

(3) The reaction time of the direct growth-response is constant for a particular intensity of illumination, provided that the duration of the exposure period exceeds a certain value. Below that value the reaction time increases as the exposure time decreases. This is also true for the phototropic response.

(4) The manner in which the reaction time of each mode of response varies as a function of the time of exposure to light is shown to be similar. It is therefore concluded that the two responses have the same functional basis, namely, the light-sensitive system under investigation. This conclusion accords with the reasonable conception of plant phototropism developed by Blaauw.

(5) With both modes of response, if an appropriate constant is subtracted from the reaction times the reciprocals of the resulting numbers follow a linear sequence when plotted against the durations of the exposure to light. The rate of the process occurring during the latent period is therefore considered to be directly proportional to the amount of preceding photochemical change.

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THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT VERY LOW PRESSURES

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§1. *Introduction.*—In a previous article¹ the results have been reported of some experiments on the rate of decomposition of gaseous nitrogen pentoxide at moderately low pressures in the range 0.2 to 2 mm. of mercury. The special features of the experimental method employed, included the use of a very large reaction vessel constructed from a 45-liter flask, thus minimizing the effect of the walls, and the use of a specially sensitive "click" gauge to follow the reaction by direct pressure measurements, thus avoiding the dangers involved in following the reaction by periodically freezing out the oxides of nitrogen and measuring the evolved

oxygen, as has sometimes been done. The results obtained at these moderately low pressures showed no falling-off in the specific unimolecular rate of decomposition below that obtained at high pressures.

In the present article we desire to report the results of some further experiments on the rate of decomposition of nitrogen pentoxide at total initial pressures down to 0.0055 mm.

§2. *The Apparatus.*—Except for the pressure-measuring device, the apparatus was essentially the same as that previously described. To follow the change in pressure we adopted the general form of the capacitance gauge devised by Olson and Hirst.² In this gauge, the gas whose pressure is to be measured presses against a thin glass diaphragm to which is attached one of the plates of an electrical condenser, the other plate having a fixed position. This condenser is connected in series with a variable condenser, the two condensers together forming the capacity of an oscillating circuit which is loosely coupled with a neighboring circuit, having a constant frequency of oscillation maintained with the help of a piezo-electric quartz crystal. Changes in pressure are then measured by the reading of the variable condenser necessary to secure resonance.

In the final form in which we used this gauge, the movable diaphragm was made from a thin sheet of mica less than 0.002 in. thick, in order to increase sensitivity. This diaphragm was 2 in. in diameter and was sealed at its circumference with "Duco" lacquer so as to close the top of a Pyrex glass chamber which was shaped like an inverted bell and connected at its lower end to a tube leading to the reaction flask.

The movable condenser plate was also made from a thin sheet of mica of approximately the same diameter as the diaphragm and made electrically conducting by gold plating with a commercial preparation used in china painting. It was placed parallel to the diaphragm and cemented at its center to a small glass spacer, cemented in turn to the center of the diaphragm. The electrical connections with this movable condenser plate were made through a narrow strip of thin tin foil so arranged as not to put any strain on the motion of the diaphragm.

The fixed plate of the condenser was made of brass. It was supported in position parallel to the movable plate by a second bell-shaped Pyrex glass chamber ring-sealed to that supporting the diaphragm, in order that temperature changes should not affect the relative position of the two condenser plates, since they were then both supported by practically the same length of Pyrex glass. The distance between the two condenser plates was about 0.3 to 0.4 mm.

Stopcocks were introduced between the gauge and the reaction vessel so that the space below the diaphragm could be opened to the reaction vessel, filled with air at any desired pressure, or completely pumped out. It was also arranged so that we could have vacuum or any desired air

pressure over the diaphragm. The air pressure on either side of the diaphragm could be measured with the help of a McLeod gauge, liquid air traps being introduced between the McLeod gauge and the capacitance gauge so that the vapor pressure of mercury was not registered on the capacitance gauge. These arrangements were made so that the gauge could be continuously calibrated throughout the individual runs.

The electrical circuits for the measurement of capacity had the same layout as given by Olson and Hirst. Except for the A and B batteries, all parts of the circuit, together with the gauge itself, were enclosed in an air thermostat provided with a regulator. During the course of a run, slight adjustments in temperature were purposely made from time to time in order to compensate for a drift in the zero that otherwise occurred. The different portions of the electrical circuits were carefully fastened in position to prevent changes in their relative positions, and electrical shielding was introduced between the circuits and the observer.

We desire to express our thanks to Dr. Arnold Beckman and Dr. Martin Nordberg for assistance in the construction of this gauge.

§3. *The Experimental Procedure.*—The runs were made in three sets. The first set consisting of runs Nos. 1 and 2 was terminated by an accident to the gauge which necessitated a new diaphragm. The second set consisted of runs Nos. 2 to 7.

Following these, a third set consisting of runs Nos. 8 to 11 was made to determine the effect of wall surface. This was done by filling the 45-liter flask with 56 pieces of previously unused soft glass tubing, having an outside diameter of approximately 2.4 cm., and ranging in length from 20 to 45 cm. The tubes were cleaned by wiping on the outside with a dry towel, and on the inside with dry waste followed by very slightly dampened waste, and this in turn again by dry waste. These tubes filled the flask practically full, increasing the ratio of surface to volume from about 0.14 cm.⁻¹ to about 0.73 cm.⁻¹, and very greatly decreasing the distance that an average molecule has to travel to come in contact with the surface.

Before each set of runs, the flask was pumped down to a pressure of about 2×10^{-5} mm. and heated to about 70° to 80°C. for a period of 15 to 20 hours, nitrogen pentoxide being admitted, allowed to decompose, and then repumped out, once or twice during this period to assist in conditioning the surface. The inside of the reaction vessel was at all times protected from mercury vapor by liquid air traps.

The runs were made at approximately 40°C. The temperature was held constant throughout each run to within 0.2°C. and usually much closer, but showed by soundings at 8 different places in the air thermostat a maximum variation of 0.8°C. between different parts of the thermostat. This variation was allowed for by averaging and the final figures given are believed to be reliable to about 0.2°C.

The pentoxide was prepared as in the previous work, and stored in crystalline form in a cooled fore-vessel from which it could be admitted to the reaction flask by evaporation. Working at the very low pressures used in this investigation, the final pressure obtained at the end of a run was never as large as would be calculated from the initial pressure on the assumption that we had pure pentoxide at the start. Such a lack of purity may have resulted from an accumulation of decomposition product in the surface layers of the pentoxide.

In making the individual runs, the rate of decomposition of the pentoxide was followed by pressure measurements made with the capacitance gauge described above. To do this, the gauge was first pumped out and a zero reading for the capacity obtained; connection was then immediately made with the reaction vessel and a new reading for the capacity made. In addition spaced throughout the run an approximately equal number of similar pairs of readings were taken with air pressure on the gauge, these pressures being then measured with a McLeod gauge. In this way the gauge was continuously calibrated against known pressures. The amount of reaction mixture removed by making the pressure measurements in this way was not serious since the reaction flask had a volume of 45,000 cc. and the gauge chamber which had to be pumped out had a volume of only 30 cc.

In obtaining the capacity measurements the procedure which it was found best to adopt was to start with such a capacity in the gauge circuit that the crystal was not oscillating, and then increase the capacity to a point where the crystal started oscillating, which was marked by a sharp decrease in plate current. When readings were not being taken the crystal was always kept not oscillating to prevent heating. In taking the readings several settings were always made in succession, since there was a tendency for a slight drift (several scale divisions) in the readings until a constant value was obtained.

The sensitivity of the pressure-measuring device depended on a number of factors, including the diaphragm used, the total pressure being measured, and the ratio between the capacity of the gauge and the variable capacity in the secondary circuit. For these reasons it varied from about 3.3×10^{-5} mm. to 13.7×10^{-5} mm. for one scale division on the variable condenser (General Radio Co., Type 222). The computed pressures appeared to be reliable to about 1 or 2%.

§4. *The Experimental Results.*—In order to give an idea of the reliability of the results we give, as examples, in tables 1 and 2 the data obtained in run No. 1 where the pressure was moderately high and the specific reaction rates checked well, and in run No. 7, which was our lowest pressure run and gave a relatively large deviation in the individual values for specific reaction rate.

The specific rates were calculated on the basis of a first order decomposition by the interval method, since it gives a fairer idea of any trend in the reaction, even though it gives a poorer check among constants than the overall method. No evidence of trend in rate was found in the case of any of the runs made in the flask without the tubes, but there was always a dropping-off in the calculated specific rates with the progress of the run after the surface had been increased by the introduction of the tubing. This dropping-off in the case of the additional surface was least at the highest pressure.

TABLE 1
Run No. 1 Temperature = 40.04°C.

TIME SECONDS	TOTAL PRESSURE MM.	PRESSURE OF N ₂ O ₅ MM.	SPECIFIC REACTION RATE $k_1(\text{SEC.}^{-1}) \times 10^4$
0			
30	0.0431	0.0370	
330	0.0472	0.0343	2.53
880	0.0534	0.0301	2.32
1650	0.0612	0.0249	2.48
2520	0.0686	0.0200	2.52
3435	0.0746	0.0160	2.44
4410	0.0796	0.0129	2.21
5450	0.0842	0.0096	2.84
16940	0.0972	0.0010	
∞	0.0986	0.0000	
		Average	2.48
		Mean deviation	0.13

TABLE 2
Run No. 7 Temperature = 40.32°C.

TIME SECONDS	TOTAL PRESSURE MM.	PRESSURE OF N ₂ O ₅ MM.	SPECIFIC REACTION RATE $k_1(\text{SEC.}^{-1}) \times 10^4$
0			
100	0.00565	0.00443	
655	0.00645		2.36
1310	0.00730	0.00333	
1950	0.00770		1.50
2735	0.00827	0.00269	
3610	0.00874		1.86
4895	0.00960	0.00180	
6190	0.00995		1.77
7680	0.01065	0.00110	
12260	0.01168		
∞	0.01230		
		Average	1.87
		Mean deviation	0.24

The specific rates were calculated for intervals so chosen as to give a fair picture of the course of the reaction. This was done by dividing the run into a reasonable number of intervals (4-7) in which approximately equal increases in pressure occurred. The first pressure reading, taken as

soon as possible ($1/2$ to 2 min.) after admission of the gas to the flask, was always used as the starting point for the calculations. The initial pressure of the nitrogen pentoxide was calculated by assuming complete decomposition at the end of the run.

A summary of the results obtained in all 11 runs is given in table 3 which is self-explanatory. The runs are arranged in the order of decreasing total initial pressures. The last column gives the ratio of the average specific rate of the run to that calculated for high pressures for the same temperature from the results of Daniels and Johnston.

§5. *Discussion of the Results.*—It is our belief that the results of runs Nos. 1 to 7, as summarized in table 3, give a reasonably correct idea of the homogeneous rate of decomposition of nitrogen pentoxide at very low pressures. In accordance with our previous work, mentioned above, no falling-off in the specific rate was found down to pressures of about 0.2 mm., but in accordance with the present results a falling-off becomes evident at a total initial pressure around 0.04 mm. and continues to become more pronounced down to our lowest pressures around 0.006 mm., where the rate has dropped to about $2/3$ of its high pressure value. Throughout the whole pressure range, however, the rate of homogeneous decomposition is essentially first order, with no trend in the calculated constants with the progress of the run.

TABLE 3

RUN. NO. (NO EXTRA SURFACE)	TEMP. °C.	TOTAL INITIAL PRESSURE MM.	INITIAL PRESSURE N ₂ O ₅ MM.	NO. CON- STANTS CALCU- LATED	SPECIFIC REACTION RATE		RATIO AVERAGE k_1 TO HIGH PRESSURE k_1
					k_1 (SEC. ⁻¹) × 10 ⁴	MEAN DEVIATION	
3	40.32	0.0470	0.0423	6	2.50	0.45	0.947
1	40.04	0.0431	0.0370	7	2.48	0.13	0.973
2	40.04	0.0142	0.0131	7	2.22	0.24	0.871
5	40.32	0.00970	0.00780	5	2.31	0.25	0.875
4	40.32	0.00850	0.00500	4	1.80	0.18	0.682
6	40.32	0.00725	0.00420	4	1.60	0.10	0.606
7	40.32	0.00565	0.00443	4	1.87	0.24	0.708
(WITH TUBES IN FLASK)					RANGE OF k_1		
10	40.32	0.0401	0.0335	7	2.96 to 1.90		1.02
8	40.32	0.0186	0.0119	5	4.69 to 2.62		1.26
9	40.32	0.0111	0.00643	6	4.24 to 2.37		1.33
11	40.32	0.01005	0.00777	5	4.58 to 1.48		1.07

These results, which seem *a priori* to be of a very reasonable nature, are in complete contradiction with the results of all previous investigators. Thus Hirst and Rideal,³ working in the range 1.450 to 0.035 mm., report an increase in specific rate with decreased pressure which became several fold at their lowest pressures. Hibben,⁴ working in the range 0.18 to 0.03 mm. found a slight increase in specific rate, which he believed to be within his experimental error. Sprenger,⁵ working in the range 0.05 to

0.01 mm., came to the conclusion that nitrogen pentoxide decomposes at approximately its high pressure rate when first introduced into the reaction flask, and later, with a considerable fraction of the original pentoxide still remaining, ceases to decompose at all. Finally, Rice, Urey and Wilson⁶ report as a preliminary result a falling-off in the rate even at pressures as high as several centimeters.

We believe that an important factor in explaining these extraordinarily discordant results of previous investigators is to be found in the effect of wall surface which was studied by us in runs Nos. 8 to 11, where we increased the surface to volume ratio from 0.14 cm.^{-1} to 0.73 cm.^{-1} . This increase in surface appears to have the effect at very low pressures of greatly increasing the rate especially at the beginning of the run. Since none of the previous investigators used a reaction vessel anywhere near as large as our 45-liter flask it appears to us quite possible that their results were seriously affected by the surface of the vessel. This consideration would explain the high results of Hirst and Rideal, especially as they found a large falling-off in the specific reaction rate with the progress of the run. In the case of Hibben, who found only a slight increase in rate in the region where we found some decrease, we should have to conclude on this basis that he had a sufficiently inactive surface so that the effect was not great with his surface to volume ratio, which we estimate to have been about 0.5 cm.^{-1} , thus lying in between the two conditions that we studied. As for the results of Sprenger, in the absence of satisfactory confirmatory experiments we cannot in the least accept his conclusion that his nitrogen pentoxide stopped decomposing with a considerable fraction of the original pentoxide still present, and believe that the discrepancy between his initial and final pressure measurements is to be accounted for on the basis of impure nitrogen pentoxide at the start. If rates for his experiments are calculated on this basis they show the same kind of behavior as those of Hirst and Rideal, and could receive the same explanation. Finally the preliminary result of Rice, Urey and Wilson, as they themselves appear to believe, may be affected by analytical inaccuracies and hardly needs discussion at the present time. Although we have discussed above the possibility of wall effect, as a factor in explaining the discordant results of other investigators, this may not be the only factor, especially as there are necessarily many unsatisfactory features about any technique that can be used in measuring the low pressure rate of decomposition of nitrogen pentoxide.

It remains to discuss some of the possible sources of error in our own results as given by runs Nos. 1 to 7 made in the large 45-liter flask in the absence of extra surface. In the first place, there must have been some residual effect of the walls even in this flask and no certain estimate of the extent of this residual effect can be given. Nevertheless, since our

surface to volume ratio was so very much smaller in these runs than in those with the tubes, and the specific rates obtained showed none of the dropping off with progress of the run characteristic of the surface effect, we are inclined to believe that our results are not greatly affected by the surface. It is of interest to note, however, that any correction which should be made for the action of the walls would be in the nature of slightly accentuating the falling-off of the specific rates below their high pressure value. In the second place, it was unfortunate that we had no runs at these very low pressures in which the calculated initial pressure of pentoxide was equal to the total initial pressure. The purity of the pentoxide, calculated after the short interval necessary for the pressure measurement, varied in runs Nos. 1 to 7 from 58 to 92%, in spite of the fact that we endeavored to get pentoxide as free as possible from its decomposition products. Nevertheless, this wide range of purities did not appear to have any effect on the consistency of our results. It is of interest to note also in this connection, however, that if we assumed that the pentoxide was really purer than calculated, the calculated specific rates would have shown even a greater falling-off below the high pressure value. For the present we do not see other possible sources of error which might be serious.

Finally, a word may be said about the bearing of these results on the theory of chemical activation by collision as developed by Rice and Ramsperger, and by Kassel. Qualitatively, the result is very satisfactory since it shows a falling-off in the rate of this unimolecular decomposition at low pressures, as is to be expected when the pressure becomes so low that the molecules cannot be activated fast enough by collisions to maintain the high pressure rate. Quantitatively, however, the result is hard to explain since if we stay within the range of kinetic theory diameters for the molecules we should expect the falling-off to occur at higher pressures. Nevertheless, the quantitative computations of the theory involve considerable complexity and possibility of choice as to assumptions. In any case, we are inclined to regard the falling-off that we have found as evidence in favor of the idea that nitrogen pentoxide receives its energy of chemical activation, at least to a considerable extent, by interaction among the molecules even if these interactions could not be called collisions in the kinetic theory sense.

¹ Ramsperger, Nordberg and Tolman, *Proc. Nat. Acad. Sci.*, **15**, 453 (1929).

² Olson and Hirst, *J. Am. Chem. Soc.*, **51**, 2378 (1929).

³ Hirst and Rideal, *Proc. Roy. Soc.*, **109A**, 526 (1925).

⁴ Hibben, *J. Am. Chem. Soc.*, **50**, 940 (1928).

⁵ Sprenger, *Zeit. physik. Chem.*, **136**, 49 (1928).

⁶ Rice, Urey and Wilson, reported by Rice at the Minneapolis meeting of the American Chemical Society, September, 1929.