

*Summary.*

The ultramicroscope has recently been used to examine turbulent flow in pipes, and to obtain information on the eddying wake behind a bluff obstacle. Photographs are given in the paper of some of the views seen when this earlier work was in progress; also of the flow around a circular cylinder at low Reynolds' number. The flows were revealed by the motions of those minute particles in water which became visible in the light beam of the ultramicroscope.

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*The Thermal Decomposition of Nitrous Oxide at Pressures up to Forty Atmospheres.*

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Nitrous oxide decomposes to nitrogen and oxygen at velocities which can be conveniently measured at temperatures between 600° and 850° C. M. A. Hunter\* investigated the reaction by streaming the gas through a porcelain bulb in a furnace and measuring the decomposition for different times of passage. No attempt was made to determine whether the reaction is homogeneous or heterogeneous. The effect of wide variation of pressure was not used to determine its order, since the reaction was followed only over small ranges of decomposition at atmospheric pressure. From the velocity of decomposition, however, bimolecular constants were obtained which could be represented by the equation:

$$\ln k = 24.12 - 31800/T,$$

where  $k$  is the bimolecular velocity constant and  $T$  the absolute temperature. If this equation holds, the activation energy of the bimolecular reaction is 62,040 cal./gm. mol.

A much more thorough examination of the reaction was made by Hinshelwood and Burk,† who measured the rate of reaction by following the pressure increase at constant volume in a silica bulb. The reaction was proved to be

\* 'Z. phys. Chem.,' vol. 53, p. 441 (1905).

† 'Proc. Roy. Soc.,' A, vol. 106, p. 284 (1924).

homogeneous. The initial pressure was varied between 50 and 500 mm. Hg, and it was found that the reciprocal of the half-lives when plotted against the initial pressures gave a straight line. True bimolecular reaction requires the straight line  $1/t_{1/2} = ka$ , where  $t_{1/2}$  is the half-life, and  $k$  the velocity constant, and  $a$  the initial concentration. The line through the experimental points showed a small intercept on the  $1/t_{1/2}$  axis for which no explanation was offered at the time. From the variation of the bimolecular constants between  $565^{\circ}$  and  $852^{\circ}$  C. the activation energy of the reaction was calculated to be 58,450 cal./gm. mol. If the reaction were a bimolecular one dependent on immediate decomposition at each activating collision of the molecules the number of molecules reacting per second should be equal to  $Z \times e^{-E/RT}$ , where  $Z$  is the number of molecules colliding per second and  $E$  is the activation energy. From the observed rate of reaction at  $1000^{\circ}$  K. a value of 55,000 cal./gm. mol. was found for the activation energy. The fairly close agreement between the two values of the activation energy, 58,450 and 55,000 cal./gm. mol. and the manner in which the half-life varied with pressure provided good grounds for believing the reaction to be a simple bimolecular one, dependent only on collisions between the molecules.

Further work on the reaction has been published by Volmer and Kummerow,\* who made velocity measurements at  $665^{\circ}$  C. between 25 and 300 mm. Hg. They came to the conclusion that the velocity of reaction was simply that to be expected from the low pressure part of a quasi-unimolecular reaction of the type, which according to the theory of Lindemann† may show a half-life independent of pressure over a very wide pressure range and yet exhibit a falling off of velocity at some sufficiently low pressure. Volmer and Kummerow expected to find that the nitrous oxide decomposition would give true unimolecular constants at some sufficiently high pressure. In a paper by Volmer and Nagasako‡ results at pressures up to 8000 mm. Hg were given, and it was claimed that these agreed with the theory of a quasi-unimolecular reaction and showed that the unimolecular constants were practically independent of pressure above a pressure of about  $6\frac{1}{2}$  atms. The activation energy was 53,000 cal./gm. mol.

Some measurements made by Musgrave and Hinshelwood§ during a study of the reaction at low pressures are shown in fig. 1. The line is almost straight

\* 'Z. phys. Chem.,' B, vol. 9, p. 141 (1930).

† 'Trans. Faraday Soc.,' vol. 17, p. 598 (1922).

‡ 'Z. phys. Chem.,' B, vol. 10, p. 414 (1930).

§ 'Proc. Roy. Soc.,' A, vol. 135, p. 23 (1932).

near the origin, but passes through a region of great curvature at about 50 mm. Hg and thereafter straightens out to a line of a much smaller slope than that near the origin. It is difficult to explain these results on the basis of Volmer's theory of a simple quasi-unimolecular reaction, since this would give a curve rising smoothly from the origin, finally becoming horizontal, without the marked change of curvature and straight lines of fig. 1. Musgrave and Hinshelwood were led to the conclusion that the observed reaction was the sum of a unimolecular reaction, the line OAB of fig. 1, and a bimolecular reaction. The intercept OC was regarded as a measure of the full extent of the unimolecular reaction and its variation with temperature gave a value of 50,500 cal./gm.

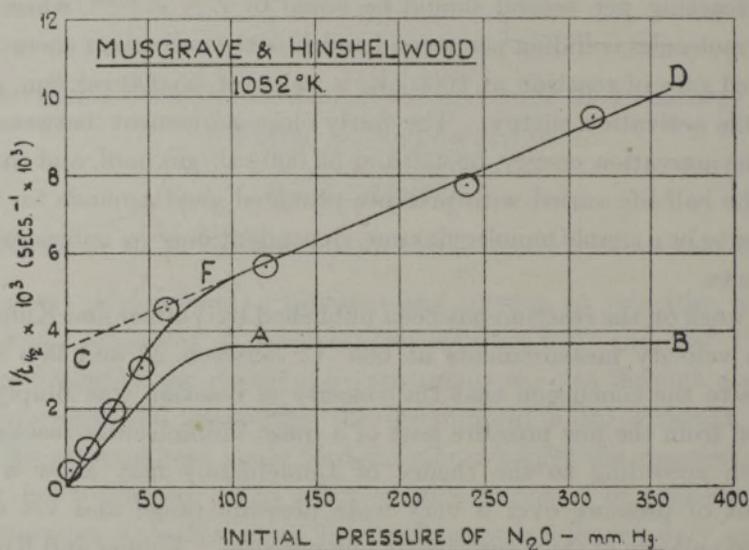


FIG. 1.

mol. for the activation energy of the unimolecular reaction. In the same paper Musgrave and Hinshelwood gave results which proved that the nitric oxide formed as a by-product catalysed the reaction slightly.

If Volmer's theory of a simple quasi-unimolecular reaction is correct, the half-life should be almost independent of pressure at all pressures above approximately 6 atms. On the other hand, Musgrave and Hinshelwood's theory of two concurrent reactions, one of which is bimolecular, suggests that the half-life might still be dependent upon pressure even above 6 atms. In order to discover the true state of affairs velocity measurements at pressures much greater than 6 atms. are needed. Such results are provided by the present paper, which reports measurements of the velocity of decomposition of nitrous oxide at pressures as high as 40 atms.

## EXPERIMENTAL.

*Apparatus.*

The reaction was studied at temperatures between 840° and 999° C. and at pressures between 0.10 and 40 atms., by measuring the rate of pressure increase of the gas at constant temperature and volume in a silica bulb. Two types of apparatus were used. The low pressure apparatus was designed for work at pressures between 50 and 2500 mm. Hg, the high pressure apparatus for work at pressures up to at least 40 atms.

(1) *Low Pressure Apparatus.*—The apparatus used by Hinshelwood and Burk (*loc. cit.*) and described by Hinshelwood and Topley\* was used for pressures up to 500 mm. Hg and was adapted for use at pressures up to 2500 mm. Hg by fitting spring-loaded taps to stand the pressure, and by employing a closed manometer for the pressure measurement. This manometer was made from a J-shaped glass capillary tube, 1 mm. internal diameter. In the longer limb, dry CO<sub>2</sub>-free air was enclosed by a mercury thread, the movement of which in the shorter limb was used to indicate the pressure. The enclosed air was kept at a constant temperature by fitting the longer limb with a water-jacket through which water from a 25° C. thermostat was circulated. The manometer was calibrated against an open mercury column and then sealed to the apparatus. The advantage of using a closed manometer of this type is that it entails only a small dead space (1.5 to 2% of the volume of the reaction bulb) and only a small correction to the results obtained with it is needed.

The nitrous oxide was stored in a glass bulb over mercury at a pressure of about 3000 mm. Hg. At pressures up to 2500 mm., the highest used with this apparatus, the gas appeared to reach the temperature of the reaction bulb within a second of its entry.

A change was made in the method of temperature measurement. In place of a millivoltmeter calibrated in degrees Centigrade, which was found to be liable to changing zero errors, the calibrated platinum-platinum rhodium thermocouple was used in conjunction with a potentiometer which made it possible to control the temperature to  $\pm 0.3^\circ$  C.

(2) *High Pressure Apparatus.*—No apparatus for this type of work at pressures up to 40 atms. has been described. Volmer and Nagasako (*loc. cit.*) used the static method at pressures up to 10 atms. They made little alteration to the apparatus used for normal pressures, the range of which is limited by the strength of the silica bulb.

\* 'J. Chem. Soc.,' vol. 125, p. 393 (1924).

The solution of the present experimental problem seemed to be to have a steel bomb whose walls could be kept at a low, safe temperature, serving as a container for an electric furnace surrounding the reaction bulb. There remain the difficulties of keeping the reaction vessel at a uniform and accurately measurable temperature, of keeping down the dead space, and of providing a sufficiently sensitive means of pressure measurement. It is believed that these difficulties have been overcome in the apparatus described below, which was designed for use at pressures up to 100 atms.

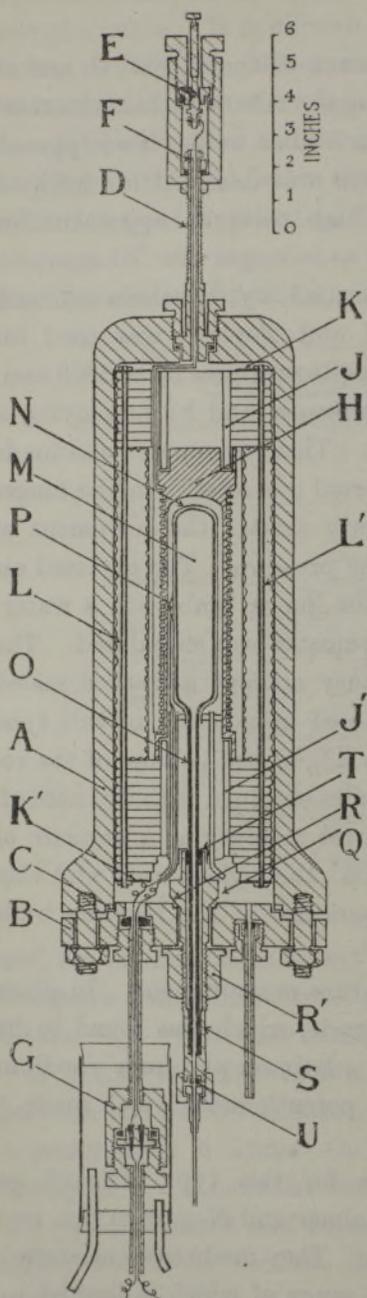


FIG. 2.

*The Bomb, Furnace, and Reaction Vessel.*—A diagram of the steel pressure vessel and its contents is given in fig. 2. The bomb A was made of mild steel, the cover plate B of "Vibrac," and the two gave a pressure-tight fitting on the copper ring C by the tightening of eight nuts over the cover plate.

It was necessary to have insulated leads into the bomb for the current supplying the furnace and for the thermocouple. The chrome-steel glass-insulated cones\* which have been in use for some time at Winnington were used. For the furnace a single insulated cone was enough, the return being via the steel body of the apparatus. The copper wire leads to the furnace were threaded through a length of twin-bore "Vitreosil" tube within the steel pressure tubing D. One wire was fastened to the inner terminal of the insulated cone E, the other was connected to the metal at F. By using the length of tube D, the cone was kept away from the heat of the furnace, which it was feared might have caused a breakage of the glass, if the cone had been fixed directly into

\* Welbergen, 'J. Sci. Instr.,' vol. 10, p. 247 (1933).

the body of the bomb. The outer part of the cone E was connected through rheostats to the positive lead of a 200-volt D.C. supply. The negative was connected to the steelwork of the apparatus. The glass insulation of the cones was much less than a millimetre thick, but care was taken to keep the bomb free from moisture, and it was found that the cone would carry a current of at least 3 amps. throughout the pressure range without trouble.

For the thermocouple leads into the bomb, two insulated cones set into one plug were needed. The platinum and platinum-rhodium wires from the hot junction were fixed to the inner terminals of the two cones, and from the outer terminals platinum and platinum-rhodium wires ran to cold junctions with copper, kept at the temperature of melting ice. The readings of a couple arranged in such a way are only correct if all the four junctions to chrome-steel are at precisely the same temperature. Because of this it was not permissible to fix the pressure cones directly into the cover plate B, where they would have been subjected to a temperature gradient along their length, as a result of the dissipation of heat from the furnace. The pressure joint was accordingly made in the separate vessel G which was attached to the cover plate by a length of steel tubing along which passed the insulated wires from the hot junction. The vessel G was water-jacketed, so preventing the occurrence of any difference in temperature along or between the insulated cones.

A connection through the cover plate was made for the entry of the nitrogen used to balance the pressure within the reaction vessel.

The furnace was designed to give as even and as steady a temperature as possible in the heating space. It was rather a difficult problem because of the necessity of having a lagging which would take up a temperature gradient between the furnace wall at 600° to 900° C., and the inner bomb wall which it was hoped to keep below 200° C. It was found to be unavoidable that the furnace space would not be much greater than the required volume of a reaction bulb. This increased the difficulty of ensuring an even temperature throughout the furnace and reaction bulb, for with the bulb filling most of the furnace space it became important to minimize any tendency for the furnace temperature to fall away at the ends.

The tendency for a furnace to show this effect of a serious temperature gradient at its ends is usually due to the efficiency of the endwise lagging of the furnace being much poorer than that of the lagging of the sides. In the design of the furnace shown in fig. 2 special attention was given to this point. The nichrome heating wire, 70 ohms resistance, insulated with porcelain "fish-spine" beads, 3 mm. in diameter, was wound in a deep helix cut in the

steel tube H. This metallic tube was used for the purpose of giving a good heat conductivity along the length of the furnace which would help to maintain an even temperature. The heating wire was covered with a thin layer of alundum cement, over which was wound sufficient asbestos string to give a diameter which would just fit the bomb. The asbestos was held in place by a jacket of wire-netting. The tube H was supported and prolonged by two lengths of wide "Vitreosil" tube J and J'. Over these were pressed a sufficient number of discs of asbestos cement board to occupy the space between the ends of the steel furnace tube and the ends of the bomb. The hollow space within the "Vitreosil" tube J was filled up with alundum cement. The whole furnace assembly was made rigid and self-supporting by bolting together two thin steel end-plates K and K', with two lengths of steel tube L and L' screwed at the ends. Tubing was used instead of rod to give a free passage for the gas between the front and the back of the bomb.

The reaction bulb M was made of silica and was about 16 cm. long with a volume of 110 c.c. To promote a rapid equalization of temperature over the whole surface of the silica, the bulb was covered with a closely fitting jacket N, made from sheet silver about  $\frac{3}{4}$  mm. thick. This jacket was made in two sections; one a test-tube shaped piece covering the whole length of the reaction vessel, the other a hemispherical cap which covered the remainder of the silica surface. The silica bulb was sealed to the silica capillary tube O, round which were arranged three "Vitreosil" tubes to pass gas into the furnace space, and a length of twin-bore "Vitreosil" tube to carry the thermocouple wires; over all these was wound asbestos string to the diameter of the tube J'. The hot junction of the thermocouple was fixed in contact with the mid-point of the silver jacket at P, by looping it round a small tang of silver raised from the body of the jacket N. The leads to the junction were kept out of contact with the silver by threading them through 1 mm. bore "Pythagoras" refractory tubing.

The above type of construction gives a reaction bulb with an outer surface of a good heat conductor, heated in a furnace tube made of a good conductor, surrounded by a considerable thickness of lagging, particularly at the ends; so that the requirements for as even a temperature as possible are fulfilled.

One of the earliest difficulties was to find a way of making the joint between the reaction bulb and the steel gas supply pipe. The first attempts were made with butt-joints, for which a flange formed on the end of the silica capillary O was held against a flange on the incoming steel tube, with a "Klingerite" washer between. The first joint made in this way was satisfactory,

but after a breakage many attempts to repair the joint were unsuccessful and the principle was discarded. The type of joint finally used was found to be quite satisfactory. It is shown in fig. 2. The mild steel tube Q was turned with a cone R, which gave a gas-tight fitting on the cover plate when the nut R' was tightened. It was found possible to join the silica to the steel by soldering the capillary O to the inside of the tube at a point S, sufficiently remote from the heat of the furnace to avoid softening the solder. From the solder at S to the interior of the bomb there was a clearance of about a millimetre between the silica and the steel. Some support was given to the capillary by the tightly fitting brass sleeve T. The length of the tube Q outside the bomb was cooled by a jet of air to make sure that there would be no softening of the joint S. The steel tube was connected to the gas supply and manometer system by a lens ring joint at U to 0.7 mm. bore copper capillary tube, running to a T-piece (G, fig. 3).

*Pressure Measurement.*—The half-life, in the decomposition of nitrous oxide, is reached when the pressure is 1.25 times the initial pressure. For an accuracy of 1% a pressure measuring instrument sensitive to 0.25% of its pressure reading would be wanted. Closed gas manometers could not conveniently be used because of the difficulty of achieving this sensitivity and at the same time avoiding a large dead space. A pressure balance\* affords the most sensitive and accurate method of measuring pressures of the order of 100 atms., but it could not readily be adapted to follow the pressure change during reaction. It provides a reservoir of fluid at a constant pressure, which can only be changed by changing the load on the balance, an operation which takes an appreciable length of time; while the reaction pressure to be measured would rise smoothly and continuously from the instant of filling the bulb.

It seemed best to use sensitive carefully calibrated Bourdon tube gauges. Six gauges were obtained and calibrated against a pressure balance. Four of these were Schaeffer and Budenberg gauges with 12-inch dials, two for 100 kg./cm.<sup>2</sup> and two for 50 kg./cm.<sup>2</sup>. The remaining two gauges were Budenberg gauges for 300 lbs./sq. inch. With practice it was found possible to read these gauges to 0.05 kg./cm.<sup>2</sup>, 0.02 kg./cm.<sup>2</sup>, and 0.4 lbs./sq. inch respectively, so that they were sufficiently sensitive for the purpose for which they were required.

If these gauges had been used connected directly to the gas, the volume of the Bourdon tube, which was several cubic centimetres, would have been a very serious addition to the dead space of the apparatus. The presence of such a

\* Michels, 'Ann. Physik,' vol. 72, p. 285 (1923); vol. 73, p. 577 (1924).

large dead space was avoided by filling completely with oil the gauge reading the reaction pressure, and separating the oil from the gas by a mercury buffer. The system used is shown in fig. 3. The gauge A was connected by steel pressure tubing to a valve B and a pressure vessel C. A Pyrex glass capillary tube D, 1 mm. bore, dipped almost to the bottom of this vessel. This capillary

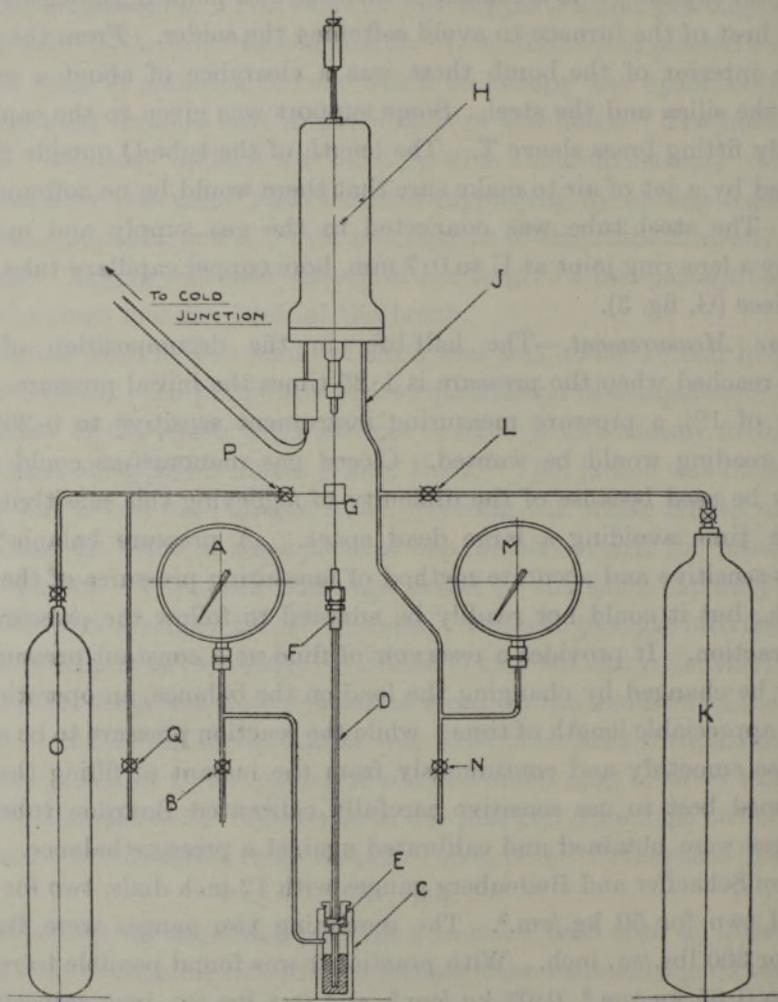


FIG. 3.

was held by a nut which pressed on a flange E, soldered to the glass. The capillary tube was about a metre long and its upper end was fitted with a soldered-on coupling F, through which it was connected to the reaction bulb, with 0.7 mm. bore copper capillary, by way of the T-piece G. The Bourdon tube was evacuated through the valve B, and at the same time the

space over the mercury in the capillary D was evacuated. Refrigerator oil was then allowed to run into the gauge through B, filling up completely all the free space and forcing mercury up the capillary tube to a height approximately barometric. The valve B was then closed. This oil filling made the gauge system so incompressible that a pressure of 80 atms. produced a movement of only 40 cm. in the mercury meniscus in the 1 mm. tube D.

*General Arrangement of the Apparatus.*—The complete apparatus is shown in fig. 3. The bomb H was held horizontally on a cradle on a bench about 3 feet high. Passing through its cover plate was a steel pressure tube J, supplying nitrogen. The nitrogen was stored under pressure in the large cylinder K, and the quantity of gas admitted to the bomb was controlled by the fine-adjustment valve L. The pressure of gas in the bomb was shown by the gauge M. A valve N was fitted for blowing off gas or for evacuating the bomb.

The nitrous oxide was stored under pressure in the cylinder O which was connected by steel tubing to a fine-adjustment valve P, leading to the bomb, and a valve Q which was used for blowing off the gas, and for evacuating the reaction bulb. The fine-adjustment valve P controlled the quantity of gas entering the reaction bulb, and its speed of entry. It was connected to the T-piece G by 0.7 mm. bore copper capillary tube. This T-piece was connected by similar tubing to the reaction bulb and the glass capillary D. By using this small bore tubing the dead space between the valve P, the reaction bulb, and the mercury meniscus in D was kept below 1 c.c.

The control valves L and P were placed together at shoulder-level on a panel, with the gauges A and M on either side.

Protection against the danger attending a burst of the glass tube D was given by a Triplex glass screen.

*Temperature Measurement and Control.*—The Johnson-Matthey platinum, platinum-rhodium couple which was used had been calibrated against a platinum resistance thermometer up to about 650° C. and checked at the salt point (801° C.) and gold point (1063° C.). The cold junction was kept at the temperature of melting ice, and the e.m.f. of the couple was measured with a Cambridge Scientific Instrument Company "Workshop potentiometer" which had been altered to give a tapping for a low resistance external galvanometer. The potentiometer dials were set to the required voltage and the current through the furnace was controlled to give no deviation of the galvanometer. A change of one microvolt in the couple e.m.f. produced a deflection of  $1\frac{1}{2}$  mm. By watching for the first signs of a deviation and taking steps to correct it immediately by changing the heating current, it was usually found to be

possible to keep the couple reading constant within less than 2 microvolts, which meant a temperature constant to about  $\pm 0.2^\circ$  C.

*Experimental Procedure.*—After assembling the apparatus the furnace was baked out at the working temperature, and at the same time evacuated through the valve N, fig. 3, by a "Hyvac" pump with a liquid-air trap. By doing this a large amount of water and grease was removed from the asbestos lagging, and the danger of shorting the insulated cones by a layer of condensed moisture averted. After this evacuation the bomb was always kept filled with nitrogen.

To prepare for an experiment the furnace temperature was adjusted to the required value and the reaction bulb evacuated through the valves P and Q. Valves P, Q, L, and N were then closed and the valves of the two cylinders N and O were opened. By opening simultaneously the fine-adjustment valves P and L, the silica bulb was filled with nitrous oxide at the same time as the bomb was filled with nitrogen, and during this filling the pressures of the two gases as shown by the gauges A and M were kept equal. The filling could be carried out at speeds up to 2 atms. per second. When the gas pressure for the experiment was reached the two valves P and L were tightly closed. One observer began immediately to take readings of the gauge A, and of the height of the mercury meniscus in the capillary D, and a second observer started a stop-watch and noted the pressure readings and the time at which they were taken, and also controlled the furnace temperature. A continual light tapping of the gauge was necessary to get the proper reading.

As the reaction proceeded the pressure in the bulb shown by the gauge A rose, and it was necessary to adjust the balancing pressure of nitrogen. This was best done continuously, by adjusting the valve L to give a steady leakage of gas into the bomb, at a rate corresponding to the rate of increase of pressure in the reaction bulb.

After the reaction had been followed for a sufficient length of time, the gas was blown out by opening valve Q and then slowly releasing valves P and N. When atmospheric pressure was reached, the reading of the gauge A and the height of the mercury column in D was taken. It was then possible to correct the observed readings for the calibration error of the gauge and for the effect of the changing head of mercury in D to obtain the absolute pressures of the gas in the reaction bulb. The results of typical experiments are shown in Table I.

When experiments were made at pressures above approximately 25 atms. there was a tendency for the furnace temperature to fall slightly during the filling, because of the larger quantities of gas which had to be heated. This

all in temperature was usually less than half a degree, but its effects on the reaction velocity were nullified by starting with the temperature half a degree high.

It is important that the time taken to fill the reaction bulb should be short. If this filling time is an appreciable fraction of the half-life, it becomes difficult to decide the initial pressure and starting time of the reaction from the experimental curve, for some of the gas will be reacting and giving a pressure change, although more gas is still entering the bulb. By choosing the working temperature to give half-lives of at least 15 to 20 minutes, the time taken to fill at a speed of 2 atms. per second, or faster, becomes such a small fraction of the half-life of the reaction that there is no difficulty in fixing the initial pressure within 0.5% and the time zero to a second or two.

Good evidence that the time taken by the gas to reach the reaction temperature was very short was provided by the shape of the reaction curves. If the gas had remained below the final reaction temperature for some length of time, the experimental pressure time curve would have shown a pronounced change of curvature near the origin, the points being low, gradually rising to the true reaction curve for a steady temperature as the rising temperature of the gas produced a higher pressure. Actually the experimental curves showed no such effect.

*Source of Nitrous Oxide.*—The nitrous oxide was taken from a cylinder of the pure liquid supplied by the British Oxygen Company, marked "for inhalation." The gas was found to be 96.7% nitrous oxide, the remainder being nitrogen and oxygen. For many of the experiments in the low pressure apparatus the gas was purified by condensing the nitrous oxide in liquid air and pumping away the permanent gas before evaporating and collecting the pure gas. This purified gas gave the same results as the gas taken directly from the cylinder. This was also the experience of Hinshelwood and Burk, and of Musgrave and Hinshelwood (*loc. cit.*) who found that even large quantities of air had no effect on the velocity of reaction except at very low pressures of nitrous oxide, *e.g.*, 30 mm. Hg.

For the high pressure apparatus cylinder gas was the only convenient source of supply of large quantities of compressed nitrous oxide, and it was used in all the experiments. There was no difficulty in filling the reaction bulb at pressures up to at least 40 atms., since the vapour pressure from liquid nitrous oxide at room temperatures is above 50 atms.

*Determination of Nitric Oxide in the Reaction Product.*—The amount of nitric oxide formed as a by-product during the high pressure reaction was

measured in a few instances. The method was one of those used by Musgrave and Hinshelwood. When the half-life had been reached the mixture of nitrous oxide and its reaction products was blown into an evacuated, calibrated 3-litre flask, and the temperature and pressure of the gas were measured. In this mixed gas the by-product was present as nitrogen peroxide formed from nitric oxide and oxygen on cooling. It was converted to nitric acid by admitting about 50 c.c. of distilled water to the flask and shaking the contents for half an hour. The acid so formed was titrated with centinormal alkali. Control experiments were made to ensure that no soda was removed from the walls of the flask by the shaking with water, and that the original nitrous oxide shaken with water gave no acid. The percentages of nitric oxide found are given in Table VII, the accuracy is probably about 10%.

*The Temperature and Pressure Ranges Employed.*—With the low pressure apparatus experiments were made between 75 mm. Hg and 2200 mm. Hg at temperatures between 999° and 888° K. The half-lives varied between 120 and 10,000 seconds. The high pressure apparatus was used between  $\frac{1}{2}$  and 40 kg./cm.<sup>2</sup> and 840° and 930° K. with half-lives varying between 10,000 seconds and about 500 seconds.

Some attempts were made to carry out experiments at pressures as high as 70 kg./cm.<sup>2</sup>. To do this it was necessary to warm the supply cylinder to obtain a high enough pressure to fill the reaction bulb, and also to heat the connections to the manometer to prevent the formation of liquid nitrous oxide which would lead to a discrepancy between the observed rate of pressure increase and the true rate of reaction. It becomes necessary to heat the dead space of the system above the critical temperature, 36.5° C., for all experimental pressures much above 40 kg./cm.<sup>2</sup>, for when the half-life is reached at about 50–60 kg./cm.<sup>2</sup> the pressure is sufficient to liquefy the unreacted nitrous oxide in the dead space if this is at room temperature. These experiments above 40 kg./cm.<sup>2</sup> were not successful. On a number of occasions the reaction bulb exploded, probably as a result of contamination of the gas with grease forced from the valve packings by the heating. It is possible that the use of valves packed with fibre or white metal might cure the trouble.

Three of these experiments, although unsatisfactory from the point of view of temperature control and reaction velocity measurement, have provided some of the data for Table VII, which shows the amount of by-product nitric oxide formed during reaction at different pressures.

Table 1.—Typical Measurements of the Velocity of Decomposition of Nitrous Oxide at High Pressures.

857·8° K.			887·7° K.			875·0° K.		
Time from entry of gas.	Thermo-couple. Millivolts.	Pressure Kg./cm. <sup>2</sup> .	Time from entry of gas.	Thermo-couple. Millivolts.	Pressure Kg./cm. <sup>2</sup> .	Time from entry of gas.	Thermo-couple. Millivolts.	Pressure Kg./cm. <sup>2</sup> .
min. sec.			min. sec.			min. sec.		
0 5	5·400	37·52	0 21	5·750	24·62	0 19	5·601	18·41
1 5	5·395	37·57	0 34	5·750	24·77	0 40	5·600	18·46
1 6	5·395	37·62	0 42	5·747	24·78	1 30	5·599	18·56
1 7	5·395	37·72	1 2	5·747	24·88	2 30	5·600	18·70
2 2	5·400	37·93	1 28	5·753	25·05	3 15	5·599	18·85
3 5	5·401	38·03	2 9	5·753	25·26	4 30	5·599	18·98
4 0	5·400	38·18	2 46	5·752	25·47	5 45	5·600	19·09
5 5	5·400	38·33	3 23	5·752	25·73	6 40	5·600	19·25
6 3	5·400	38·53	4 19	5·749	25·95	7 30	5·600	19·35
7 5	5·400	38·68	5 4	5·750	26·21	8 52	5·600	19·51
8 0	5·397	38·94	5 50	5·749	26·42	10 5	5·600	19·66
10 0	5·400	39·19	7 20	5·750	26·83	12 13	5·599	19·92
11 0	5·400	39·44	8 28	5·750	27·14	13 33	5·601	20·07
12 2	5·399	39·59	9 31	5·750	27·30	15 6	5·601	20·22
13 7	5·399	39·64	10 40	5·750	27·56	16 36	5·600	20·36
15 2	5·400	39·94	11 33	5·748	27·82	18 37	5·602	20·61
16 7	5·400	40·20	12 40	5·750	28·07	19 40	5·602	20·71
18 5	5·401	40·50	13 35	5·749	28·21	20 30	5·601	20·81
19 3	5·399	40·65	14 25	5·749	28·41	21 25	5·600	20·90
21 0	5·402	40·84	16 0	5·748	28·75	22 28	5·598	21·00
23 8	5·402	41·14	17 15	5·750	28·99	23 27	5·600	21·10
24 2	5·397	41·29	18 30	5·750	29·22	25 5	5·601	21·23
26 0	5·400	41·54	19 45	5·750	29·41	26 30	5·600	21·36
28 0	5·399	41·84	21 23	5·750	29·71	28 0	5·600	21·50
30 0	5·402	42·03	22 30	5·752	29·99	29 0	5·599	21·60
31 5	5·400	42·23	23 50	5·750	30·09	30 20	5·598	21·70
33 0	5·403	42·43	25 10	5·750	30·28	32 10	5·600	21·85
37 8	5·402	42·93	26 20	5·747	30·43	33 27	5·600	21·95
38 2	5·402	43·13	27 25	5·750	30·58	34 55	5·597	22·00
40 5	5·400	43·32	28 35	5·747	30·75	37 0	5·600	22·24
41 7	5·399	43·43	29 43	5·750	30·87	39 0	5·597	22·33
43 0	5·401	43·53				40 45	5·603	22·48
45 8	5·402	43·78				42 28	5·601	22·57
47 7	5·400	44·03				43 30	5·600	22·66
48 5	5·403	44·23				44 50	5·601	22·76
49 0	5·402	44·33				46 30	5·602	22·85
51 8	5·400	44·43				47 52	5·600	22·94
53 0	5·400	44·73				49 17	5·600	23·03
55 2	5·403	44·94				51 28	5·601	23·12
58 5	5·403	45·14				54 30	5·600	23·27
60 0	5·400	45·39				56 0	5·602	23·36
62 0	5·402	45·59						
64 5	5·399	45·74						
65 52	5·402	45·84						
67 17	5·400	46·00						
69 18	5·400	46·20						
71 15	5·400	46·35						
74 30	5·400	46·55						
75 10	5·400	46·65						
76 20	5·401	46·74						
78 15	5·398	46·93						
81 5	5·399	47·19						

## RESULTS.

*The Velocity of Reaction at Pressures up to 2000 mm. Hg (2.72 kg./cm.<sup>2</sup>). Low Pressure Apparatus.*

The results at pressures below 500 mm. were obtained with the normal low pressure apparatus; those above this pressure with the low pressure apparatus fitted with closed manometer.

Table II.

913.5° K.		971° K.		996.5° K.	
Initial pressure, mm. Hg.	Half-life, secs.	Initial pressure, mm. Hg.	Half-life, secs.	Initial pressure, mm. Hg.	Half-life, secs.
180	7350	220	910	228	416
400	4760	390	675	375	317
759	3270	832	494.4	829	231.6
1137	2778	988	436.5	932	207.4
1506	2226	1119	399.3	1049	195
1816	2160	1315	369	1126	182.3
2120	1893	1683	307.5	1208	175
		1896	286.2	1278	178.1
		2002	287.5	1385	166.7
				1460	159.7
				1574	148.6
				1728	142.7
				1853	139.2
				1930	131.4
				1983	129.6
				2026	132.2
				2165	122.2

*The Velocity of Reaction at Pressures up to 40 atms. High Pressure Apparatus.*

Table III.—Temperature: 614.7° C., 887.7° K. 1 kg./cm.<sup>2</sup> = 0.967 atms.

Pressure, kg./cm. <sup>2</sup> .	Half-life, secs.	Pressure, kg./cm. <sup>2</sup> .	Half-life, secs.
0.36*	13,824	10.63	2,415
0.46*	11,394	12.50	2,093
0.54	9,540	12.84	2,123
2.44	4,815	19.20	1,836
3.40	3,490	24.61	1,542
3.97	3,220	26.67	1,560
4.65	2,970	30.40	1,493
5.64	2,835	32.86	1,482
6.76	2,850	36.45	1,459
8.70	2,425	39.56	1,454

\* Low pressure apparatus.

Table IV.—Temperature : 644.7° C., 917.7° K. 1 kg./cm.<sup>2</sup> = 0.967 atms.

Pressure, kg./cm. <sup>2</sup> .	Half-life, secs.	Pressure, kg./cm. <sup>2</sup> .	Half-life, secs.
0.53	3,115	7.24	762
2.21	1,680	9.26	711
3.05	1,240	10.78	663
3.59	1,044	12.20	665
4.64	863	12.85	604
5.80	819		

Table V.—Temperature : 657.5° C., 930.5° K. 1 kg./cm.<sup>2</sup> = 0.967 atms.

Pressure. kg./cm. <sup>2</sup> .	Half-life, secs.	Pressure, kg./cm. <sup>2</sup> .	Half-life, secs.
0.52	2,195	6.40	534
2.20	957	7.99	473
2.97	767	9.22	429
3.98	658	11.26	398
5.13	585	12.73	348

Table VI.—Change of Reaction Velocity with Temperature and Change of Activation Energy with Pressure at Constant N<sub>2</sub>O Concentration.

Temperature, ° K.	Pressure, kg./cm. <sup>2</sup> .	log <sub>10</sub> (1/t <sub>4</sub> ).		Activation energy E, cals./gm. mol.
		Observed.	Calculated.	

1. Pressure 37½ kg./cm.<sup>2</sup>.

840.9	37.0	4.0545	4.054	} 64,900
857.8	37.4	4.383	4.386	
866.2	38.1	4.544	4.546	
875.0	37.85	4.711	4.710	

2. Pressure 18¼ kg./cm.<sup>2</sup>.

840.9	18.2	5.948	5.935	} 63,900
857.8	18.05	4.256	4.261	
866.2	18.6	4.421	4.419	
875.0	18.4	4.5755	4.581	

3. Pressure 0.53 kg./cm.<sup>2</sup>, 390 mm. Hg.

904.3	} 61,000	0.526	4.2645	4.280
919.6		0.524	4.542	4.528
934.7		0.536	4.501	4.761
951.5		0.533	4.796	3.013
968.5		0.546	3.0075	3.260
		0.536	3.2640	

Table VI.—(continued).

Temperature, ° K.	Pressure, kg./cm. <sup>2</sup> .	$\log_{10}(1/t_1)$ .		Activation energy E. cals./gm. mol.
		Observed.	Calculated.	
4. Pressure 0.26 kg./cm. <sup>2</sup> , 190 mm. Hg.				
904.3	0.250	4.095	4.109	} 55,200
934.7	0.256	4.558	4.542	
951.5	0.252	4.7545	4.770	
968.5	0.265	4.770	4.994	
985.8	0.255	4.985	3.213	
	0.258	3.220		
5. Pressure 0.14 kg./cm. <sup>2</sup> , 105 mm. Hg.				
904.3	0.143	5.930	5.943	} 53,750
	0.137	5.900		
919.6	0.137	4.1845	4.160	
	0.137	4.1725		
951.5	0.143	4.540	4.588	
	0.146	4.631		
968.5	0.141	4.790	4.805	
999.0	0.144	3.192	3.175	
6. Pressure 0.10 kg./cm. <sup>2</sup> , 73.5 mm. Hg.				
916.5	0.10	4.0575	4.050	} 53,000
934.7	0.10	4.2775	4.298	
951.5	0.10	4.510	4.518	
968.5	0.10	4.750	4.732	
985.8	0.10	4.941	4.941	
999.0	0.10	3.103	3.096	

Table VII.—The Amount of By-Product Nitric Oxide formed at various Pressures at 590° C.

Initial pressure of N <sub>2</sub> O, kg./cm. <sup>2</sup> .....	11.4	18.2	24.1	33.3	45.3	51.0	63.3
Molecules % NO at the half-life .....	0.11	0.10	0.09	0.07	0.07	0.08	0.09

Nitrous oxide from cylinder (97 % N<sub>2</sub>O) ... 0.0065 mols. % NO.

### Discussion.

The results obtained with the low pressure apparatus, which are shown in fig. 4, are clearly in agreement with the observations of Hinshelwood and Burk and Musgrave and Hinshelwood (*loc. cit.*), since straight-lines can be drawn for  $1/t_1$  against the pressure as far as 2000 mm. Hg. From the work of Musgrave and Hinshelwood we know that these lines can be expected to bend sharply towards the origin at some pressure in the neighbourhood of 60 mm. Hg.

Table VIII.—Temperature 888° K.

1	2	3	4	5	6	7	8
Pressure kg./cm. <sup>2</sup> .	Reacting molecules ÷ 2.5 × colliding molecules	$e^{-E/RT}$ .	Ratio Col. 2/Col. 3.	$f(E)$ $n = 4$ .	Ratio Col. 2/Col. 5.	$f(E)$ $n = 6$	Ratio Col. 2/Col. 7.
0.54	$1.93 \times 10^{-14}$	$9.3 \times 10^{-16}$	20.7	$144 \times 10^{-16}$	1.34	$11.8 \times 10^{-14}$	0.164
2.44	$0.856 \times 10^{-14}$	$5.01 \times 10^{-16}$	17.1	$79 \times 10^{-16}$	1.08	$6.55 \times 10^{-14}$	0.130
3.40	$0.87 \times 10^{-14}$	$4.17 \times 10^{-16}$	20.8	$66 \times 10^{-16}$	1.32	$5.50 \times 10^{-14}$	0.158
3.97	$0.78 \times 10^{-14}$	$3.89 \times 10^{-16}$	20.0	$62 \times 10^{-16}$	1.25	$5.15 \times 10^{-14}$	0.152
4.65	$0.736 \times 10^{-14}$	$3.39 \times 10^{-16}$	21.7	$54 \times 10^{-16}$	1.36	$4.50 \times 10^{-14}$	0.164
5.64	$0.63 \times 10^{-14}$	$3.16 \times 10^{-16}$	19.9	$50.4 \times 10^{-16}$	1.25	$4.24 \times 10^{-14}$	0.148
6.76	$0.52 \times 10^{-14}$	$2.95 \times 10^{-16}$	17.6	$47.1 \times 10^{-16}$	1.10	$3.97 \times 10^{-14}$	0.132
8.70	$0.476 \times 10^{-14}$	$2.51 \times 10^{-16}$	19.0	$40.1 \times 10^{-16}$	1.19	$3.40 \times 10^{-14}$	0.140
10.63	$0.39 \times 10^{-14}$	$2.34 \times 10^{-16}$	16.7	$37.6 \times 10^{-16}$	1.04	$3.19 \times 10^{-14}$	0.122
12.50	$0.385 \times 10^{-14}$	$2.04 \times 10^{-16}$	18.9	$32.9 \times 10^{-16}$	1.17	$2.80 \times 10^{-14}$	0.138
12.84	$0.366 \times 10^{-14}$	$2.04 \times 10^{-16}$	17.9	$32.9 \times 10^{-16}$	1.11	$2.80 \times 10^{-14}$	0.130
19.20	$0.404 \times 10^{-14}$	$1.66 \times 10^{-16}$	24.4	$26.9 \times 10^{-16}$	1.50	$2.30 \times 10^{-14}$	0.176
24.61	$0.265 \times 10^{-14}$	$1.45 \times 10^{-16}$	18.3	$24.6 \times 10^{-16}$	1.08	$2.02 \times 10^{-14}$	0.130
26.67	$0.240 \times 10^{-14}$	$1.35 \times 10^{-16}$	17.8	$22.0 \times 10^{-16}$	1.09	$1.90 \times 10^{-14}$	0.126
30.40	$0.222 \times 10^{-14}$	$1.23 \times 10^{-16}$	18.0	$20.0 \times 10^{-16}$	1.11	$1.74 \times 10^{-14}$	0.128
32.86	$0.207 \times 10^{-14}$	$1.18 \times 10^{-16}$	17.5	$19.3 \times 10^{-16}$	1.07	$1.67 \times 10^{-14}$	0.124
36.45	$0.190 \times 10^{-14}$	$1.07 \times 10^{-16}$	17.7	$17.5 \times 10^{-16}$	1.09	$1.52 \times 10^{-14}$	0.124
39.56	$0.176 \times 10^{-14}$	$1.00 \times 10^{-16}$	17.6	$16.4 \times 10^{-16}$	1.07	$1.42 \times 10^{-14}$	0.124

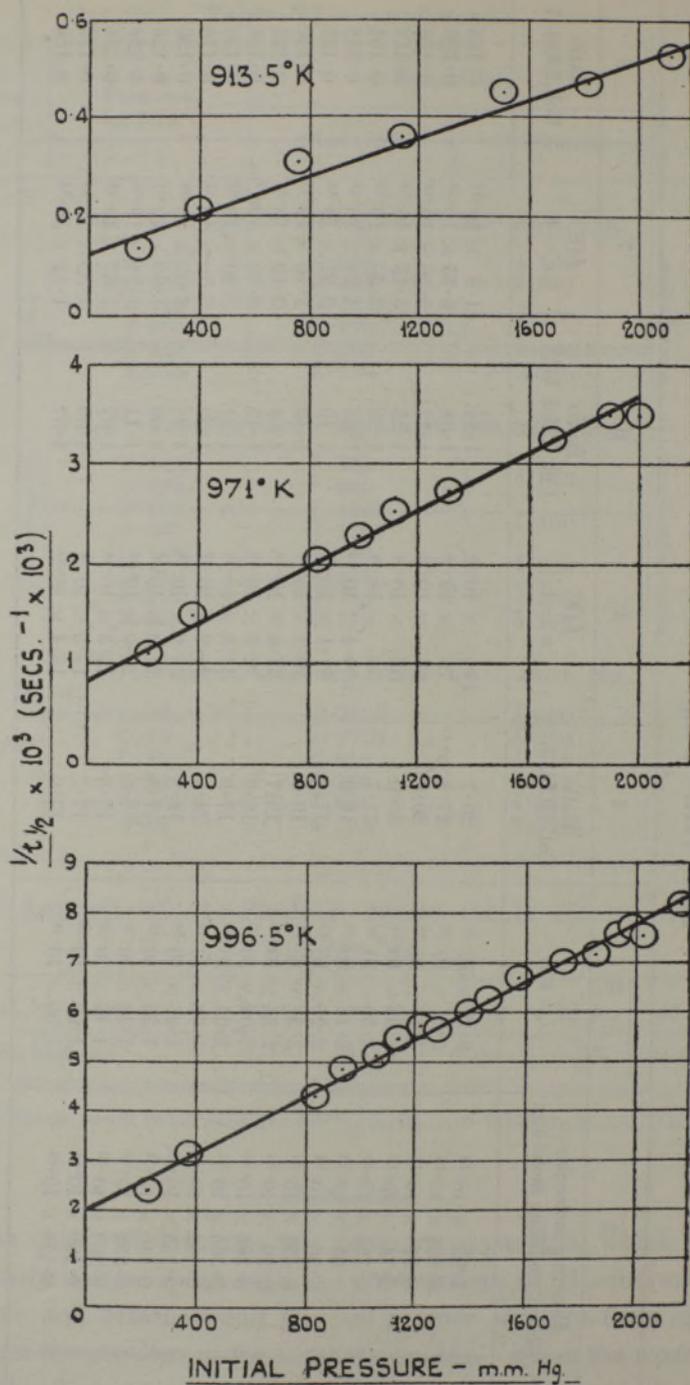


FIG. 4.

At 2000 mm. Hg, a pressure at which Volmer found an approach to true unimolecular velocity constants, there are no indications whatever of the line  $1/t_{1/2}$  against  $p$  tending to become horizontal.

The curve for the complete pressure range at 888° K. is shown in fig. 5; the straight line extending to at least 3 kg./cm.<sup>2</sup> in fig. 4 is found to bend over fairly sharply at about 4 kg./cm.<sup>2</sup> to another straight line of smaller slope which persists to about 26 kg./cm.<sup>2</sup> before curving away. Above 30 kg./cm.<sup>2</sup> the half-life is almost independent of pressure.

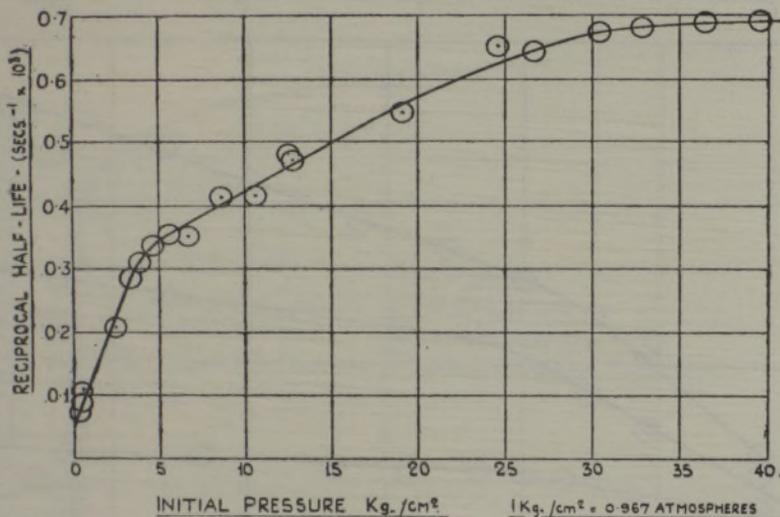


FIG. 5.

The measurements given in Tables IV and V were made to see whether any shifting of the bend at 4 kg./cm.<sup>2</sup> with change of temperature could be discovered. The curves of fig. 6 show that within the range of temperature employed, change of temperature produces no definite change of the pressure at which the bend occurs.

The results of Table VII, which show the amount of nitric oxide formed during reaction, give an assurance that at high pressures catalysis by this by-product is no more serious than it is at low pressures. Musgrave and Hinshelwood found that at an initial pressure of 200 mm. Hg of nitrous oxide, about 3½% of nitric oxide was formed during reaction; at 500 mm. Hg this had fallen to less than 2%. Table VII shows that the percentage of nitric oxide formed continues to decrease with rising pressure.

The results of measurements made to determine the activation energy are given in Table VI. For each series straight lines are obtained by plotting

$1/K^\circ$  against  $\log 1/t_{1/2}$ . The values of  $\log 1/t_{1/2}$  calculated back from these straight lines are tabulated in column 4. The inferior accuracy of the two series at the lowest pressures, 75 and 100 mm. Hg, is due to the difficulty of measuring accurately with an ordinary manometer, a pressure increase of only 18 to 25 mm. Hg. An attempt was made to carry out each series at constant initial concentration of  $N_2O$  rather than at constant initial pressure, by taking into account the variation of pressure with temperature at constant concentration, and adjusting the initial pressures accordingly. The activation energies, calculated on the assumption that the slopes of the lines  $1/K^\circ$  against

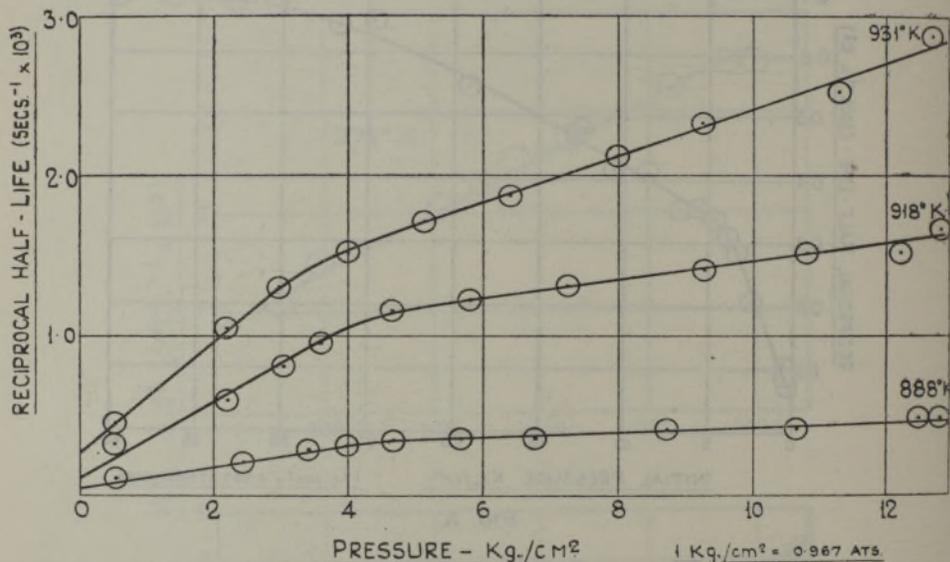


FIG. 6.

$\log_e 1/t_{1/2}$  at constant initial concentration are equal to  $E/R$ , are given in column 5, and are plotted against the pressure in fig. 7. In this graph the results of Musgrave and Hinshelwood for zero pressure, Hinshelwood and Burk for pressures between 100 and 400 mm. Hg, and M. A. Hunter for atmospheric pressure are included. Between 0 and 4 kg./cm.<sup>2</sup> there is a great increase of activation energy with increasing pressure. Above this pressure there is little further change to 40 kg./cm.<sup>2</sup>. These results are at variance with those of Volmer and Nagasako,\* who give an activation energy of 53,000 cal./gm. mol. for all pressures up to 10 kg./cm.<sup>2</sup>. There is little doubt, however, that fig. 7 shows the true behaviour, since it is supported both by the satisfactory results of Table VI and by the results of other workers. It is likely that we

\* 'Z. phys. Chem.,' B, vol. 9, p. 141 (1930).

are concerned with at least two, and possibly more, simultaneous reactions, each with a different activation energy. It remains to be decided whether or not the hypothesis that a unimolecular reaction proceeds alongside a bimolecular one is sufficient. Fig. 5 shows that it is not. The straight line for  $1/t_{1/2} - p$  does not continue indefinitely, but bends to another practically straight line of smaller slope, which in turn is succeeded by one which is almost horizontal.

Recent work on the thermal decomposition of acetaldehyde by Hinshelwood and Fletcher\* has produced results which correspond closely to those for

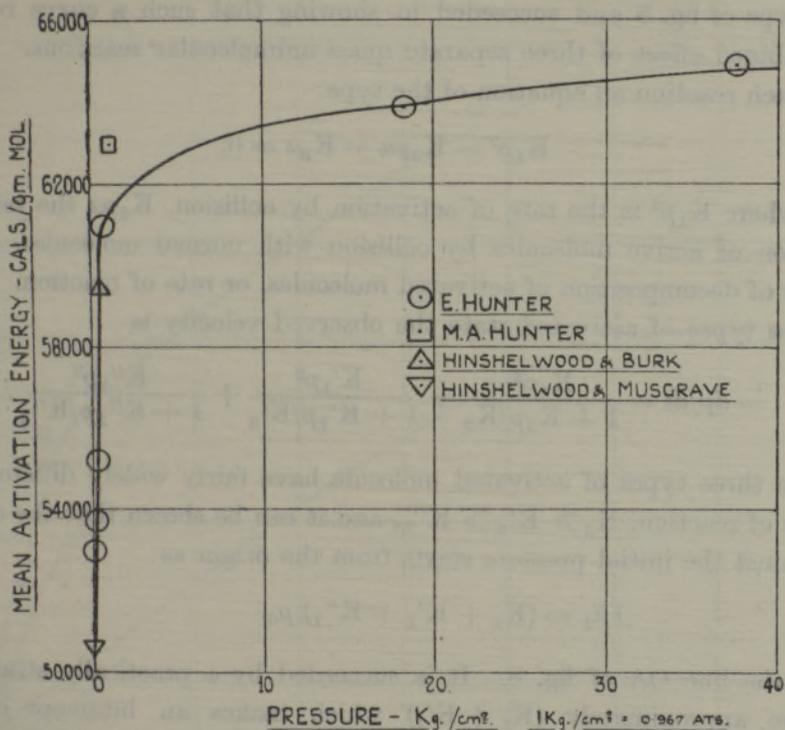


FIG. 7.

nitrous oxide, except for their much smaller pressure scale. The same type of segmented curve was obtained, with sharp bends at 3, 45, and 250 mm. Hg. In order to account for the behaviour of acetaldehyde the theory was put forward that the molecule can be activated in a definite number of different ways, according to the manner in which the energy is divided within the molecule between the different modes of vibration or rotation. In quasi-unimolecular reactions the time lapse between the instant of activation of the molecule by collision and the instant of its decomposition probably arises

\* 'Proc. Roy. Soc.,' A, vol. 141, p. 41 (1933).

from the necessity for a re-arrangement of the energy within the molecule before a state favouring decomposition is brought about. It is conceivable that the time taken for this re-arrangement will depend on how the energy has been distributed between the modes of vibration according to the particular way in which the molecule has been activated. If a definite number of different ways of activation are possible they will lead to the same definite number of independent quasi-unimolecular reactions.

In their paper, Hinshelwood and Fletcher made a rough analysis of a curve of the type of fig. 5 and succeeded in showing that such a curve represents the combined effect of three separate quasi-unimolecular reactions.

For each reaction an equation of the type

$$K_1 p^2 - K_2 p a - K_3 a = 0,$$

holds, where  $K_1 p^2$  is the rate of activation by collision,  $K_2 p a$  the rate of deactivation of active molecules by collision with normal molecules, and  $K_3 a$  the rate of decomposition of activated molecules, or rate of reaction. If there are three types of activated state the observed velocity is

$$- dp/dt = \frac{K_1 p^2}{1 + K_2 p/K_3} + \frac{K'_1 p^2}{1 + K'_2 p/K'_3} + \frac{K''_1 p^2}{1 + K''_2 p/K''_3}.$$

If the three types of activated molecule have fairly widely different probabilities of reaction,  $K_3 \gg K'_3 \gg K''_3$ , and it can be shown that the curve for  $1/t_1$  against the initial pressure starts from the origin as

$$1/t_1 = (K_1 + K'_1 + K''_1) p_0.$$

This is the line OA of fig. 8. It is succeeded by a practically straight line of slope approximately  $(K_1 + K'_1)$  which makes an intercept of about  $K''_1 K''_3 / K''_2 \log 2$ , on the axis of  $1/t_1$ . This line, AB in fig. 8, represents the reaction velocities at pressures between 50 and about 3000 mm. Hg, and its intercept is that which appears in figs. 4 and 5. In this region one of the three reactions has reached its limiting velocity constant. At a higher pressure the second reaction reaches its limiting velocity constant, and the line of slope  $(K_1 + K'_1)$  is followed by a line of slope  $K_1$ , directed to a still larger intercept on the axis of  $1/t_1$ . This third line is BC in fig. 8 which eventually becomes practically horizontal as the rising pressure causes the third reaction to approach its limiting velocity constant.

The methods of this analysis give for the nitrous oxide decomposition the three quasi-unimolecular curves OEF, OGH, and OJK of fig. 8. Although it

is clear that three separate curves can account for the shape of the experimental curve OABCD, fig. 8 does not show more than the approximate magnitudes and shapes of the three curves, since the limiting velocity constants LF, LH, and LK are not sufficiently widely separated to fulfil the condition  $K_3 \gg K'_3 \gg K''_3$ , which is necessary before the above analysis can be expected to hold almost quantitatively.

It is now possible to explain the activation energy curve of fig. 7. Each of the three reactions has its own activation energy. At low pressures ( $< 50$  mm.

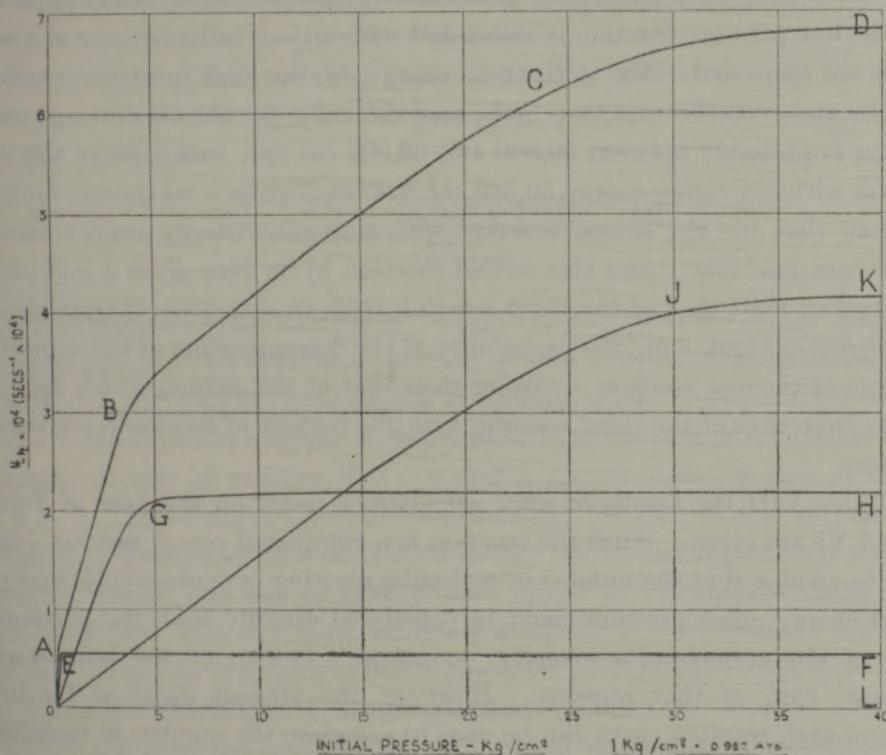


FIG. 8.

Fig) the low pressure reaction OEF of fig. 8 contributes a greater fraction to the decomposition than either the medium pressure reaction OGH, or the high pressure reaction OJK, but as the pressure rises these latter two reactions participate to a greater and greater extent. The curve for the average activation energy consequently shows a rapid change in E with increasing pressure. At about 5 kg./cm.<sup>2</sup>, however, both the low pressure and the medium pressure reactions are giving their maximum possible reaction velocities, and their combined contributions are quite a large fraction of the total. The increase in

velocity on increasing the pressure above about 5 kg./cm.<sup>2</sup> is due solely to the growth of the high pressure reaction OJK of fig. 8 and the measured mean activation energy no longer shows such a rapid change with increasing pressure. Above a pressure of about 30 kg./cm.<sup>2</sup> the limiting velocity constants of all three reactions are reached and the observed activation energy becomes independent of pressure, since the relative contributions of the three reactions do not vary with pressure.

The absolute values of all three activation energies cannot be deduced from fig. 7 since each may itself vary continuously with pressure. It is apparent that the low pressure reaction is associated with an activation energy of about 50,500 cal./gm. mol. The activation energy of the high pressure reaction must be above 65,000 cal./gm. mol., and the value for the medium pressure reaction is probably between 50,500 and 62,000 cal./gm. mol. Since the first reaction with activation energy 50,500 cal./gm. mol. gives a maximum velocity less than that for the second reaction with activation energy approximately 60,000 cal./gm. mol.; and this second reaction in its turn gives a maximum velocity less than that of the third reaction with an activation energy greater than 65,000 cal./gm. mol., the probability of the decomposition of the activated molecule of the first reaction is smaller than that of the second, which again is smaller than that of the third reaction with the highest of the three activation energies.

In Table VIII the results of some calculations based on the data of Tables III and VI are given. Since the reaction is a compound one it was not justifiable to assume that the number of molecules reacting per cubic centimetre per second at any given pressure could be calculated directly from the particular value of the unimolecular velocity "constant"  $\ln 2/t_{\frac{1}{2}}$ , or the bimolecular constant,  $1/at_{\frac{1}{2}}$  at that pressure. However, the tangent  $dp/dt$  at the time origin of each reaction curve can be used to calculate the number of molecules reacting, since the pressure increase is brought about by the formation of three molecules in place of two of nitrous oxide. It was found that the number calculated in this way always agreed to within 10% of the number calculated from the different values of  $\ln 2/t_{\frac{1}{2}}$  (the unimolecular "constant") over the pressure range. The numbers calculated in the latter way were used in Table VIII since the values of  $t_{\frac{1}{2}}$  were known more accurately than the values of the tangents at the very start of the reactions, which were not easy to determine accurately.

In column 2 of Table VIII is shown the ratio, reacting molecules/(2.5 × calc. no. of colliding molecules). The number of collisions was calculated

on the assumption that the diameter of the nitrous oxide molecule is  $3.32 \times 10^{-8}$  cm. The factor 2.5 is used to compensate for the increased number of collisions due to the higher than average velocity of the high translational energy molecules which are likely to be concerned in activating collisions and for the possibility that a particular orientation of the molecules at the moment of impact is necessary.

The values calculated for the expression  $e^{-E/RT}$  from the data of Table VI are given in column 3 of Table VIII, and it will be seen that activation energy associated with only two square terms can only account for one-twentieth of the observed reaction, as is shown in column 4.

The fraction of the molecules possessing energy greater than  $E$ , distributed between a number of degrees of freedom is given as a sufficient approximation by the expression

$$\frac{e^{-\left(\frac{E + (\frac{1}{2}n - 1)RT}{RT}\right)} \cdot [E/RT + (\frac{1}{2}n + 1)]^{\frac{1}{2}n - 1}}{\frac{1}{2}n - 1},$$

where  $n$  represents the number of "square terms" between which the energy is distributed. This expression, worked out for nitrous oxide, gives for  $n = 4$  and  $n = 6$ , the values which appear in columns 5 and 7, respectively of Table VIII. The ratios in columns 6 and 8 show that the rate of activation can be equated to rate of reaction if  $n = 4$  and is greater than the rate of reaction if  $n = 6$ . This implies a distribution of energy between two, or at most three degrees of freedom, so that activation energy can be distributed between translational energy and one or perhaps two modes of vibrational energy within the molecule. It is now fairly generally accepted that the atoms of the nitrous oxide molecule lie in a straight line in the order NNO; two or even three degrees of freedom is therefore not an unreasonable number.

Since the observed reaction can be regarded as the resultant of three quasi-unimolecular reactions, the thermal decomposition of nitrous oxide is principally concerned with the isolated molecule, which presumably breaks up according to the scheme:  $N_2O \longrightarrow N_2 + O$ . This free oxygen atom must react rapidly, either with a second free atom,  $O + O \longrightarrow O_2$ , or with a fresh nitrous oxide molecule  $O + N_2O \longrightarrow N_2 + O_2$ , and the measured pressure increase will be that corresponding to the stoichiometric equation  $2N_2O \longrightarrow 2N_2 + O_2$ .

The author wishes to thank Mr. C. N. Hinshelwood for his help and advice throughout the work, and Mr. W. R. D. Manning, of the Department, for his help in the design of the apparatus.

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*Summary.*

Apparatus for the study of gas reactions by the static method at pressures up to 100 atms. and at temperatures up to 900° C. is described.

Results of measurements of the velocity of thermal decomposition of nitrous oxide at pressures up to 40 atms. are given. In conjunction with the work of Musgrave and Hinshelwood\* they show clearly that the observed reaction is the resultant of three separate quasi-unimolecular reactions which become independent of pressure at approximately 0.08, 5, and 30 atms., respectively.

The average activation energy of the reaction has been measured at different pressures and is found to rise rapidly from the value 50,500 cal./gm. mol. at zero pressure until a pressure of about 6 atms. is reached. As the pressure rises above 6 atms. it becomes less and less dependent upon pressure, and is practically independent of pressure above 30 atms.

The behaviour of the reaction suggests that there are three separate modes of activation, each with a different mean activation energy and a different probability of decomposition of the activated molecule.

\* 'Proc. Roy. Soc.,' A, vol. 135, p. 23 (1932).

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