The Rate of Thermal Decomposition of Deuterium Iodide

John C. L. Blagg and G. M. Murphy

values for k_1 in the series H_2O, H_2S, and H_2Se: with uncorrected data these are 7.8, 4.0, and 3.2×10^5 dynes/cm.

For the sake of completeness we will remark that Végard[20] from an x-ray analysis gave a rectilinear structure for H_2S, at least in the solid. It is noteworthy that the observed frequencies give reasonable force constants if introduced into equations for a rectilinear model: the peculiar shape of the long wave fundamental would then have to be explained by invoking the presence of an unresolved Q branch; while all observed bands other than ω_2 and ω_3 must be interpreted as combination tones involving an inactive frequency. The only band in H_2S which cannot be so assigned is $2\omega_2$ at 2423 cm^{-1}, but the last point, together with the irregular nature of the rotational lines in the band at 2.6 μ resolved by Nielsen and Barker,[3] is sufficient to exclude the rectilinear structure.

While this paper was in preparation, Nielsen and Nielsen[21] published a brief note as a preliminary account of similar work. They confirm the existence of the long wave band at 8.0 μ for H_2S, and the corresponding bands for D_2S and HDS. They do not appear to have located the fundamental ω_3 for D_2S; in its place they give a band at 4.55 μ and relate it to ω_3 of H_2S. This wave-length corresponds to a force constant of some 5.2×10^5 dynes/cm, and hence the frequency is much too high. The strong peak in HDS at 988 cm^{-1} also seems to have escaped observation. The following comparative table is given by Nielsen and Nielsen:

H_2S	HDS	D_2S
1.9 μ	2.1 μ	—
2.65	3.15	3.65μ
3.70	4.1	4.55
7.9	9.0	10.8

We wish to express our acknowledgments to Professor F. G. Donnan, F.R.S., for his continued interest in our work.

[20] L. Végard, Nature **126**, 916 (1930).

[21] A. H. Nielsen and H. H. Nielsen, J. Chem. Phys. **4**, 229 (1936).

The Rate of Thermal Decomposition of Deuterium Iodide

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The partition functions for deuterium iodide have been calculated at temperatures from 300 to 1500°K. Constants were calculated for an equation to give the value of the free energy function at any temperature within this range. A similar calculation was made for D_2 using the data of Johnston and Long. Combining these with the data for the other molecules involved, the equilibrium constant for the decomposition of deuterium iodide and for the exchange reaction was calculated. These results can be differentiated and integrated to give values for ΔH^0, ΔC_p and ΔS^0. The equilibrium constant for the reaction $H_2 + 2DI \rightleftharpoons D_2 + 2HI$ has been plotted against the temperature from 300 to 1500°K. The equilibrium constant for the reaction $DI \rightleftharpoons \frac{1}{2}D_2 + \frac{1}{2}I_2$ has been calculated. The rate of thermal decomposition of deuterium iodide was measured between 660 and 719°K. The experimental ratio of the rate constants for the reactions $HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$ and $DI \rightarrow \frac{1}{2}D_2 + \frac{1}{2}I_2$ has been compared with the theoretical value of Wheeler, Topley and Eyring. Contrary to their expectations, it was found to be lower than the theoretical value.

THE effect on the rate of several chemical reactions produced by substituting deuterium for hydrogen has been studied by various investigators.[1] Because of the simple homogeneous and bimolecular character of the thermal decomposition of hydrogen iodide, the corresponding reaction with deuterium appears to be one of the most important reactions to study at the present time, since theoretical calculations can be made for this case with some certainty. We have therefore studied the rate of thermal decomposition of deuterium iodide between 660 and 719°K.

Since the reverse reaction also occurs, the rate of decomposition of hydrogen iodide depends

[1] For a review of the subject, see Urey and Teal, Rev. Mod. Phys. **7**, 34 (1935).

TABLE I.

	DI
B_e	3.301
α	6.180×10^{-2}
D_e	-5.347×10^{-6}
ω_e	1640.307
$x_e\omega_e$	20.043

TABLE II.

T	Q	$-(F^0-E_0^0)/T$
300	64.550	43.828
500	108.585	47.399
800	182.750	50.768
1000	240.238	52.420
1500	404.875	55.471

upon the equilibrium constant. The latter has been determined experimentally by Bodenstein[2] who has also made an extensive study of the rates of formation and decomposition. Additional experiments have been made by Kistiakowsky[3] and others and a critical review of both the experimental and theoretical aspects of the reaction has been given by Kassel.[4] The equilibrium constant for deuterium iodide has not yet been measured but Rittenberg and Urey[5] have investigated the reaction

$$H_2+2DI\rightarrow D_2+2HI \qquad (1)$$
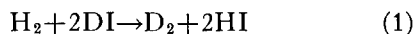
and have shown that the experimentally determined equilibrium constants are in agreement with those calculated from spectroscopic data. Since the energy levels and their statistical weights are well known for hydrogen, iodine and hydrogen iodide and since the corresponding data for the isotopic deuterium compound are readily obtainable,[6] we may proceed with confidence and use the equilibrium constant for deuterium iodide as calculated from the statistical theory. This calculation has been made recently for hydrogen iodide by Murphy[7] who has shown that the experimental results are in reasonable agreement with the theory. It appears, however, that the temperatures at which Bodenstein has worked may be in error and an attempt has been made to correct them. The other difficulty lies in the uncertainty in the heat of dissociation of hydrogen iodide which cannot be determined from spectroscopic data. We have therefore used Bodenstein's data to determine

this quantity.[8] The calculated values of log K are plotted against the reciprocal of the absolute temperature in Fig. 1 together with the experimental points of Bodenstein and of Rittenberg and Urey. A more certain value of the heat of dissociation of hydrogen iodide would only result in a parallel shift of the whole curve in either direction, but it seems impossible to adjust the statistical theory in any way so as to obtain agreement with experiment at the highest and lowest temperatures studied by Bodenstein.

The method of calculating the equilibrium constants for deuterium iodide is similar to that for hydrogen iodide, the partition functions,

$$Q=\sum_{v,\ J} p_J \exp\left[-E(v,J)/kT\right]. \qquad (2)$$

being summed by the method of Kassel.[9] The summation is taken over vibrational and rotational quantum numbers, v and J, $p_J=(2J+1)$ is the quantum weight of the Jth rotational level and E is the vibrational and rotational energy of the molecule as given by analysis of the molecular spectra. The molecular constants were obtained from those of hydrogen iodide and are given in Table I. Following Giauque and his co-workers, the natural constants found in the International Critical Tables[10] were used. The summation was made at 300, 500, 800, 1000 and 1500°K and the values for the partition function, Q, are given in Table II. The free energy may then be obtained by the relation

$$\begin{aligned}-(F^0-E_0^0)/T=&(3/2)R\ln M\\&+(5/2)R\ln T+R\ln Q-7.267 \quad (3)\end{aligned}$$

[2] Bodenstein, Zeits. f. physik. Chemie **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).
[3] Kistiakowsky, J. Am. Chem. Soc. **50**, 2315 (1928).
[4] Kassel, *Kinetics of Homogeneous Gas Reactions* (The Chemical Catalog Co., New York, 1932), p. 148.
[5] Rittenberg and Urey, J. Am. Chem. Soc. **56**, 1885 (1934).
[6] Jevons, *Report on Band-Spectra of Diatomic Molecules* (The University Press, Cambridge, 1932).
[7] Murphy, J. Chem. Phys. **4**, 344 (1936).

[8] Bodenstein has also neglected to correct for the decomposition of iodine molecules into atoms. This has been done in the points as plotted in Fig. 1, although it is nearly negligible at his temperatures. The decomposition of H_2 and D_2 into atoms is also negligible at these temperatures. We have therefore neglected these slight corrections in our rate constant.
[9] Kassel, J. Chem. Phys. **1**, 576 (1933); Phys. Rev. **43**, 364 (1933).
[10] Int. Crit. Tab., Vol. I, p. 16. The numerical constant of the free energy equation was taken as 7.267; $R=1.9869$; $hc/k=1.4324$.

where M is the molecular weight, $E_0{}^0$ is the energy at the absolute zero and the other quantities have their usual thermodynamic meaning. Since the normal state of deuterium iodide is $^1\Sigma$ the electronic statistical weight is unity. There are no other electronic states to be considered. The nuclear spin contributions have been omitted which is valid for temperatures above 25°C as shown by Gibson and Heitler.[11] With the use of Eq. (3) and the values of the Q's as shown in Table II, we have obtained values for the free energy function as given in the same table. The atomic weights for deuterium and iodine were taken as 2.01363[1] and 126.932,[12] respectively. For convenience in interpolation, the values obtained from Eq. (3) have been fitted to a formula of the type

$$-(F^0-E_0{}^0)/T = a/T + b \log T + cT + dT^2 + i. \quad (4)$$

The coefficients in this equation for deuterium iodide together with those obtained for D_2 from the calculations of Johnston and Long[13] are shown in Table III. An equation of the form of (4) will reproduce the value of the free energy function to within at least 0.001 cal./mole between the temperatures of 298.1 and 1500°K as shown by comparison with the results obtained by summation at other temperatures within this range. It should probably not be extrapolated beyond these limits. The coefficients in Eq. (4) may now be combined with the corresponding constants for I_2 as calculated by Murphy,[7] to give

$$-R \ln K = \Delta F^0/T = \Delta H_0/T - \Delta\Gamma_0 \ln T$$
$$-\tfrac{1}{2}\Delta\Gamma_1 T - \tfrac{1}{6}\Delta\Gamma_2 T^2 + I, \quad (5)$$

providing the value for $\Delta E_0{}^0$ is known. This may be obtained from the value 971.83 14 cal./mole

TABLE III.

	DI	D_2
a	-365.512	-6.92285
b	11.1051	15.7301
c	3.642×10^{-3}	2.85×10^{-5}
d	-6.78×10^{-7}	1.09×10^{-7}
i	16.5063	-11.1506

[11] Gibson and Heitler, Zeits. f. Physik **49**, 465 (1928).
[12] Int. Crit. Tab., Vol. I, p. 44.
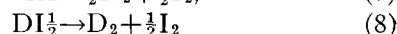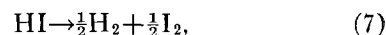[13] Johnston and Long, J. Chem. Phys. **2**, 389 (1934).

TABLE IV.

DI$\to\tfrac{1}{2}D_2+\tfrac{1}{2}I_2$	
ΔH_0	562.08
$\Delta\Gamma_0$	2.8930
$\Delta\Gamma_1$	-6.8113×10^{-3}
$\Delta\Gamma_2$	4.1889×10^{-6}
I	19.8513

for the hydrogen iodide reaction and the zero-point energies of the various molecules involved, by using the equation

$$^2\Delta E_0{}^0 = {}^1\Delta E_0{}^0 + (\tfrac{1}{2}E_{0D_2}{}^0$$
$$- E_{0DI}{}^0 - \tfrac{1}{2}E_{0H_2}{}^0 + E_{0HI}{}^0), \quad (6)$$

where the superscripts one and two refer to reactions (7) and (8) respectively.

$$HI\to\tfrac{1}{2}H_2+\tfrac{1}{2}I_2, \quad (7)$$
$$DI\tfrac{1}{2}\to D_2+\tfrac{1}{2}I_2 \quad (8)$$
and
$$E_0{}^0 = (\tfrac{1}{2}\omega_e - \tfrac{1}{4}x_e\omega_e)\cdot hcN. \quad (9)$$

We have used constants as given by Urey and Teal[1] from the spectroscopic data of Jeppeson[14] for H_2 and D_2, obtaining for the zero-point energies of H_2, D_2, hydrogen iodide and deuterium iodide the values 2175.02 1545.62, 1144.84 and 815.142 cm^{-1}, respectively.[15] The value of $^2\Delta E_0{}^0$ obtained from Eq. (6) is 1014.52 cal./mole. The principal uncertainty in this quantity is that due to $^1\Delta E_0{}^0$ and therefore $^2\Delta E_0{}^0$ is probably good to about 14 calories. The constants for Eq. (5) are given in Table IV.

The equilibrium constant for reaction (8) is now obtained from Eq. (5), the constants of

[14] Jeppeson, Phys. Rev. **44**, 165 (1933).
[15] The vibrational constants used by Giauque (J. Am. Chem. Soc. **52**, 4816 (1930)) and by Johnston and Long, reference 13, which we have used in calculating the partition functions for H_2 and D_2 give somewhat different zero-point energies for these two molecules than the ones we give above. The use of their zero-point energies changes $^2\Delta E_0{}^0$ by about 50 cal. but this affects the final constants by a negligible amount as we have discovered by calculation. It seems better to use the more recent vibrational constant for H_2 and D_2 as determined by Jeppeson. A similar conclusion was reached by Davis and Johnston (J. Am. Chem. Soc. **56**, 1045 (1934)) who report that the use of Jeppeson's data in place of that used by Giauque changes the entropy by only 0.001 cal./mole/degree. Teal and MacWood (J. Chem. Phys. **3**, 760 (1935)) have given vibrational constants for H_2 and D_2, obtained from Raman Spectra, which differ slightly from those of Jeppeson and which are probably better due to the method in which they were obtained. However, the use of these constants instead of those of Jeppeson would change $\Delta E_0{}^0$ for reaction (8) by only 0.98 cal./mole which is much less than the other uncertainties involved. We have taken 1 cm^{-1} = 2.8461 cal./mole.
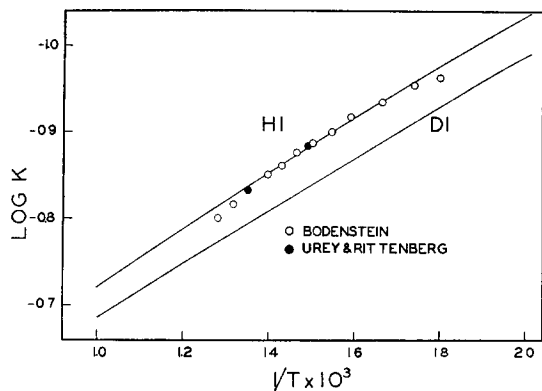
FIG. 1.

Table IV and this value of $^2\Delta E_0{}^0$, and the results are shown in Fig. 1. Since the principal uncertainty in the whole procedure is that in $^1\Delta E_0{}^0$, a better value of this would only shift both curves parallel to themselves in either direction by an equal amount. There are at present no experimental data to check the deuterium iodide curve.

The well-known methods of thermodynamics[16] may also be used to give reliable values of ΔS^0, ΔC_p, and ΔH^0 from Eq. (4). Although the results obtained are not as exact as those for the free energy, the precision is sufficient for most applications and the tedious task of summing the partition functions a second time is unnecessary. We obtain in this way, from the constants of Table IV

$$\Delta H^0{}_{298.1} = 1159 \pm 15 \text{ cal./mole}$$

and

$$\Delta S^0{}_{298.1} = -1.303 \text{ cal./mole}.$$

Using the value $S_{298.1}$ $(I_2) = 62.29$ as calculated by Giauque[17] and $S_{298.1}$ $(D_2) = 34.36$ as given by Johnston and Long,[13] we find $S_{298.1}$ $(DI) = 49.62$ cal./mole. The values of ΔH^0 and ΔS^0 at this temperature are higher than the corresponding

TABLE IVa.

$H_2 + 2DI \rightarrow D_2 + 2HI$	
ΔH_0	-306.80
$\Delta \Gamma_0$	2.6378
$\Delta \Gamma_1$	-1.03694×10^{-2}
$\Delta \Gamma_2$	7.7832×10^{-6}
I	14.3158

[16] Lewis and Randall, Thermodynamics (McGraw-Hill Book Co., New York, 1923), Chapter XV, p. 173.
[17] Giauque, J. Am. Chem. Soc. **53**, 507 (1931).

quantities for hydrogen iodide by 46 and 0.1 cal./mole, respectively.

The equilibrium constant for reaction (1) may also be calculated from the constants of Table IV and smilar constants for reaction (7) as obtained by Murphy.[7] The resulting coefficients in Eq. (5) are found in Table IVa and a plot of K against temperature is shown in Fig. 2. The partition functions of the four molecules involved vary in a very complicated way with the temperature and so it is difficult to make any exact statements as to the way in which the various factors involved contribute to the free energy change of the reaction. There is no reason, however, to doubt the statistical calculations and, if the equilibrium should be measured for this exchange reaction over a wide temperature range, this curious variation with temperature will probably be found.

RATE OF DECOMPOSITION OF DEUTERIUM IODIDE

The rate constant for the decomposition of deuterium iodide is given by the expression

$$k_2 = (K_2/(0.4343 \cdot a \cdot t)) \log ((\alpha+z)/(\alpha-z)), \quad (10)$$

where K_2 is the equilibrium constant for reaction (8), a is the initial concentration of deuterium iodide in moles per cc, t is the time expressed in seconds, $\alpha = 2K_2(1-z)$ and z is the fraction of deuterium iodide decomposed at time t. This is essentially the equation used by Bodenstein, although expressed in different units and rearranged to facilitate computation. As may be seen from Eq. (10) and as pointed out by Kistiakowsky,[3] the errors involved in determining k_2 are smallest when the time of heating is so
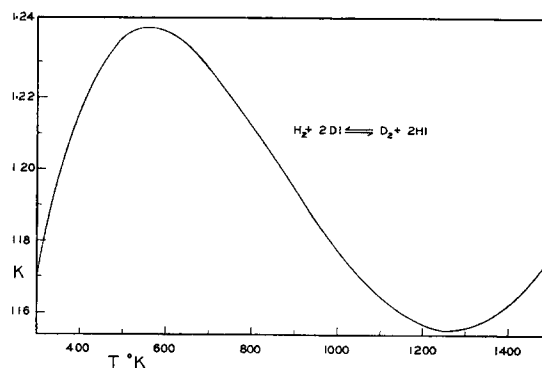

FIG. 2.

chosen that a small but uniform decomposition occurs as far as possible from the equilibrium concentration. Our experiments have been carried out, for the most part, at the same time for each temperature. This is valid for the deuterium iodide decomposition since the reaction is known to be homogeneous and bimolecular from Bodenstein's work on hydrogen iodide.

EXPERIMENTAL MATERIALS

Deuterium was prepared by decomposing 99.9 percent deuterium oxide in an electrolytic cell so designed as to separate the oxygen and deuterium as they were generated. The iodine was resublimed before using. Deuterium iodide was prepared by passing a mixture of deuterium and iodine gases over two platinum spirals, burning at red heat, in the manner described by Cook and Bates.[18] An excess of iodine was used to insure almost complete combination of the deuterium. The deuterium iodide was purified by distillation from a trap surrounded by a dry ice-alcohol mixture to a trap immersed in liquid air. Three or four distillations were made to insure the purity of the deuterium iodide as shown by the colorless product which was obtained. The deuterium iodide was kept frozen by liquid air until the cells were ready to be filled. Hydrogen iodide was prepared in a similar manner using tank hydrogen, which had been passed over a roll of red hot copper screen, and was used to check our experimental procedure as described below. All chemicals used in the analysis were of high grade analytical purity.

FURNACE AND REACTION VESSELS

The furnace was a sulfur boiler in which the temperature was controlled by keeping the pressure over the sulfur constant. The device for controlling the pressure was developed in this laboratory and is described by Rittenberg and Urey[5] and independently by C. C. Coffin.[19]

The temperature was measured with a thermocouple made from No. 28 Chromel-P and No. 28 Alumel wire and the voltage read with a Leeds and Northrup type K potentiometer. The standard cell used with the potentiometer was a

TABLE V.

Run	Temp (°K)	Time (sec.)	Mol/cc ×10⁵	z (%)	k_2 ×10	k_2 ave ×10	K ×10
25	660	18,003	1.963	3.90	1.16		
26		15,421	1.970	3.68	1.26		
27		18,063	1.963	3.92	1.16	1.19	1.430
22	671	14,457	1.949	5.29	2.01		
23		12,354	1.967	4.73	2.06		
24		14,344	1.935	4.93	1.88	1.98	1.455
11	686	10,805	1.933	7.19	3.80		
12		10,857	1.664	6.66	4.03		
13		10,800	1.678	6.57	3.96		
14		10,810	1.683	6.50	3.89	3.92	1.487
15	708	3,599	1.948	7.30	11.49		
16		3,600	1.959	6.92	10.75		
17		18,003	1.963	20.83	11.12	11.12	1.537
18	719	3,623	1.924	11.03	18.82		
19		3,602	1.925	10.54	17.88		
20		3,734	1.693	10.02	18.43		
21		3,603	1.709	9.74	18.23	18.34	1.560
1*	681	3,630	2.144	3.94	5.31		
2		3,599	2.159	3.86	5.21		
3		7,219	1.819	5.92	4.88		
4		7,207	1.832	6.23	5.10		
5		7,203	2.064	5.70	4.14		
6		7,196	2.057	6.36	4.69		
7		7,204	2.011	5.80	4.33		
8		7,208	2.024	6.68	5.03	4.84	1.332

* Runs 1 to 8 inclusive were made with hydrogen iodide. All other runs were made with deuterium iodide.

new Eppley cell which had a negligible temperature coefficient. The thermocouple was calibrated against the ice point and boiling point of water, the boiling point of naphthalene and the boiling point of sulfur. These are all approved standards of pyrometry.[20] The boiling points were corrected to atmospheric pressure by the equations given in the *International Critical Tables*.[20] A least square equation was calculated for the temperature. The temperature remained constant to better than $\frac{1}{2}°$ since it was impossible to notice fluctuations with the potentiometer.

Quartz reaction cells were used. They were approximately six inches long with an outside diameter of about one inch. The volumes were between 50 and 60 cc. The volume of each cell was determined by one of two methods. One, by weighing empty and then filled with water, and two, by filling with water from a burette. The two methods checked to within 0.05 cc. The volume was needed in order to determine a.

[18] Cook and Bates, J. Am. Chem. Soc. **57**, 1775 (1935).
[19] C. C. Coffin, J. Am. Chem. Soc. **55**, 3636 (1933).

[20] Int. Crit. Tab., Vol. I, p. 53.

EXPERIMENTAL PROCEDURE

The cells were pumped for from twelve to twenty-four hours and heated to a dull red heat four or five times during the pumping. When the cells were ready to be filled, the liquid air was removed from the storage trap containing the deuterium iodide and a bath of alcohol dry ice was substituted. The amount of dry ice used was such that the temperature of the bath was between -50 and $-45°C$ as measured by a pentane thermometer. This gave a pressure of deuterium iodide desirable for our experiments and was reproducible as can be seen from column four in Table V. The pressure of deuterium iodide was allowed to build up for about ten minutes and then a stopcock between the storage trap and the cells was opened. The gas flowed into the cells through capillary stopcocks which were closed after about fifteen minutes from the time the liquid air was removed from the storage trap. The gas in the cells was then frozen with liquid air and the cells sealed off from the vacuum system. Contact with the stopcock grease caused a slight amount of decomposition, but since the cells were filled through capillary tubes the diffusion of the decomposition products was slow and no color was shown by the deuterium iodide in the cells. Bates and Lavin[21] have shown that stopcocks lubricated with vaseline may be used with hydrogen iodide. In these experiments Lubriseal was used throughout. The cells for runs with hydrogen iodide were filled in a similar manner and, since a good check with Bodenstein's results was obtained, any error introduced by the use of greased stopcocks is negligible. Before each set of runs the deuterium iodide was redistilled.

After a measured length of time in which the cells were kept in the constant temperature furnace, the reaction was stopped by placing the cells in a blast of cold air and then freezing the deuterium iodide and iodine with liquid air. The total time elapsed between removal from the furnace and complete freezing never exceeded two minutes. Any error thus introduced was balanced out by the time necessary to bring the cell up to temperature when placed in the furnace. The reaction was timed by an electric clock and was measured to the nearest second from the time the cell was placed in the furnace until it was removed and placed in the blast of air. The cells were then opened, sealed to the vacuum system and the gases collected in a trap filled with a four percent solution of potassium iodide which was free from dissolved carbon dioxide and which had been tested for neutrality and for the presence of iodate.[22]

METHOD OF ANALYSIS

The trap containing the iodine and deuterium iodide dissolved in potassium iodide was emptied into a flask and thoroughly washed. A standard solution of sodium thiosulfate, free from dissolved carbon dioxide, was used to titrate the iodine. The thiosulfate solution was standardized each day by means of a standard ceric sulfate solution.[23] This latter solution had been standardized against Bureau of Standards sodium oxalate, using orthophenanthroline ferrous complex, as the indicator since a back titration with ferrous sulfate was necessary. For iodine-thiosulfate titrations a one percent freshly prepared potato starch solution was used. Weight burettes were used for all titrations and all titrations were made in a reproducible light.

The iodate method for acid determination was used in analyzing for deuterium iodide.[24] After analysis for iodine had been made, two grams of potassium iodate were added and the solution allowed to stand for twenty minutes and then titrated with thiosulfate. The titration was completed within twenty-five minutes after the addition of the iodate. A blank was run over the same period of time by adding the same amount of iodate to twenty-five cc of the same potassium iodide solution in which the deuterium iodide and iodine were dissolved. Since the volume of each cell was known, the number of moles of deuterium iodide at the start could be calculated. The fraction decomposed was determined by dividing the number of grams of thiosulfate solution used to titrate the iodine by the total number of grams used in both titrations.

The validity of our experimental method was tested by means of eight experiments on the rate

[21] Bates and Lavin, J. Am. Chem. Soc. 55, 81 (1933).

[22] Fales, *Inorganic Quantitative Analysis* (The Century Co., New York, 1925), p. 353.
[23] Suggested by Dr. G. W. Walden of this laboratory.
[24] Kolthoff and Furman, *Volumetric Analysis*, Vol. II, p. 389.

of decomposition of hydrogen iodide and the results obtained were in good agreement with those of Bodenstein. The data obtained for both hydrogen iodide and deuterium iodide will be found in Table V. The equilibrium constant, K, was calculated for deuterium iodide from Eq. (5) and for hydrogen iodide from a similar equation given by Murphy.[7] The values obtained are given in the last column of Table V. Our constants refer to reactions (7) and (8) and the subscripts one and two refer to the hydrogen iodide and deuterium iodide reactions, respectively. All of our experimental rate constants will be found plotted in Fig. 3, together with those of Bodenstein and Kistiakowsky on hydrogen iodide.

We have considered all the factors involved in calculating our rate constants and each constant is good to the average deviation from the mean which ranges from two to four percent. This precision is as good as that obtained by Bodenstein and Kistiakowsky on the hydrogen iodide reaction. Any error due to K is due to the uncertainty in the zero-point energy and is well within the precision which we have claimed.

DISCUSSION OF RESULTS

It is now well known that the simple Arrhenius equation is not valid for reaction rate constants over a very wide temperature range. Moreover, there are objections to the simple collisional formulas as used in the past. We have, however, used the latter theory to derive an equation for our results of the form

$$\log k_2 = -9333/T + 0.5 \log T + 11.799 \quad (11)$$

which may be compared with the similar equation given by Kassel[4] for hydrogen iodide

$$\log k_1 = -9555/T + 0.5 \log T + 12.311. \quad (12)$$

Eq. (11) will reproduce $\log k_2$ to ± 0.01 and should be regarded merely as an interpolation formula, rather than ascribing any reality to the heat of activation, number of collisions, temperature dependence or cross-sectional molecular areas. On the basis of this theory, if we assume that the collision cross sections of HI and DI are equal and that there is no zero-point energy in the activated complex, the ratio of the rate constants for the two reactions is given by
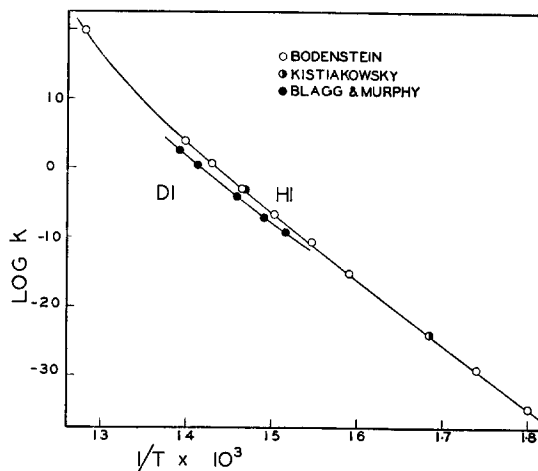

FIG. 3.

$$k_1/k_2 = (M_2/M_1)^{\frac{1}{2}} e^{\Delta E_0^0/RT}, \quad (13)$$

where M_1 and M_2 are the molecular weights of HI and DI and ΔE_0^0 is the difference in their zero-point energies and equals 938.4 cal./mole. Evaluation of Eq. (13) at 700°K gives 1.97 as the ratio of the rate constants. Using Eq. (11) based upon our experimental results and the corresponding constant for HI as determined by Bodenstein, we find the experimentally observed ratio at 700°K of

$$k_1/k_2 = 1.156/0.757 = 1.528.$$

The definitely slower rate for DI seems to indicate that some zero-point in energy is required in the activated state.

Eyring[25] and his collaborators have calculated the absolute rate of reactions in terms of potential surfaces, which in general are those obtained from the Morse formula. Statistical considerations enable the probability of the activated state to be calculated and symmetry considerations furnish considerable information about its potential and vibrational properties. Later developments of this theory by Wheeler, Topley and Eyring[26] have resulted in numerical results for the reaction rates between the halogens and hydrogen and deuterium. They have predicted for the rate of formation of hydrogen and deuterium iodides, the values $k_1'/k_2' = 2.6$, 2.34 and 2.26 at 575, 700 and 781°K where the primes on the rate constants refer to the reverse reaction

[25] Eyring, J. Chem. Phys. **3**, 107 (1935).
[26] Wheeler, Topley and Eyring, J. Chem. Phys. **4**, 178 (1936).

of that measured by us. Using the equilibrium constant as calculated above we find for 700°K, which is in our temperature range,

$$k_1/k_2 = (K_1/K_2)^2 \cdot k_1'/k_2' = 0.818 \times 2.34 = 1.92$$

according to the theory of Wheeler, Topley and Eyring. This result is based upon 14 percent additive binding in the potential surfaces, the zero-point energy of the activated state being ignored. Approximately 20 percent is required to give the experimental result for the HI reaction, if activated zero-point energy is included. However, they have used Bodenstein's experimental results to determine the proper frequencies, activation energy and moments of inertia and since the DI reaction uses the same potential surface, their result should give the correct constant for the DI reaction. Because of the difficulties involved in the theoretical calculations, however, we feel the agreement with our experimental ratio of 1.528 is highly satisfactory. Unfortunately, Wheeler, Topley and Eyring expected the observed ratios to be somewhat larger than the value cited above, since they believe their calculated frequencies for the activated complex to be too stiff. Since the experimental ratio for this reaction has been highly desirable as a check of the theory, it will no doubt suggest to the theoretical chemists the proper way to adjust the potential surfaces in order to obtain closer agreement.

Recently, Geib and Lendle[27] have presented some results on the rate of formation of DI. Their ratio at 700°K is 2.45 and converting to the decomposition reaction as before by means of the equilibrium constant, we find $k_1/k_2 = 2.00$. This is considerably higher than our result and also somewhat higher than the theoretical one of Wheeler, Topley and Eyring. They followed the course of the reaction by measuring the extinction coefficient of iodine by a photometric method. Since they did not use monochromatic light, rather large corrections were necessary for the effect of H_2 and HI on the calibration curves of the iodine absorption. Their precision is therefore rather low and since their agreement with Bodenstein's results for HI is not very satisfactory, the individual rate constants, as well as their ratio, may be in error.

ACKNOWLEDGMENT

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The Far Ultraviolet Absorption Spectrum of N₂O

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The absorption spectrum of nitrous oxide below 2200A has been reinvestigated. Much new material has been found, particularly below 1550A, including some discrete systems of bands, and some continuous regions of absorption. No bands are found below 997A, but only continous absorption down to about 850A, the limit of observation. A Rydberg series was found, converging to an ionization potential of 12.66 volts. Evidence was found for a total of ten electronic states including the members of the Rydberg series. The vibration frequency in the electronic transition around 1500A is 621 cm⁻¹.

THE near ultraviolet absorption spectrum of N₂O has been studied by many investigators.[1-3] The absorption above 2000A appears to be continuous, and very weak. Below 2000A Leifson[4] found two broad bands, one whose center was apparently about 1850A and the other extending from about 1550A to the limit of his observation. These regions have also been studied

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[2] O. R. Wulf and E. H. Melvin, Phys. Rev. 39, 180 (1932).
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[4] S. Leifson, Astrophys. J. 63, 73 (1926).