tions. The maximum rise in temperature occurred in the first minute and was only 0.3°, which is negligible. Finally, the α-bromonaphthalene manometer was almost instantaneous in its response to pressure changes within the system. None of the photographs obtained in the investigation given in the second paper shows any evidence of a lag.

Summary

An apparatus has been described which is capable of measuring accurately the velocity of a rapid gaseous reaction.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES ON THE RATE OF OXIDATION OF NITRIC OXIDE[1] II. THE VELOCITY OF THE REACTION BETWEEN NITRIC OXIDE AND OXYGEN AT 0° AND 30°

BY R. LEONARD HASCHE AND WALTER A. PATRICK

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A number of investigators have studied the kinetics of the reaction between nitric oxide and oxygen. It was the subject of a long controversy between Raschig and Lunge. They used similar experimental methods, absorbing the reacting gaseous mixture in sodium hydroxide or sulfuric acid and titrating the amount of nitrogen dioxide formed with potassium permanganate. Raschig claimed experimental evidence pointing to the formation of nitrogen trioxide as an intermediate product; while Lunge's results indicated that nitrogen dioxide was formed directly, strictly in accordance with the law of a third-order reaction. Raschig's view regarding the intermediate, nitrogen trioxide, is also held by Briner and co-workers,[2] and by Jolibois and Sanfourche.[3] That the reaction possesses a small, but marked, negative temperature coefficient was first noted by Foerster and Blich.[4] Recently, Briner, Pfeiffer and Malet[5] have studied the reaction at low temperatures, down to —193°; Bodenstein,[6] in 1918, worked at the temperatures 0°, 30°, 60° and 90°; later, Bodenstein and Linder[7] con-

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[1] The material in this article is taken from a dissertation submitted by R. Leonard Hasche in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University.

[2] Briner and Fridori, *J. chim. phys.*, **16**, 279 (1918). Briner and Fridori, *Helvetica Chim. Acta*, **16**, 181 (1918). Briner, Niewiazski and Wiswald, *J. chim. phys.*, **19**, 290 (1921).

[3] Jolibois and Sanfourche, *Compt. rend.*, **168**, 235 (1919). Sanfourche, Bl, **25**, 533, 646 (1919).

[4] Foerster and Blich, *Z. angew. Chem.*, **23**, 2017 (1910).

[5] Briner, Pfeiffer and Malet, *J. chim. phys.*, **28**, 25 (1924).

[6] Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918).

[7] Bodenstein and Linder, *Z. physik. Chem.*, **100**, 87 (1922).

tinued the velocity measurements at still higher temperatures, up to 394°. The results confirm those of Lunge that the reaction is one of the third order. Furthermore, Bodenstein states that the reaction occurs entirely in the gas volume, in other words, is a homogeneous gaseous reaction uncatalyzed by the walls of the reaction vessel. If this were true, it would be an exceptional case. It seemed more questionable in the light of recent research, as day by day the number of reactions that are uncatalyzed by the surface of the reaction vessel is being narrowed down. In order to answer this question, the present work was undertaken. The surface-to-volume ratio was increased approximately 140 times by filling the reaction chamber with glass wool.

The apparatus and experimental procedure described in the preceding paper was employed. With partial pressures of nitric oxide and oxygen of approximately 20 mm. of mercury, the reaction proceeded at a rate that could be measured very satisfactorily.

Method of Calculation

An excess of oxygen was used in all of the experiments. Calculations of the velocity constants, therefore, are based on the decrease in pressure in terms of nitric oxide with time expressed in seconds. In order to make the calculations of the velocity constants for the different experiments comparable, all readings of the α-bromonaphthalene manometer were corrected to 15°. The temperature coefficient of expansion and density of the manometer liquid were determined under actual experimental conditions. The mercury and α-bromonaphthalene manometers were opened to the same pressure and read at two different temperatures. Correction for the association of nitrogen dioxide into the tetra-oxide was applied to the observed pressure decrease expressed in millimeters of α-bromonaphthalene corrected to 15°. The speed of this reaction is so great that it may be neglected, and the degree of dissociation calculated from the equilibrium constant. Bodenstein and Linder[8] made a careful study of the equilibrium and give an empirical formula which expresses the relation between their observed value of K_p and the absolute temperature, pressure being expressed in atmospheres: $\text{Log } K_p = (2692/T) + 1.751 \log T + 0.0048\, T - 7.144 \times 10^{-6} + 3.0622$. Calculation according to this formula gives a value for K_p of 0.0178 at 0° and 0.2105 at 30°.

The degree of dissociation of nitrogen tetra-oxide, designated by α, may be calculated according to the equation, $\alpha = \sqrt{\dfrac{K_p}{4P + K_p}}$, where P denotes the pressure due to the equilibrium, $N_2O_4 \rightleftharpoons 2NO_2$, and is expressed in atmospheres. Different values of P (converted over into millimeters of α-bromonaphthalene at 15°) were substituted in Equation 1 and the values

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[8] Ref. 7, pp. 37–105.

of α thus obtained furnished the necessary data for the construction of the curves shown in Fig. 1. The curves give the relation between the observed decrease in pressure, denoted by Δp, and the degree of dissociation of nitrogen tetra-oxide. The decrease in pressure, which is represented by the equation, $2NO + O_2 = 2NO_2$, we have designated by x and it is expressed in mm. of α-bromonaphthalene at 15°. It is obtained by substitution in the expression $x = \Delta p/(\alpha - 2)$.

The method for the calculation of the velocity constants differed from that employed by other investigators. The constants found in the paper are "instantaneous" velocity constants. The decrease in pressure of nitric oxide expressed in millimeters of α-bromonaphthalene was plotted on a large scale against time in seconds; the slope of the curve at any point was read directly by the mirror method developed in this Laboratory by Latshaw.[9] This method seems far superior to the evaluation of velocity constants by the use of the integrated expression; it certainly leads to truer values than are obtained by taking the mean slope between two pressure readings, and is much easier to use than an interpellation formula. It is very essential that the curves be drawn accurately for the successful use of the mirror method. The velocity constants were obtained by substitution in the equation for a reaction of the third order, $k = (dp/dt/[NO]^2[O_2]$.

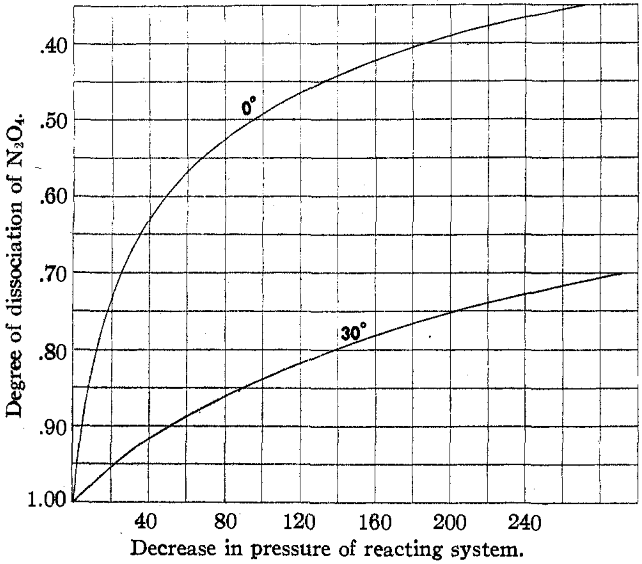

Fig. 1.—Mm. of α-bromonaphthalene at 15°.

In the tables that follow, a and b represent measured initial pressures of oxygen and nitric oxide, respectively, both expressed in millimeters of α-bromonaphthalene. In the column marked Δp is found the decrease in

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[9] Latshaw, This Journal, **47**, 793 (1925).

pressure as read from the film, corrected to 15°. The image of the meniscus on the film was very sharp and could be read by the aid of a vernier scale and reading glass with an accuracy of ±0.1 mm. This is well within the accuracy of the mercury manometer readings which was ±0.05 mm. The column designated α gives the degree of dissociation of nitrogen tetraoxide corresponding to each pressure reading.

Table I

Results

Experiment 2

Small surface at 30°. a = 145.7; b = 210.0

T''	Δp	α	x	dp/dt	$k \times 10^{-7}$
6	8.0	0.980	7.9	2.350	4.52
12	15.2	.963	14.7	2.050	4.80
18	21.1	.950	20.0	1.846	5.08
24	26.3	.939	24.8	1.650	5.30
30	31.4	.931	29.4	1.433	5.39
36	35.8	.923	33.2	1.250	5.39
42	39.1	.918	36.1	1.107	5.32
48	43.3	.911	39.8	0.970	5.39
54	46.5	.906	42.5	.857	5.31
60	49.4	.901	45.0	.795	5.48
66	52.1	.898	47.3	.690	5.27
72	54.3	.895	49.1	.643	5.32
78	56.4	.891	50.9	.590	5.32
84	58.5	.889	52.7	.543	5.33
90	60.4	.886	54.2	.510	5.40
96	62.3	.883	55.8	.464	5.33
102	63.9	.880	57.0	.443	5.42
108	65.2	.879	58.2	.420	5.48
114	66.6	.877	59.3	.384	5.32
120	68.2	.875	60.6	.362	5.39
126	69.5	.873	61.7	.340	5.40
132	70.8	.871	62.7	.324	5.46
138	71.9	0.869	63.5	0.304	5.37
144	72.8	.868	64.3	.294	5.38
150	73.9	.866	65.1	.276	5.38
160	75.5	.865	66.7	.252	5.44
170	77.1	.863	67.8	.236	5.47
180	78.5	.861	68.9	.219	5.44
190	79.9	.859	70.0	.204	5.50
200	81.2	.858	71.1	.186	5.43
210	82.4	.857	72.1	.172	5.40
220	83.3	.856	72.8	.168	5.56
230	84.2	.854	73.5	.154	5.38
240	85.4	.853	74.5	.144	5.43
250	86.2	.851	75.1	.140	5.55
260	87.1	.850	75.7	.132	5.49
270	87.9	.849	76.3	.123	5.34
280	88.6	.848	76.9	.116	5.46
300	90.1	.847	78.2	.106	5.47
320	91.4	.846	79.1	.096	5.37
370	94.3	.842	81.4	.078	5.44
420	96.8	.840	83.4	.062	5.39
470	98.8	.838	85.0	.053	5.46
				Av.	5.40

Experiment 4

Large surface at 30°. a = 146.4; b = 200.5

T''	Δp	α	x	dp/dt	$k \times 10^{-7}$
6	7.8	0.979	7.7	4.300	9.05
12	14.2	.964	13.7	2.025	5.09
18	19.7	.952	18.9	1.625	4.96
24	24.9	.943	23.6	1.483	5.14
30	29.7	.933	27.9	1.283	5.17
36	33.9	.928	31.6	1.117	5.16
42	37.4	.921	34.7	1.023	5.33
48	40.6	.915	37.5	0.900	5.25
54	43.8	.910	40.2	.800	5.20
60	46.6	.906	42.6	.724	5.25
66	49.0	.902	44.6	.675	5.36
72	51.4	.899	46.6	.638	5.33
78	53.6	.896	48.6	.590	5.63
84	55.6	.893	50.3	.548	5.71
90	57.5	.891	51.9	.504	5.70
96	59.3	.888	53.3	.468	5.70
102	60.8	.885	54.5	.440	5.72
108	62.4	.883	55.8	.412	5.76
114	63.9	.880	57.1	.388	5.82
120	65.3	.878	58.2	.364	5.84
126	66.7	.877	59.4	.351	5.99
132	67.9	.875	60.4	.330	6.04
138	69.1	.873	61.3	.316	6.12
144	70.2	0.872	62.3	0.295	6.09
150	71.3	.871	63.1	.280	6.09
160	73.4	.869	64.9	.254	6.24
170	74.7	.866	65.9	.243	6.40
180	76.1	.864	67.0	.234	6.66
190	77.5	.863	68.1	.224	6.92
200	78.8	.861	69.2	.210	7.05
210	80.2	.859	70.3	.194	7.10
220	81.3	.858	71.2	.185	7.25
230	82.4	.857	72.1	.172	7.30
240	83.4	.856	72.9	.161	7.32
250	84.3	.855	73.7	.151	7.37
260	85.3	.853	74.4	.144	7.48
270	86.2	.852	75.1	.138	7.65
280	87.1	.851	75.8	.130	7.70
300	88.6	.849	77.0	.124	8.26
320	90.0	.847	78.1	.118	8.80
370	93.3	.844	80.8	.092	9.24
420	95.9	.842	82.8	.076	9.81
470	98.4	.840	84.8	.062	10.54
520	100.3	.837	86.2	.052	10.93

TABLE I (*Concluded*)

EXPERIMENT 6

Large surface at 0°. $a = 127.5$; $b = 168.7$

T''	Δp	α	x	dp/dt	$k \times 10^{-7}$	T''	Δp	α	x	dp/dt	$k \times 10^{-7}$
8	15.1	0.773	12.3	2.050	8.90	88	69.0	.547	47.5	0.436	10.03
12	20.5	.734	16.2	1.875	9.07	92	70.3	.544	48.3	.410	9.96
16	25.8	.698	19.8	1.625	9.05	96	71.5	.542	49.0	.390	9.94
20	29.4	.678	22.2	1.483	9.11	100	72.7	.540	49.8	.368	9.92
24	33.0	.661	24.6	1.327	9.03	104	73.8	.538	50.5	.348	9.89
28	36.7	.642	27.1	1.184	8.99	108	75.0	.535	51.2	.330	9.84
32	40.0	.630	29.2	1.083	9.04	112	76.0	.532	51.8	.320	9.98
36	43.1	.619	31.2	0.983	9.06	116	77.0	.530	52.4	.310	10.11
40	46.3	.607	33.2	.887	8.98	120	78.0	.529	53.0	.300	10.27
44	48.8	.598	34.8	.833	9.15	124	79.0	.527	53.6	.286	10.24
48	51.2	.592	36.3	.790	9.38	128	79.9	.525	54.1	.281	10.44
52	53.5	.585	37.8	.740	9.52	132	80.8	.523	54.7	.270	10.55
56	55.8	.578	39.2	.707	9.82	136	81.6	.522	55.2	.258	10.50
60	57.8	.573	40.5	.648	9.68	140	82.4	.521	55.7	.252	10.69
64	59.7	.568	41.7	.600	9.61	148	83.8	.518	56.6	.226	10.35
68	61.4	.564	42.8	.570	9.77	160	86.0	.514	57.9	.201	10.37
72	63.2	.560	43.9	.530	9.69	180	89.1	.509	59.8	.176	10.78
76	64.7	.556	44.8	.502	9.71	200	92.0	.504	61.5	.152	11.03
80	66.1	.553	45.7	.472	9.88	220	94.3	.500	62.9	.128	10.77
84	67.6	.550	46.8	.450	9.99	240	96.4	.497	64.3	..	...

EXPERIMENT 9

Small surface at 0°. $a = 232.4$; $b = 215.6$

T''	Δp	α	x	dp/dt	$k \times 10^{-7}$	T''	Δp	α	x	dp/dt	$k \times 10^{-7}$
12	44.9	0.611	32.3	3.600	9.89	114	134.5	0.447	86.6	0.340	12.97
18	60.6	.566	42.3	3.170	9.72	120	136.1	.446	87.6	.318	13.45
24	72.4	.540	49.6	2.280	9.20	126	137.6	.444	88.4	.290	13.38
30	83.1	.519	56.1	1.900	10.08	132	138.9	.443	89.2	.270	13.63
36	90.5	.506	60.6	1.417	9.47	138	140.0	.442	89.9	.256	14.02
42	97.5	.495	64.7	1.217	9.76	144	141.2	.441	90.6	.232	13.82
48	103.1	.487	68.2	1.109	10.74	150	142.3	.440	91.3	.208	13.53
54	107.7	.480	70.9	0.933	10.44	160	143.7	.438	92.0	.197	13.84
60	112.2	.474	73.5	.833	11.15	170	145.8	.436	93.2	.176	14.84
66	115.9	.469	75.7	.706	10.93	210	150.6	.431	96.0	.124	16.07
72	119.0	.465	77.5	.620	10.90	250	154.4	.427	98.7	.096	18.19
78	121.9	.462	79.1	.551	10.90	310	157.8	.424	100.1	.064	20.39
84	124.4	.459	80.7	.490	11.00	360	161.0	.421	101.9	.056	26.19
90	126.8	.456	82.1	.450	11.24	410	163.0	.419	103.1	.040	35.01
96	129.0	.454	83.5	.420	11.93	460	164.6	.418	104.1	.028	39.86
102	130.9	.452	84.6	.402	12.63	510	165.7	.417	104.7	..	...
108	132.8	.449	85.6	.380	13.13						

Discussion of Results

We have included in the tables only one experiment showing the results obtained under a given set of conditions. Duplicate runs were made and excellent checks obtained in every instance. Expt. 2 shows that the equation for a third-order reaction is obeyed rigidly. Another experiment, not included, gives an average for the constants of 5.46 which compares well with 5.40, the average of Expt. 2. In Expt. 4, where the reaction chamber was filled with glass wool, the increasing velocity constants toward the end of the reaction indicate that the order of the reaction has been reduced; in other words, the mechanism has been changed. A similar effect of increased glass surface on the rate of reaction of nitric oxide and chlorine has been noted by Kiss[10] and by Trautz and Henglein.[11] A duplicate experiment fully confirms Expt. 4, the constants being accelerated in an analogous manner.

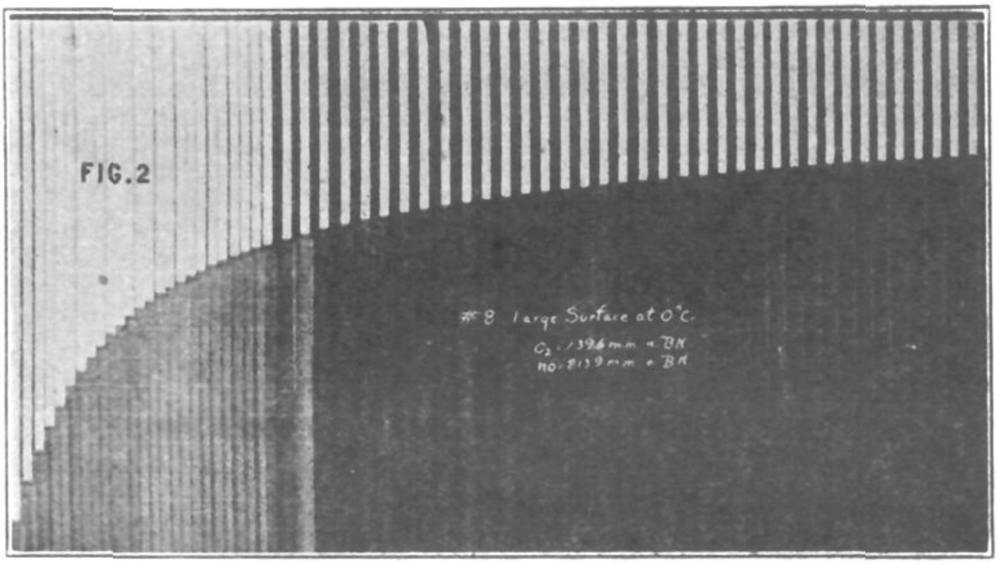

FIG.2

The experiments at the lower temperature, 0°, show a different state of affairs. Acceleration in the constants in Expt. 6 is very slight; while with the small surface in Expt. 9 the constants have increased four-fold at the end of the run. This large increase in the case of the small surface may be

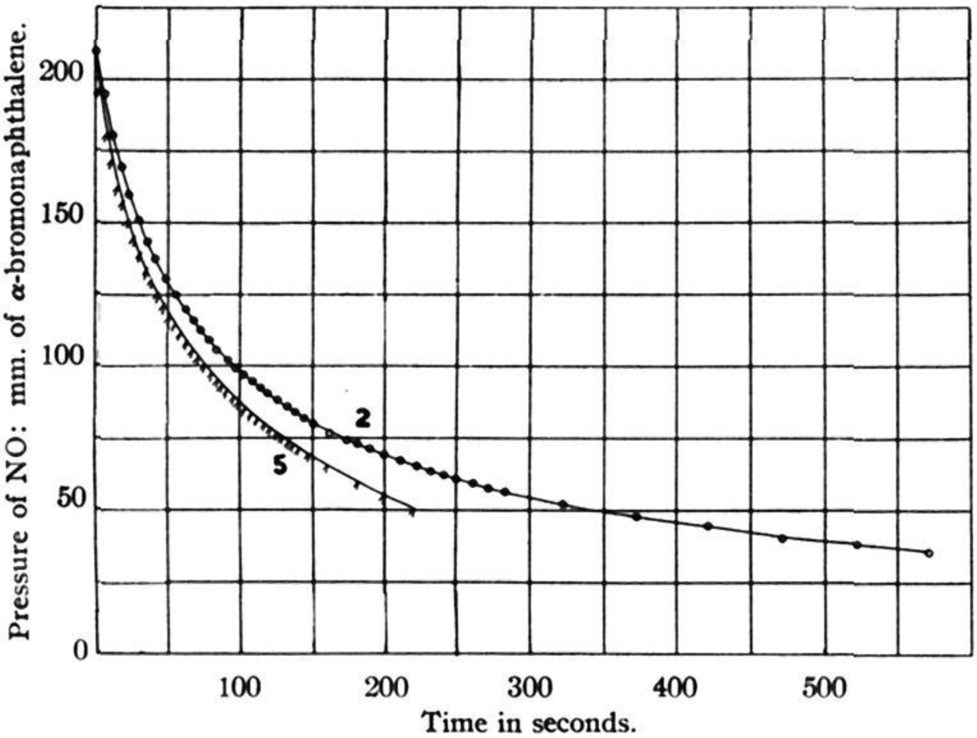

Fig. 3.—Temperature, 30°. No. 5, large surface.
No. 2, small surface.

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[10] Kiss, *Rec. trav. chim.*, **4,** 112 (1923).

[11] Trautz and Henglein, *Z. anorg. Chem.*, **110, 246** (1920).

due to the formation of nitrogen trioxide as a side reaction. The state of dryness in the two reaction vessels is not the same, considering the increase in surface-to-volume ratio of approximately 140 times produced by the glass wool, and it is not possible to pump off traces of moisture at the low temperature. The experiments of Baker[12] indicate that the decomposition of nitrogen trioxide is catalyzed by moisture. Another influence that should be considered and which would operate in the same direction is the imperfect state of the gas, nitrogen tetra-oxide, so close to its boiling point. It will be noted that the pressures used in Expt. 9 were considerably higher than those in Expt. 6. Other experiments, not included in the tables, closely agree with Expts. 6 and 9. In all cases, however, where acceleration in the velocity constants occurs, it is noticeable only in the latter half of the reaction.

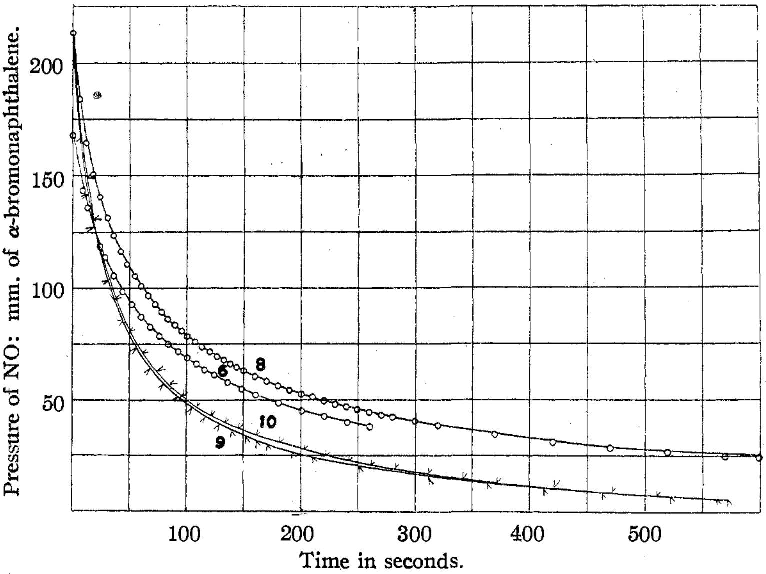

Fig. 4.—Temperature, 0°. Nos. 6 and 8, large surfaces. Nos. 9 and 10, small surfaces.

Plots of some of the experiments are shown in Figs. 3 and 4. It was from these curves that the slopes were read. The curves give some idea of the accuracy of the data and check the calculated initial pressures. No evidence of autocatalysis was apparent from the curves.

A comparison of the velocity measurements in the present work with those of Bodenstein shows a fairly good agreement. The average of all the experiments at 30° with the small surface is 5.43×10^{-7}. In the first half of all the experiments at 0° there is little difference between the large

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[12] **Baker**, *J. Chem. Soc.*, **91**, 1862 (1907).

and small surface. Taking an average of all the experiments when 50% of the nitric oxide has been converted gives a value of 9.10×10^{-7} for the lower temperature. These constants may be converted into terms of moles per liter with time expressed in minutes by the formula

$$K_c = 2 \times 60 K_p \frac{1}{a^2} = 2 \times 60 K_p \left(\frac{1.5}{13.6} \times \frac{1}{760} \times \frac{273}{T} \times \frac{1}{22.4}\right)^{-2}$$

(It is necessary to multiply by two, since Bodenstein used only one-half the measured pressure of nitric oxide in the calculation of his velocity constants.)

The table shows the comparison.

	273°K.	303°K.	$\frac{K_{t+10}}{K_t}$
k_c(Bodenstein)	2.09×10^{-6}	1.70×10^{-6}	0.933
k_c(Our value)	2.60×10^{-6}	1.94×10^{-6}	.916

The customary 10° temperature coefficient is given in the last column.

Negative Temperature Coefficient

The negative temperature coefficient of this reaction seems to point to an unstable intermediate compound which is in the state of rapid equilibrium. Gay Lussac, in 1842, first stated the general principle that in complex reactions, that compound is first formed which is the least stable. Skrabal[13] presents the corollary that, when intermediates are possible, a slow reaction produces the most stable end product. Of the possible intermediates, N_2O_2 and an iso N_2O_4 may be considered. The latter would probably be a peroxide as suggested by G. N. Lewis.[14] The reactions involving these intermediates would be represented as follows

$$2NO \rightleftharpoons N_2O_2 \text{ (fast)} \tag{1}$$

$$N_2O_2 + O_2 = 2NO_2 \text{ (measurably slow)} \tag{1a}$$

$$2NO + O_2 \rightleftharpoons N_2O_4 \text{ (iso) (fast)} \tag{2}$$

$$\text{(iso)}N_2O_4 = 2NO_2 \text{ (measurably slow)} \tag{2a}$$

Assuming that Reactions 1 and 2 are in rapid equilibrium, the reaction the speed of which we were measuring would be that of 1a or 2a. In all cases the establishment of the equilibrium between nitrogen dioxide and the tetra-oxide is immediate as far as we are concerned. Since an increase in temperature would shift the equilibrium in Reactions 1 and 2 toward the left, we should expect a negative temperature coefficient. Whenever, then, an equilibrium of the type given above is superimposed upon a normal reaction, a reversed temperature coefficient should result. Skrabal[15] has described such a reaction in solution, between iodic acid and sulfurous acid. As to what intermediate is formed in the reaction between nitric oxide and oxygen, that question awaits more experimental evidence for its answer. A minute amount of the intermediate would account for the speed of the

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[13] Skrabal, *Z. Elektrochem.*, **14,** 529 (1908).

[14] Lewis, *Chem. Reviews,* **1,** 231 (1924).

[15] Skrabal, *Z. Elektrochem.*, **21,** 461 (1915).

reaction. An attempt is being made to isolate and identify an intermediate at liquid-air temperatures.

Summary

1. The velocity of the reaction between nitric oxide and oxygen has been studied at 0° and 30°. The reaction was found to be one of the third order at the higher temperature; while the acceleration in the velocity constants at 0° may be due to the formation of N_2O_3 or to the imperfect state of N_2O_4.

2. A large increase in surface-to-volume ratio by the introduction of glass wool into the reaction chamber caused a marked acceleration in the velocity constants in the latter half of the reaction at 30°; the acceleration was less marked at the lower temperature.

3. No evidence of autocatalysis was obtained.

4. The negative temperature coefficient of the reaction has been ascribed to intermediate compound formation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NO. 468]

EXPERIMENTAL STUDIES ON THE HYDROGEN ELECTRODE[1]

BY H. T. BEANS AND L. P. HAMMETT

RECEIVED OCTOBER 14, 1924 PUBLISHED MAY 5, 1925

Two or more hydrogen electrodes in the same solution must agree in potential and their common potential will be the true hydrogen electrode potential of the solution, provided the system is at equilibrium. The present investigation is an attempt to classify some of the conditions which give rise to variable potentials of hydrogen electrodes with platinum catalysts and to show how the variability may be eliminated.

Apparatus and Materials.—Electrical measurements were made with a Leeds and Northrup Type K potentiometer, using a carefully standardized Weston cell. The constant temperature bath was a Freas water thermostat, set at 25.00°. The electrical system was carefully tested for leakage. The saturated calomel half-cell[2] was used as reference electrode. Several cells prepared at different times and from different materials showed a maximum variation of 0.3 mv. The hydrogen electrode vessel is shown in Fig. 1. An apparatus on the Soxhlet principle designed by Dr. Walden of this Laboratory was used for cleaning electrodes.

Hydrogen was prepared by electrolysis of 15% sodium hydroxide solution. It was passed successively through a column of cotton, an electrically-heated silica tube containing platinized asbestos, a bead tower through which dil. sulfuric acid was continu-

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[1] The material of this article is taken from a dissertation submitted by L. P. Hammett to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Fales and Mudge, THIS JOURNAL, 42, 2434 (1920).