of this phenomenon. In dilute acid the adsorption is more than monionic, and there may be an adsorption of the dye acid itself together with the exchange adsorption.

Summary

1. Wool violet is very suitable for the determination of the specific surface of lead sulfate. In the saturated state 1 dye ion is adsorbed per 1.5 lead ions in the surface of lead sulfate when the supernatant liquid is neutral. The dye adsorption increases in acid medium.

2. Wool violet gives an exchange adsorption on the surface of lead sulfate. The sulfate ions in the surface are replaced by an equivalent amount of dye ions, thus causing the precipitation of some lead sulfate from the supernatant liquid and yielding a solution containing sulfate in excess of lead.

3. Adsorbed wool violet inhibits the speed of kinetic exchange of lead ions at the interface lead sulfate–solution, and virtually prevents the recrystallization of lead sulfate from 0.01 *N* nitric acid at room temperature.

4. On shaking a coarsely crystalline product of lead sulfate in 0.01 *N* nitric acid a recrystallization takes place.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 11, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Thermal Decomposition of Nitrogen Pentoxide at Low Pressures[1,2]

BY E. F. LINHORST AND J. H. HODGES

Introduction

The generally accepted theory of the mechanism of unimolecular reaction was proposed in 1922 by Lindemann, and elaborated in succeeding years by others.[3] It is a consequence of this theory that at sufficiently low pressures, when the mean interval between collisions has increased until it is of the same order of magnitude as the mean interval between the activation of a molecule and its decomposition, the specific reaction rate will decrease as the pressure is lowered. If the activation process depends on the collision between two molecules, the reaction should approach a second order process at very low pressures. Experimental confirmation of this predicted decrease in the specific reaction rate has been obtained in a number of cases, which have been summarized by Ramsperger.[4]

The results of previous work on the rate of decomposition of nitrogen pentoxide at low pressures are somewhat discordant. Hunt and Daniels[5] find the specific reaction rate essentially constant down to 0.01 mm., though the value at their lowest pressure is slightly lower than at higher pressures. Hirst and Rideal[6] find the specific reaction rate to increase at pressures below 0.26 mm., but no other work has indicated an increase at low pressures. Hibben[7] finds no decrease in the specific reaction rate from 0.2 mm. down to 0.03 mm. Sprenger[8] concludes that the reaction slows down and stops before all the nitrogen pentoxide has decomposed, but these conclusions are supported by no other work. Schumacher and Sprenger[9] report a decrease in the specific reaction rate becoming apparent at pressures below 0.06 mm. Ramsperger and Tolman[10] report careful measurements at pressures down to 0.001 mm. showing a decrease in the specific reaction rate evident below 0.05 mm., but giving no indication that the reaction during any given experiment deviates appreciably from the first order even at their lowest pressures. Preliminary results obtained in the present research[11] using comparatively small reaction vessels and working at the temperature of 35° indicated a

---

(1) From a dissertation submitted by E. F. Linhorst to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1931.

(2) Presented in part at the Buffalo meeting of the American Chemical Society, September, 1931.

(3) (a) Lindemann, *Trans. Faraday Soc.*, **17**, 598–99 (1922); (b) Rodebush, THIS JOURNAL, **45**, 606 (1923); (c) Hinshelwood, *Proc. Roy. Soc.* (London), **A113**, 230 (1926); (d) Fowler and Rideal, *ibid.*, **A113**, 570 (1926); (e) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); (f) Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928); (g) Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, 1932.

(4) Ramsperger, *Chem. Rev.*, **10**, 27 (1932).

(5) Hunt and Daniels, THIS JOURNAL, **47**, 1602 (1925).

(6) Hirst and Rideal, *Proc. Roy. Soc.* (London), **A109**, 526 (1925).

(7) Hibben, THIS JOURNAL, **50**, 940 (1928).

(8) Sprenger, *Z. physik. Chem.*, **136**, 49 (1928).

(9) Schumacher and Sprenger, *Proc. Nat. Acad. Sci.*, **16**, 129 (1930).

(10) Ramsperger and Tolman, *ibid.*, **16**, 6 (1930).

(11) Hodges and Linhorst, *ibid.*, **17**, 28 (1931).

falling off in the value of the specific reaction rate at pressures below 0.06 mm., and in several measurements at pressures below 0.004 mm. the decomposition approximated a second order reaction.

In the present paper are reported results of a study of the reaction at the temperatures 35, 45, 55 and 65° in a reaction vessel of 22 liters capacity. Most of the experiments were conducted with partial pressures of nitrogen pentoxide ranging from 0.005 down to 0.0005 mm.

Apparatus, Materials, Procedure

The method of measuring the rate of decomposition of nitrogen pentoxide consisted briefly in confining a small quantity of the gas in a closed vessel and determining at intervals the pressure of oxygen developed by decomposition.

Apparatus.—The important parts of the apparatus used are illustrated in Fig. 1. It was constructed of Pyrex glass. The mercury diffusion pump could reduce the pressure to 10^{-6} mm. Next to the liquid air trap was a greaseless ground-glass valve, completely enclosed and operated from the outside by a strong magnet. This valve would not hold against large pressure differences, but for preventing diffusion at low pressures (never exceeding 0.1 mm.) it proved to be entirely satisfactory. After the valve came a side tube leading through another magnetically operated valve to a reservoir containing solid nitrogen pentoxide kept cool continuously by solid carbon dioxide and ether. Beyond this came the reaction system consisting of a spherical 22-liter flask to which were attached a side-tube for condensing the oxides of nitrogen in liquid air, and the quartz fiber manometer. The reaction vessel was cleaned by a brief treatment with warm chromic acid before being put in place. To restore the glass surface to its normal condition after the treatment with chromic acid, the reaction flask was kept for several hours at a temperature above 500°.

The reaction vessel was enclosed in a box made of monel metal, insulated on the outside with asbestos. This box, when provided with heating coils on the inside, served as an oven for baking out the apparatus; and the same box, when filled with water and provided with a thermoregulator and heating unit, served as a thermostat. The temperature was kept constant within 0.03°, and the absolute values for the four temperatures used in the work were determined with a thermometer standardized by the Bureau of Standards.

A quartz fiber manometer of the bifilar type described by Coolidge[12] was used for the pressure measurements. Each manometer used in the work was calibrated in air against the readings of the McLeod gage. Mercury vapor was excluded from the fiber by a liquid air trap. Between 0.05 and 0.0005 mm. pressure, we believe this manometer gives pressure readings accurate to 2%.

Preparation of Nitrogen Pentoxide.—Nitrogen pentoxide was prepared by dehydrating pure nitric acid with phosphorus pentoxide. The method was similar to that described by Daniels and Bright.[13] The nitrogen pentoxide distilling from the original mixture of pure nitric acid and phosphorus pentoxide was collected in a large U-tube containing more phosphorus pentoxide (sublimed in oxygen). From this U-tube it was distilled into the reservoir which was then sealed directly to the apparatus as shown in Fig. 1. This last distillation was conducted in a slow stream of ozonized oxygen. Once in the reservoir tube, the material can be kept for many months when continuously cooled by carbon dioxide snow. It is kept pure by the frequent evacuation incident to the experimentation.

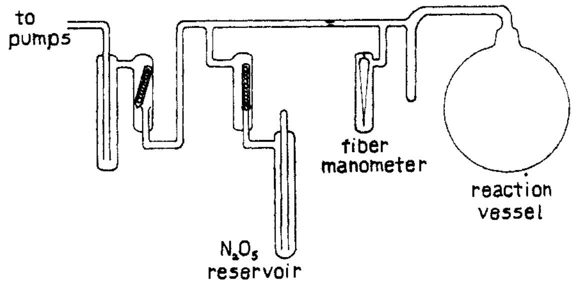

Fig. 1.—Apparatus.

Experimental Procedure.—The reaction vessel was baked in the oven at 400° for two or more hours under the lowest pressure attainable with the pumps. Connecting tubes not in the oven were flamed for about ten minutes. The fiber manometer could not be placed in the oven because it was found that the temperature warped the fibers.

After the vessel had cooled to about 100° from the baking process, the side valve leading to the nitrogen pentoxide was opened. The temperature of the reservoir was adjusted to about −60° to give a vapor pressure of about 0.03 mm. of nitrogen pentoxide, and as the reaction vessel further cooled to room temperature it was kept in communication with the reservoir and the vacuum pumps. Toward the end of this step the reaction flask was cooled in ice water, which makes the decomposition so slow that most of the decomposition products are eliminated by diffusion and there remains in the flask nitrogen pentoxide containing relatively small amounts of nitrogen dioxide, oxygen and perhaps nitric acid. This seasoning process, which continued for an hour or more, removed any traces of moisture or oxidizable material and allowed the surface of the reaction vessel to come to equilibrium with the reacting system before the measurements were started.

At the end of the seasoning operation, with the vessel still in ice water, the valve leading to the pumps was closed, the temperature of the pentoxide reservoir was adjusted to give the desired initial pressure, and sufficient time allowed for this vapor pressure to become established throughout the system. The valve in the reservoir line was closed, and the nitrogen pentoxide frozen in the condensing tube with liquid air. The valve leading to the pumps was now opened and after all the uncondensed gases were removed, the reaction system was sealed off from the rest of the apparatus. The thermostat was brought to the desired temperature, warm water substituted for a moment in place of the liquid air around the condensing tube and the reaction was started. At con-

---

(12) Coolidge, This Journal, **45**, 1637 (1923).

(13) Daniels and Bright, *ibid.*, **42**, 1131 (1920).

venient intervals the oxides of nitrogen were frozen out with liquid air, and the pressure of the residual oxygen measured with the quartz fiber. Total decomposition was obtained by leaving the vessel at 60 to 100° overnight. The thermostat was covered practically all the time, and the apparatus was never exposed to bright daylight.

The initial pressure of nitrogen pentoxide was taken as twice the final pressure of oxygen (corrected for any oxygen initially present), since the decomposition is represented by the equation $2N_2O_5 = 4NO_2 + O_2$.

Results

The results of all successful runs with the 22-liter vessel are expressed in Tables I and II. The experiments are arranged in order of decreasing initial pressures. Although the reaction is no longer of the first order in our pressure range, we have calculated the specific reaction rate, K, according to the usual formula for a first order reaction, as is customary in this work.

TABLE I

DECOMPOSITION OF N_2O_5, 22-LITER FLASK, 35.0°

Run	Time, min.	O_2 press. $\times 10^3$, mm.	N_2O_5 press. $\times 10^3$, mm.	$K \times 10^3$, (min.$^{-1}$)
59	0	2.4	81.1	
59	30	11.7	62.6	8.6
59	86.5	23.1	39.8	8.0
59	186.5	33.4	19.0	7.3
59	∞	43.0	0	
58	0	0.1	25.8	
58	36.3	2.9	20.3	6.7
58	96.3	6.06	13.9	6.2
58	206.3	9.28	7.5	5.6
58	∞	13.03	0	
57	0	0.07	5.83	
57	50	.69	4.59	4.8
57	140	1.47	3.034	4.6
57	311	2.185	1.600	3.7
57	∞	2.985	0	
56	0	0.043	3.494	
56	35.5	.264	3.052	3.8
56	95.5	.560	2.460	3.6
56	201.5	.928	1.724	3.5
56	∞	1.79	0	
60	0	0.026	1.776	
60	161	.274	1.280	2.04
60	461	.510	0.808	1.53
60	∞	.914	0	
61	0	.016	1.728	
61	165	.292	1.176	2.33
61	540	.568	0.624	1.69
61	∞	.880	0	
55	0	.034	1.402	
55	158	.237	0.996	2.16
55	560	.466	.538	1.53
55	∞	.735		

TABLE II

DECOMPOSITION OF N_2O_5, 22-LITER FLASK AT 45, 55, 65°

Run	Temp., °C.	Time, min.	O_2 press. $\times 10^3$, mm.	N_2O_5 press. $\times 10^3$, mm.	$K \times 10^3$, (min.$^{-1}$)
52	45.0	0	0.032	3.016	
52	45.0	40	.515	2.05	9.65
52	45.0	130	1.015	1.05	7.45
52	45.0	∞	1.540	0	
53	45.0	0	0.032	1.596	
53	45.0	54	.277	1.104	6.8
53	45.0	179	.516	0.626	4.54
53	45.0	∞	.829	0	
54	45.0	0	.036	1.539	
54	45.0	56	.265	1.084	6.25
54	45.0	206	.535	0.544	4.6
54	45.0	∞	.807	0	
49	55.0	0	.029	1.857	
49	55.0	50	.530	0.854	15.5
49	55.0	∞	.957	0	
50	55.0	0	.043	1.830	
50	55.0	20	.354	1.208	20.75
50	55.0	60	.593	0.730	12.60
50	55.0	∞	.958	0	
51	55.0	0	.047	1.594	
51	55.0	20	.258	1.172	15.35
51	55.0	70	.502	0.684	10.75
51	55.0	∞	.844	0	
48	65.0	0	.032	1.827	
48	65.0	15	.464	0.962	42.7
48	65.0	∞	.945	0	
46	65.0	0	.076	1.650	
46	65.0	20	.482	0.838	33.9
46	65.0	∞	.901	0	
47	65.0	0	.035	1.526	
47	65.0	15	.352	0.892	35.8
47	65.0	∞	.798	0	

The results from Table I and the results at 55° from Table II are expressed graphically in Fig. 2 by plotting the logarithm of K/K_∞ for each interval against the logarithm of the mean pressure for the interval. K/K_∞ is the ratio of the value of K at the pressure of the experiment to the value of K at higher pressures where the reaction is of the first order. There are also included in Fig. 2 the results obtained in the 1500-cc. flask at 35°.[11] Figure 2 contains, furthermore, for comparison the results of Schumacher and Sprenger[9] at 35° and of Ramsperger and Tolman[10] at a temperature of about 40°. The former are represented by taking the average value of the specific reaction rate and the average value of the initial and final pressure for each experiment; the latter are expressed by taking the value of the specific reaction rate and the initial pressure for each experiment (this method is not quite comparable with that of expressing the other results, but since Ramsperger and Tolman find no decrease in rate during the course of an experiment this is probably the fairest basis of comparison).

It will be observed that the agreement between the present results and those of Schumacher and Sprenger is very good. The results of Ramsperger and Tolman deviate somewhat in the direction of a more rapid reaction. Their results also differ from ours in that they find, even at their lowest initial pressure of 0.004 mm., that the specific reaction rate remains essentially constant throughout the course of an experiment. This is usually taken to mean that the reaction products are about as effective in activating collisions as are the reactant molecules. The present results show a consistent decrease in the value of K during the course of each run; within our limits of experimental error, the rate of the reaction seems to depend only on the partial pressure of the nitrogen pentoxide, and to be entirely independent of the concentration of the reaction products. As to their bearing on this point, the results of Schumacher and Sprenger occupy an intermediate position; the average of their K is always less for the last half of a run than for the first half, but there is a somewhat irregular fluctuation in K during the experiment.

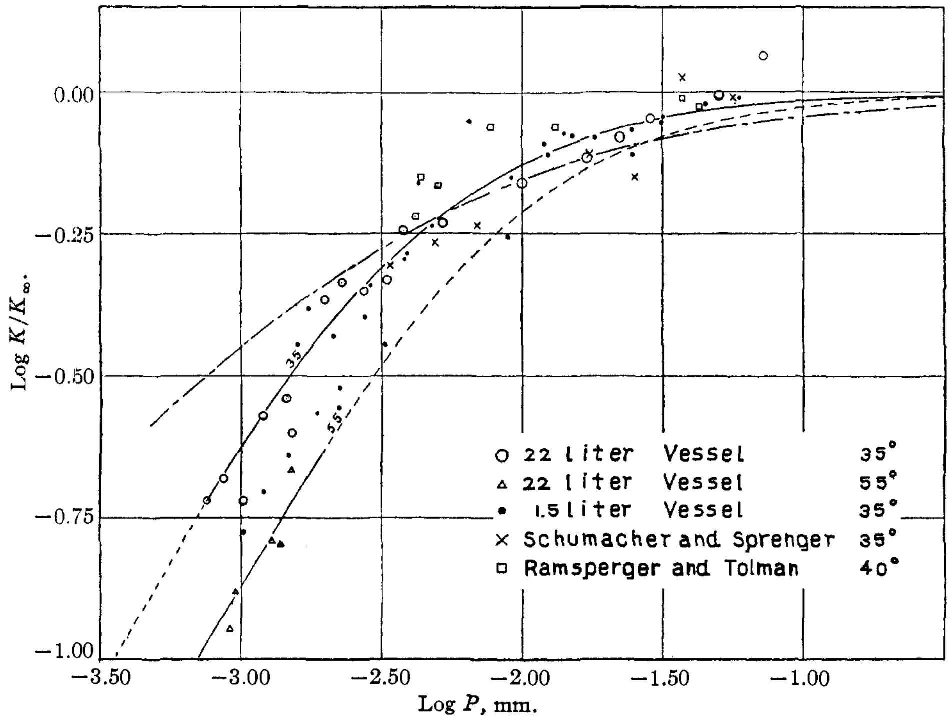

Fig. 2.—Experimental results, empirical and theoretical equations: empirical equation curves ——— - - - -; theoretical equation curve —— - —— - ——.

In Fig. 3, the measurements at 35, 45 and 55° in the 22-liter flask are presented in the form of a plot of $1/K$ against $1/P$. The linear relationships shown in Fig. 3 indicate that our experimental results are well expressed by an empirical equation of the form $1/K = 1/K_\infty + B/P$, where B is a constant. Introducing the value of the constant and rearranging, this equation can be expressed as

$$\frac{K}{K_\infty} = \frac{1}{1 + (0.00329/P)} \text{ (at 35°) and}$$

$$\frac{K}{K_\infty} = \frac{1}{1 + (0.00645/P)} \text{ (at 55°)}$$

Graphs of the values of log K/K_∞ against log P as given by these equations are shown in Fig. 2. From the empirical equation it is possible to calculate the apparent order of the reaction at any pressure. At 35°, for pressures of 0.1, 0.01 and 0.001 mm., the apparent order is, respectively, 1.03, 1.25 and 1.77.

The extent to which possible surface effects interfere with the homogeneous decomposition is a question of great importance in connection with the theoretical bearing of the present results. Ramsperger and Tolman,[10] by packing their 45-

liter flask with glass tubing, increased the ratio of surface to volume from 0.14 to 0.73 cm.$^{-1}$. Comparing results in the empty flask with those in the packed flask at similar pressures, the value of K in the empty flask remained essentially constant over an entire run, whereas in the packed flask the initial value of K was from 20 to 100% greater than in the unpacked flask, falling off as the run proceeded to values equal to or less than those in the empty vessel. In our preliminary work[11] an attempt was made, by using two different reaction vessels constructed of glass tubing, to increase the surface by considerable amounts. The results indicated a rate of reaction distinctly lower in the vessels with the larger surface, but the values were so erratic in comparison with the results in the flask that we considered them to be of somewhat doubtful significance. There was no evidence of an accelerating effect at the beginning of a run as found by Ramsperger and Tolman. Further evidence on the effect of the glass surface upon this reaction comes from a comparison of the results obtained in the 1.5-liter flask with those in the 22-liter flask. Both sets of data are included in Fig. 2. It will be observed that down to a pressure of 0.005 mm. (log P = -2.3) there is no significant variation between the data obtained in these two vessels. The surface-to-volume ratio in the smaller flask is 0.5 cm.$^{-1}$, and that in the larger flask is 0.2 cm.$^{-1}$; although a 2.5-fold variation in this ratio is not as severe a test as might be desired, we believe that the consistency of the two series of results is so high that this comparison constitutes good evidence for the homogeneous character of this reaction down to a pressure of about 0.005 mm. Below this pressure, however, there seems to be some divergence between the two series of results, with indications of a somewhat retarded rate in the smaller vessel.

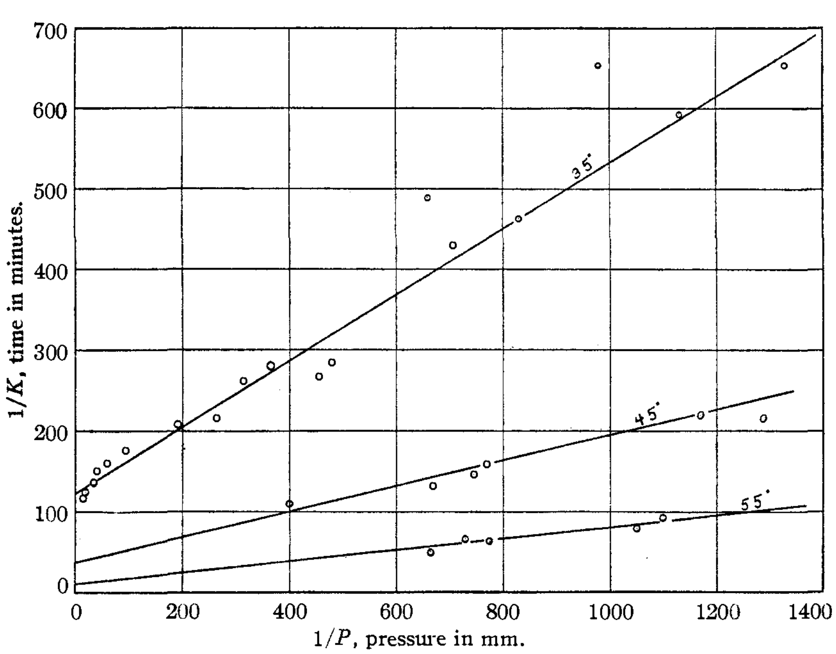

Fig. 3.—Relation between $1/K$ and $1/P$.

Theoretical Discussion

The theoretical picture of the unimolecular reaction as elaborated by Hinshelwood, Rice and Ramsperger, and Kassel[3] has already been outlined. In developing the general theory two different assumptions have been made concerning the probability of reaction of an activated molecule. The simplest of these assumptions, frequently referred to as Theory I, states that any activated molecule has a constant probability of reacting, independent of the amount or the distribution of the internal energy. Ramsperger[4] has listed some of the consequences of Theory I which are subject to experimental test. The present results, as shown in Fig. 3, display the linear relation between $1/K$ and $1/P$ which is one of the consequences of Theory I. However, the slope of this straight line can be expressed according to Theory I by an equation involving the diameter and the number of degrees of freedom of the molecule. It is easily shown that no reasonable assumptions concerning the diameter and the complexity of the nitrogen pentoxide molecule will account for the slope of this line. It is another consequence of Theory I that the temperature coefficient should have practically the same value at low pressures as at high. The energy of activation at low pressures has been calculated from the present results by taking the values of K corresponding to a pressure of 0.001 mm. at our four temperatures. The average value of the energy of activation is 20,000

(±2000) calories; at high pressures the activation energy is 24,700 calories. These discrepancies between the experimental results and Theory I indicate that this form of the general theory is inadequate for this reaction.

The second form of the general theory is based on the assumption that the critical energy must be localized in some one degree of freedom (Theory II) or in some one bond, which involves two degrees of freedom (Theory III). Kassel[14] has already compared the actual behavior of nitrogen pentoxide with the behavior to be expected from Theory III. We have inserted in Fig. 2 the theoretical curve given by the quantum form of Theory III, using 15 as the number of oscillators in the molecule, 22 as the number of quanta necessary to furnish the critical energy, and 26×10^{-8} cm. as the diameter of the molecule (a considerably larger value than kinetic theory considerations would allow). Even if we disregard the divergence between this theoretical curve and the experimental results below 0.005 mm., where the possible evidence of surface effects makes our results less significant, nevertheless there is a definite discrepancy in the region between 0.06 and 0.02 mm., where the results are more reliable, and where agreement between the different workers is reasonably good. Better agreement at the high pressure end of the curve could be obtained by assuming a larger diameter for the molecule, but this is already unreasonably large.

This reaction has always presented the severest test for the theories of unimolecular reaction. Theory III has given a reasonable interpretation of several other unimolecular reactions, but it is apparent from the present summary of results at low pressures that there is a definite conflict between any reasonable deductions from Theory III and the best existing results on the decomposition of nitrogen pentoxide.

Summary

1. The rate of thermal decomposition of nitrogen pentoxide has been measured in a 22-liter flask at temperatures of 35, 45, 55 and 65°, and at pressures ranging from 0.05 mm. to less than 0.001 mm.

2. Over this pressure range the reaction undergoes a transition from a first order to a second order mechanism. Deviation from a first order reaction becomes apparent around 0.05 mm. pressure, and at 0.001 mm. the reaction is apparently of the order 1.8.

3. The effect on the reaction of the glass walls has been observed by comparing the present results with previous results obtained in a 1.5-liter flask in which the ratio of surface to volume is 2.5 times greater. The surface appears to have no effect down to pressures around 0.005 mm.; below this pressure the surface appears to retard the reaction slightly.

4. The data have been compared with two of the existing theories of unimolecular reaction and differences that seem difficult to reconcile have been pointed out.

ANN ARBOR, MICH. RECEIVED DECEMBER 15, 1933

---

[14] Ref. 3g, p. 191.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Reduction of Silver Salts with Hydroxylamine

BY M. L. NICHOLS

Introduction

In their investigation of the photographic process, Sheppard and Mees studied the method of alkaline development. They state that[1] "the concentration of the alkali has a direct and controlling influence both on the composition of the solution and on the development." They also say that[1] "so long as we are ignorant of the quantitative relation between reducer oxidized and silver halide reduced, as also of the former's oxidation product, the survey of development can only be tentative and approximate."

In order to determine this relationship they studied the action of hydroxylamine on silver bromide in the presence of sodium hydroxide, on ammoniacal silver nitrate, and on silver nitrate in the presence of sodium sulfite and sodium hydroxide. In all these experiments they determined the grams of silver obtained per gram molecule of hydroxylamine used and formulated the

---

[1] Sheppard and Mees, "Investigations on the Theory of the Photographic Process," Longmans, Green and Co., London, 1907, p. 140.