Summary

1. The vapor pressure of carbon dioxide at the ice point was accurately measured to obtain a pressure system for the calibration of piston gages which would be less complicated than the mercury column. A description of the apparatus used in these measurements is given.

2. All of the gages in this Laboratory (nine in number) were balanced in turn against the vapor pressure of pure liquid carbon dioxide at 0°. On the basis of the constants of these gages, determined by comparison against a mercury column during the period from 1911 to 1924, a preliminary value of 26144 ± 2.6 mm. of mercury was obtained for the vapor pressure, omitting the measurements on one gage whose constant was obviously in error.

3. Three gages were calibrated with an improved, water-jacketed mercury column, yielding constants consistent to 1 part in 25,000, and a fourth one was compared directly with one of these three standard gages.

4. A number of new measurements of the vapor pressure were made with these standard gages and the preliminary values with these were recalculated, using the constants obtained by comparison with the improved mercury column. The value for the vapor pressure of liquid carbon dioxide at 0° thus deduced is 26144.7 ± 1.0 international millimeters of mercury, or 34.4009 ± 0.0013 atmospheres ($g = 980.665$).

5. It is suggested that the carbon dioxide liquid-vapor system at the ice point is suitable for adoption as a definite calibration point for pressure gages, since it satisfies the requirements as to accuracy, simplicity and ease of manipulation.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 135]

THE THERMAL DECOMPOSITION OF OZONE. I. THE HOMOGENEITY, ORDER, SPECIFIC RATE AND DEPENDENCE OF RATE ON TOTAL PRESSURE

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1. Introduction

For several years the authors have been engaged in an investigation of the kinetics of the thermal decomposition of ozone. The justification for such an extended research upon this bothersome chemical change is three-fold. In the first place, there existed remarkable discrepancies in the results of the several researches previously carried out upon it, and these discrepancies were of sufficient significance to leave the kinetics of the decomposition entirely in doubt; second, it seemed desirable, from the point of view of developing the experimental technique of chemical

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kinetics, to discover and remove the causes of the apparent difficulties; third, although the conditions influencing the decomposition are apparently difficult to control, the reaction possesses certain features which would make it particularly useful as a tool in the general study of reaction mechanism, if its true nature could be determined. As these investigations progressed, the importance of this last point became increasingly apparent.

As a result of the work to be described in this and two following papers, we believe that considerable light has been thrown on the discrepancies present in the literature, and that sufficient advance has been made in the technique of ozone experimentation to make it now possible for different experimenters to obtain reasonably concordant results.

2. The Problems to Be Studied

There were several questions concerning the thermal decomposition of ozone which were definitely in doubt as the result of previous investigations. In the first place, there was lack of agreement as to the *homogeneity* of the reaction, even at temperatures high enough so that the known slow first-order decomposition on the walls could be neglected. In the second place, although the early careful measurements of Warburg and Jahn had shown the reaction to be closely of the *second order* with respect to ozone, later measurements had in some cases shown considerable deviations in the direction of the first order, especially towards the end of the decompositions. In the third place, although the *specific rates* obtained by Warburg and Jahn were in approximate agreement, other investigators had sometimes obtained considerably higher specific rates. In the fourth place, although Jahn had found the rate to be inversely proportional to the *total pressure* of the decomposing oxygen-ozone mixture, later investigators had sometimes obtained an effect of pressure which was less than the inverse first power. In the fifth place, although Jahn had obtained some direct and much indirect evidence that the rate was inversely proportional to the concentration of *oxygen*, Chapman and Jones had added oxygen to ozone and found almost no inhibiting effect. And finally, although Clement had made measurements to determine the *temperature coefficient* of the rate of decomposition of ozone, his specific rates at a given temperature were much higher than those obtained by Warburg and by Jahn.

In the present paper we shall discuss the homogeneity, order, specific rate, and effect of total pressure on the rate. In a second paper, we shall consider the effect of oxygen on the rate. A third paper will discuss the temperature coefficient of the reaction rate. The material to be presented necessarily consists partly of a critique of previous work and partly of a description of our own experiments which were pertinent to the phase of the subject under discussion.

3. The Homogeneity of the Reaction

The decomposition of ozone, as is the case for a number of other gas reactions, may apparently take place under suitable conditions, either homogeneously in the gas phase or heterogeneously through catalysis on the walls. The first evidence on this point was obtained by Warburg,[2] who measured the rate of decomposition of ozone both at room temperature and at temperatures of 100° and above. He found the reaction at room temperature to be of the first order with respect to ozone, and the specific rate to vary markedly from tube to tube. At the higher temperatures the reaction was of the second order and of approximately the same specific rate in a number of his good tubes. Certain of his tubes, however, which gave very high first-order rates at room temperature, still tended to give rates between the first and second order at the higher temperatures. This furnishes strong evidence that the reaction at low temperatures is predominantly of the first order and catalyzed by the walls, but that at temperatures of 100° and above, in suitable containers with proper cleaning, the reaction can be made to take place substantially homogeneously.

This conclusion was made more certain by the work of Clarke and Chapman,[3] who followed the decomposition of two portions of the same sample of ozone in two bulbs of different surface to volume ratio set side by side and both at 100°. In the course of their work the surface-volume ratio for the two bulbs differed as much as seven fold, but the pressure change with the time was practically the same for each bulb. In the six experiments, the results of which Clarke and Chapman gave graphically in their article, the second-order character of the decomposition is indeed only fairly well exhibited, and the second-order constant shows considerable fluctuation from run to run.[4] But this does not affect the conclusion in regard to the homogeneity of the reaction since, regardless of the character of the pressure change with time, it could not have been the same in the two bulbs if the major portion of the reaction were taking place on the walls.

Although it thus appears that the decomposition at 100° and higher can be carried out under conditions such that it is at least predominantly homogeneous, this of course does not mean that heterogeneous decomposition may not enter under certain circumstances. Thus, as already noted, Warburg had difficulty with some of his tubes at the higher temperatures. In addition, Perman and Greaves[5] obtained different rates of decomposition in different tubes and found also, as perhaps might be

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[2] Warburg, *Ann. Physik*, **9**, 1286 (1902).

[3] Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908).

[4] These conclusions result from calculations which we have made on the curves given by Clarke and Chapman.

[5] Perman and Greaves, *Proc. Roy. Soc.*, **80A**, 353 (1908).

expected, that the rate was markedly accelerated in a tube filled with clay pipe stems. Griffith and McKeown[6] also found different rates in different tubes.

For the purposes of the present considerations we shall only be interested in the homogeneous decomposition of ozone. We have, however, considerable evidence that we were able to obtain the homogeneous reaction, as will become apparent in the course of the articles. In the first place, working by the static method at 100° in a Pyrex tube, with a ratio of volume to surface of 0.87 cm., we obtained second-order rates of decomposition which agreed reasonably with those of Warburg,[2] Jahn,[7] and Chapman and his co-workers,[3] carried out in tubes of quite different glass. In the second place, working by the dynamic method in a tube with a ratio of volume to surface of 0.13 cm., we obtained at temperatures higher than 100° values of the specific second-order rate which extrapolate back to the ones mentioned above, which we obtained by the static method at 100°. In the third place, we also made measurements at a single higher temperature by the dynamic method with a tube having a ratio of volume to surface of 0.34 cm., and obtained concordant results. Finally, we carried out at 100° by a modified static method, a number of decompositions in Pyrex tubes having a ratio of volume to surface of 0.49 to 0.59 cm., and although the experiments were not designed for great accuracy, most of the results nevertheless were consistent with those obtained at 100° with the larger bulb. (See, however, Ref. *a* of Table XII in this article and Ref. *a* of Table III in the next article of the series.[8]) These results furnish strong evidence that we were actually working with the homogeneous change.

4. Order of the Reaction at 100° and Above

Critique of the Literature.—As already mentioned, the earlier careful researches of Warburg and Jahn apparently showed that the homogeneous decomposition of ozone at temperatures of 100° and above was of the second order with respect to the ozone. This was also substantiated, although less satisfactorily, by the work of Clarke and Chapman[3] and of Chapman and Jones.[9] Our own work, as will be shown below, also confirms at 100° and higher temperatures the second-order character of the decomposition.

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[6] Griffith and McKeown, *J. Chem. Soc.*, **127**, 2086 (1925).

[7] The comparison with Jahn's results involves an extrapolation to the conditions of the other experimenters.

[8] Wulf and Tolman, THIS JOURNAL, **49**, 1202 (1927).

[9] Chapman and Jones, *J. Chem. Soc.*, **97**, 2463 (1910). A majority of the runs made by Clarke and Chapman and by Chapman and Jones on pure ozone have been tested for order by the present authors, using the method of Ref. 10, and have been found to exhibit an approximately second-order character.

In contrast to these five independent confirmations of the second-order character of the decomposition are the results of Perman and Greaves[5] and Griffith and McKeown.[6]

Perman and Greaves worked at a variety of temperatures and total pressures, and found at 60, 80, 100 and 120° that the specific rate of the decomposition calculated as second order increased seriously during their runs. It is difficult to account for the divergence of these results from those of the majority of other investigators.

The fact already mentioned, that they found that the rate of decomposition depended on the particular tube used and its condition, would at first sight indicate that Perman and Greaves were measuring the combined results of the homogeneous second-order decomposition and a first-order wall reaction, which would indeed lead to an increase during the run in the specific rate, calculated as second order. It is difficult, however, to reconcile this explanation with the fact that at total pressures of one atmosphere and less they obtained at the beginning of their runs rates of decomposition as low as or lower than those made probable by the work of Warburg and Jahn. Hence, in order to maintain this explanation we should have to assume that the second-order part of their decompositions had an unusually low rate. This is not impossible, however, since as we shall see later, different samples of ozone, all of which decompose with a second-order rate, may vary widely in their specific rates.

Besides the uncertainty as to the possibility of contact catalysis on the walls of their tubes, it is to be noted that Perman and Greaves employed stopcocks in their apparatus, and do not appear to specify the lubricant. Any organic lubricant would, of course, be very dangerous in experiments on ozone decomposition. Their technique of determining the final pressures after all the ozone was decomposed is also open to criticism, and the calculated constants are very susceptible to small errors in their final pressure. The method consisted in decomposing the ozone left at the end of the run by heating a portion of the bulb for ten minutes with a Bunsen burner. They give, however, no description of the test which they made, to show that this actually leads to complete decomposition. In spite of such possible sources of error, we have no certain explanation of the deviation from a second-order decomposition found by Perman and Greaves.

Somewhat similar remarks must also be made with respect to the deviations from second order given by the more recent work of Griffith and McKeown. They too found, at total pressures of one atmosphere or less, rates of decomposition early in the runs, as low as or lower than those we must accept as usual for the second-order homogeneous decomposition, these rates increasing as the runs progressed. It must be mentioned, however, that certain portions of their technique were not above criticism. In the first place, their apparatus contained "dead space," which necessitated corrections to their pressure readings. In the second place, their final pressures to be used in the calculations were determined not from a decomposition of the ozone left at the end of their runs, but from a chemical analysis of the ozone remaining at that time. The resulting combination in a single calculation of concentrations determined by different methods is, of course, unfortunate in view of the sensitiveness of the calculations to the value of the final pressure. Here too, however, we have no certain explanation of the deviations which they found from a second-order decomposition.

Experiments on Order at 100° by the Static Method.—Our own experiments on the order of the reaction were made at 100° by the static method of following the pressure change in a bulb of decomposing ozone, also at 100° by a modified static method in which bulbs containing ozone were heated and the contents analyzed, and at higher temperatures by the dynamic method based on analyses of the ozone entering and leaving a heated tube.

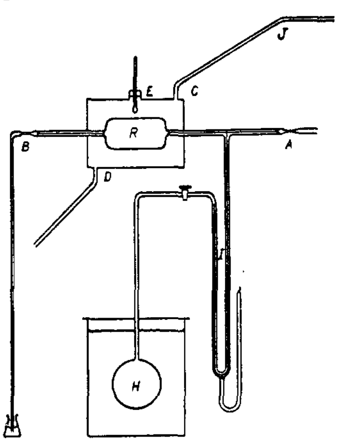

Fig. 1.

The apparatus used for the measurements at 100° by the static method did not differ in principle from those heretofore employed, so that a diagram (see Fig. 1) and a brief description of it will be sufficient.

The reaction tube *R* is of Pyrex and has an approximate capacity of 109 cc. with a surface of 126 sq. cm. It is connected by capillary tubing to a capillary U-shaped manometer *I*, containing sulfuric acid of known density, and thence to a buffer bulb *H* containing dry air, in a carefully thermostated water-bath. The reaction tube is enclosed in a brass steam chamber, provided with stuffing boxes for the exit tubes, covered with asbestos insulation, and furnished with a thermometer at *E*. A boiler with an electric heater is arranged to give a constant supply of saturated steam which enters the chamber at *C* and leaves at *D*. Arrangements are also made for superheating the steam to 150° to secure complete decomposition of the ozone at the end of each run.

The reaction tube was filled by first sweeping at room temperature for a period of one to four hours with ozonized oxygen dried by passage over sulfuric acid. Without altering the gas flow, the chamber was then brought to 100° in about 12 minutes and the flow continued for five minutes longer. The reaction tube was then sealed off at the constrictions *A* and *B*.

The decomposition was followed by reading the pressure of the manometer, and the final pressure was determined after raising to 150° and holding at that temperature for 15 minutes. In view of the extremely slow rate of change at the end of a second-order decomposition, and the sensitiveness of the calculations to the value of the final pressure, it is now believed that it would have been better to heat to a higher temperature. The capillaries were of small enough bore so that the reaction could be regarded as taking place at constant volume, and no corrections had to be applied.

In Table I the data and results of two typical runs, Nos. 10 and 15, are given at length, the calculations of the specific second-order rate being made for each observation in the conventional way using the relation

$$k_2 = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_0}\right) = \frac{RT}{t}\left(\frac{1}{p} - \frac{1}{p_0}\right) \qquad (1)$$

where p_0 and p are the partial pressures of ozone present at time 0 and t, respectively.

The time in Table I is given in minutes, and the pressures in cm. of sulfuric acid; d., 1.832. The values of P in the table are the differences between the final pressure after complete decomposition and the instantaneous pressure, and hence must be multiplied by 2 to give the instantaneous partial pressure of ozone. Hence the calculation of k_2 in cc./

TABLE I

DATA AND RESULTS OF TWO EXPERIMENTS PERFORMED BY THE STATIC METHOD

Run 10

t, min.	P, cm. of H_2SO_4	$k_2 \times 10^{-2}$, cc./(moles sec.)
0	9.61	
10	8.41	2.13
11	8.32	2.11
12	8.24	2.07
13	8.15	2.06
14	8.08	2.02
15	7.98	2.03
16	7.87	2.07
17	7.80	2.04
19	7.65	2.01
21	7.47	2.04
23	7.33	2.02
25	7.22	1.98
27	7.12	1.93
29	6.97	1.95
31	6.82	1.97
33	6.70	1.97
35	6.60	1.95
37	6.49	1.94
40	6.33	1.94
43	6.17	1.94
46	6.03	1.93
50	5.86	1.91
54	5.68	1.92
58	5.52	1.91
62	5.36	1.91
67	5.18	1.91
72	5.04	1.88
77	4.89	1.88
82	4.76	1.86
87	4.60	1.87
92	4.45	1.89
97	4.33	1.88
102	4.22	1.87
107	4.12	1.86
112	4.00	1.87
117	3.90	1.87
122	3.81	1.87
127	3.74	1.85
132	3.63	1.87
137	3.55	1.87
148	3.41	1.84
160	3.23	1.85
172	3.09	1.84
187	2.93	1.83
202	2.77	1.83

TABLE I (*Concluded*)

t, min.	P, cm. of H_2SO_4	$k_2 \times 10^{-2}$, cc./(moles sec.)	t, min.	P, cm. of H_2SO_4	$k_2 \times 10^{-2}$ cc./(moles sec.)
		Run 15			
0	4.72		49	3.69	1.74
10	4.48	1.63	54	3.59	1.78
12	4.42	1.71	59	3.52	1.76
14	4.37	1.74	64	3.44	1.77
16	4.31	1.81	69	3.35	1.81
18	4.28	1.73	74	3.29	1.79
20	4.22	1.81	79	3.23	1.78
23	4.18	1.71	84	3.17	1.77
26	4.12	1.70	94	3.02	1.82
29	4.05	1.74	104	2.92	1.81
32	3.98	1.77	106	2.90	1.80
36	3.91	1.75	108	2.88	1.80
40	3.83	1.77	110	2.86	1.80
44	3.78	1.72	112	2.84	1.80

(moles sec.) can be made from the data given with the help of the numerical equation

$$k_2 = \frac{82.07 \times 373 \times 76 \times 13.596}{60 \times t \times 1.832 \times 2}\left(\frac{1}{P} - \frac{1}{P_0}\right) \qquad (2)$$

where P_0 is the pressure at our arbitrarily chosen starting time. The actual temperature at which these runs were made was about 0.4° below 100°, owing to an atmospheric pressure somewhat less than 760 mm. The fluctuation in the barometer during any given run was not sufficient to introduce difficulties.

The results of eleven runs made under our best experimental conditions are also shown graphically in Fig. 2, in which the reciprocal of half the pressure of ozone for each observation is plotted for each run against the corresponding value of the time. Since Equation 1 can be rewritten in the form

$$1/p = (k_2/RT)t + 1/p_0 \qquad (3)$$

it is evident that a straight line is the criterion for a second-order change with this method of plotting. Furthermore, the slope of this line can be used for calculating the specific reaction rate k_2.[10]

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[10] The calculation of k_2 from the plots in accordance with Equation 3 is certainly superior to the calculation from Equation 1 as given in Table I. The use of Equation 1 makes the calculated value of k_2 depend on the particular observation chosen for the initial pressure, and if this is slightly off, a trend not actually given by the experimental data will appear in the successive values obtained for k_2.

We have also devised and used in this work another graphical method for treating second-order reactions which is less accurate, but which can be applied to cases where the final pressure is not known. The partial pressure of ozone p_0 present at the start of the run is evidently twice the difference between the final and initial pressures read, $p_0 = 2(p_f - p_i) = 2\Delta p_\infty$, and the partial pressure of ozone present at time t is $p = 2(p_f - p_i - \Delta p) = 2(\Delta p_\infty - \Delta p)$. Substituting in Equation 3 and rearranging we obtain $1/\Delta p = RT/[2(\Delta p_\infty)^2 k_2 t] + 1/\Delta p_\infty$. Hence, by plotting the reciprocal of

It will be noted that the results given in Table I and graphically in Fig. 2 (lines inserted with a straight edge) amply confirm the fact that at least under suitable conditions the decomposition is of the second order with respect to the concentration of ozone. Furthermore, the consistency of the readings within each run is evidence for the accuracy with which the pressure change was experimentally followed.

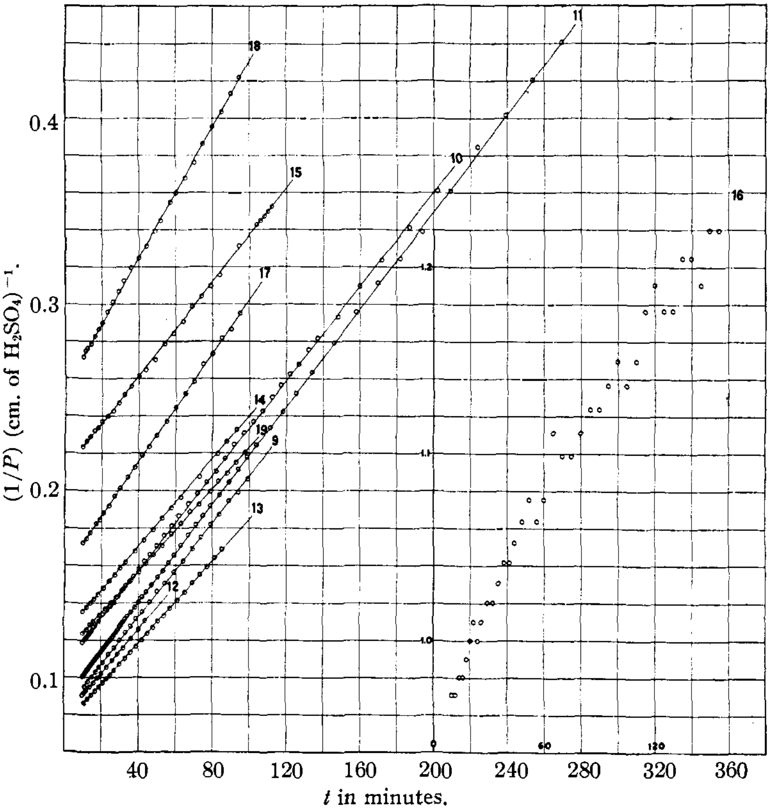

Fig. 2.

Although the above results show that each of these individual samples of ozone decomposed at 100° with a rate which was second order almost within the limits of the experimental accuracy, the specific second-order rates for the different decompositions are not in exact agreement, as shown in Table II.

pressure rise against the reciprocal of time, we obtain for a second-order reaction a straight line, whose slope and intercept permit a simultaneous determination of final pressure and specific rate. The method is not very accurate, owing to the error in $(\Delta p_\infty)^2$. It is, we believe, superior to previous methods that have been employed, in cases where the final pressure is not known, since the straightness of the line affords an immediate check on the order of the reaction.

TABLE II

RESULTS OF ELEVEN EXPERIMENTS PERFORMED BY THE STATIC METHOD

Expt. no.	Initial concn., moles/cc. × 10^7	$k_2 \times 10^{-2}$, cc./(moles sec.)
Ozone made by electrolysis of sulfuric acid solution		
9	14.46	1.82
10	11.13	1.83
11	13.21	1.89
17	7.38	2.09
18	4.60	2.52
19	10.31	1.59
	Av.	1.96
Ozone made by silent discharge, using Linde tank oxygen		
12	14.64	1.69
13	15.44	1.59
14	9.31	1.67
15	5.47	1.82
16	1.22	(3.54-2.16)[a]
	Av.	1.69

[a] The concentration of ozone in this run was too low to permit an accurate measurement of the pressure change with time. It may be seen from Fig. 2 that the measurements showed some deviation from the second order. In Table II, approximate limits of the variation in the coefficient are given. This result is not included in the average.

These deviations from constancy in the specific rate k_2 for different samples indicate that certain factors, having only a moderate effect, however, on the rate of decomposition of ozone, are not yet completely controlled. Such deviations in specific rate will be more completely discussed in Section 5.

The eleven runs presented in Fig. 2 and Table II are chosen as being those made under the best experimental conditions from a total of 37 runs made at 100° by the static method. A true picture of the nature of the results cannot be obtained, however, unless we briefly describe the character of the other runs.

Runs 1 to 5 were made before the technique had been completely developed. The apparatus corrections were large, since the buffer bulb had not yet been thermostated, and the manometer tube was not a capillary so that corrections had to be introduced for the motion of the manometer liquid. Furthermore, no value was obtained for the total ozone by decomposing at the higher temperature, and this had to be determined from the run itself by the graphical method.[10] This made the values of the calculated constants inaccurate. Nevertheless, the results were sufficiently good to show that these decompositions were very closely of the second order, but had specific rates which varied markedly among themselves and were, on the average, some two-fold higher than the eleven runs reported above. We have no certain explanation for this, although it may be a more extreme illustration of the fact already noted that ozone may decompose with a good second-order rate, and yet the constant vary markedly from run to run. (See also Section 5.)

Runs 6, 7 and 8 were made with electrolytic ozone immediately after fresh sulfuric acid had been put in the generator, and gave very high rates of decomposition, up to ten-fold greater than for the eleven best runs, and only one of the three runs gave a second-order decomposition. This indicates some catalyst present in the fresh sulfuric acid (oxides of nitrogen?) which was gradually eliminated as the generator was used.

Runs 9 to 19 are the eleven runs reported in Table II and made as already described. The electrolytic ozone was made from the same acid as in Runs 6, 7 and 8.

In the remaining runs, stopcocks were introduced instead of constrictions at *A* and *B* in an attempt to cut down the time of experimentation. These stopcocks were first lubricated with sulfuric acid, which made it difficult to go to the higher temperatures for complete decomposition without leaks.

Runs 20 and 21 gave second-order rates somewhat higher than the average of the eleven best runs.

Runs 22 and 23 were made with electrolytic ozone from fresh sulfuric acid and again gave very high rates of decomposition which were not second order.

Runs 24 to 29 were made using calcium chloride as a drying agent instead of the superior material, sulfuric acid. All of these runs but one gave good second-order constants, but somewhat higher than those in the eleven best runs.

Runs 30 to 37 were made with vaseline-lubricated stopcocks. All of the rates of decomposition were quite high and only four of the eight runs followed the second order, rather convincingly indicating catalyst from the vaseline.

One probable conclusion to be drawn from these data is that the rate of decomposition of ozone is easily influenced by traces of catalyst, and that the lowest rates are most likely to correspond to the true decomposition process of pure ozone.

Experiments on Order at 100° by a Modified Static Method.—In addition to these experiments in which the decomposition was followed by the pressure change, experiments were also made at 100° in which four Pyrex bulbs of about 30cc. capacity were filled with ozone, one of them being kept as a control, and the others heated in boiling water for varying lengths of time. The ozone contents of the tubes were then determined iodimetrically.

After some preliminary experiments, in which no mixing bulb was present in the line leading to the four bulbs and which gave erratic results, the four experiments shown in Table III were performed with ozonized Linde oxygen at a total pressure of about 71 cm.

TABLE III

EXPERIMENTS USING THE MODIFIED STATIC METHOD

Reaction time, min.	$C \times 10^7$, moles/cc.	$k_2 \times 10^{-2}$, cc./(moles sec.)	$k_1 \times 10^{-4}$, sec.$^{-1}$
	Experiment 1		
0	10.53	..	..
15	9.08	1.69	1.65
40	7.38	1.70	1.49
100	5.07	1.70	1.22
	Experiment 2		
0	14.91	..	..
15	12.24	1.62	2.19
40	9.96	1.39	1.68
100	6.47	1.46	1.39
	Experiment 3		
0	13.86	..	..
15	(Bulb cracked)	..	..
40	8.57	1.85	2.00
100	5.27	1.96	1.61
	Experiment 4		
0	12.74	..	..
25 + 25 + 50 = 100	5.78	1.58	..
40 + 60 = 100	5.68	1.62	..
100	5.75	1.59	..
	Av.	1.65	

In the last experiment the three bulbs were heated for the same total time, 100 minutes, but two of the bulbs were cooled after part of the run and then put back into the boiling water. This was done to test the possibility that the instantaneous rate of decomposition of ozone might depend on the previous history of the decomposition mixture. This possibility was also tested in Run 35, performed by the original static method. No evidence of such an effect was ever found.

It will be noted that all the samples decomposed at closely the same second-order rate, as given by the approximate equality of the calculated second-order constants k_2. The calculated first-order constants k_1, however, deviate widely.

The average value for k_2 for all these runs made at a total pressure of 70 cm. was 1.65×10^2 cc./(moles sec.), and this corrected to 76 cm. (see Section 6) corresponds to a value of k_2 at one atmosphere of 1.54×10^2 cc./(moles sec.), thus being even lower than the lowest values given in Table II.

Experiments on Order at Temperatures Above 100° by the Dynamic

Method.—In addition to the foregoing experiments specifically made for the purpose of testing the order of the decomposition of ozone at 100°, incidental tests of order at higher temperatures were obtained from dynamic experiments made primarily for other purposes. The method consisted in passing ozonized oxygen through a tube heated in a paraffin bath to a constant high temperature (about 148°) and analyzing the inflowing and outflowing gas for ozone. The apparatus and method will be more fully described in the second article of this series.

The tests of order were made on two different kinds of ozone. The first kind was made electrolytically from sulfuric acid and will be called "acid" ozone. The second kind was made by generating oxygen from caustic solution and then ozonizing by the silent discharge; this will be called "caustic" ozone. The "caustic" ozone undoubtedly contained catalyst as will appear more clearly in the second article of the series. Tables IV and V show the results obtained with the two kinds of ozone.

TABLE IV

"ACID" OZONE

Reaction time, sec.	$C_0 \times 10^7$, moles/cc.	$C \times 10^7$, moles/cc.	$k_2 \times 10^{-4}$, cc./(moles sec.)
38.4	8.20	5.47	1.58
38.4	7.86	5.17	1.73
48.0	7.77	4.70	1.75
48.0	7.52	4.65	1.71
64.1	7.21	4.12	1.63
64.1	7.33	4.37	1.45
96.1	6.10	3.07	1.68
96.1	6.23	2.91	1.91
		Av.	1.68

TABLE V

"CAUSTIC" OZONE

Reaction time, sec.	$C_0 \times 10^7$, moles/cc.	$C \times 10^7$, moles/cc.	$k_2 \times 10^{-4}$, cc./(moles sec.)
38.4	11.46	6.37	1.81
38.4	10.23	5.85	1.90
48.0	8.73	4.51	2.23
48.0	8.21	4.31	2.29
64.1	7.14	3.31	2.53
64.1	7.15	3.26	2.60
90.6	6.31	2.62	2.47
90.6	6.41	2.53	2.63
		Av.	2.32

The fair constancy of k_2, even when the reaction time was more than doubled, shows that these kinds of ozone actually decomposed nearly with a second-order rate. The results with the "caustic" ozone are less constant but, as we shall see in the second article of this series, "caustic" ozone has a tendency to give low values of k_2 when C_0 is high.

Again, we notice that different kinds of ozone may decompose in accordance with the second order, and yet with different specific rates.

5. The Specific Rate of Ozone Decomposition

The results presented in the preceding section show that in agreement with all other experimenters, except Perman and Greaves, and Griffith and McKeown, we have been able to prepare ozone which decomposes with a rate which is very closely of the second order with respect to the ozone. We have found, however, different specific rates for different samples of ozone, and must examine this further. Let us first consider the experience, in this connection, of other investigators who have obtained second-order decompositions.

Warburg[2] made eight experiments on the order at 100° and a pressure somewhat greater than 1 atmosphere (average, 92.4 cm.). He used five different tubes in this work, all of which were chosen from apparatus which showed only a small rate of decomposition at room temperature, and obtained good second-order decompositions in them. The specific rates found in the different pieces of apparatus were as shown in Table VI.

TABLE VI

EXPERIMENTS OF WARBURG AT 100°

Apparatus no.	VII	VIII	IX	II	III	
No. of expts.	2	2	2	1	1	
$k_2 \times 10^{-2}$ cc./(moles sec.)	1.42	1.37	1.28	1.07	1.08	Av. 1.24

It will be seen that Warburg also obtained considerable variation in his constants for experiments apparently made under just the same conditions. Moreover, similar deviations were obtained even in a single tube. Thus, the two individual runs made in Tube IX on two successive days gave specific rates which differed by 10% from the average value of 1.28×10^2. Hence Warburg's actual deviations are greater than indicated by the averages in Table VI.

Warburg's experiments were made by ozonizing a given amount of oxygen directly in his tubes and then heating to 100°. Hence, his total pressures at the time of decomposition were greater than 1 atmosphere and, as calculable from the data in his article, the average pressure for the decompositions in Table VI was 92.4 cm. Hence, assuming k_2 to be inversely proportional to total pressure (see Section 6), Warburg's average result then gives 1.54×10^2 cc./(moles sec.) as the value for k_2 at 1 atmosphere and 100°.

The experiments of Clement[11] were made by the dynamic method. At 100° and 1 atm. pressure he made only two experiments on the rate of decomposition of ozone and obtained for k_2 the two rather high and

[11] Clement, *Ann. Physik*, **14**, 341 (1904).

discordant results 3.26×10^2 and 4.96×10^2 cc./(moles sec.) with a mean of 4.11×10^2.

Jahn[12] worked only at 127°, but at a variety of pressures and by both the static and dynamic methods. The largest group of experiments under the same pressure consisted of eleven runs made at one atmosphere by the dynamic method, using both dry and moist ozone. The values which he obtained for k_2 are given in Table VII.

TABLE VII

EXPERIMENTS OF JAHN AT 127°

Expt. no.	Reaction time, min.	$k_2 \times 10^{-3}$ cc./(moles sec.)	Condition of ozone
16	7.10	2.22	Dry
17	7.20	1.83	Dry
18	7.15	2.02	Dry
19	5.13	2.23	Dry
20	5.13	2.07	Dry
21	13.8	9.25[a]	Dry
22	13.6	2.07	Dry
		Av. 2.07	
23	6.71	3.22	Moist
24	4.90	1.92	Moist
25	13.3	2.75	Moist
26	13.3	1.98	Moist
		Av. 2.47	

[a] Jahn believes this result should be eliminated.

This table also shows variations in specific rate, although perhaps there is a tendency for the specific rates to agree better at temperatures higher than 100°, as we have also found in our own later work.

Chapman and his co-workers give curves for a number of runs at one atmosphere and 100°, and from these we have calculated the second-order constants, using the graphical method of extrapolation for determining the total concentration of ozone.[10] The method of computation should give fair accuracy. We obtain the results shown in Tables VIII and IX.

TABLE VIII

EXPERIMENTS OF CLARKE AND CHAPMAN IN TUBES WITH SMALL RATIO OF SURFACE TO VOLUME, AT 100° AND 1 ATM.

Fig.	2	3	4	5	6	7	8	
$k_2 \times 10^{-2}$, cc./(moles sec.)	1.78	1.37	1.18	3.28	1.77	1.09	1.43	Av. 1.70

TABLE IX

EXPERIMENTS OF CHAPMAN AND JONES ON DRY OZONE AT 100° AND 1 ATM.

Fig. 4, Curve	I	II	III	IV	
$k_2 \times 10^{-2}$, cc./(moles sec.)	2.31	2.16	1.96	1.91	Av. 2.09

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[12] Jahn, *Z. anorg. Chem.*, **48**, 260 (1906).

Here, too, we obtain considerable fluctuations in the specific rates for runs which were, for the most part, individually approximately of the second order.

We can give no certain explanation for these variations in specific rates found by ourselves and others for samples of ozone, each of which decomposes individually in accordance with the second order. Perhaps the most probable explanation is that of varying amounts of positive catalyst, whose action, nevertheless, leaves the reaction of the second order. This explanation is made reasonable by our results given in Tables IV and V on "acid" and "caustic" ozone, and further evidence as to the nature of the catalyst in "caustic" ozone will be given in the second article of this series.

The question now arises whether we can speak of any true specific rate for the second-order homogeneous decomposition of pure ozone. The following table giving the average values obtained by different investigators for k_2 at 100° and 1 atm. pressure will be helpful.

TABLE X

AVERAGE VALUES OF k_2 AT 100° AND 1 ATM.

Investigator	Source of oxygen	Method of ozonization	Number of runs	Method of experiment	$k_2 \times 10^{-2}$, cc./(moles sec.)
Warburg	From $KClO_3$, then well purified	Silent discharge	8	Static	1.51[a]
Clement	....	Electrolysis from H_2SO_4	2	Dynamic	4.11
Clarke and Chapman	From $KMnO_4$, then purified	Silent discharge	7	Static	1.70
Chapman and Jones	From $KMnO_4$, then purified	Silent discharge	4	Static	2.09
Wulf and Tolman	....	Electrolysis from H_2SO_4	6 (best)	Static	1.96[b]
Wulf and Tolman	Linde tank	Silent discharge	4 (best)	Static	1.69[b]
Wulf and Tolman	Linde tank	Silent discharge	11	Modified static	1.52[a]

[a] Corrected to 1 atm.

[b] Actually at about 74.5 cm. of Hg.

We can only conclude from the results presented in this table that the specific second-order rate for the decomposition of pure ozone at 100° and 1 atm. might at least be as low as 1.5 to 1.7 × 10^2 cc./(moles sec.). It seems possible, moreover, that even lower values might be encountered.[13]

[13] See Ref. *a* of Table XII in this article and Ref. *a* of Table III in the second article for examples of ozone which appeared to decompose with very low rates. Both these samples of ozone were prepared from "caustic" oxygen generated after fresh water had been added to the generator. This seemed in general to lead to very stable ozone.

6. The Effect of Total Pressure on the Rate of Ozone Decomposition

a. Critique of the Literature.—Having found individual samples of ozone to decompose in accordance with the second order, it is natural to investigate next the effect of total pressure on the rate of decomposition. If the rate of decomposition should be proportional solely to the square of the ozone concentration, no change should result in the calculated value of the second-order constant k_2, from a change in the total pressure of the gas mixture. It was found in 1906 by Jahn,[12] however, that the second-order constant was decreased by increasing the total pressure of the gas mixture, a result which he ascribed to an inhibiting effect of oxygen on the rate of decomposition. Later investigators have also found the calculated specific rate to decrease with total pressure, and we must now consider this phenomenon.[14]

The results of Jahn[12] on the decrease in the specific rate of ozone decomposition with total pressure are very satisfactory, and indeed show quantitatively within the limits of experimental error that the specific rate is inversely proportional to total pressure. His results, all obtained at 127°, and changed to our units, are presented in Table XI.

TABLE XI

RESULTS AS GIVEN BY JAHN AT DIFFERENT TOTAL PRESSURES AT 127°

No. of expts.	Method	Pressure, atm.	$k_2 \times 10^{-3}$, cc./(moles sec.)	$k_2 \times 10^{-3} \times$ press.
	Static (Warburg)	About 1.32	1.45	1.91
3	Static	1.25	1.80	2.25
6	Dynamic	1.01	2.07	2.09
3	Static	0.929	2.32	2.16
2	Static	.612	3.00	1.84
3	Static	.457	4.20	1.92
5	Dynamic	.395	5.37	2.12

The figures in Col. 5 show quite satisfactorily the inverse proportionality of k_2 to the pressure. It is also interesting to note that Warburg's results at 127° are also brought into agreement with those of Jahn by considering the effect of pressure.

Chapman and Jones,[9] in the course of their work, also decomposed samples of ozone at 100° at the two pressures 1 and 0.5 atm., although not for the purpose of determining the effect of pressure. To make the comparison, we have calculated by the method of Ref. 10, the specific

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[14] It is interesting to note that Jahn's results might at first sight be taken as indicating a first-order rather than a second-order rate of decomposition, since doubling the pressure of ozone mixture in a bulb actually only doubles the rate of decomposition instead of quadrupling it. Such a suggestion, however, must be ruled out owing to the adherence to second order during each given run, and as we shall see in the next article, the inhibiting effect of oxygen must be accepted as the real explanation of the results.

rates for the four runs which they made on dry ozone at 1 atm. and obtained as already shown in Table IX, the average value $k_2 = 2.09 \times 10^2$ cc./(moles sec.). In calculating the specific rates for their runs at 0.5 atm., a difficulty has been encountered, since it seems almost certain that they employed incorrect units in labeling their Fig. 3, which gives the data for these runs. In the first place, if we accept their pressure units, we find that the original concentration of the ozone which they prepared for use in Expt. III was of the order of 7.8% of ozone by volume, which is rather high for ozone prepared by the silent discharge, especially as the highest concentration which they obtained for the ozone that they used for their 1-atm. experiments was 4.6%. In the second place, if we accept their pressure units in Fig. 3, we obtain a rate of decomposition in the four experiments in which they add oxygen to ozone only half as great as in the five exactly similar experiments which they give in Figs. 5 and 6. And in the third place, if we accept their units in Fig. 3, we find that they did not obtain any appreciable increase in decomposition rate with decrease in total pressure. For these reasons we conclude that one division in Fig. 3 really corresponds not to 1 cm. of sulfuric acid but to 0.5 cm. of sulfuric acid, just as in Figs. 5 and 6. Accepting this conclusion, we have then calculated for the specific rates for the four runs made at 0.5 atm., the values (51.6), 5.01, 4.75 and 4.81 $\times 10^2$, and neglecting the one anomalous value, obtain for the average specific second-order rates for their ozone at 100° and 0.5 atm. pressure $k_2 = 4.86 \times 10^2$ cc./(moles sec.), very close to twice the value 2.09×10^2 which we calculated for their ozone at 1 atm. Hence, accepting our conclusion as to their units of plotting, the work of Chapman and Jones also shows that k_2 is inversely proportional to the total pressure.

Perman and Greaves[5] and Griffith and McKeown[6] also experimented on the effect of total pressure on the rate of ozone decomposition. Since, however, they were unable to obtain second-order decompositions, their results are not of special interest in the present connection. They obtained in general a decrease in rate with increase in total pressure somewhat less than would be expected on the basis of inverse proportionality.

b. Experiments on the Effect of Total Pressure.—Our own experiments on the effect of total pressure were not carried out in a very satisfactory manner, and we present them with some hesitancy primarily for the confirmation they afford of Jahn's findings. The apparatus consisted of four Pyrex bulbs, each of approximately 30 cc. volume, connected together so that they could be filled with the same ozone at atmospheric pressure. After filling, the pressure in two of them was reduced to somewhat less than an atmosphere, and in the other two was reduced to half this value. Keeping one bulb at each of the pressures as a control, the other two were immersed for equal lengths of time in a water-bath at 100°. After removing and "freezing" in tap water, all four bulbs were then analyzed for ozone by iodimetric methods, and the specific rates calculated assuming second order.

The results of six such experiments performed with ozone prepared by the silent discharge from two different kinds of oxygen are given in Table XII.

Table XII

Experiments on the Effect of Total Pressure, Using the Modified Static Method

Expt. no.	Kind of oxygen	Time, min.	Initial concn. at higher pressure, moles/cc. × 10^6	p, mm.	p', mm.	$k_2 \times 10^{-2}$, cc./(moles sec.)	$k_2' \times 10^{-2}$, cc./(moles sec.)	$\frac{pk_2}{p'k_2'}$
1	Linde	37	1.73	556	263	2.85	5.71	1.05
2	Linde	37	1.44	556	263	2.67	6.41	0.88
3	Caustic	30	1.64	556	250	1.50[a]	2.73	1.22
4	Caustic	40	2.25	552	248	1.55	2.79	1.24
5	Caustic	45	0.58	553	240	2.95	10.15	0.67
6	Caustic	45	.65	553	239	2.60	6.47	.93
							Av.	1.00

[a] Correcting by the inverse pressure effect to 1 atm. we should here obtain the very low value $k_2 = 1.10 \times 10^2$ cc./(moles sec.).

A further experiment was performed, just the reverse of these, in which the pressure in two of the bulbs was increased by the addition of ozone rather than diminished by exhaustion, using a fifth auxiliary bulb filled with ozone at atmospheric pressure. The pressure in all four reaction bulbs was first reduced to something less than half an atmosphere and then ozone injected back into two of them from the auxiliary bulb. The ratio corresponding to the figures in the last column of Table XII came out 1.19.

These results show clearly a large effect of total pressure on the value of the specific reaction rate, and the average of the rather widely varying ratios agrees with Jahn's quantitative relation of inverse proportionality.

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Summary

As a result of the work described in the foregoing article on the thermal decomposition of ozone at temperatures of 100° and above, the following conclusions appear probable, although not all of them are absolutely certain.

1. The decomposition can be made to take place as a homogeneous reaction in Pyrex and in certain other glasses.
2. The homogeneous decomposition can be carried out so as to be very closely of the second order with respect to ozone.
3. The specific reaction rate for different samples which decompose in accordance with the second order may vary markedly.
4. If there is a true second-order rate for pure ozonized oxygen, it has at 100° and 1 atm. total pressure a specific rate as low as $1.5 - 1.7 \times 10^2$ cc./(moles sec.).
5. For ozonized oxygen which decomposes in accordance with the second order, the specific rate is closely inversely proportional to the total pressure.

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THE THERMAL DECOMPOSITION OF OZONE. II. THE EFFECT OF OXYGEN AND ACCIDENTAL CATALYSTS ON THE RATE

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1. Introduction

As shown in the preceding article of this series,[2] all investigators agree that the rate of decomposition of ozonized oxygen is markedly decreased by increase in total pressure, and for ozone that decomposes as a second-order reaction, the specific rate is very closely inversely proportional to the total pressure. Two possible explanations of this fact present themselves. (a) The decomposition of ozone is inhibited by oxygen, the specific second-order rate being inversely proportional to the concentration of oxygen. This hypothesis was believed by Jahn to be true, and was the fact used by him in support of his mechanism of ozone decomposition. In the present article, however, we shall especially avoid any assertions as to mechanisms. (b) The decomposition of ozone is inhibited by some unknown negative catalyst present in ozonized oxygen (perhaps formed at the time of ozonization), and the specific second-order rate is inversely proportional to the concentration of this negative catalyst, so that with changes in pressure the specific rate is inversely proportional to total pressure. This entirely logical but somewhat artificial hypothesis has not previously been considered. Its consideration at the present time is forced by the experiments of Chapman and Jones,[3] who actually added

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[1] National Research Fellow in Chemistry.

[2] Wulf and Tolman, THIS JOURNAL, **49**, 1183 (1927).

[3] Chapman and Jones, *J. Chem. Soc.*, **97**, 2463 (1910).