T - 19.971$$

TABLE 3  
 DECOMPOSITION OF NITROUS OXIDE

$T$	$\log k_{obs.}$	$\log k_{calc. I}$	$\Delta$	$\log k_{calc. II}$	$\Delta$
1125°	4.064	4.031	-0.033	4.056	-0.006
1085	3.575	3.599	+0.024	3.607	+0.032
1053	3.223	3.230	+0.007	3.227	+0.004
1030	2.940	2.951	+0.011	2.941	+0.001
1001	2.580	2.582	+0.002	2.565	-0.015
967	2.133	2.122	-0.011	2.101	-0.032
838	0.040	0.036	-0.004	0.055	+0.015

$$\log k_{calc. I} = -12921/T + 0.5 \log T + 13.990$$

$$\log k_{calc. II} = -8946/T + 10 \log T - 18.502$$

The data on the decomposition of hydrogen iodide are the most accurate, and in this case the improvement in the fit brought about by using (2) is very marked; the agreement between calculated and observed values is within 2% except at 647°K.; here there is a 5% discrepancy, but this is clearly due to an error in this value, since no matter what formula is used, there is a bad kink in the deviation plot at this temperature. The experiments on the formation of hydrogen iodide show more irregular deviations, but even here it seems indicated that equation (2) is preferable, since the deviation between the calculated and the observed value changes sign seven times with (2) and only twice with (1); the coefficient of  $\log T$  is less here than for the decomposition experiments, and for this reason also the improvement produced by using (2) is less marked. The best evidence, however, for the occurrence of a  $\log T$  term for the case of the formation of hydrogen iodide is obtained from the equilibrium constants, which could not be even approximately fitted by using a formula of type (1) for the formation together with the formula chosen for the decomposition.

In the case of nitrous oxide the experiments are hardly accurate enough to draw any definite conclusions, but the deviation plot is of a more plausible appearance when (2) is used.

In fitting (1) to the experimental data, the method of least squares has been used; with (2) a suitable coefficient for  $\log T$  has first been determined, and the remaining coefficients have then been found by least squares; there is thus a chance to improve the fit with (2) somewhat by a better choice of  $B$ . Throughout this paper the reaction rate constants are given in the units cc. moles<sup>-1</sup> sec.<sup>-1</sup>

*Theory.*—It thus appears that for the experiments on the decomposition of hydrogen iodide, the only case in which there are really accurate measurements over a wide temperature range, it is necessary to abandon (1) in favor of some such formula as

$$k = cT^B e^{-E/RT} \quad (4)$$

in which  $B$  has a value of about 16. The question then arises whether it is possible to account for an expression of this type by elaboration of the theory previously mentioned. It seems that this can be done, and probably in various ways. The essential feature is that the chance of reaction at a collision must be made to increase as the energy available in the collision increases. For definiteness, suppose that the energy to be considered is that in six squared terms, two vibrational ones for each molecule, and two representing the relative translational energy.<sup>5</sup> The fraction of all collisions for which the energy in these terms lies between the limits  $E$  and  $E + dE$  is

$$W(E)dE = e^{-E/RT} E^2 dE / 2(RT)^3. \quad (5)$$

Suppose that the chance of reaction at a collision with energy  $E$  is

$$\varphi(E) = \begin{cases} 0 & \text{for } E \leq E_0 \\ b(E - E_0)^s / E^2 & \text{for } E_0 \leq E \leq E' \\ 1 & \text{for } E \geq E' \end{cases} \quad (6)$$

where  $s$ ,  $E_0$ ,  $E'$  and  $b$  are constants and

$$b(E' - E_0)^s / E'^2 = 1. \quad (6a)$$

Any steric factor which persists for high energy collisions can be taken account of by using a suitable diameter for calculating the collision number, so that no generality is lost by setting  $\varphi(E) = 1$  for large  $E$  instead of some other constant value. The factor  $E^2$  in the denominator of (6) does not make much difference physically, but the resulting formula is simpler because of its presence.

Now the rate of the reaction may be written

$$k = \alpha \int_0^{\infty} W(E) \varphi(E) dE, \quad (7)$$

where  $\alpha$  is the rate at which collisions occur. For low enough temperatures the essential contribution to this integral will be made by values of  $E$  much less than  $E'$ , and we may write as a first approximation, good at low temperatures

$$k^0 = \alpha \int_{E_0}^{\infty} e^{-E/RT} E^2 / 2(RT)^3 b(E - E_0)^s / E^2 dE, \quad (8)$$

which may be immediately integrated to give

$$k^0 = \alpha b \Gamma(s + 1) / 2 (RT)^{s-2} e^{-E_0/RT}. \quad (9)$$

This is of the same form as (4) if we put<sup>6</sup>

$$s = B + 3/2 \quad (10)$$

$$\alpha b R^{s-2} \Gamma(s + 1) / 2 = c T^{3/2}. \quad (11)$$

The integration of (7) may be carried out term by term; it does not lead to a simple formula, and the result will not be written down here; the necessary numerical calculations can be made with little difficulty. For comparison with experiment, it is convenient to give the simple formula for  $k^\circ$  together with numerical values of  $k/k^\circ$  for various temperatures; this ratio will be nearly unity for low temperatures, and will decrease with increasing temperature. The theory thus leads to the prediction that a reaction may follow an equation of type (4) at low temperatures, but that it must deviate in the direction of lower rates as the temperature is increased.

*Applications.*—We shall now apply this theory to the decomposition of hydrogen iodide. Since the results are in good agreement with (4), we conclude that the ratio  $k/k^\circ$  is but little less than unity even at the highest experimental temperature. Taking a diameter of  $3.3 \times 10^{-8}$  cm. we find from (9) and (6a) that  $E' = 57,900$  cal., and by the use of this value in (7) we obtain the ratio  $k/k^\circ = 0.861$  at  $781^\circ\text{K}$ . This result is much too low to be acceptable, since the actual rate is probably within 2% of the value given by the empirical equation. If the cross-section is taken three times larger, this discrepancy is somewhat reduced:  $E' = 60,280$  cal., and  $k/k^\circ = 0.918$ . We may next reconsider the choice  $B = 16$ ; this value is uncertain, and might be changed by as much as three units; with  $B = 13$  a new empirical equation is found:

$$\log k_{\text{calc. II}} = -6091/T + 13 \log T - 28.264.$$

If this equation is used, and the large value for the diameter is retained, it is found that  $E' = 60,970$  cal. and  $k/k^\circ = 0.953$ . This ratio is now close enough to unity so that it cannot be rejected. Nevertheless it may not be out of place to consider an additional change which results in a further increase; this is the use of an energy function with seven squared terms instead of six; the extra term is a contribution from rotation, since it may be supposed that of the four squared terms brought in by the rotations of the colliding molecules three are always unavailable because of the conservation of angular momentum, while the fourth might contribute to the activation. If this change is made the value of  $E'$  becomes 63,916 cal. and  $k/k^\circ$  at  $781^\circ\text{K}$ . is now 0.973.

At higher temperatures the correction will become rapidly larger, so that (9) will no longer represent the results of the theory. Calculations have been made for  $T = 900^\circ$ ,  $1000^\circ$  and  $1100^\circ\text{K}$ . using the large value for the cross-section,  $B = 13$ , and six squared terms in the energy function. The ratio  $k/k^\circ$ , which was 0.953 at  $781^\circ$ , has at these higher temperatures the values 0.855, 0.735 and 0.605. It is certain that no reasonable numerical modifications of this form of theory will be able to increase these values very much, and it may therefore be stated that this theory demands

that the rate of decomposition of hydrogen iodide at temperatures above 800°K. shall fall below the predictions of the empirical equations given here; in particular, (4) corresponds to a linear increase in the energy of activation with the temperature; actually this energy must approach some limiting value.

Of course, by varying the form of (6) different types of temperature dependence could be derived. The form given was chosen for mathematical convenience, but it is improbable that any other form would lead to a fundamentally different result. This belief is borne out by the results of extensive calculations dealing with the rates of unimolecular reaction, where integrals of the same general form occur; for it was found in those calculations that the results were insensitive to what might have seemed very great variations in the assumed specific reaction rates of molecules with different energy contents. It thus seems necessary that the rate of decomposition of hydrogen iodide shall deviate from the predictions of the empirical equations given here, in the direction of lower rates, and that this deviation shall become apparent at temperatures very little above the highest at which the rate has yet been measured. It can be seen that this deviation will be of such a character that the energy of activation, which is increasing linearly with the temperature, will approach a constant value at very high temperatures.

There is a possibility that the rate of decomposition of hydrogen iodide is to be represented by the sum of two terms which are both pure exponentials and have slightly different activation energies; this representation also would require the measured energy of activation to approach a constant value at high temperatures.

It is quite possible that those simpler bimolecular reactions which involve a free atom may, to a much better approximation, be represented by a constant energy of activation, equal to the heat of reaction at the absolute zero. There is as yet almost no experimental knowledge by which this question might be decided.

*Conclusions.*—It has been shown that the most accurate existing measurements of the rates of second-order gas reactions show deviations from pure exponential temperature dependence, which can be empirically represented by a linear increase of the energy of activation with temperature. It is pointed out that this requires the chance of reaction to increase with the energy of the collision in a continuous fashion. Assuming a particular form for this variation, a theory is worked out which predicts that this linear increase shall fail at temperatures only slightly higher than those yet reached in the hydrogen iodide decomposition. There is reason to believe that the numerical results of this theory are substantially correct, even though the detailed assumptions are doubtless far from right.

In any case, it does not seem reasonable to express the temperature dependence of second-order reactions by a single constant energy of activation or to regard the agreement between the rate of reaction and the product of the collision number with a simple exponential containing an average value for the energy of activation as having any deep theoretical significance. The empirical knowledge that this agreement usually exists, within a factor of ten or so, will of course remain useful.

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<sup>1</sup> See, for example, Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, Oxford University Press, 1929, p. 51.

<sup>2</sup> Rice and Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1617 (1927); Kassel, *J. Phys. Chem.*, **32**, 225 (1928); also various later papers by these same authors.

<sup>3</sup> Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

<sup>4</sup> Hinshelwood and Burk, *Proc. Roy. Soc.*, **106A**, 284 (1924).

<sup>5</sup> It is probable that only that component of the relative velocity which is parallel to the line of centers is available, and the distribution law for the kinetic energy resident in this component is the same as for the energy in two squared terms.

<sup>6</sup> The collision rate  $\alpha$  is itself proportional to  $T^{1/2}$ .

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## ON THE PREDICTIONS OF TRANS-NEPTUNIAN PLANETS FROM THE PERTURBATIONS OF URANUS

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1. It has always been difficult to understand why predictions of an exterior planet by Lowell and his predecessors, Gaillot, Lau and W. H. Pickering, were possible from the very small residuals which the longitude of Uranus exhibits. The definiteness of these predictions appeared to be quite outside the possibilities of the material under discussion and yet it was not easy to point out any fundamental error in the arguments. The discovery, at the Lowell Observatory, of a new planet in the region predicted suggested a fresh examination of Lowell's work.

The oscillations in the residuals during the interval which has elapsed since the observations were fairly continuous, seem to have periods too short for an explanation on the basis of the existence of an exterior planet, and neither of the two hypothetical planets of Lowell seem to account for them; in any case, their amplitudes are very small. It therefore occurred to me to make an analysis of the following problem. *What are the elements of a planet of given mass and between given limits of distance which will produce small APPARENT perturbations on another planet during a given interval of time, with much larger apparent perturbations*