greatly increased by the addition of one oxygen atom to form octyl alcohol, indicates by similar reasoning that the oxygen atoms turn toward the water at their interface. Thus the *adhesional energy* toward water is determined by the *strongest electromagnetic fields* in the molecule, while the *tensile energy* is determined by the *weakest fields, provided the molecules are unsymmetrical.*

4. The solubilities of heptylic acid, heptin, and heptaldehyde have been determined, and are found to be nearly the same, which indicates that the length of the hydrocarbon chain is of more importance in determining the solubility than the nature of the active group at the end of the molecule, provided that the activity of the latter is not too widely varied.

5. For the first time the surface energy relations of a paraffin with a triple bond at the end of the molecule have been worked out. The triple bond is found to increase the adhesional work from about 42 to 67, and the total adhesional energy from 105 to 147, the lower values given being those of the corresponding saturated compounds. The introduction of one oxygen atom increases the adhesional work to 90 and the energy to 164. This indicates that the triple bond has a greater relative effect on the adhesional energy than on the adhesional work at 20° as compared with an hydroxyl oxygen atom.

6. The relations worked out in this paper should be of fundamental importance in connection with the study of lubrication, flotation, and all other adhesional phenomena. Similar data for the adhesional relations between mercury and organic liquids have been worked out in this laboratory.

The writers wish to thank Professor Nicolet, of this laboratory, for the preparation of the heptin used and for advice in regard to the methods for purifying heptaldehyde, and the other organic liquids.

The apparatus used was purchased by the use of a grant from the C. M. Warren Fund of the American Academy of Arts and Sciences, to which we express our indebtedness.

CHICAGO, ILL.

THE THERMAL DECOMPOSITION OF GASEOUS NITROGEN PENTOXIDE. A MONOMOLECULAR REACTION.

BY FARRINGTON DANIELS AND ELMER H. JOHNSTON.

In connection with the work of the Fixed Nitrogen Research Laboratory, it became desirable to measure the rate of decomposition of gaseous nitrogen pentoxide. The reaction was found to be monomolecular, a matter of considerable interest, since only one other gaseous monomolecular reaction, the decomposition of phosphine, has been reported in the literature.[1] Since such reactions are of great importance for the theory

[1] Trautz and Bhandarkar, *Z. anorg. allg. chem.*, **106**, 95 (1919).

of chemical kinetics and since the work on phosphine had to be carried
out under very disadvantageous experimental conditions, it seemed de-
sirable to publish the results of the present investigation.

Experimental.

The apparatus in which the decomposition rates were measured is
shown in Fig. 1. It was made entirely of glass, the pressure being trans-
mitted through a platinized glass diaphragm making electrical contact
with a platinized glass knob and then measured with a mercury manom-
eter. The construction and operation of the manometer were the same
as described before[1] except that improvements were made in the platin-
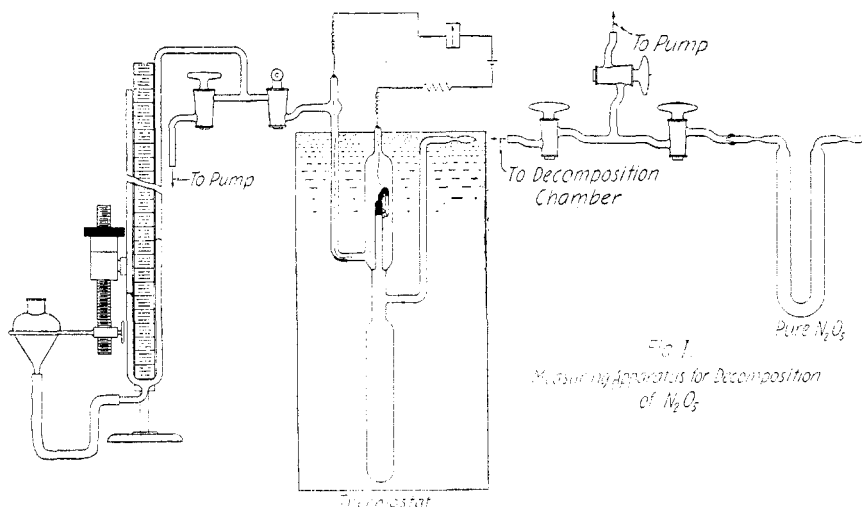izing process.

Fig. 1.
Measuring Apparatus for Decomposition
of N_2O_5

The best platinum coatings were obtained by dipping the bulbs into
absolute alcohol in which were dissolved approximately 1.5 g. of an-
hydrous platinic chloride and an equal weight of oil of lavender per 100
cc. After dipping, the bulbs were immediately held over a piece of sheet
copper heated by a blast lamp. Heating in this manner avoids the
presence of moisture which results in an uneven deposit. The platinum
was burnt in with an alcohol flame in a dark room, since otherwise it is
difficult to avoid overheating. Two or more coats were applied. It
was necessary to have the platinum well burnt in and in the case of the
diaphragms this could not be satisfactorily accomplished if the deposit

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

was too thick. On the other hand, it was necessary to have the deposit as thick as possible to assure a long life. The bulbs were flattened by holding in the flame of a gas blast lamp. It was essential to have the platinum coating so firm that it could not be scratched off with a sharp piece of glass.

The outside of the whole apparatus was painted with a thick coat of black shellac, for the reaction is affected by light. It was immersed completely in a large water thermostat kept at the required temperature within 0.02 or 0.03° as read on a thermometer checked against one which had been calibrated by the Bureau of Standards.

In carrying out a determination the decomposition chamber was connected through a system of 3 stopcocks with a Nelson pump and a tube of purified crystals of nitrogen pentoxide.[1] Temporary joints were made with overlapping glass tubes and de Khotinsky cement. A zero reading with the chamber evacuated was obtained by subtracting the manometer difference from the barometer height. It usually amounted to 20 or 30 mm., which was the excess of external pressure necessary to force the diaphragm away from the knob, plus the 1 or 2 mm. of air which was not removed by the pump. The crystals were next partly evaporated with the help of the pumps; this was done to insure a high degree of purity. The stopcocks were then turned so that the gaseous nitrogen pentoxide passed over into the decomposition chamber, where it was sealed off after reaching the desired pressure. For the high pressure at the higher temperatures it was necessary to raise the vapor pressure of the solid by immersing the tube in warm water. After placing a rubber cap over the sealed-off tube to exclude light the apparatus was lowered into the thermostat until completely immersed.

The course of the reaction was then followed in a simple manner. The air pressure on the manometer side of the diaphragm was made greater than the pressure in the decomposition chamber, so that the electrical circuit was broken. As the reaction proceeded the pressure in the chamber increased until the diaphragm touched the knob, whereuopn the galvanometer gave a sudden deflection. The time at which this deflection occurred was taken with a stopwatch. After raising the leveling bulb and taking the new manometer reading, the galvanometer was again watched and the time of the closing of the electrical circuit recorded. This procedure was repeated as frequently as desired until the reaction was completed and no further increase in pressure was observed over a long period of time (overnight in most cases). All readings were corrected to 0°.

The results are shown in Figs. 2 and 3, where pressure is plotted against time. In the original, the scale was great enough so that one linear

[1] See THIS JOURNAL, **42**, 1133 (1920) for preparation of pure N_2O_5.

millimeter was equivalent to one millimeter of mercury in pressure. Graphical interpolation for regular time intervals on these curves gave the values for pressure (P) and time (t), found in Table II and used in calculating the reaction velocity constants. The starting point of the time readings was taken as the time of lowering the decomposition chamber into the thermostat. The absolute time values have no significance, for the time between admitting the gas and sealing off varied in each experiment, as did also the amount of nitrogen pentoxide decomposed by the hot glass in sealing off the connecting tube. Accordingly, the curves cannot be compared directly with each other. To follow the course of the reaction only the time *difference* between successive pressures is necessary.
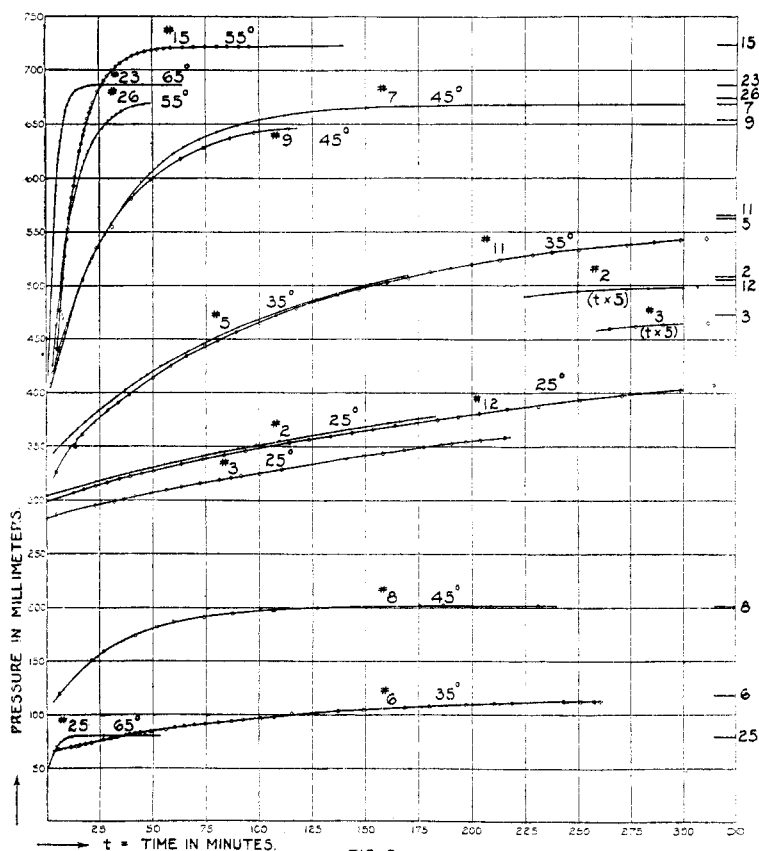

FIG. 2.

Experiments were not made above 65° because accuracy would have to be sacrificed for speed in the observations and because the reaction time would be no longer than the indefinite period of thermal lag, nor below 25° because of the long time involved and the difficulty of operating the

thermostat. Experimental data obtained in the previous research on the vapor pressure of nitrogen pentoxide[1] permitted a calculation of the reaction velocity at these lower temperatures as shown presently.

Calculation of Results.

To obtain the reaction velocity constant it was necessary to know the amount of nitrogen pentoxide taken and the amount remaining undecomposed after each particular time interval. To determine these quantities, it was assumed that the reaction took place in accordance with the following equation

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2. \tag{1}$$

$$4NO_2$$
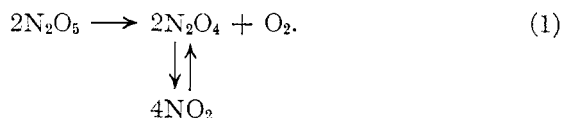
The calculations assumed further that the reaction is irreversible and that the gaseous nitrogen pentoxide exists as N_2O_5 rather than as some higher polymer. There is evidence for both of these assumptions in the literature.[2] Experimental proof of these facts was made, however, in this laboratory with Mr. A. C. Bright. Weighed bulblets of nitrogen pentoxide were broken in a thermostated glass vessel provided with a platinum diaphragm. The final pressures checked with those calculated from the weight of pentoxide taken, on the assumption that the decomposition was complete. Extrapolation of the time pressure curves to zero time showed that without decomposition the molecular weight was 108, corresponding to the formula N_2O_5.

FIG. 3.

A complication which necessitated laborious calculations resulted from the shifting of the $2NO_2 \rightleftharpoons N_2O_4$ equilibrium toward the tetroxide (smaller volume) as the reaction proceeded and the pressure of the mixed oxides increased. An allowance for this effect was made possible, however, from a knowledge of the equilibrium constant,

$$K = \frac{P_{N_2O_4}}{P^2_{NO_2}}.$$

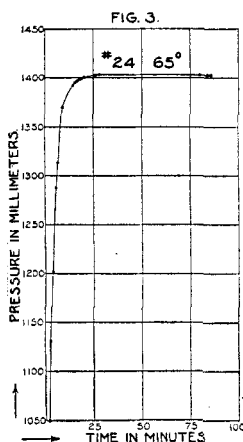From Equation 1 for the reaction, since the total pressure is equal to the sum of the partial pressures, it is evident that we have at any instant,

$$P_{total} = P_{N_2O_5} + P_{N_2O_4} + P_{NO_2} + P_{O_2}. \tag{2}$$

Furthermore, it should be noted that one mol of O_2 results from the de-

[1] *Loc. cit.*

[2] Ehrlich and Russ, *Monatsh.,* **32,** 917 (1911); Russ and Pokorny, *ibid.,* **34,** 1027 (1913).

composition of 2 mols of N_2O_5, and corresponds to 2 mols of N_2O_4 or 4 mols of NO_2.

Expressing all the partial pressures in terms of the partial pressure of oxygen we have then,

$$P_{N_2O_4} = 2P_{O_2}(1-\alpha)$$
$$P_{NO_2} = 4P_{O_2}(\alpha) \qquad (3)$$
$$P_{N_2O_5} \text{ (initial)} = 2P_{O_2} \text{ (final)}$$

where α is the degree of dissociation of the tetroxide.

When decomposition is complete $P_{N_2O_5} = 0$, and we have

$$\begin{aligned} P_f &= P_{N_2O_4} + P_{NO_2} + P_{O_2} \\ &= 2(1-\alpha)P_{O_2} + 4\alpha P_{O_2} + P_{O_2} \\ &= 3P_{O_2} + 2\alpha P_{O_2}. \end{aligned} \qquad (4)$$

The degree of dissociation, α, at different temperatures was calculated from Natanson's[1] work on the equilibrium between nitrogen tetroxide and dioxide, using the following equation,

$$\log K = \log \frac{P_{N_2O_4}}{P_{NO_2}^2} = \frac{2866}{T} - \log T - 9.132 \qquad (5)$$

which Schreber[2] gives as the best expression for Natanson's data. Equation 5 leads to the following values for K at different temperatures.

Temp., ° C.	K.
0	0.08518
15	0.02290
20	0.01516
25	0.01026
35	0.00484
45	0.00239
55	0.00123
65	0.000656

Expressing the partial pressures in terms of the partial pressure of oxygen,

$$K = \frac{P_{N_2O_4}}{P_{NO_2}^2} = \frac{2P_{O_2}(1-\alpha)}{(4P_{O_2}\alpha)^2}$$
$$\frac{\alpha^2}{1-\alpha} = \frac{1}{8KP_{O_2}} \qquad (6)$$

α may be easily obtained from $\alpha^2/(1-\alpha)$ with the help of mathematical tables after substituting the proper numerical values for K and P_{O_2}.

Table I was constructed by giving arbitrary values to P_{O_2} from 1 to 500 millimeters and calculating P_f from Equations 4 and 6.

P_i, the intial pressure of nitrogen pentoxide assuming no decomposition, was obtained by doubling P_{O_2}, since one mol of O_2 is formed by the decomposition of 2 mols N_2O_5.

[1] Natanson, *Wied. Ann.*, **24**, 454 (1885); **27**, 606 (1896)

[2] Schreber, *Z. physik. Chem.*, **24**, 651 (1897).

The results of only a few caculations are given in Table I. These and many others were used for constructing the curves shown in Fig. 4, in which values of P_f, the final pressure after complete decomposition, were plotted as abscissas and P_i, the initial pressures of nitrogen pentoxide without decomposition, as ordinates. Graphical interpolation on these curves was accurate for they were carefully constructed on a large scale, one linear millimeter being equivalent to one millimeter of pressure. It was thus possible to find the initial pressure of pentoxide from the final pressure by use of the curve, whereas it could not be observed experimentally on account of the decomposition occurring while the gas was being introduced and sealed off.

Fig. 4.
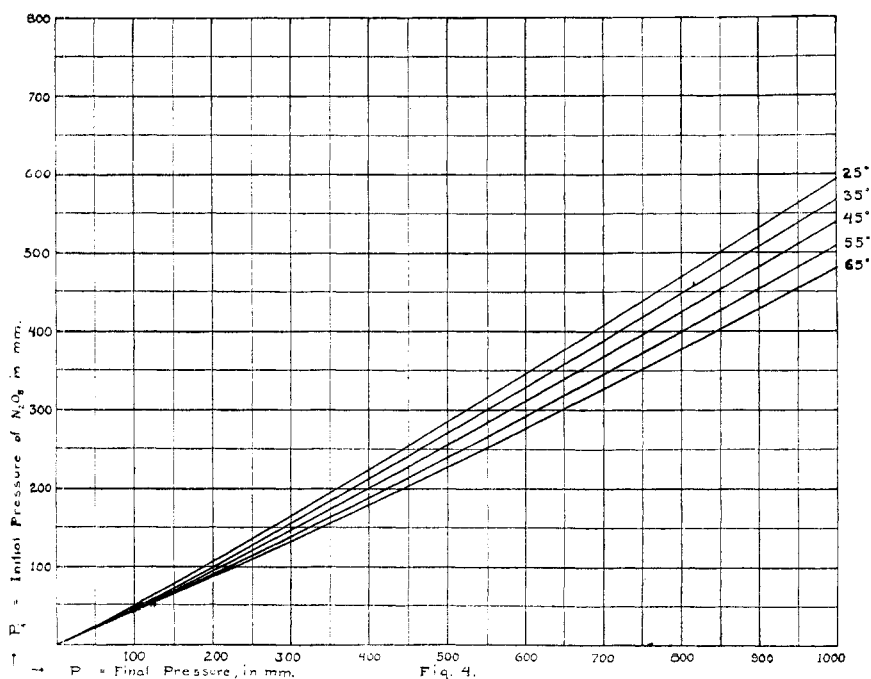
For the reaction velocity constant, it was necessary to know also the amount of pentoxide decomposed at any time t during the course of the reaction. This was obtained in a manner very similar to that just described by putting the increase in pressure, i. e., the observed pressure minus the initial pressure, $(P - P_i)$ equal to $P_{O_2} + 2\alpha P_{O_2}$, where P_{O_2} is the partial pressure of oxygen at the time t.

The reason for this is evident from the following,

$$P = P_i + P_{O_2} + P_{N_2O_4} + P_{NO_2} - p, \qquad (7)$$

where P is the observed pressure at the time t, P_i is the initial pressure of pentoxide, and p is the partial pressure which would be exerted by the

pentoxide which has decomposed up to the time t; p is equal to $2P_{O_2}$ since 2 mols pentoxide give one mol of oxygen on decomposition. $P_{N_2O_4}$ and P_{NO_2} can be expressed in terms of P_{O_2} as before. We obtain,

$$
\begin{aligned}
P &= P_i + P_{O_2} + 2(1 - \alpha)P_{O_2} + 4\alpha P_{O_2} - 2P_{O_2} \\
&= P_i + P_{O_2} + 2\alpha P_{O_2} \\
P - P_i &= P_{O_2} + 2\alpha P_{O_2} = (^1/_2 + \alpha)p.
\end{aligned}
\tag{8}
$$

It is easy, therefore, with the help of Equation 8, to calculate the pressure increase which results when any definite quantity of pentoxide has decomposed. The reverse process, that of calculating the amount of pentoxide

Fig 5
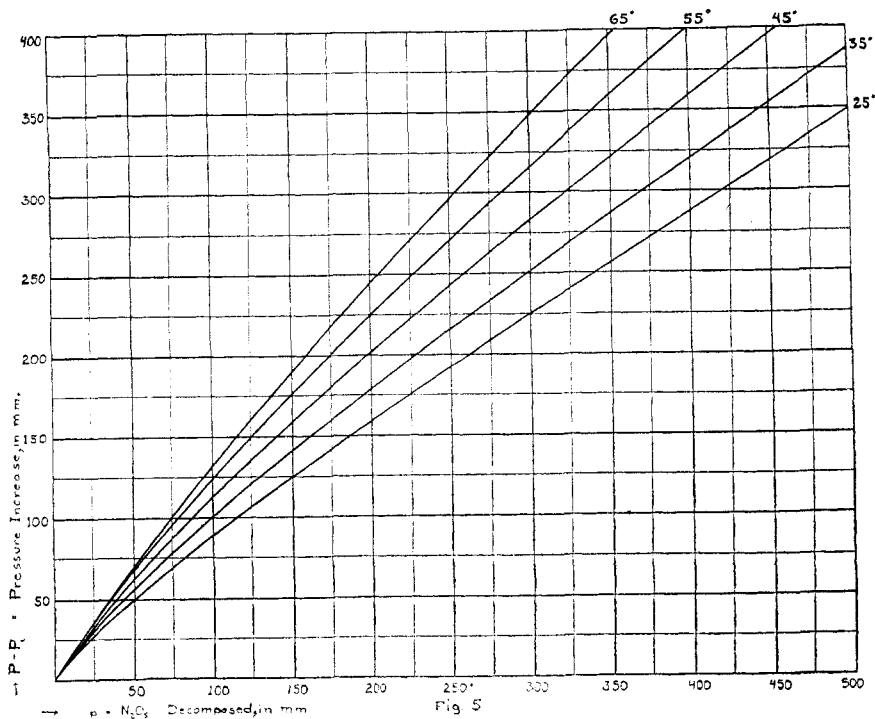
decomposed from the pressure rise can be most easily carried out by the use of a graphical interpolation. Assuming arbitrary values for the instantaneous values of P_{O_2} just as was done in the previous calculation of the final values of P_{O_2}', a series of curves were plotted with p as abscissas and $P - P_i$ as ordinates. The procedure for calculating α was identical with that already described. In the last two columns of Table I, the values for p and $P - P_i$ are recorded. From these values and many others not given here the curves shown in Fig. 5 were drawn. They were plotted accurately on a large scale where one mm. was equivalent to 0.5 mm. of pressure.

TABLE I.

25°.

P_{O_2} (Assumed.)	$\dfrac{\alpha 2}{1-\alpha.}$	$\alpha.$	$P_i.$	$P_f.$	$p.$	$P - P_i.$
5	2.43	0.761	10	22.6	10	12.6
25	0.487	0.496	50	99.8	50	49.8
50	0.243	0.386	100	188.6	100	88.6
100	0.1218	0.292	200	358.4	200	158.4
150	0.0813	0.247	300	524.1	300	224.1
200	0.0609	0.217	400	687.8	400	287.8
400	0.0305	0.160	800	1328.0	800	528.0

35°.

5	5.166	0.858	10	23.6	10	13.6
25	1.033	0.624	50	106.2	50	56.2
50	0.5166	0.505	100	200.5	100	100.5
100	0.2583	0.395	200	379.0	200	179.0
150	0.1722	0.338	300	551.4	300	251.4
200	0.1291	0.300	400	720.0	400	320.0
400	0.0646	0.224	800	1379.2	800	579.2

45°.

5	10.44	0.919	10	24.2	10	14.2
25	2.087	0.739	50	112.0	50	62.0
50	1.044	0.625	100	212.5	100	112.5
100	0.5230	0.507	200	401.4	200	201.4
150	0.3486	0.441	300	582.3	300	282.3
200	0.2615	0.397	400	758.8	400	358.8
400	0.13075	0.302	800	1441.6	800	641.6

55°.

5	20.32	0.955	10	24.5	10	14.5
25	4.065	0.830	50	116.5	50	66.5
50	2.032	0.735	100	223.5	100	123.5
100	1.016	0.621	200	424.2	200	224.2
150	0.6775	0.551	300	615.2	300	315.2
200	0.5080	0.503	400	801.0	400	401.0
400	0.2541	0.393	800	1514.4	800	714.4

65°.

5	38.10	0.975	10	24.7	10	14.7
25	7.622	0.895	50	119.7	50	69.7
50	3.811	0.823	100	232.2	100	132.3
100	1.905	0.724	200	444.8	200	244.8
150	1.270	0.659	300	647.7	300	347.7
200	0.9530	0.610	400	844.0	400	444.0
400	0.4765	0.492	800	1593.6	800	793.6

Table II presents the calculations of the reaction velocity constants from the data. The first and second columns give the time (t) and the observed pressure (P), the values being taken from the curves in Figs. 2 and 3. The third column gives the pressure increase due to decomposition, which is obtained by subtracting the initial pressure (P_i) from the values of (P) given in the second column. The initial pressure (P_i)

TABLE II.
25°.

	No. 2 ($P_i = 288.7$).				No. 3 ($P_i = 268.7$).				No. 12 ($P_i = 290.4$).			
t.	P.	$P-P_i$.	p.	$k\times10^{-3}$.	P.	$P-P_i$.	p.	$k\times10^{-3}$.	P.	$P-P_i$.	p.	$k\times10^{-3}$.
20	315.1	26.4	23.9	....	293.0	24.3	21.5	....	310.8	20.4	17.8	....
40	325.6	36.9	35.2	2.18	302.2	34.5	32.5	2.32	320.0	31.6	29.6	2.21
60	335.1	46.4	46.1	2.20	311.0	42.3	41.6	1.92	331.7	41.4	40.7	2.18
80	344.0	55.3	57.0	2.29	318.9	50.2	50.9	2.09	340.2	49.8	50.0	1.90
100	351.2	62.5	65.5	1.87	325.9	57.2	59.2	1.95	348.2	57.8	59.9	2.11
120	359.0	70.3	75.9	2.38	332.3	63.6	66.9	1.87	355.1	64.7	68.5	1.90
140	365.2	76.5	83.9	1.92	338.8	70.1	75.5	2.18	361.9	71.5	77.5	2.07
160	371.7	83.0	92.7	2.20	344.4	75.7	82.9	1.96	368.1	77.7	85.3	1.87
180	377.3	88.6	100.1	1.92	350.0	81.3	90.4	2.06	374.2	83.8	93.8	2.12
200	....	....	....	....	355.1	86.4	96.0	1.60	380.0	89.6	101.2	1.92
220	....	....	....	....	360.0	91.3	103.8	2.30	385.1	94.7	108.2	1.89
260	....	....	....	....	369.3	100.6	116.3	1.97	395.0	104.6	121.8	1.94
300	....	....	....	....	....	....	....	....	403.6	113.2	134.3	1.92
340	....	....	....	....	....	....	....	....	410.4	120.0	144.0	1.61
1200	492.8	204.1	268.7	2.20	....	....	....	....	....	....	....	....
1300	495.6	206.9	272.7	2.23	459.3	190.6	247.8	1.91	491.9	201.5	264.5	1.81
1400	....	....	....	....	462.0	193.3	251.9	2.18	495.0	204.6	269.3	2.05
1500	....	....	....	....	464.1	195.4	254.9	1.97	497.1	206.7	272.7	1.76
1700	....	....	....	....	467.0	198.3	259.3	1.92	500.2	209.8	277.1	1.44
∞	505.0	.....	288.7	....	473.0	.....	268.7	....	508.0	.....	290.4	....
				Av., 2.14				Av., 2.01				Av., 1.93

35°.

	No. 5 ($P_i = 306.5$).				No. 6 ($P_i = 56.0$).				No. 11 ($P_i = 308.2$).			
t.	P.	$P-P_i$.	p.	$k\times10^{-3}$.	P.	$P-P_i$.	p.	$k\times10^{-3}$.	P.	$P-P_i$.	p.	$k\times10^{-3}$.
10	356.6	50.1	43.8	....	69.2	13.2	9.7	....	345.7	37.5	31.1	....
20	375.2	68.7	63.3	7.71	73.9	17.9	13.2	7.87	368.1	59.9	53.8	8.54
30	391.7	85.2	82.0	8.00	78.0	22.0	16.8	8.80	385.3	77.1	72.7	7.74
40	406.2	99.7	99.0	7.89	81.4	25.4	19.9	8.24	400.2	92.0	90.0	7.62
50	419.8	113.3	115.3	8.20	84.9	28.9	22.8	8.38	414.0	105.8	106.2	7.74
60	431.3	124.8	129.7	7.83	88.0	32.0	25.7	9.12	426.5	118.3	121.4	7.83
70	441.8	135.3	143.0	7.82	90.0	34.0	27.6	7.78	438.0	129.8	135.8	8.03
80	451.1	144.6	154.6	7.36	92.6	36.6	30.0	8.84	448.1	139.9	148.8	7.86
90	460.0	153.5	166.4	8.10	94.7	38.7	32.1	8.41	457.2	149.0	160.2	7.42
100	468.2	161.7	177.1	7.95	97.0	41.0	34.5	10.59	465.2	157.0	171.0	7.58
120	482.2	175.7	195.7	7.76	100.3	44.3	37.6	7.79	480.0	171.8	190.4	7.63
140	494.2	187.7	211.8	7.85	103.2	47.2	40.4	8.26	492.3	184.1	206.8	7.50
160	504.3	197.8	225.2	7.64	106.2	50.2	44.0	13.11	503.2	195.0	221.3	7.72
180	513 0	206.5	237.6	8.27	108.0	52.0	45.6	7.15	512.0	203.8	233.8	7.77
200	....	....	....	....	109.8	53.8	47.3	8.92	519.4	211.2	244.6	7.84
240	....	....	....	....	112.2	56.2	50.0	9.29	531.4	223.2	260.9	6.89
280	....	....	....	....	....	....	....	....	539.5	231.3	272.0	7.22
320	....	....	....	....	....	....	....	....	545.2	237.0	279.8	6.07
360	....	....	....	....	....	....	....	....	549.9	241.7	286.6	6.85
∞	562.2	.....	306.5	....	119.0	.....	56.0	....	565.3	.....	308.2	....
				Av., 7.89				Av., 8.83				Av., 7.54

TABLE II (*Continued.*)
45°.

$t.$	No. 7 ($P_i = 348.4$).				No. 8 ($P_i = 94.8$).				No. 9 ($P_i = 340.2$).			
	$P.$	$P-P_i.$	$p.$	$k \times 10^{-3}.$	$P.$	$P-P_i.$	$p.$	$k \times 10^{-3}.$	$P.$	$P-P_i.$	$p.$	$k \times 10^{-3}.$
10	462.0	113.6	101.1	....	129.0	34.2	25.6	....	467.3	127.1	115.4	....
20	518.5	170.1	163.2	28.9	148.7	53.9	42.3	27.6	519.5	179.3	173.5	29.9
30	556.4	208.0	208.0	27.7	162.6	67.8	55.0	27.7	555.5	215.3	217.0	30.2
40	585.2	236.8	243.0	28.7	173.1	78.3	65.2	29.6	581.0	240.8	248.0	29.0
50	607.0	258.6	270.0	29.6	108.3	85.5	72.5	28.4	600.0	259.8	271.1	28.9
60	622.5	274.1	289.8	29.1	185.6	90.8	78.0	28.3	614.1	273.9	289.1	30.2
70	634.3	285.9	304.4	28.7	189.9	95.1	82.2	28.8	624.6	284.4	302.7	31.0
80	642.7	294.3	315.3	28.5	192.8	98.0	85.1	26.2	632.5	292.3	312.8	31.4
90	649.1	300.7	324.0	30.5	195.1	100.3	87.7	31.2	638.9	298.7	320.9	35.1
100	653.4	305.0	329.8	27.1	197.2	102.4	89.9	37.1	642.5	302.3	326.2	32.1
120	660.0	311.6	338.4	31.0	199.6	104.8	92.0	28.0	.....	.....	.....	....
140	664.0	315.6	343.5	35.6	.....	.....	.....	....	.....	.....	.....	....
160	665.7	317.3	345.6	28.0	.....	.....	.....	....	.....	.....	.....	....
∞	668.0	.....	348.4	....	202.0	.....	94.8	....	653.7	.....	340.2	...
			Av., 29.4				Av., 29.3				Av., 30.9	

55°.

$t.$	No. 15 ($P_i = 357.8$).				No. 26 ($P_i = 331.3$).			
	$P.$	$P-P_i.$	$p.$	$k \times 10^{-3}.$	$P.$	$P-P_i.$	$p.$	$k \times 10^{-3}.$
3	...	...	...	..	424.5	93.2	72.9	..
4	...	...	...	..	449.0	117.7	95.0	89.5
5	...	...	...	..	471.5	140.2	115.9	92.6
6	465.0	107.2	85.3	..	491.8	160.5	135.2	94.0
7	492.5	134.7	110.2	96.0	509.0	177.7	151.9	89.0
8	514.0	156.2	136.1	88.7	524.8	193.5	168.0	94.2
9	532.0	174.2	148.8	81.0	539.8	207.7	182.8	95.0
10	549.5	191.7	166.2	87.0	551.3	220.0	195.7	90.5
12	582.0	224.2	200.0	97.2	572.2	240.9	217.8	89.1
14	607.0	249.2	226.7	92.8	589.4	258.1	236.4	89.6
16	628.2	270.4	250.0	98.0	604.0	272.7	252.2	91.1
18	644.0	286.2	267.3	87.5	616.3	285.0	265.9	95.1
22	668.0	310.2	294.3	88.6	634.0	302.7	285.7	90.2
26	686.0	328.2	314.9	98.1	646.0	314.7	299.3	88.6
30	697.3	339.5	327.6	87.8	654.5	323.2	309.0	90.9
38	709.9	352.1	342.5	85.1	664.2	332.9	320.0	85.1
46	716.1	358.3	349.8	81.1	...	...	...	..
54	719.3	361.5	353.6	80.6	...	...	...	..
∞	722.4	...	357.8	..	673.7	...	331.3	..
			Av., 89.2				Av., 90.9	

TABLE II (Continued).

65°.

	No. 23 (P_i = 319.5).				No. 24 (P_i = 696.0).				No. 25 (P_i = 32.6).			
t.	P.	$P-P_i$.	p.	$k\times10^{-8}$.	P.	$P-P_i$.	P.	$k\times10^{-8}$.	P.	$P-P_i$.	p.	$k\times10^{-8}$.
2	484.5	165.0	128.2	...	1055.0	359.0	311.4	...	59.5	26.9	18.6	...
3	534.5	215.0	172.4	263.0	1147.5	451.5	408.2	290.0	65.3	32.7	22.6	337.0
4	571.8	252.3	207.2	270.0	1211.5	515.5	477.6	276.0	69.0	36.4	25.1	288.0
5	600.0	280.5	234.2	278.0	1260.0	564.0	531.3	282.0	71.8	39.2	27.2	329.0
6	621.7	302.2	255.1	278.0	1295.0	599.0	571.6	280.0	74.2	41.6	29.1	434.0
7	638.8	319.3	271.6	296.0	1321.9	625.9	602.4	285.0	76.0	43.4	30.1	337.0
8	650.7	331.2	283.7	291.0	1347.0	651.0	631.3	371.0	..	..	..	...
9	659.7	340.2	292.7	290.0	1363.5	667.5	650.1	344.0	..	..	..	...
10	666.5	347.0	299.4	288.0	1374.0	678.0	662.8	324.0	..	..	..	...
12	675.0	355.5	308.0	279.0	1385.9	689.9	677.2	284.0	..	..	..	...
14	680.3	360.8	313.5	325.0	1391.9	695.9	684.2	216.0	..	..	..	...
16	683.2	363.7	316.5	347.0	1396.0	700.0	689.2	292.0	..	..	..	...
18	...	...	...	...	1398.8	702.8	692.1	278.0	..	..	..	...
∞	685.7	...	319.5	...	1402.5	...	696.0	...	79.1	..	32.6	...

| Av., 290.0 | Av., 293.0 | Av., 345.0 |

was obtained from the final pressure (P_f) through the use of the curves shown in Fig. 4. The fourth column gives the pressure p which would be exerted by the pentoxide which has decomposed in the time t. The values of p were obtained from the values of $P — P_i$ by means of the curves shown in Fig. 5.

The reaction velocity constant shown in the last column were calculated directly from the figures in the first and fourth columns on the assumption that the reaction was monomolecular with the help of the formula,

$$k = \frac{2.303}{t_2 - t_1} \log_{10} \frac{p_\infty - p_1}{p_\infty - p_2}, \tag{9}$$

where p_∞ is equal to P_i.

The values of t_2 and t_1 chosen for the calculation were successive times in the first column of Table II.

Discussion of Results.

The experiments are numbered chronologically in the order in which they were performed. The missing numbers show the experiments which failed. Expts. 4 and 10 gave erratic experimental data due to failure of the diaphragm to function properly. From No. 13 to No. 22 a series of failures resulted, due to impure pentoxide and to unsatisfactory diaphragms in which changes in the platinizing process were being tried out. The gaps in some of the experiments were due to time consumed in manipulation, or to absence from the laboratory overnight.

In all, 4 different decomposition chambers were used in the experiments recorded, which varied from 20 cc. to 130 cc. in volume and from

10 mm. to 30 mm. in diameter. The length of all the chambers up to the air compartment was approximately 20 cm. Since no difference in the results was detected it may be assumed that the size and shape of the vessel have no influence on the reaction.

Expts. 9 and 11 were carried out with the chamber (130 cc.) packed full with half a g. of glass wool. Since the velocity constant is not increased by this increased surface distributed throughout the whole mass, it is evident that the velocity observed is not that of a diffusion process to the glass surface. Furthermore, the very large temperature coefficient, 300% for 10°, shows that the rate measured is that of a true chemical reaction. Although a diffusion process may appear to be a monomolecular reaction, its temperature coefficient would be very small.

The accuracy of the pressure readings was about one mm. and in many cases less. In all, 376 pressure readings were taken, which are shown in Figs. 2 and 3, and out of this number there are only 11 which fall more than a millimeter from the smooth curves. The time was taken with a stopwatch to one or two seconds—a greater accuracy than was necessary. The thermostat was constant to 0.03°. The results were plotted on coordinate paper 40 $\times$ 50 cm. on the largest scale possible for each experiment. The errors in the mathematical and graphical operations which were necessary in the correction for the shifting $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium were negligible. The greatest error in the work lies in the fact that in some parts of the curves there were not a sufficient number of points to determine the true course.

The velocity constant in Expt. 25 does not check with the others at the same temperature. The errors in it, however, are greatly magnified because the experiment was carried out at a very low pressure in order to contrast it with Expt. 24, in which a high pressure was used. Probably there is nothing significant in its higher value, the discrepancy being due merely to the magnification of errors. Accordingly, it is excluded in determining the average velocity constant at 65°.

The velocity constants are consistent and show conclusively that the reaction is monomolecular. The fluctuations which do occur are eratic and can be traced readily to uncertainties in the curves, or to magnification of errors occasioned by very small pressure changes. In Table III, in order to show that the reaction is not bimolecular, the velocity constants for one of the experiments (26) are compared with those calculated for a bimolecular reaction with the help of the formula

$$k = \frac{1}{t_2 - t_1} \frac{p_2 - p_1}{(p_\infty - p_1)(p_\infty - p_2)} \tag{10}$$

t_2 and t_1, being taken as successive times as was done in the calculations on the monomolecular basis.

To show further that the corrections for the $N_2O_4 \rightleftarrows 2NO_2$ equilibrium are appreciable, the values in the sixth column of Table III are calculated directly from the *observed* pressures on the basis of a monomolecular reaction.

TABLE III.

Experiment No. 26.

t.	p.	$k \times 10^{-2}$. (monomolecular).	$k \times 10^{-2}$. (bimolecular).	$P - P_i$.	$k \times 10^{-2}$. (monomolecular).
3	72.9	..	...	93.2	(uncorrected)
4	95.0	89.5	0.362	117.7	103.0
5	115.9	92.6	0.410	140.2	105.0
6	135.2	94.0	0.457	160.5	105.0
7	151.9	89.0	0.475	177.7	99.3
8	168.0	94.2	0.549	193.5	100.9
9	182.8	95.0	0.610	207.7	100.3
10	195.7	90.5	0.641	220.0	95.8
12	217.8	89.1	0.718	240.9	93.6
14	236.4	89.6	0.864	258.1	94.4
16	252.2	91.1	1.053	272.7	93.4
18	265.9	95.1	1.324	285.0	97.1
22	285.7	90.2	1.660	302.7	92.2
26	299.3	88.6	2.33	314.7	90.0
30	309.0	90.9	3.40	323.2	91.7
38	320.0	85.1	5.46	332.9	88.00
∞	331.3	..	...	342.4	...

Reaction Velocity Constants from 0° to 25°.—The reaction velocity constants at temperatures of 25° and below were readily calculated from the data of a previous research on the vapor pressure of nitrogen pentoxide,[1] in which the rate of pressure increase in the presence of the solid phase was observed. By extrapolation to zero time, the true vapor pressure without decomposition was obtained. The time pressure curves shown in Fig. 5 of the previous research were plotted on a large scale and corrections made for the shifting $N_2O_4 \rightleftarrows 2NO_2$ equilibrium as follows, ,

$$P = \text{observed pressure} = P_{N_2O_5} + P_{N_2O_4} + P_{NO_2} + P_{O_2}. \quad (11)$$

When a molecule of nitrogen pentoxide decomposes its place is immediately taken by another molecule from the solid, since the presence of the solid phase assures a constant partial pressure equal to its vapor pressure. The pressure increase during decomposition is thus equal to the sum of the partial pressures of the decomposition products, or,

$$P - P_i = P_{N_2O_4} + P_{NO_2} + P_{O_2}, \quad (12)$$

where P is the observed pressure and P_i is the initial pressure of undecomposed pentoxide, *i. e.*, its vapor pressure.

Substituting in Equation 12 for the partial pressures their values in terms of the partial pressure of oxygen, we obtain

[1] *Loc. cit.*

$$P - P_i = 2(1 - \alpha)P_{O_2} + 4\alpha P_{O_2} + P_{O_2} = 3P_{O_2} + 2\alpha P_{O_2}. \quad (13)$$

The pressure p corresponding to the pentoxide decomposed is equal to $2P_{O_2}$. Taking arbitrary values for P_{O_2} and plotting $p(= 2P_{O_2})$ against $P - P_i (= 3P_{O_2} + 2\alpha P_{O_2})$ on a large scale in the manner already described, a series of curves at temperatures from 0 to 25° was constructed. From these curves the partial pressure of the pentoxide decomposed at any time could be obtained from the pressure increase. There are given in Table IV some of the data from which the curves were constructed, but the curves themselves are not reproduced. They are very similar to those shown in Fig. 4.

TABLE IV.

25°.

P_{O_2} (assumed).	p (N₂O₅ decomp.).	$\dfrac{\alpha^2}{1-\alpha}$.	α.	$P - P_i$ (press. increase).
1	2	12.18	0.930	4.8
3	6	4.06	0.830	14.0
7	14	1.74	0.710	31.0
15	30	0.813	0.583	62.5
30	60	0.406	0.466	118.0

20°.

1	2	8.240	0.901	4.8
3	6	2.746	0.779	13.7
7	14	1.177	0.646	30.0
15	30	0.5490	0.516	60.5
30	60	0.2748	0.405	114.0

15°.

1	2	5.4585	0.863	4.7
3	6	1.8195	0.717	13.3
7	14	0.7797	0.575	29.0
15	30	0.3639	0.448	58.5
30	60	0.1820	0.345	111.0

0°.

1	2	1.468	0.682	4.4
3	6	0.4893	0.496	12.0
7	14	0.2097	0.365	26.0
15	30	0.09785	0.268	53.0
30	60	0.04893	0.198	101.9

In a monomolecular reaction the amount of material reacting in a given time is proportional to the concentration. Mathematically expressed, $dx/dt = kA$, where dx is the quantity changed in the time dt, A is the concentration of the reacting substance and k is the reaction velocity constant. A in this case is equal to the vapor pressure and is constant. The reaction velocity constant may then be calculated in a very simple manner in accordance with the formula,

$$k = \frac{p}{P_i t}. \quad (14)$$

The results are shown in Table V, where the first 2 columns give the time and corresponding pressures as taken from the experimental data of the previous research after plotting on a large scale. The vapor pressures, P_i, are calculated from the formula[1] instead of from the curves, because the error of extrapolation was so large.

TABLE V.

0°.

t.	P.	$P - P_i$.	p.	p/t.	$k = p/P_i t$.
0	51	0	..	...	.....
1380	58	7	3.2	0.00232	0.0000456
2870	64	13	6.5	0.00226	0.0000442
5695	79	28	15.1	0.00265	0.0000520

Av., 0.0000472

15°.

0	181	..	..	...	.....
20	187	6	2.5	0.125	0.000690
30	189	8	3.5	0.117	0.000645
40	191	10	4.4	0.110	0.000608
50	193	12	5.4	0.108	0.000597
60	195	14	6.3	0.105	0.000580

Av., 0.000624

20°.

0	275	..	..	...	.....
20	290	15	6.6	0.33	0.00120
30	296	21	9.5	0.32	0.00117
40	302	27	12.4	0.31	0.00113
50	308	33	16.7	0.33	0.00120
60	314	39	18.5	0.31	0.00113

Av., 0.00117

25°.

0	414	0	..	...	.....
20	446	32	14.0	0.70	0.00169
30	464	50	23.5	0.78	0.00188
40	481	67	34.3	0.86	0.00207
50	496	82	40.4	0.81	0.00196
60	512	98	49.0	0.81	0.00196

Av., 0.00191

The results show in a conclusive manner that a monomolecular reaction is being measured. It follows, therefore, that the reaction velocity constant should be independent of the initial pressure. The experimental facts show this to be the case. At 45° the same constant was obtained, starting with 345 mm. of pentoxide as with 95 mm. At 65° the same constants were obtained with 696 mm. and 319 mm. With an initial pressure

[1] *Loc. cit.*

of 33 mm. at 65° the constant was appreciably higher, but, as already pointed out, the experimental errors are greatly magnified at these lower pressures. The same thing holds true for one experiment at 35° where only 56 mm. were taken.

The temperature coefficient of the velocity constant is a matter of considerable interest. It has long been realized that the increase in the number of molecular collisions with increasing temperature is not sufficient to explain the large temperature coefficients of reaction velocities. For a 10° rise, reaction velocities increase 200 or 300% or more, whereas the number of collisions increases by only about one per cent. One of the earliest attempts to explain this large temperature coefficient has been the hypothesis of Arrhenius, in which there is supposed to be an equilibrium existing between "active" and "passive" molecules. An increase in temperature increases greatly the ratio of "active" molecules. to "passive" ones. Only the "active" ones can react chemically and the reaction velocity depends on the frequency of collision between "active" molecules. Since a monomolecular reaction does not depend on molecular collision, information concerning its velocity constant should throw light on the mechanism of this large increase in the ratio of "active" to "passive" molecules with temperature rise.

On the basis of his considerations, Arrhenius advanced the following equation to express the effect of temperature (T) on the reaction velocity constant (k),

$$\frac{d \log k}{dT} = \frac{E}{RT^2},$$

(15)

in which E is a quantity having the dimensions of energy which is found experimentally to be dependent but slightly on the temperature.

The quasi-thermodynamic derivation for Equation 15, presented by Arrhenius is only partially satisfactory—nevertheless, the newer treatments of W. M. C. Lewis, Perrin and Tolman, are found to lead to an equation of this same form. According to Tolman[1] the quantity E, which is sometimes called the "critical increment," is the difference between the average energy of the molecules and modes of electromagnetic vibration which actually take part in the reaction, and the average energy of these same elements whether or not they are in a reactive condition. On this basis, it would be expected that the quantity A should vary but slightly with the temperature.

Integrating Equation 15, we obtain for the "critical increment" in calories,

$$E = \frac{1.98 \, T_2 T_1 \times 2.302 \log_{10} k_2/k_1}{T_2 - T_1}.$$

(16)

[1] THIS JOURNAL, **42**, 2506 (1920).

This equation was used in calculating the critical increment from the reaction velocity constants given in Tables II and V. The results are given in Table VI.

TABLE VI.

Calculation of the Critical Increment.

Temp., ° C.	k.	Critical increment.	Mean Temp., ° C.
65	0.293		
65	0.290		
	Av., 0.292	25830	60
55	0.0909		
55	0.0892		
	Av., 0.0900	22750	50
45	0.0309		
45	0.0293		
45	0.0294		
	Av., 0.0299	25370	40
35	0.00754		
35	0.00883		
35	0.00789		
	Av., 0.00808	25100	30
25	0.00193		
25	0.00801		
25	0.00214		
	Av., 0.00203	24240	12.5
0	0.0000472		
	Av., 24700		

The important thing about these calculations is that E is shown experimentally to be practically constant with a greater accuracy and over a wider range of temperature than has been possible hitherto. In the *only* other monomolecular gas phase reaction recorded in the literature[1] the temperature range in which the walls of the vessel did not exert a catalytic influence was quite small, and because of the high temperature necessary the experimental accuracy was unsatisfactory.

From the average critical increment, 24,700 calories, the reaction velocity constants may be calculated with the help of Equation 16 at different temperatures, taking the constant at one temperature (25°) for a starting point. The agreement between observed and calculated velocity constants is shown in Table VII.

[1] Trautz and Bhandarkar, *Z. anorg. allg. Chem.*, **106**, 95 (1919).

TABLE VII.

Temperature, °C.	k(observed).	k(calculated).
65. .	0.292	0.286
55	0.0900	0.0932
45	0.0299	0.0283
35	0.00808	0.00790
25	0.00203	0.00203
25 (solid present)	0.00191	0.00203
20 (solid present)	0.00117	0.000992
15 (solid present)	0.000624	0.000475
0 (solid present)	0.0000472	0.0000440

The experimental values at 25, 20 and 15 with the solid present are less accurate than the others on account of the error of extrapolating for the vapor pressure.

The value of the critical increment for this reaction, 24,700 calories, is of very considerable interest since the theories of W. C. M. Lewis and Perrin[1] make it possible to predict from the critical increment, the frequency of light which will be photochemically active in producing the same reaction. The results of photochemical experiments on this reaction will be the subject of a following report. It may be stated in advance, however, that the frequency predicted by the Lewis, Perrin theory was *not* photochemically active. This result, which contradicts the Lewis-Perrin theory, is not in disagreement, however, with the treatment proposed by Tolman.[2]

Summary.

1. The decomposition of gaseous nitrogen pentoxide is a monomolecular reaction which takes place at room temperature. Such a system is valuable for studying new theories concerning the relation of radiant energy to chemical action.

2. The rate at which gaseous nitrogen pentoxide decomposes was determined experimentally between 0° and 65°. The course of the reaction was followed by pressure observations with a glass manometer.

3. The large temperature coefficient of the reaction velocity showed that catalysis by the glass walls and diffusion, was not a factor. Furthermore, the addition of glass wool with a large surface caused no change in the reaction rate.

4. The quantity of nitrogen pentoxide taken was calculated from the pressure after complete decomposition. Corrections for the $N_2O_4 = 2NO_2$ equilibrium were necessary.

5. At the lower temperatures the reaction velocities were calculated from the data of a previous research in which the solid phase was present.

6. The experimental facts show that the critical increment is independent of the temperature.

WASHINGTON, D. C.

[1] W. C. M. Lewis, *J. Chem. Soc.*, **113,** 471 (1918); Perrin, *Ann. phys.*, **11,** 5 (1919).

[2] *Loc. cit.*