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# HOMOGENEOUS GAS REACTIONS AT HIGH CONCENTRATIONS. I. DECOMPOSITION OF HYDROGEN IODIDE

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Kinetic studies of homogeneous gaseous reactions have revealed in a number of cases a perfect agreement between the predictions of the mass action law as deduced from the stoichiometric equation of the process and the observed influence of concentration on the reaction velocity. It has been generally assumed that, in these cases, the observed reactions directly follow a collision of two molecules in the case of bimolecular and of three molecules in the case of trimolecular reactions. There exist, however, many reactions which follow a more complicated course even in the small concentration interval investigated and the postulation of intermediary processes seems to be necessary for their kinetic interpretation. Moreover, the mechanism of bimolecular reactions may not be quite as simple as it appears, although this cannot be definitely established by the existing experiments. It is possible that experiments on a larger scale of concentrations would reveal deviations from the simple bimolecular law. Hibben[1] found, for example, that the decomposition of nitrous oxide is no longer bimolecular at very low concentrations. This deviation is due, apparently, to the predominance of a heterogeneous wall reaction and is therefore in no direct relation to the mechanism of the homogeneous reaction. The increase of relative probability of a wall reaction with increasing mean free path of the gaseous molecules is of course inherent in all bimolecular gaseous reactions and may considerably complicate their investigation at very low concentrations. Conversely, reactions which are homogeneous at ordinary concentrations will very probably remain so at higher concentrations and their investigation in this region, therefore, should not meet the difficulty mentioned above. Here, however, the homogeneous rate itself may become influenced by factors, the effect of which is negligible under ordinary experimental conditions ("atmospheric pressure" and below) owing to an increasing probability of three-

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[1] J. H. Hibben, *Proc. Nat. Acad. Sci.*, **13**, 626 (1927).

and poly-molecular collisions or, speaking more generally, owing to the close proximity of the molecules. A hypothesis concerning a retarding effect of "three body" collisions on the rate of bimolecular reactions which the writer had in mind when starting these experiments has not been substantiated and its discussion therefore appears to be unessential; the experiments, however, offer one the possibility of drawing certain conclusions concerning the mechanism of bimolecular processes and should, therefore, be of some interest in connection with the theory of gaseous reactions.

The decomposition of hydrogen iodide was chosen as the object of study partly from considerations of an experimental nature, partly because this reaction has been most thoroughly investigated at ordinary concentrations and is known to have no complicating side reactions.

The rate of hydrogen iodide decomposition, the rate of its formation from molecular iodine and hydrogen and the position of the gaseous equilibrium have been extensively investigated by Bodenstein[2] over a wide range of temperatures (283–508°). He obtained good agreement between the rate and the equilibrium measurements, showing furthermore that the rate of decomposition is bimolecular—at least in the somewhat narrow concentration interval (around 0.042 mole per liter) investigated—and that this reaction is homogeneous in glass vessels. The more recent experiments of Taylor,[3] who found the rate of decomposition to be influenced by extension of the surface of the Pyrex glass used by him, can hardly affect Bodenstein's last conclusion, since his velocity constants are throughout considerably larger than those of Bodenstein. Furthermore, from Bodenstein's values of $d \ln k/dT$, a constant heat of activation[4] is calculable, whereas Taylor's results give a heat of activation decreasing with temperature. His experiments only show, therefore, that, in addition to the homogeneous decomposition, a wall reaction can be created by a suitable choice of the material for the containing vessels. Quite recently, Lewis and Rideal[5] doubted the simple bimolecular character of the reaction, suggesting that the decomposition is caused by free iodine atoms and finding that the rate (and similarly the position of the equilibrium) is influenced by minute quantities of water vapor. Bodenstein and Jost[6] pointed out, however, that phosphorus pentoxide, used by Lewis and Rideal as the drying agent, reacts at the temperature of their experiments with hydrogen iodide and probably causes all the observed effects. The experiments of Lewis and Rideal, therefore, do not prove the active influence of water vapor on the reaction velocity, but, as Bodenstein and

[2] Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).

[3] H. A. Taylor, *J. Phys. Chem.*, **28**, 984 (1924).

[4] W. C. McC. Lewis, *J. Chem. Soc.*, **113**, 471 (1918).

[5] B. Lewis and E. K. Rideal, THIS JOURNAL, **48**, 2553 (1926).

[6] M. Bodenstein and W. Jost, *ibid.*, **49**, 1416 (1927).

Jost conclude, there is on the other hand no experimental evidence available contradicting the existence of such influence.

## Experimental Details

The method chosen for the purpose of the present investigation was the static one and was in principle very similar to that used by Bodenstein. Sealed vessels filled with hydrogen iodide were heated in a thermostat for a desired length of time and their contents later analyzed.

Since, however, the details of both methods are somewhat different and the technique of rate measurements on gases at pressures up to about 500 atmospheres is not yet quite developed, the more important details will be here briefly described.

**Gas Preparation.**—Hydrogen iodide was prepared by passing a mixture of hydrogen and iodine through a heated furnace. It was distilled once in a vacuum to free it from larger quantities of iodine and was stored in a glass vessel cooled by liquid air.

**Preparation of Gas Samples.**—In order to fill the experimental vessels with hydrogen iodide they were sealed (through a graded seal) to a larger glass bulb (about 200 cc.) provided with a Daniels[7] glass membrane manometer and a dry inner ground glass stopper, magnetically operated, which connected it through a trap and, further, through a greased stopcock with the hydrogen iodide container. The only greased stopcock in direct connection with the filling bulb was at the end of a long capillary (to prevent decomposition of larger quantities of hydrogen iodide) and connected it through a mercury vapor trap to a mercury diffusion pump. After thorough evacuation of the system some hydrogen iodide was distilled into the intermediary trap with the pump still working. This operation resulted always in a slight decomposition due to the passage of hydrogen iodide through the greased stopcock but the iodine formed remained during the subsequent operations in the trap on account of its low vapor pressure. The stopcocks to the container and to the pump were now closed and hydrogen iodide in the trap was slowly warmed up until a desired pressure (from 50 to 300 mm.) was created in the system. Then the inner glass stopper was closed and the trap and one of the experimental vessels were simultaneously cooled by liquid air. Experiments showed that practically no hydrogen iodide diffused from the large bulb through the stopper but that all condensed in the vessel. After about two minutes the stopcock to the pump was opened again and a few minutes later the vessel, which had been filled, was sealed off. It was found impossible to prevent slight decomposition of hydrogen iodide, particularly during the sealing off; the liquid hydrogen iodide, after the vessels were warmed up, was always slightly colored by iodine. Analysis of the contents of those vessels, which were somewhat more than usually dark colored and thus were considered unsuitable for experiments, showed that the free iodine content of these was not greater than 0.02%. The amount of iodine present initially in other vessels must, therefore, be lower than this figure. The experimental vessels were made of fused quartz, since the only other possible material—Pyrex glass—has been shown by H. A. Taylor to be catalytically active. The vessels were of cylindrical shape of some 50 cc. volume (2 × 15 cm.) for low pressure experiments, of about 8cc. volume (0.8 × 15 cm.) for medium pressures and of about 3.3 cc. (0.5 × 15 cm.) and 0.7 cc. (0.2 × 20 cm.) for high pressures. The 3.3cc. vessels (two of them) used initially were found to be impractical. On account of their very thick walls (10 mm.) the quartz showed signs of considerable inner strain, manifested from time to time by small cracks in the surface. One of these vessels exploded

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[7] Daniels and Bright, THIS JOURNAL, **42**, 1131 (1920).

a few minutes after cooling, the other during the first experiment after about five minutes of heating in the thermostat. The hydrogen iodide concentrations were in both cases only about one-fifth of those which the smaller vessels with the same ratio of internal diameter to wall thickness (1:2) were later found to withstand.

One end of each vessel was drawn to a fine tip, the other to a capillary about 0.5 mm. in diameter used in sealing the vessels to the filling system. The volume of all vessels, determined by weighing, varied slightly from experiment to experiment on account of the impossibility of sealing off the capillaries at exactly the same length. The errors so introduced are negligibly small for the larger vessels; for the small ones they were partly corrected for, the length of the capillary being measured each time and also the average area, the volume thus determined being added to the main volume. The errors introduced through the somewhat irregular shape of the capillaries may amount to as much as 0.5% of the total volume.

**Conduct of the Reaction.**—For heating the vessels a large lead-bath thermostat, electrically heated, was used. The temperature, measured by a Chromel-Alumel thermocouple, was read on a potentiometer to 0.2°. The thermostat contained an efficiently working stirrer, an additional knife heater and a mercury thermoregulator. Due to a special design this latter was very sensitive; it responded to a sudden change of temperature of 0.5° within ten seconds and the periodic variations of the temperature in the thermostat did not amount to more than 0.2°. During longer periods of time, however, the temperature of the thermostat, when left without attention, showed a slow drift amounting sometimes to as much as 1.5° in twenty-four hours. The insertion of the cold quartz vessels into the thermostat lowered its temperature by a few degrees and several minutes were required for the temperature to become stationary again. In the later part of the work this inconvenience was avoided by heating the thermostat before each experiment to an appropriately higher temperature, so that even initially the temperature was within 0.5° of the average.

To obtain a rapid cooling, the vessels, after taking them out of the thermostat, were immediately put into a steel pipe attached to a carbon dioxide tank and were cooled by a stream of cold gas. Two minutes were found to be sufficient (except for the 3.3cc. vessels) to bring them below room temperature.

**Analysis.**—The analysis was initially beset with considerable difficulties. They were overcome by applying a cotton pad soaked in liquid air to one side of the vessel[8] and breaking the fine tips in distilled and degassed water under a specially designed small gas receiving apparatus. The rush of evaporating hydrogen iodide was so violent, however, that sometimes a fraction of it escaped from the receiver and more than one analysis was ruined in this way. It was fortunate that escaping hydrogen iodide immediately formed a fog in the air and so was easily detected. The tip of the capillary at the other end of the vessel was finally broken off and the vessel washed out with a degassed potassium iodide solution. For the subsequent titration of iodine and hydrogen iodide a standard solution of sodium thiosulfate approximately 0.1 *N* and two potassium hydroxide solutions 0.1 and 0.03 *N* were used. Before each titration a 0.01 or 0.005 *N* solution was freshly prepared from the standard thiosulfate by dilution. All titrating solutions were checked at regular time intervals according to the usual standard methods. For the iodine determination a certified micro buret was used almost exclusively. The other volumetric apparatus was recalibrated. The volumetric determination of free hydrogen, which, as a check, proved to be so useful to Bodenstein, had to be abandoned here on account of considerable complications resulting in the method of analysis

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[8] The simpler procedure of freezing one end of the vessels failed, hydrogen iodide melting first at the far end of the narrow and relatively thin-walled capillary and the resulting expansion cracking the quartz.

adopted. However, Bodenstein had to use this determination only in order to correct errors in analysis due to a reaction of hydrogen iodide with the alkaline constituents of his soft glass vessels. Pure quartz, which was used in the present work, is very unlikely to react in this way and therefore the omission of the hydrogen determination is more or less admissible (see, however, later pages).

## Calculation of Results

By integrating the equation

$$-\frac{d[\mathrm{HI}]}{dt} = k[\mathrm{HI}]^2 - k_1[\mathrm{I_2}][\mathrm{H_2}] \tag{1}$$

Bodenstein has derived an expression which gives the velocity constant $k$ of the decomposition reaction as a function of the time $t$, the fraction decomposed, $x$

$$x = \frac{\mathrm{I_2}}{\mathrm{I_2} + {}^1/_2\mathrm{HI}} \tag{2}$$

and of the fraction decomposed at equilibrium $\zeta$. The equation is

$$k = \frac{\log\left[\dfrac{\dfrac{\zeta}{2\zeta - 1} - x}{\zeta - x}(2\zeta - 1)\right]}{0.8686\,\dfrac{1-\zeta}{\zeta}\,t} \tag{3}$$

This equation is valid for experiments in which pure hydrogen iodide was present initially. The reaction of hydrogen iodide being bimolecular, the constant $k$ of the above equation is still proportional to the concentration and must therefore be divided by this latter in order to obtain a bimolecular velocity constant independent of concentration. The measurements of the equilibrium between gaseous hydrogen iodide, iodine and hydrogen at total concentrations not far from 0.04 mole per liter have been summarized by Bodenstein in the following interpolation formula for the equilibrium decomposition, $\zeta$

$$\zeta = 0.13762 + 7.221 \times 10^{-5}t + 2.5764 \times 10^{-7}t^2 \tag{4}$$

where $t$ is the temperature in centigrade degrees. From this equation the equilibrium decomposition can be calculated for every temperature.

Equation (3) shows immediately that the closer the observed decomposition is to that at equilibrium, the more sensitive will the calculated value of the velocity constant $k$ be to small errors or to changes in the equilibrium constant. For this reason the time of heating in the following experiments was always chosen so as to give only a small and almost uniform decomposition. Such a decision, however, in conjunction with the bimolecular character of the reaction, limited the choice of convenient temperatures to the lower part of the range investigated by Bodenstein.

## Experimental Results

Table I gives the results of rate measurements at an average temperature of 321.4°. The temperature of each experiment is a graphical average of all readings during the time of heating. The constant $k$ given in the seventh column has been calculated by means of Equation (3), using for $\zeta$

TABLE I

THE RATE OF HI DECOMPOSITION AT 321.4°

| No. | Average temp., °C. | Time, secs. | Decomp., % | Vol. of the vessel, cc. | Initial concn. of HI, mole/liter | $k$(sec.$^{-1}$) × $10^6$ | $k_0 \times 10^6$ (moles/liter, sec.) |
|---|---|---|---|---|---|---|---|
| 1 | 322.4 | 82800 | 0.826 | 51.38 | 0.02337 | 0.1004 | 3.96 |
| 2 | 321.6 | 172800 | 2.567 | 59.80 | .03838 | .1543 | 3.98 |
| 3 | 322.1 | 180000 | 3.286 | 59.80 | .04333 | .1900 | 4.22 |
| 4 | 322.7 | 173100 | 3.208 | 51.38 | .04474 | .1927 | 3.98 |
| 5 | 321.6 | 81000 | 2.942 | 51.38 | .1027 | .3763 | 3.61 |
| 6 | 321.6 | 57560 | 2.670 | 7.899 | .1126 | .4778 | 4.20 |
| 7 | 322.4 | 61320 | 4.499 | 7.899 | .1912 | .7792 | 3.85 |
| 8 | 321.4 | 19200 | 2.308 | 7.899 | .3115 | 1.235 | 3.96 |
| 9 | 321.6 | 18000 | 2.202 | 7.899 | .3199 | 1.255 | 3.87 |
| 10 | 321.3 | 16800 | 2.071 | 7.899 | .3279 | 1.262 | 3.87 |
| 11 | 321.4 | 17400 | 2.342 | 7.899 | .3464 | 1.383 | 3.99 |
| 12 | 321.4 | 17700 | 2.636 | 7.899 | .4075 | 1.537 | 3.77 |
| 13 | 320.4 | 18000 | 2.587 | 7.899 | .4228 | 1.482 | 3.80 |
| 14[a] | 321.3 | 23400 | 4.343 | 7.899 | .4736 | 1.967 | 4.18 |
| 15 | 321.6 | 6000 | 2.224 | 3.280 | .9344 | 3.802 | 4.03 |
| 16 | 321.7 | 5400 | 1.903 | 0.778 | .9381 | 3.597 | 3.76 |
| 17 | 321.1 | 8160 | 3.326 | .781 | 1.138 | 4.251 | 3.81 |
| 18 | 321.2 | 3600 | 1.986 | .703 | 1.201 | 5.642 | 4.74 |
| 19 | 321.7 | 5400 | 2.741 | .713 | 1.231 | 5.253 | 4.19 |
| 20 | 321.7 | 5400 | 3.089 | .779 | 1.317 | 5.940 | 4.42 |
| 21 | 321.1 | 8160 | 4.116 | .715 | 1.339 | 5.305 | 4.04 |
| 22 | 321.1 | 3600 | 1.830 | 3.280 | 1.351 | 5.187 | 3.92 |
| 23[a] | 321.3 | 4380 | 2.972 | 0.810 | 1.624 | 7.033 | 4.36 |
| 24 | 321.2 | 3600 | 2.369 | 3.280 | 1.714 | 6.767 | 3.99 |
| 25 | 321.4 | 3600 | 2.959 | 0.777 | 2.067 | 8.520 | 4.12 |
| 26 | 321.1 | 3600 | 3.360 | 3.280 | 2.414 | 9.523 | 4.02 |
| 27 | 321.2 | 3600 | 3.710 | 0.782 | 2.532 | 10.80 | 4.31 |
| 28 | 321.4 | 3600 | 4.224 | .785 | 2.678 | 12.40 | 4.63 |
| 29 | 321.3 | 3600 | 3.912 | .729 | 2.680 | 11.43 | 4.31 |
| 30 | 321.4 | 3600 | 4.505 | .777 | 2.682 | 13.29 | 4.95 |
| 31 | 321.4 | 1560 | 1.786 | .788 | 2.742 | 11.68 | 4.26 |
| 32 | 321.5 | 2400 | 2.947 | .780 | 2.762 | 12.72 | 4.56 |
| 33 | 321.4 | 3600 | 4.316 | .729 | 2.822 | 12.68 | 4.50 |
| 34 | 321.6 | 2400 | 3.168 | .732 | 2.886 | 13.72 | 4.71 |
| 35 | 321.6 | 2400 | 3.215 | .710 | 2.982 | 13.94 | 4.63 |
| 36 | 321.6 | 1560 | 2.093 | .735 | 2.999 | 13.74 | 4.54 |
| 37 | 321.3 | 1440 | 2.078 | .740 | 3.310 | 14.78 | 4.51 |
| 38 | 321.3 | 1440 | 2.214 | .780 | 3.360 | 15.77 | 4.74 |
| 39 | 321.1 | 1500 | 2.415 | .785 | 3.751 | 16.56 | 4.50 |
| 40 | 321.4 | 1470 | 2.865 | .782 | 3.769 | 20.17 | 5.35 |
| 41 | 321.4 | 1470 | 2.687 | .731 | 3.914 | 18.87 | 4.82 |
| 42 | 321.1 | 1500 | 2.936 | .720 | 4.093 | 20.28 | 5.05 |
| 43 | 321.4 | 1470 | 2.822 | .780 | 4.146 | 19.87 | 4.79 |

Table I (*Concluded*)

| No. | Average temp., °C. | Time, secs. | Decomp., % | Vol. of the vessel, cc. | Initial concn. of HI, mole/liter | $k$(sec.$^{-1}$) × $10^6$ | $k_0 \times 10^6$ (moles/liter, sec.) |
|---|---|---|---|---|---|---|---|
| 44 | 321.4 | 1470 | 3.047 | .718 | 4.353 | 21.52 | 4.94 |
| 45 | 321.2 | 1140 | 3.426 | .773 | 5.742 | 31.38 | 5.52 |
| 46 | 321.4 | 1200 | 4.178 | .709 | 6.272 | 36.77 | 5.86 |
| 47 | 321.4 | 1200 | 4.607 | .778 | 6.502 | 40.83 | 6.28 |
| 48 | 321.4 | 1200 | 4.646 | .835 | 6.722 | 41.22 | 6.09 |
| 49 | 321.4 | 1200 | 4.976 | .657 | 6.807 | 44.40 | 6.52 |
| 50 | 321.4 | 1200 | 5.487 | .712 | 7.131 | 49.43 | 6.93 |

the value 18.745% computed from Bodenstein's interpolation formula and counting the time in seconds. In order to obtain the constant $k_0$ of the last column, the $k$'s were divided by the initial concentration of hydrogen iodide expressed in moles per liter (sixth column) and were reduced to the same temperature, 321.4°, by using a value 1.061 as the temperature coefficient of the rate at 321° per degree, calculated from Bodenstein's data. The table reproduces actually the results of all the experiments made which were not interrupted by an explosion of the vessel or by a failure in the analysis of the contents. A group of seven experiments in vessels which, contrary to the usual procedure, were not heated and degassed thoroughly during the evacuation process previous to filling, have been recorded separately in Table II. All these experiments, scattered throughout the range of concentrations investigated, yield values of $k_0$ considerably larger than the rest of the experiments and indicate, therefore, the presence of some additional catalytic decomposition. Supporting this view is an observation made occasionally when degassing the reaction vessels, that microscopic amounts of some yellow substance—possibly of mercuric iodide—were deposited in the colder parts of the apparatus.

Table II

Catalyzed Decomposition

| No. | Av. temp., °C. | Time, secs. | Decomp., % | Vol., cc. | Init. HI, mole/liter | $k \times 10^6$ (sec.$^{-1}$) | $k_0 \times 10^6$ (mole/liter/sec.) |
|---|---|---|---|---|---|---|---|
| 51 | 321.4 | 61200 | 6.501 | 10.015 | 0.1130 | 1.171 | 10.4 |
| 52 | 321.6 | 18000 | 3.674 | 7.899 | .3128 | 2.152 | 6.81 |
| 53 | 321.3 | 8160 | 4.879 | 0.779 | 1.194 | 6.685 | 8.03 |
| 54 | 321.5 | 6120 | 4.806 | .733 | 1.514 | 8.367 | 5.50 |
| 55 | 321.4 | 3600 | 5.384 | .732 | 3.092 | 16.13 | 5.22 |
| 56 | 321.3 | 1500 | 3.175 | .733 | 3.772 | 22.02 | 5.87 |
| 57 | 321.7 | 1200 | 5.141 | .763 | 5.873 | 46.02 | 7.75 |

**Experiments with Specially Dry Hydrogen Iodide.**—In order to investigate how far the rest of the experiments represented the true velocity of decomposition of pure hydrogen iodide and were not influenced by the presence of someun known impurities (water), the filling apparatus was modified at the end of the present work. The stopcock and the capillary leading to the pump were removed and replaced by a wide tubing with a constriction for sealing off; between the trap, mentioned in the description of the apparatus, and the hydrogen iodide container were introduced three additional traps with inner glass seals at both ends of the line. Freshly prepared hydrogen iodide was used. All the separated (by the inner seals) parts of the system were baked out in a vacuum at 450–400° for ten hours. The quartz part of the apparatus with the reaction vessels sealed to it was heated to a somewhat higher temperature than the rest. Hydrogen iodide was distilled four times in a vacuum from a bath of melting carbon disulfide (−112°), only the first fraction being used each time and the rest being sealed off after cooling. Unfortunately the glass membrane manometer failed to work after the heating and the pressure of hydrogen iodide in the filling system had to be guessed. The result was that too much was filled into two of the vessels and they exploded on heating; the remaining two experiments are Nos. 14 and 23 of the first table. Hydrogen iodide prepared in this way must have been not only extremely dry but also incomparably freer from all foreign matter than the quality normally used. Incidentally, it contained only very small quantities of free iodine and appeared to the eye absolutely colorless. This was secured by allowing a long time for complete condensation of hydrogen iodide before the vessels were sealed off.

**The Influence of Temperature.**—Table III represents nine experiments made at a lower temperature. The value of $\zeta$ used in the calculation of the constants $k$ was computed from Bodenstein's data to be $\zeta = 18.247\%$. The bimolecular constants $k_0$ of the last column have been corrected to the mean temperature of 300.0°.

TABLE III

THE RATE OF HI DECOMPOSITION AT 300.0°

| No. | Temp., °C. | Time, secs. | Decomp., % | Vol., cc. | Concn. | $k \times 10^6$ | $k_0 \times 10^6$ |
|---|---|---|---|---|---|---|---|
| 58 | 299.7 | 10500 | 1.075 | 0.702 | 1.000 | 1.036 | 1.05 |
| 59 | 299.7 | 10500 | 1.433 | .838 | 1.353 | 1.387 | 1.04 |
| 60 | 300.0 | 9600 | 1.523 | .830 | 1.455 | 1.614 | 1.11 |
| 61 | 300.0 | 9600 | 1.946 | .655 | 1.957 | 2.070 | 1.06 |
| 62 | 300.0 | 9600 | 1.933 | .709 | 1.959 | 2.125 | 1.09 |
| 63 | 299.6 | 2400 | 0.6966 | .827 | 2.405 | 2.818 | 1.20 |
| 64 | 300.0 | 9600 | 2.745 | .835 | 2.482 | 2.956 | 1.19 |
| 65 | 299.6 | 2400 | 1.547 | .645 | 4.847 | 6.558 | 1.38 |
| 66 | 299.8 | 1320 | 1.145 | .613 | 5.998 | 8.818 | 1.49 |

**Equilibrium Measurements.**—Table IV gives the results of equilibrium measurements at 321.4°. The analysis of these experiments was particularly difficult on account of large amounts of non-condensable hydrogen present and a considerable number were rendered useless by losses of hydrogen iodide. The number of experiments offered is somewhat limited also because the quartz vessels did not seem to withstand well the long heatings necessary to attain equilibrium. Numerous explosions which, of course, ruined the rather costly quartz vessels were the unpleasant result.

Table IV

The Thermal Equilibrium at 321.4°

| No. | Time, secs. | HI init., moles per liter | Decomp., % | Time, secs., calcd. |
|---|---|---|---|---|
| 67 | 275400 | 1.02 | 18.67 | 139000 |
| 68 | 357000 | 1.30 | 19.03 | 109000 |
| 69 | 198000 | 1.64 | 18.68 | 86000 |
| 70 | 198000 | 1.79 | 18.93 | 79000 |
| 71 | 357000 | 1.92 | 19.72 | 74000 |
| 72 | 230400 | 2.08 | 19.27 | 68000 |
| 73 | 230400 | 2.12 | 19.40 | 67000 |
| 74 | 194400 | 2.21 | 18.78 | 64000 |
| 75 | 172800 | 2.24 | 18.48 | 63000 |
| 76 | 108000 | 2.29 | 18.71 | 62000 |
| 77 | 108000 | 2.30 | 18.81 | 61500 |
| 78 | 141000 | 2.65 | 19.02 | 53500 |
| 79 | 126000 | 3.73 | 20.75 | 38000 |
| 80 | 68700 | 5.39 | 19.46 | 26200 |

## Errors

**Influence of Impurities.**—Before discussing the theoretical significance of the experiments made, it is well worth while to consider in detail the possible errors. Table II shows quite plainly that hydrogen iodide decomposition is rather sensitive to the presence of impurities. Whether the observed catalytic acceleration is really due to the mercuric iodide noticed or is due to oxygen occluded in quartz and driven off in most of the experiments by heating cannot be decided. It is important to note that the results of Table I very probably represent the true velocity of decomposition of pure hydrogen iodide, as is best demonstrated by the complete agreement between the main body of the results and those of experiments Nos. 14 and 23 made with unquestionably pure and dry hydrogen iodide.

**Accidental Errors.**—The mean of the first 14 experiments up to 0.5 mole per liter concentration (the reasons for this limitation will be seen from a later discussion) is $k_0 = 3.95 \times 10^{-6}$ with an average deviation of single values amounting to 3.1% and with a probable error of the mean itself of 0.73%. But, aside from one or two values with larger deviation—and these are very likely due to unobserved small losses of hydrogen iodide or of iodine (in the broken tip of the capillary)—the average deviation is even much smaller. It is fully accounted for by unavoidable errors in buret readings and other uncertainties of the analysis and of volume determinations and also by errors made in averaging the temperature;

these latter may amount easily for longer time intervals (overnight) to 0.3° and will therefore account for about 2.0% deviation in the constants, $k_0$. All this shows that the rate measurements gave completely reproducible results.

**Systematic Errors.**—The calculated probable error of the mean does not include, however, systematic errors. The more important of these are: (1) Incorrect titers of solutions used and errors in the calibration of the volumetric apparatus. Assuming an error of 0.5% to be thus involved in each titration, we are on the safe side. This gives a possible error of 1.5% in $k_0$, since iodine determination enters here in the first power, that of hydrogen iodide as the square. (2) More important still is the error in determination of the absolute temperature of the thermostat. The Chromel-Alumel thermocouple was calibrated in boiling water, mercury and sulfur. As the result of these determinations, repeated several times with almost identical results, a three-constant equation has been calculated which gives the temperature of the thermostat, designated in Table I as 321.4 to 321.6°. Independent check of the temperature was made by means of a platinum resistance thermometer and a high-precision Mueller type bridge. The first determination—in an early part of the work—yielded 321.2°; the second one, made somewhat later, 321.3°. Attributing a statistical weight unity to the thermocouple determination and a weight 2 to the mean of the platinum thermometer temperatures, the final mean temperature is calculated to be 321.4° with an uncertainty of not more than 0.3° or with an error in the $k_0$ not exceeding 2%.

**Errors at High Concentrations.**—The experiments at higher concentrations of hydrogen iodide are, of course, equally subject to all these errors and, in addition, to two others which will now be considered. The time intervals required for the heating up and for the cooling down of the vessels have been neglected so far, the "true" time of heating being equated to the actual time of immersion in the thermostat. This source of error will obviously affect the results more considerably the shorter the time of immersion. Therefore, four experiments, represented in Table V, have been made of only very short duration; the "true" time of heating has then been calculated after assuming an appropriate velocity constant

TABLE V

THE CORRECTION OF HEATING TIME

| No. | Av. temp., °C. | Decomp., % | Vol., cc. | HI, moles per liter | $k_0 \times 10^6$, assumed | Time in seconds Immersion | Time in seconds Calcd. "true" |
|---|---|---|---|---|---|---|---|
| 81 | 321.4 | 0.339 | 0.783 | 2.052 | 4.35 | 365 | 381 |
| 82 | 321.4 | .316 | .783 | 2.062 | 4.35 | 365 | 352 |
| 83 | 321.4 | .389 | .704 | 2.225 | 4.40 | 365 | 399 |
| 84 | 321.4 | .526 | .731 | 2.809 | 4.55 | 365 | 413 |
| | | | | | Av. | 365 | 388 |

$k_0$ (see the latter part of the article) for each experiment. The difference between the mean "true" and the actual immersion time amounts to only twenty-three seconds, the iodine initially present and the decomposition during the cooling apparently more or less compensating the slower rate during the warming up period. Therefore, the systematic error of time determination even in the shortest experiment (No. 45, Table I, 1140 seconds) amounts to only 2% and a correction of the results in Table I in this respect was considered unnecessary. The other error may arise from a change in the equilibrium decomposition due to the non-ideal character of the gases at high concentrations. The observed deviation of the decomposition velocity under these conditions from the normal course is rather in favor of such possibility. Table IV, containing the equilibrium measurements, could also be interpreted as supporting it. A closer comparison shows, however, that there is no systematic change of equilibrium decomposition with concentration of hydrogen iodide but rather a steady, although a slow, increase with time of heating for about equal concentrations. Different interpretations of the effect can be offered. (1) The time of heating was possibly too short. The last column of the table gives, however, the calculated times at which the equilibrium should be reached within 1% (that is, $x = 0.18558$ for $\zeta = 0.18745$) and shows that this time is throughout much shorter than the actual time of heating. It would remain so even if the equilibrium decomposition was shifted to $\zeta = 0.22000$ (this last calculation of course, was made with a suitably modified value of $k_0$). (2) The equilibrium mixture becomes inhomogeneous, liquid iodine being separated. Unfortunately a calculation of the iodine vapor pressure at 321° would be of no value since the composition of a liquid phase under the experimental conditions is unknown. Another consideration, however, will help. If a condensation does take place, there must be a critical concentration of hydrogen iodide with which at equilibrium a saturation concentration of iodine obtains. Above this, the extent of decomposition would increase very rapidly with increase of initial concentration of hydrogen iodide. No evidence of such behavior, at least in the concentration range investigated, can be found in Table IV. (3) Hydrogen is slowly consumed in the walls of the quartz vessels. The vessels showed, however, no visible signs of any change on the inner surfaces and so a reduction of silica appears improbable. It is more likely that hydrogen under high pressure is slowly diffusing through quartz. That helium diffuses through quartz even at room temperature has been shown by Elsey[9] and it is well known that at temperatures considerably higher than 320° quartz is quite permeable to hydrogen. The presence of such a diffusion process would not only account for the observed slow shift in the equilibrium decomposition but would also indi-

[9] H. M. Elsey, This Journal, **48**, 1600 (1926).

cate that the true decomposition values at high concentrations are somewhat lower than the figures recorded in Table IV and, hence, either about equal to or slightly lower than Bodenstein's value, $\zeta = 0.18745$, obtained for concentrations not in excess of 0.08 mole per liter. The velocity constants $k_0$ in the upper range of concentrations represent therefore in all probability either the true or slightly smaller values.

## Kinetic Interpretation of the Results

For convenience in the following discussion the results of the first table have also been represented in Fig. 1. The ordinates give the velocity constant $k_0$, the abscissas the initial concentration of hydrogen iodide plotted on a logarithmic scale. The constants $k_0$ obtained at the mean temperature, 300.0° (Table III), have also been plotted on Fig. 1 (as large circles) after having been multiplied by a factor of 3.85. This graphical representation will be of value in showing that the bimolecular velocity constant $k_0$ (the range 0.02 to 1.0 mole/liter) is quite independent of the size of the vessels used. Since, however, the surface-volume ratio of the different quartz vessels varied by at least a factor of 10, it means that the decomposition velocity measured was at least almost exclusively that of the homogeneous reaction. The experiments with dried hydrogen iodide mentioned earlier show, furthermore, that it was the true velocity of decomposition uninfluenced by the presence of impurities. Possibly even more convincing in this respect is a comparison with Bodenstein's results. His empirical interpolation formula for the velocity constant $k_0$[10] yields for the temperature 321.4° a value $1.10 \times 10^{-5}$ (mole/22.4 liters, minutes). Converted to our units (mole/liter, seconds) the value is $4.12 \times 10^{-6}$. The same value 4.12 is obtained when for the calculation of the reaction velocity at 321.4° the equation

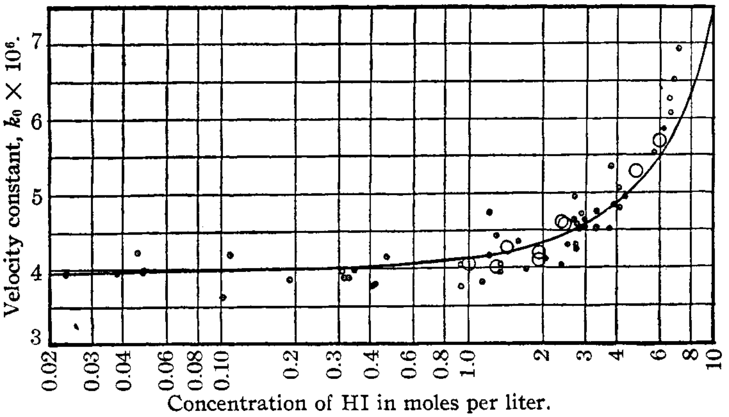

Fig. 1.—The bimolecular velocity constant of HI decomposition.

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[10] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

$$\ln \frac{k_{T_1}}{k_{T_2}} = A \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \qquad (5)$$

and the two nearest values (302 and 356°) of Bodenstein are used. The agreement between Bodenstein's and the present values is quite unusually good. The difference amounts to only 4% and is thus even within the limits of the maximum possible error estimated for these experiments alone, although about the same error (5%) must be inherent in Bodenstein's measurements. In consideration of the fact that he used soft glass vessels instead of pure quartz and that his method of filling the vessels (and therefore the amount of impurities) was quite different from ours, such agreement is the best proof that in both cases the true homogeneous rate has been measured.

Fig. 1 shows quite clearly that the velocity constant, $k_0$, which remains unchanged in a wide range of concentrations, starts to rise from about 1 mole per liter, reaching a value higher by more than 50% for the concentration of 7 moles per liter. Furthermore, as the values of $k_0$ at 300.0° indicate, the slope of the rise is essentially independent of the temperature; the temperature coefficient of the reaction rate at different concentrations therefore is the same.[11] The most natural explanation of this rise, that does not involve a postulate of some tri- or of still higher order molecular processes, is that the reaction rate is strictly proportional to the number of bimolecular collisions, but that the number of these latter is not proportional to the square of the concentration, provided the concentration is rather large. Indeed, van der Waals[12] has already shown that the equation for the total number of collisions

$$Z = 2\sqrt{\pi}\, N^2 \sigma^2 \sqrt{\frac{RT}{M}} \qquad (6)$$

($N$ the number of molecules per unit volume of the only kind present, $\sigma$ their diameter, $M$ the molecular weight, $R$ the gas constant and $T$ the absolute temperature) is only a first approximation and that the next step in refining it is the multiplication of it by a factor

$$\frac{1}{1 - Nb} \qquad (7)$$

The constant $b$ has been found to be equal to four times[13] the volume of a molecule assumed to be a sphere. The same correction of course must be applied to the constants $k_0$ in order to retain the proportionality between the collision number and the reaction velocity. In Fig. 1 the curve has been drawn with a value of $Nb$ equal to 47 cc. per mole or with $\sigma$ =

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[11] It is appropriate to point out that the factor 3.85, by which the constants at 300.0° have been multiplied, is within 1% of the temperature coefficient of the rate between 300.0 and 321.4° determined from Bodenstein's data.

[12] J. D. van der Waals, "Over de continuiteit van den gas-en vloeistoftoestand," Leiden, **1873.**

[13] O. E. Meyer, "Die kinetische Theorie de Jase," Breslau, **1899.**

$3.33 \times 10^{-8}$ cm. This value of $b$ fits best the numerous experiments between $c = 2.5$ and $c = 4.5$ moles per liter concentration. The experiments at very high concentrations are unsuitable for the determination of $b$ because, as Jaeger[14] pointed out, even the corrected collision equation is only an approximation and must fail when $Nb$ approaches unity. The experiments in the region $c = 0.9$ to $c = 2.5$ moles per liter show somewhat too large irregular deviations to be used for the calculation of $b$. They yield, however, a mean ($k_0 = 4.14 \times 10^{-6}$; $c = 1.31$ moles/liter), which is within 1% of the curve[15] drawn. The introduction of the quantity $b$ into the expression for the collision number is equivalent to the introduction of the volume correction $b$ into the equation of state of van der Waals. The other correction "$a$" which takes care of the attracting forces between the molecules has, however, a different influence on the form of the collision equation. As Sutherland[16] has shown, only the apparent diameter of the molecules is increased by forces of attraction, whereas, at least as long as only forces acting between two (colliding) molecules are considered, the number of collisions remains proportional to the square of the molecular concentration. No more general calculations taking care of the influence on the collision frequency of forces exerted by other neighboring molecules are recorded in the literature.

The agreement of the value of $\sigma$ obtained ($\sigma = 3.3 \times 10^{-8}$ cm.) with that calculated by Rankine[17] from viscosity data, $\sigma = 3.5 \times 10^{-8}$ cm., is rather good.

Summarizing, the conclusions arrived at can be stated as follows. The decomposition of hydrogen iodide is kinetically strictly bimolecular; Bodenstein's measurements of the reaction velocity seem to be very accurate; an exact value for the velocity constant at 321.4° and a fairly accurate value of the molecular diameter[18] have been obtained.

**Activation Energy and Collision Area.**—With these data on hand an investigation of the mechanism of activation[19] and reaction can now be attempted. The writer has repeated the graphical determination of the

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[14] G. Jaeger, *Sitz. Akad. Wien*, **105** (2A), 111 (1896).

[15] The larger deviations of these experiments arise partly from uncertainties in the analysis of the very small amounts of iodine formed in the small 0.7cc. vessels. The two experiments with the 3.28cc. vessel (Nos. 24 and 26) have not been included in the above average. It is very doubtful whether the "true" time of heating coincides with the time of immersion in the thermostat so well for this large and very thick walled vessel, as it does for the small 0.7cc. vessels.

[16] Sutherland, *Phil. Mag.*, **36**, 507 (1893).

[17] Rankine, *Trans. Faraday Soc.*, **17**, 719 (1922).

[18] The probable error in this latter is somewhat uncertain. It is easy to show, however, that a change of $b$ by 25% (therefore a change in $\sigma$ by about 8%) completely destroys the agreement between calculation and experiments in Fig. 1.

[19] For the following considerations compare, for instance, C. N. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, **1926**.

activation energy[4] from the temperature coefficient data of Bodenstein. The values of $\ln k_0 - {}^1/_2 \ln T$, from the equation

$$\ln k = {}^1/_2 \ln T - E/RT + C \qquad (8)$$

have been plotted on a large scale against $1/T$. All values of Bodenstein from 508 to 302° lie on a straight line with maximum deviation not exceeding 5% in the value of $k$ (not $\ln k$). The slope yields for $E$, 44,300 cal.[20] In order to estimate the probable limit of error of this figure, we may assume that the velocity constants at 508 and 302° are wrong each by 20%—a rather exaggerated error in view of the agreement earlier demonstrated. The upper limit of $E$ under these conditions is calculated to be 45,900 cal. Assuming that the reaction occurs on each collision in which the energy of both molecules exceeds the above value, we may calculate the rate of hydrogen iodide decomposition at 321.4°.

$$k_0c^2 = 2Z\, e^{-E/RT} \qquad (9)$$

$Z$, the total number of collisions per cc. per second at unit concentration (1 mole per liter), is calculated to be $2.82 \times 10^{31}$, if $\sigma = 3.3 \times 10^{-8}$ cm. The exponential with $E = 45{,}900$ cal. is equal to $1.28 \times 10^{-17}$, so that the number of molecules reacting, which is twice the number of effective collisions, is calculated to be at least $7.25 \times 10^{14}$. This must be compared with the experimentally determined number ($k_0 = 3.95 \times 10^{-6}$) $2.39 \times 10^{14}$. The agreement obtained cannot be considered as quite good because, it must be remembered, the calculated reaction velocity represents the lower limit, still consistent with Bodenstein's measurements of the temperature coefficient, and should probably be raised by a factor close to 2.

As has been frequently pointed out, Equation 9 holds strictly only if the energy of activation of the colliding molecules is assumed to be distributed in two degrees of freedom only. It is of some interest to consider another possible source of activation energy: the total kinetic energy of relative motion of colliding molecules.

In such a case the number of collisions (therefore half the rate of decomposition) with the relative kinetic energy larger than a given one is expressed not by Equation (9) but by[21]

$$k_0c^2 = 2Z\left(1 + \frac{E}{RT}\right) e^{-\frac{E}{RT}} \qquad (10)$$

To calculate the theoretical reaction velocity of hydrogen iodide decomposition with Equation 10 it must be first noted that the temperature coefficient of the reaction rate is given now by

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[20] The value of $k_0$ at 283° is considerably off the straight line (by some 20% in $k$) and its inclusion would *decrease* the average activation energy. The deviation is possibly due to a wall reaction becoming marked at this low temperature. Since we are interested here in the upper limit of $\epsilon$ only, the value of $k$ at 283° has been neglected.

[21] Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Company, New York, 1927.

$$\frac{d \log k_0}{dT} = \frac{1}{2T} + \frac{E}{RT^2} - \frac{1}{T} \tag{11}$$

(the term $(1 + E/RT)$ being substituted in Equation (10) with a sufficient degree of accuracy by $E/RT$) and that therefore $RT$ must be added to the previously determined value of $E$.

The upper limit of $E$ at 321° now becomes 47,100 cal., and from this and Equation 10 the *minimum* number of effective collisions is calculated to be $4.45 \times 10^{15}$, the rate therefore to be $8.9 \times 10^{15}$. The experimentally determined value was $2.4 \times 10^{14}$.

Without going into further calculation it may be pointed out here that the discrepancy between the calculated and experimental rates will be still considerably increased if the assumption is made that all forms of energy present in a diatomic molecule, that is, energy of translation, of rotation and of oscillation, contribute to the activation of hydrogen iodide.[22] The only error which could have entered into the calculations of the theoretical reaction rate (provided the theory of activation is correct generally) lies in the assumption that the diameter of the reacting molecules or, better, their effective cross section, is the same as the kinetic cross section of an average molecule. And, since the calculated rate was found to be greater than the observed, it means that the effective cross section of molecules in collisions leading to reaction is considerably smaller than the average. If only two degrees of freedom are acting in the activation, the effective cross section is still not far from the normal—probably one-half to one-fourth of it. But if we assume that at least three—the translational—degrees of freedom are responsible for the activation, the effective cross section of reacting molecules must be smaller than 0.03 of the normal. This result is rather striking because, as has been shown repeatedly,[23] atoms (and probably also molecules) in the state of electronic excitation have cross sections considerably greater than the calculated kinetic averages for normal atoms. Some light on the process of activation in thermal reactions could possibly be obtained by similar studies of the cross sections of molecules excited to higher oscillation and rotation quantum states by absorption of light in their infra-red absorption bands. At present very little can be said definitely as to the origin of the small effective cross sections of the activated molecules. They may be due to a "steric factor"[24]—the

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[22] For the form of equations determining the number of collisions with energy greater than a given one, as a function of the number of degrees of freedom, see Herzfeld, "Die Kinetische Theorie der Wärme," Braunschweig, **1925**; Hinshelwood, *Proc. Roy. Soc., London*, **113A**, 230 (1926); Fowler and Rideal, *ibid.*, **113A**, 570 (1926); O. K. Rice and H. C. Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

[23] K. A. Stuart, *Z. Physik*, **36**, 262 (1925); Schutz, *ibid.*, **35**, 260 (1925); compare also Franck and Jordan, "Anregung von Quantensprüngen durch Stösse," Berlin, **1926**, p. 243.

[24] Herzfeld, *Ann. Physik*, **59**, 635 (1919); Tolman, THIS JOURNAL, **47**, 1524 (1925).

orientation of the molecules in the moment of their collision—or to some other causes. Prior to deciding this question, it is necessary to know the exact origin of the activation energy.

**The Molecular Volume Factor in the Velocity Experiments.**—The experiments here described offer—at least in principle—the possibility of solving this last problem. A more careful consideration of the meaning of the term $Nb$ which, according to the suggested interpretation, caused the observed increase of the velocity constant at high concentrations, will show that this quantity is somewhat different from the ordinary $Nb$ entering the van der Waals equation of state. In this equation $b$ determines, so to speak, that part of the total volume of a gas which, being occupied by the rest of the molecules, is excluded from the space which can be occupied by an average molecule. Therefore, $b$ of van der Waals is determined by the nearest distance to which the centers of two average molecules can approach each other, that is, by the sum of their radii. In contrast to this the experiments on reaction rate describe not the behavior of average molecules but the behavior of certain[25]—activated—molecules; $Nb$, therefore, represents that fraction of the total volume which is excluded to these particular molecules, is thus determined by the nearest distance to which the center of an activated molecule can approach the center of an average molecule in an average collision. The knowledge of this distance will make possible at least an indirect conclusion as to the forms of energy sharing in the thermal activation. If it is the kinetic energy we may expect[15] that $b$, determined from the rate measurements, will be somewhat smaller than the usual $b$ at the same temperature. On the other hand it is quite likely that increased energy of rotational and vibrational degrees of freedom[26] increases somewhat the dimensions of the molecules and should be therefore manifested by a larger volume correction in the rate experiments. Unfortunately, the present state of knowledge of the exact volume of average molecules of hydrogen iodide at the temperature of the experiments here recorded as also possible errors in $b$, determined, from the rate measurements, make a successful comparison rather improbable.

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[25] The case is equivalent to the case of a mixture of two kinds of molecules, although we must assume that there is a continuous exchange of individual molecules, of which each has a chance to be either activated or deactivated. Provided the concentration of one (the "activated") kind is negligibly small, the volume correction for it is given by $4N[4/3\pi((r' + r)/2)^3]$, $r'$ and $r$ being the radii of both kinds, whereas for the other kind (the "average") the correction is $4N(4/3\pi r^3)$. In reality molecules in different (higher) rotational or oscillational quantum states or molecules with different velocities are probably capable of reaction on collision with a suitable other molecule. The above calculation gives, therefore, only their average cross section.

[26] A. Sommerfeld, "Atombau und Spectrallinien," Vieweg und Sohn, Braunschweig, **1924.**

In conclusion the writer wishes to thank Professor Hugh S. Taylor for his active interest and encouragement during the course of this work.

## Summary

1. The decomposition of gaseous hydrogen iodide has been investigated at concentrations from 0.02 to 7 moles per liter.

2. The rate of decomposition is bimolecular in the whole range of concentrations investigated and is not influenced by extreme drying.

3. At higher concentrations a correction taking care of the volume of the molecules in the expression for the number of bimolecular collisions must be introduced in order to retain the bimolecular character of the reaction rate.

4. Calculations of the reaction rate from the data on the activation energy show that the effective cross section of activated molecules in collisions leading to reaction are smaller than the average kinetic cross section of molecules.

5. A way of deciding which forms of molecular energy are contributing to the activation process has been indicated from considerations on the nature of the volume correction obtained from the rate measurements here recorded.

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# THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VII. THE ELECTRIC MOMENTS OF CERTAIN DIPHENYL DERIVATIVES. THEIR RELATION TO THE SEVERAL STRUCTURES

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A study of the chemical properties of diphenyl and its derivatives has led to interesting speculations concerning the structures of the various molecules. For the purpose in hand it is considered unnecessary to review the work which has been done in this field; it will be sufficient simply to state the conclusions given in two more recent publications These articles contain numerous references to previous investigations.

Adkins, Steinbring and Pickering,[3] as a result of their studies, conclude that the non-formation of the anhydrides is due to the fact that in the dinitro and dihydroxy acids the rings are extended as in the conventional formula, while in the amino or benzidine type of acids the rings are super-

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[3] Adkins, Steinbring and Pickering, This Journal, **46**, 1917 (1924).